1 Composite ultrafiltration membrane tailored by MOF@GO with highly
2 improved water purification performance

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10 **Abstract**

11 Developing advanced filtration membrane with high flux, good solute rejection and excellent
12 antifouling performance is highly demanded. Hydrophilic graphene oxide (GO) nanosheets are
13 attractive fillers for the preparation of composite membranes for water purification. However, strategies
14 that can fully exploit the advantages and remedy the drawbacks of GO nanosheets are still needed. In
15 this work, UiO-66 was specifically anchored to the GO layers as a porous modifier. The incorporated
16 UiO-66 can effectively prevent the GO layers from stacking and introduce unique properties into the
17 composite (UiO-66@GO). A series of novel composite membranes were prepared with the obtained
18 UiO-66@GO composite and polyethersulfone (PES). As a result, the prepared composite membranes
19 (UiO-66@GO/PES) exhibit high hydrophilicity and water purification performance. Especially, the
20 water flux of composite membrane with 3.0 wt % UiO-66@GO loading shows an increase of 351 %
21 and 78 % respectively in comparison with that of the PES and GO/PES membranes. Moreover, the
22 UiO-66@GO/PES membranes exhibit good solute rejection and impressive antifouling performance,
23 which is appealing for the application of industrial water purification.

24 **Keywords:** Metal-organic framework, Graphene oxide, Ultrafiltration membrane, Water purification

25

26 **1. Introduction**

27 Over the past several decades, emission of contaminants into the environment has sharply increased
28 due to the rapid industrial expansion and fast population growth. The water pollution deserves special
29 attention, since water quality relates directly to the health of human and wildlife. Among the
30 contaminants in water, dyes from textile, paper, printing, and food industries have become a major
31 threat to the water security. The development of water pollution will result in serious water shortage
32 and ecological damage. Thus, there is an urgent need to purify the waste water before being released
33 into the environment [1, 2].

34 Among the various technologies, as an efficient and environmentally friendly separation technology
35 with relatively simple operation process, ultrafiltration is widely used for water purification. For high-
36 efficiency industrial ultrafiltration processes, high flux, good solute rejection and excellent antifouling
37 performance are highly needed, which mainly depend on the pore structure and surface property of the
38 ultrafiltration membranes [3]. Generally, enhancing the pore quantity with molecular sieving property
39 can effectively improve the water permeation, and increasing the surface hydrophilicity of the
40 ultrafiltration membrane can endow the membrane with excellent wettability and antifouling
41 performance. Recently, great efforts have been made to develop advanced ultrafiltration membranes.
42 Polyethersulfone (PES) is one of the most widely used commercial polymers for ultrafiltration
43 membrane fabrication because of its excellent chemical resistance and thermal stability. Up to now,
44 several modification approaches of PES membrane have been proposed to improve the water
45 purification performances, such as chemical modification, blending with fillers, etc. [4, 5] However,
46 chemical modification would change the structure of the PES molecule chains and the procedure is
47 hard to control. In contrast, blending with fillers to prepare composite ultrafiltration membranes has
48 been demonstrated to be an effective and straightforward method. Thus composite ultrafiltration
49 membrane can combine the advantages of polymer matrix and filler. Moreover, it is more feasible for

industrial production [6]. In this case, the choice of fillers primarily determines the filtration performance of the composite ultrafiltration membranes. Therefore, it is critical to develop advanced fillers to achieve the overall performance improvement.

As a two-dimensional carbon material with rich functional groups (*e.g.*, carboxyl, hydroxyl, and epoxy groups), large surface area, strong hydrophilicity, and outstanding chemical stability, graphene oxide (GO) is considered as a promising filler material in composite membranes for water purification [7-11]. Zinadini *et al.* [4] prepared GO/PES ultrafiltration membrane and found that the composite membranes exhibited improved water flux and antifouling performance due to the hydrophilic property of GO. Besides, GO possesses remarkable mechanical property, which can reinforce the mechanical strength of the composite membranes [6]. However, there are still some problems need to be solved. For instance, GO nanosheets can easily stack together because of the strong interactions between the neighboring nanosheets. The narrowed interlayer space is detrimental to the increase of water flux due to the hindered transportation of water molecules through the layers. In this respect, there is a need to seek solutions to effectively avoid the stacking and fully utilize the unique properties of GO nanosheets.

Metal-organic frameworks (MOFs), a new class of porous crystalline materials that constructed from metal-containing units and organic linkers, may be promising candidates as modifiers for GO nanosheets because of their highly designable pore structure and tunable surface chemical properties [12-19]. Until now, several MOF modified GO composite materials (MOF@GO) have been explored [2, 11, 20]. While the research on MOF@GO composite material as fillers to prepare composite membranes is very limited. Recently, Dong *et al.* [21] studied ZIF-8@GO/Pebax composite membranes for gas separation. Yang *et al.* [22] reported ZIF-8@GO/Nafion hybrid membrane to improve the proton conductivity. ZIF-8@GO/Polyamide membrane has been prepared for water purification with enhanced antimicrobial activity [23]. Therefore, research on the design of diversely MOF@GO functionalized composite membranes is highly desirable, especially for the application as the ultrafiltration membrane for water purification.

In the present work, MOF@GO modified composite ultrafiltration membranes were investigated. To achieve the high water purification performance, we selected UiO-66, a prototypical Zr-MOF with hydrophilic surface, as modifier for GO nanosheets. The structure is given in Figure 1. The aperture size of UiO-66 is about 6.0 Å, which falls between the size of water molecules (~2.8 Å) and most organic contaminants (larger than 6.0 Å) [24]. Based on the coordination effect between metal ions of UiO-66 and carboxyl groups of GO, UiO-66 could be specifically anchored to the GO layers via in situ crystallization, widening the interlayer space and forming porous structure on GO layers. Besides, the hydrophilic UiO-66 with molecular sieving pores for water molecules can endow the composite material more favorable properties for water purification. The composite ultrafiltration membranes (UiO-66@GO/PES) were prepared through phase inversion method by incorporating the UiO-66@GO composite into the PES matrix. The water purification performance of the resulted membranes was examined by water flux and solute rejections based on various filler loadings, and systematic characterizations were applied to investigate the influence of UiO-66@GO composite on membrane performance. The antifouling property of the prepared composite membranes was also studied to explore the potential of the membranes being used in industrial water purification. This work might give guidance to the fabrication of advanced ultrafiltration membranes for water treatment.

2. Materials and methods

2.1. Materials

PES (Ultrason E6020P) was kindly supplied by BASF, Germany. Polyvinylpyrrolidone (PVP, $M_w = 24,000$ g/mol) was purchased from Beijing HWRK Chem Co., Ltd. GO with a particle size less than 2 µm was purchased from Nanjing Jicang Nanotechnology Co., Ltd. Bovine serum albumin (BSA, 98 %), zirconium chloride ($ZrCl_4$, 99 %), and terephthalic acid (H_2BDC , 99 %) were purchased from J&K Scientific Co., Ltd, China. Methyl Orange (MO, $C_{14}H_{14}N_3NaO_3S$, $M_w = 327.3$ g/mol) was purchased from Maikun chemical Co., Ltd, China. Direct Red 80 (DR 80, $C_{45}H_{26}N_{10}O_{21}S_6$, $M_w = 1373.1$ g/mol) was purchased from TCI. *N,N'*-dimethylformamide (DMF, 99 %) and *N,N'*-dimethylacetamide (DMA,

99 %) were purchased from Sinopharm Chemical Reagent Co., Ltd. Methanol (CH_3OH , 99 %) was purchased from Beijing Chemical Works.

2.2. Synthesis of UiO-66

UiO-66 was synthesized according to the reported procedure [25]. 0.386 g (1.67 mmol) of ZrCl_4 and 0.276 g (1.67 mmol) of H_2BDC were dissolved in 50 mL of DMF. Then, the mixture was transferred into a 100 mL Teflon liner within a stainless-steel autoclave and kept at 120 °C for 24 h. After the reaction, the product was centrifuged and washed with fresh DMF and methanol for several times. Finally, the product was dried at 80 °C in air and further activated at 150 °C in a vacuum oven.

2.3. Synthesis of UiO-66@GO

10 mg GO was dispersed into 50 mL DMF by sonication for 8 h. Then, ZrCl_4 (0.386 g) was added to the GO solution and stirred at room temperature overnight. Afterwards, H_2BDC (0.276 g) was added. After solvothermal reaction at 120 °C for 24 h, the resulting composite material was centrifuged and washed with fresh DMF and methanol for several times. Finally, the product was dried at 150 °C in a vacuum oven.

2.4. Fabrication of the membranes

All the membranes were fabricated by phase inversion method. For the fabrication of PES membrane, the casting solution was prepared by dissolving 18 wt % PES and 8 wt % PVP in DMA. For the fabrication of composite membranes, different amounts of fillers were firstly dispersed in DMA to achieve a homogeneous suspension by sonication and agitation. Then, PES and PVP were added to the suspension in 3 additions to get a viscous solution. The loadings of the fillers were varied from 0 wt % to 3.0 wt % based on the weight of PES. The resulting solutions were stirred overnight. A sonication-assisted method was adopted to fully remove the trapped air bubbles. Afterwards, the solutions were cast onto a clean glass plate with a hand-casting knife (with a thickness of 100 μm). The wet membrane accompanied with the glass plate was immersed in a distilled water bath immediately after casting. Then, the membranes were transferred to a fresh water bath for 24 h to accomplish phase inversion.

125 Finally, the fabricated membranes were sandwiched between filter papers and dried for 24 h at room
126 temperature.

127 *2.5. Characterization of UiO-66 and UiO-66@GO*

128 Powder X-ray diffraction (PXRD) analysis was recorded on a SHIMADZU XRD-6000-X-ray
129 diffractometer in reflection mode using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The 2θ range of 5° to 50° was
130 scanned with a step size of 0.01° . Fourier transform infrared spectroscopy (FT-IR) analysis was carried
131 out on a Nicolet 6700 FT-IR spectrophotometer. Powder samples were prepared using the KBr wafer
132 method and the measurements were performed in a diffuse reflectance module. Transmission electron
133 microscopy (TEM) images were obtained using a Tecnai G20 equipment. Scanning electron
134 micrographs (SEM) analysis was applied using a JSM-7800F equipment.

135 *2.6. Characterization of the membranes*

136 Membrane morphologies were analyzed by SEM images. The cross-sectional samples were prepared
137 by fracturing the membranes in liquid nitrogen. Before analysis, the samples were sputtered with Au
138 under 10-20 kV acceleration voltage to increase the electrical conductivity. The surface morphology
139 was studied through AFM analysis (DMFASTSCAN-SYS, Bruker, Germany). The membrane samples
140 were fixed on a glass holder and $5 \mu\text{m} \times 5 \mu\text{m}$ areas were scanned at a rate of 1 Hz. The parameters
141 including the mean roughness (R_a), the root mean square of the Z data (R_q) and the mean difference
142 between the five highest peaks and the five lowest valleys (R_z) were used to quantify the surface
143 roughness of the membranes. The static water contact angles of the composite membranes were tested
144 at 25°C on a contact angle goniometer (OCA20, Dataphysics Instrument, Germany). Before the
145 measurement, dried sample was fixed on a glass plate using double sided tape. Then, a water droplet
146 was carefully dropped on the top surface and the contact angle between the water and membrane was
147 measured immediately. The result for each sample was calculated by averaging at least five values
148 obtained from different areas of the sample.

149 *2.7 Permeation and rejection measurements*

150 Permeation and rejection measurements of the membranes were carried out in a custom-built
151 stainless-steel permeation cell equipped with a nitrogen gas line as the driving force. The effective area
152 of the tested membrane is about 10 cm². The maximal pressure of the equipment can reach 2.50 MPa
153 with an accuracy of 0.05 MPa. The accuracy for the water flux measurement is 0.001 kg·m⁻²·h⁻¹.
154 Herein, the measurements were carried out at 25 °C under constant stirring speed of 300 rpm. For the
155 permeation test, each membrane was compacted at 0.3 MPa with distilled water for 30 min to achieve a
156 steady flux. Then, the data was recorded at least three times at the interval of 10 min. The water flux
157 $J_{w,1}$ (kg·m⁻²·h⁻¹) was calculated using the following equation [3-6]:

$$158 \quad J_{w,1} = \frac{M}{A\Delta t} \quad (1)$$

159 where $J_{w,1}$ is the pure water flux of the membrane (kg·m⁻²·h⁻¹), M is the weight of the permeated water
160 (kg), A is the effective area of the tested membrane (m²), and Δt is the permeation time (h).

161 The rejection tests were carried out using aqueous solutions of MO and DR. The concentrations of
162 dyes in the feed solution were 200 ppm. Typically, 100 ml solution was used as the feed solution, and
163 20 ml permeated solution was collected. The concentrations of dyes in permeate and feed sides were
164 measured using ultraviolet spectrophotometer (TU-1901). The measured wavelength ranges from 190
165 nm to 900 nm with an accuracy of 0.3 nm. The repeatability of the measured wavelength is about 0.1
166 nm. For the concentration measurement of MO and DR, the minimum concentration can reach 1 ppm
167 and 2 ppm with an accuracy of 0.01 ppm. Rejection ratio (R) was defined as the following equation [3-
168 6]:

$$169 \quad R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

170 where C_p and C_f are the concentrations of dyes in the permeate and feed sides, respectively.

171 2.8 Antifouling measurements

For the measurement of antifouling performance, first, the membrane was subjected to pure water permeation for 60 min to obtain the pure water flux ($J_{w,1}$). Then, the BSA solution at a concentration of 1000 ppm was used as the feed solution and filtered for 60 min to obtain the water flux of BSA solution (J_p). After this, the fouled membrane was cleaned with distilled water for 10 min before measuring the water flux of the cleaned membrane ($J_{w,2}$). The flux recovery ratio (FRR) was calculated using the following equation [3-6]:

$$FRR(\%) = \left(\frac{J_{w,2}}{J_{w,1}} \right) \times 100 \quad (3)$$

To analysis the antifouling performance in detail, several parameters including total fouling ratio (R_t), reversible fouling ratio (R_r), and irreversible fouling ratio (R_{ir}) were also used to describe the fouling resistance of the membranes. These parameters were calculated according to the following equations [3-6]:

$$R_t(\%) = \left(1 - \frac{J_p}{J_{w,1}} \right) \times 100 \quad (4)$$

$$R_r(\%) = \left(\frac{J_{w,2} - J_p}{J_{w,1}} \right) \times 100 \quad (5)$$

$$R_{ir}(\%) = \left(\frac{J_{w,1} - J_{w,2}}{J_{w,1}} \right) \times 100 = R_t - R_r \quad (6)$$

3. Results and discussions

3.1. Characterization of UiO-66 and UiO-66@GO

Figure 2 shows the PXRD patterns of GO, UiO-66, and UiO-66@GO composite. The pattern of UiO-66 is in good agreement with that reported in literature, indicating the successful synthesis [26]. The almost identical peaks of UiO-66@GO with UiO-66 demonstrate that the crystalline structure of UiO-66 in the composite material is not changed during the in situ crystallization. The characteristic diffraction peak of GO at around 10° corresponds to the interlayer space of 0.87 nm. However, the same peak was not observed in the pattern of UiO-66@GO. One possible explanation is that the

194 anchored UiO-66 can effectively reduce the van der Waals binding energy between the GO layers and
195 promote the layer exfoliation, demonstrating the successful loading of UiO-66 on GO layer [26]. This
196 speculation can be further verified by FT-IR, SEM and TEM analyses.

197 Figure 3 shows the FT-IR spectra of GO, UiO-66 and UiO-66@GO composite to characterize the
198 functional groups. For UiO-66, the absorption peaks at wavenumbers of 1660 cm^{-1} , 1585 cm^{-1} (1395
199 cm^{-1}) and 1506 cm^{-1} represent the C=O symmetric stretching in the carboxylate group of the BDC
200 ligand, the O–C–O asymmetric stretching in the BDC ligand and the typical vibration present in the
201 C=C stretching of benzene ring, respectively [26]. For GO, the peaks at 1740 cm^{-1} , 1625 cm^{-1} , 1380
202 cm^{-1} and 1050 cm^{-1} correspond to the stretching vibrations of the C=O bond of carbonyl or carboxyl
203 groups, the O–H bond in water, C–OH group and C–O bond. These absorption peaks demonstrated the
204 presence of oxygen-containing functional groups in GO [26]. The spectrum of the UiO-66@GO
205 composite does not change much compared with UiO-66. However, the peaks belong to the oxygen-
206 containing bands of GO disappear in the spectrum of UiO-66@GO. This may happen because these
207 groups on the GO layers are bonded with the metal sites of UiO-66 [25, 26].

208 The morphology of GO, UiO-66, and the UiO-66@GO composite were investigated by SEM and
209 TEM. As shown in Figure 4, UiO-66 exhibits as aggregates of particles with the size of 150 nm, while
210 GO presents as a dense multilayer plane. For UiO-66@GO composite, the UiO-66 particles distribute
211 orderly on the GO layers, indicating that UiO-66 nanoparticles are anchored to the GO layers rather
212 than physically mixed with GO. Moreover, the reduced UiO-66 particle size (about 80 nm) because of
213 the limited grown space between GO layers is another firm evidence for the successfully loading of
214 UiO-66 on GO layers. This favorable structure of the UiO-66@GO composite can effectively avoid the
215 layer stacking of GO.

216 3.2. Characterization of the membranes

217 3.2.1 Membrane morphology

218 To visually investigate the effect of UiO-66@GO on the microstructure of the composite membranes,
219 SEM analysis was carried out. The cross-sectional SEM images of the membranes with different UiO-
220 66@GO loading are exhibited in Figure 5. All the membranes exhibit the typical asymmetric porous
221 structure with a dense skin layer connected by a porous sub-layer having finger-like pore structure.
222 Compared with PES membrane, the finger-like pores of all the UiO-66@GO blended membranes are
223 slightly wider. Additionally, it can be seen that with the increased filler loading of the composite
224 membranes, a microcellular-like structure could be observed. This phenomenon may be attributed to
225 the fast solvent (DMA) and non-solvent (deionized water) exchange during the membrane fabrication
226 process because of the hydrophilic nature of UiO-66@GO [6]. These microcellular pore structure and
227 increased pore size may provide new pathways for water molecules and enhance the water transport
228 efficiency.

229 3.2.2 AFM analyses of the membrane surfaces

230 Figure 6 shows the three-dimensional AFM images of the membrane surfaces. The height
231 information of the membrane surface is reflected by the variation of brightness in the pictures. The
232 brighter region represents the higher membrane surface. The roughness parameters, including R_a , R_q ,
233 and R_z , are obtained in a scan area of $5\ \mu\text{m} \times 5\ \mu\text{m}$. The results are presented in Table 1. It is observed
234 that the large peaks and valleys in the PES membrane surface are substituted by many small ones in the
235 composite membranes, leading to an obvious decrease in the surface roughness [3-5]. The decreased
236 surface roughness would reduce the contact areas between the contaminants and the membrane surface,
237 which is favorable to the improvement of antifouling performance. With the increase of UiO-66@GO
238 loading, the surface roughness of the composite membrane grows gradually due to the accumulation of
239 the hydrophilic UiO-66@GO in the skin layer of the membrane. When the loading of UiO-66@GO is
240 3.0 wt %, the average roughness of the composite membrane is still lower than that of the pure PES
241 membrane. The reason can be explained by the introduction of UiO-66@GO. The regularly dispersed
242 UiO-66@GO in membrane makes the membrane surface become smooth. With the increase of filler

loading, the exchange of solvent and non-solvent during the membrane preparation process also be influenced, inducing the membrane becomes roughness again [4, 27, 28]. Therefore, the UiO-66@GO/PES membrane at the loading of 3.0 wt % exhibits smoother surface than PES membrane surface, while it is rougher than the membranes at the loading of 2.0 wt%.

3.2.3 Hydrophilicity of the membranes

The water contact angle measurements were conducted to characterize the hydrophilicity of the membranes. In general, a lower contact angle indicates a more hydrophilic property [4]. The membranes with higher surface hydrophilicity will have greater ability to attract water molecules and reduce the adsorption of contaminants, which would play a positive role in improving water flux and antifouling ability [27]. As shown in Figure 7, the pure PES membrane shows a water contact angle of 85.7° due to the inherent hydrophobic property of PES. The water contact angles of the membranes are reduced (that is, hydrophilicity is improved) with the addition of GO and UiO-66@GO. Moreover, the contact angle decreases gradually with the increase in GO and UiO-66@GO loadings. These results indicate that adding GO and UiO-66@GO into PES matrix could enhance the hydrophilicity property of PES membrane. It is supposed that the hydrophilic GO and UiO-66@GO in the casting solutions may spontaneously migrate to the membrane surface to decrease the interface energy during the phase inversion process, thus increasing the surface hydrophilicity [4]. In addition, the water contact angles of the UiO-66@GO/PES membranes are lower than that of the GO/PES membranes, indicating a more hydrophilic property of UiO-66@GO than the pristine GO.

3.2.4 Permeation flux and rejection performance

Figure 8 shows the pure water flux of the prepared composite membranes with different GO and UiO-66@GO loadings. It can be observed that the addition of UiO-66@GO in PES matrix induces a much higher water flux in comparison with that of the pure PES membrane. Meanwhile, the water flux increased with the filler loading at the range of 0 wt % to 3.0 wt %. When the loading of UiO-66@GO reaches 4.0 wt %, the water flux of the composite membrane shows a decrease though it is 277 %

higher than that of the pure PES membrane. This can be explained as follows. The small amount of UiO-66@GO (lower than 3.0 wt %) can increase the inner space in the dense skin layer, thus providing more water transport ways to enhance water flux. However, with the further increase of the loading (like 4.0 wt %), a relatively thicker skin layer may be generated and the partial agglomeration of UiO-66@GO in the porous sub-layer may block the pathways, resulting in the resistance for water transport [4, 29]. Thus, we studied the UiO-66@GO/PES composite membrane with the filler loading up to 3.0 wt % in the following sections. Compared with the pure PES membrane, the composite membranes with UiO-66@GO loadings of 0.5 wt %, 1.0 wt %, 2.0 wt %, and 3.0 wt % show the increases of 80 %, 157 %, 269 %, and 351 % in water flux, respectively. Besides, the water flux of the UiO-66@GO/PES membrane is also much higher than that of the GO/PES membrane, achieving an increase up to 77.5 % at 3.0 wt % loading. The large enhancement of water flux can be explained by two reasons. First, the enhanced surface hydrophilicity can attract more water molecules close to the membrane and facilitate the transport of water molecules in the membrane. It can be observed that the change of water flux shares the same trend with the hydrophilicity property of the membranes (Figure 7). In this respect, membranes with higher surface hydrophilicity have greater advantages. Second, the large pore size of UiO-66@GO/PES membranes (as shown in Figure 5) can reduce the resistance to water molecules and provide additional space for water transportation. The above results demonstrate that the UiO-66@GO composite is a favorable filler for the preparation of ultrafiltration membranes with high flux.

The rejection performance for organic pollutants in water was evaluated on two organic dyes (MO and DR 80). The results were shown in Figure 9. The PES membrane shows good rejection ratios for these two dyes because of the relatively compact skin layer. After blending with GO, the GO/PES membrane exhibit higher retention ratios than that of unfilled PES membrane. For the DR 80 rejection, the best retention ratio of the pure PES and GO/PES membranes are 92.9 % and 93.8 % respectively. For the MO rejection, the best retention ratio of pure PES and GO/PES membrane are 84.9 % and 87.0 %

respectively. The slightly increased retention ratios were due to the acidic functional groups of GO. It has been reported that GO can induce negative charge on the surface of the prepared membranes, causing high retention between negative dye and negative surface [4]. However, the stacking tendency of GO in membrane matrix will seriously hinder the positive effect of functional groups. In this respect, the anchored UiO-66 on GO layers can effectively avoid the stacking of GO and endow the resulting composite molecular sieve property. As a result, for the UiO-66@GO/PES membrane, the best rejection ratios of DR 80 and MO enhanced to be 98.3 % and 89.0 %, higher than that of GO/PES membrane. Meanwhile, the rejection effectiveness of dyes was tested and the results are shown in Figure 10 by taking UiO-66@GO/PES membrane at the loading of 3.0 wt % as an example. It can be seen that the rejection ratios of dyes remain stable during 50 h measurement, indicating the favorable operation stability that is important for the industrial application of membranes.

3.2.5 Antifouling performance of the membranes

Membrane fouling is a major obstacle for the large-scale application of membrane separation technology. It occurs frequently and is harmful for the membrane permeability [29-32]. In waste water, protein is one of the most common pollutants. Besides, protein can act as the representative of organic pollutants because of their complex structures. During the water purification processes, the protein tends to be adsorbed on the membrane surface, causing the fouling of membrane. On the basis of these, protein has been widely used as fouling substances for the antifouling measurement [3-6]. Herein, antifouling performance of the prepared membranes was examined using aqueous solution of BSA. Figure 11 shows the variation of the water flux as a function of fouling time. Obviously, there was a large drop in water flux when pure water is substituted by protein solution in the feed side. The maximum loss of water flux (57.1 %) was observed in the pure PES membrane because of the fouling on the membrane surface. While, the UiO-66@GO/PES composite membranes showed the decreased loss of water flux. Meanwhile, with the increase of UiO-66@GO loading, the antifouling performance of the composite membranes was improved correspondingly. When the loading of UiO-66@GO

increases to 3.0 wt %, the loss of water flux successfully decreased as 11.4 %, indicating the largely improved antifouling ability.

To understand the antifouling performance more specifically, several parameters for the evaluation of antifouling performance were calculated and gathered in Table 2. One important parameter is FRR, The higher FRR indicates the better antifouling property of the membrane. As seen from Table 2, the UiO-66@GO/PES membranes have higher FRR than the pure PES and GO/PES membranes. Especially, the UiO-66@GO/PES composite membrane with 3.0 wt % UiO-66@GO loading showed the highest FRR of 88.6 %, while that value of the pure PES and GO/PES membranes were 42.9 % and 84.3 %. The difference between these results indicates that UiO-66@GO/PES membranes exhibit better antifouling performance than pure PES and GO/PES membranes, which can be further demonstrated by the total, reversible, and irreversible fouling resistance ratios of the membranes (Table 2). The total fouling ratios of PES, GO@PES, and UiO-66@GO/PES membranes are 71.4 %, 49.4 % and 26.6 % respectively. After the fouling processes with BSA solution, the irreversible fouling ratios of PES, GO@PES, and UiO-66@GO/PES membranes are 57.1 %, 15.7 % and 11.4 % respectively. The above different antifouling performance is believed to come from the different hydrophilicity and surface roughness of the membranes. The membrane with more hydrophilic property and smooth surface could effectively decrease the affinity and the contact area between the membrane surface and the contaminants [3, 4]. From this point, the UiO-66@GO/PES membranes possessing more hydrophilic and smooth surfaces than PES and GO/PES membranes could take more advantages on antifouling performance. Considering the above results and discussions, we think that UiO-66@GO is promising filler to improve the antifouling performance of the ultrafiltration membrane.

Remarkably, from the above discussions, the UiO-66@GO/PES membranes exhibit highly improved water purification performance than PES and GO/PES membranes. The favorable results highlight the critical role of UiO-66@GO in membranes for water purification. Besides, the concerned PES composite membranes at their best performance were summarized in Table 3 to compare the effect of

different fillers in PES matrix for water purification. Compared with the reported PES composite membranes, UiO-66@GO/PES showed a comprehensive high performance in water flux, rejection ratio and antifouling performance. The results indicated that designing MOF modified GO composite material as filler in polymer matrix is indeed an effective route to enhance the water purification performance, and will be extended to fabricate other kinds of advanced membranes.

4. Conclusions

The development of advanced filtration membrane has crucial importance to address the global challenges of water scarcity and the pollution of aquatic environments. In this work, UiO-66@GO composite was synthesized and a series of novel composite membranes were prepared by blending this composite material into the PES membrane matrix for water purification. The results revealed that the combination of UiO-66 with GO can effectively remedy the drawbacks of GO and endow GO new possibilities. After blending UiO-66@GO into the PES membrane matrix, the hydrophilicity and water purification performance of the UiO-66@GO/PES membranes were effectively improved. The pure water flux of the UiO-66@GO/PES membrane at 3.0 wt % loading increased by 351% compared with that of the pure PES membrane, together with increased rejection ratio to organic dyes (MO and DR 80). The antifouling measurements demonstrated that the UiO-66@GO/PES composite membranes have impressive antifouling performance. The simultaneously improved water flux, retention ratio and antifouling performance demonstrated that using MOF@GO composite materials as fillers to prepare composite ultrafiltration membranes is a high efficient and promising way to develop advanced membranes for water purification.

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459 **Figure list:**

460 **Figure 1.** The structure of UiO-66 (Zr₆ cluster, green; O, red; C, gray).

461 **Figure 2.** XRD patterns of GO, UiO-66 and UiO-66@GO composite.

462 **Figure 3.** FT-IR patterns of GO, UiO-66 and UiO-66@GO composite.

463 **Figure 4.** SEM images of (a) UiO-66, (b) UiO-66@GO. TEM images of (c) GO, (d) UiO-66@GO.

464 **Figure 5.** SEM images of the cross-section morphology of (a, b) PES membrane, composite
465 membranes with different UiO-66@GO loadings of (c, d) 0.5 wt %, (e, f) 1.0 wt %, (g, h) 2.0 wt %, (i,
466 j) 3.0 wt %.

467 **Figure 6.** AFM images of (a) PES, (b) 1.0 wt % UiO-66@GO/PES membrane, (c) 2.0 wt % UiO-
468 66@GO/PES membrane, (d) 3.0 wt % UiO-66@GO/PES membrane.

469 **Figure 7.** Water contact angles of the membranes with various filler loadings.

470 **Figure 8.** Pure water fluxes of the prepared membranes.

471 **Figure 9.** Dye rejection performance of the prepared membranes.

472 **Figure 10.** The rejection effectiveness versus time of 3.0 wt % UIO-66@GO/PES membrane.

473 **Figure 11.** Flux versus time of the prepared membranes during the fouling processes.

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507 **Table 1** Surface roughness parameters of PES, GO/PES and UiO-66@GO/PES membranes.

Membranes	Roughness parameters		
	R _a (nm)	R _q (nm)	R _z (nm)
PES	21.7	28.2	259.0
0.5 wt % UiO-66@GO/PES	7.8	10.0	79.1
1.0 wt % UiO-66@GO/PES	9.3	12.0	89.0
2.0 wt % UiO-66@GO/PES	9.8	12.2	112.0
3.0 wt % UiO-66@GO/PES	11.8	20.6	184.0

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509 **Table 2** Fouling resistance ratios of the prepared membranes.

Filler content (wt %)	UiO-66@GO/PES				GO/PES			
	FRR (%)	R _t (%)	R _r (%)	R _{ir} (%)	FRR (%)	R _t (%)	R _r (%)	R _{ir} (%)
0.0	42.9	71.4	14.3	57.1	42.9	71.4	14.3	57.1
0.5	79.4	49.2	28.6	20.6	58.2	70.7	28.9	41.8
1.0	85.6	38.9	24.4	14.5	61.8	70.6	32.4	38.2
2.0	88.0	27.1	15.1	12.0	85.4	48.8	34.2	14.6
3.0	88.6	26.6	15.2	11.4	84.3	49.4	33.7	15.7

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512 **Table 3** Water purification performance of PES composite membranes.

Membranes	Filler loadings (based on PES weight)	Relative increased percentage of water flux	Percentage of rejection	Percentage of water flux recovery	Ref.
SBMA@CNT/PES	1.5 wt %	13.0 %	--	84.5 %	12
Oxidized MWCNTs/PES	1.3 wt %	63.6 %	70.0 % (Na ₂ SO ₄)	50.0 %	33
AgNPs–HNTs–rGO/PES	1.0 wt %	90.9 %	78.0 % (PEG)	60.0 %	6
SiO ₂ /PES	11.1 wt %	104.8 %	97.8 % (BSA)	98.0 %	34
NH ₂ -MWCNTs/PES	3.1 wt %	220.0 %	87.0 % (BSA)	48.0 %	27
CNTs/PES	0.6 wt %	660.0 %	87.3 % (Na ₂ SO ₄)	87.7 %	29
GO/PES	3.0 wt %	154.3 %	88.8% (DR)	84.3 %	This work
UIO-66@GO/PES	3.0 wt %	351.4 %	98.3% (DR)	88.6 %	

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Graphical abstract