Hydrophilic hollow zeolitic imidazolate framework-8 modified ultrafiltration membranes with significantly enhanced water separation properties

Huazhen Sun, Beibei Tang, Peiyi Wu⁎

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, PR China

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ABSTRACT

Metal-organic frameworks (MOFs) are being intensively investigated for the design of advanced composite membranes, primarily due to their favorable polymer affinity, and highly tunable porous structure and surface properties. However, the development of engineered MOF-based ultrafiltration (UF) membranes for water treatment remains in its infancy. In the present study, hydrophilic hollow zeolitic imidazolate framework-8 (hZIF-8) was meticulously synthesized via surface functionalization-assisted etching approach by using tannic acid (TA), and then incorporated into polysulfone (PSf) casting solution to fabricate novel hybrid UF membranes via phase inversion method. The resultant hZIF-8 not only possessed a highly hydrophilic surface derived from the coated TA but also yielded a unique hollow structure without destroying the intrinsic frameworks. Thanks to the well-tailored surface property and nanostructure of hZIF-8, the obtained PSf/hZIF hybrid UF membranes showed highly improved water permeation (597 L m⁻² h⁻¹), which was 2.8 times that of the pristine PSf membrane (210 L m⁻² h⁻¹), while well maintaining the rejection property. What's more, the incorporation of hZIF-8 rendered the membrane with enhanced resistance to fouling. These results indicated the great application potential of such MOF/polymer hybrid UF membranes in wastewater treatment and separation in many industrial fields.

1. Introduction

Over the past few decades, membrane technology has advanced significantly for wastewater treatment and water purification because of its small footprint, low energy consumption, and environmental friendliness [1–3]. Especially, ultrafiltration (UF) membranes are widely studied and industrially applied due to their excellent performance in the removal of suspended nanoparticles, bacteria, macromolecules, etc. [4,5]. To date, many polymers such as poly(vinylidene fluoride) (PVDF), polysulfone (PSf) and bromomethylated poly(phenylene oxide) (BPPO) have been used to produce UF membranes via a nonsolvent induced phase inversion method [6–9]. However, the inherent hydrophobicity of these commonly used polymer matrices usually induces a high tendency towards membrane fouling, which can diminish the separation performance and shorten membrane lifetime [10]. Additionally, the water flux of the current polymer membranes is relative low. Therefore, the development of high-performance UF membranes is highly desirable to improve the filtration efficiency and meet the industrial and environmental requirements [11,12].

To improve the membrane performance, hydrophilic inorganic materials, such as SiO₂, TiO₂, graphene oxide (GO), ZnO and their corresponding nanocomposites, have been incorporated into polymeric UF membranes to tailor the porous structure and other fundamental properties of membranes [13–18]. The obtained organic/inorganic hybrid membranes combine the advantages of both inorganic fillers and organic polymers, thus boosting membrane performance with an enhanced permeability and antifouling performance. However, the poor compatibility of inorganic particles with soft polymer matrices presents a major challenge in the fabrication of organic/inorganic hybrid membranes. Problems such as aggregation of nanoparticles, poor dispersion, and nonselective interface voids arise frequently, which may compromise the overall separation performance of the obtained membranes [19,20]. Meanwhile, the control of inorganic-particle size is also a challenge in making a good membrane [21]. In this case, the choice of inorganic nanoparticles plays a fundamental role in determining the filtration performance of hybrid membranes. Therefore, research on the design and preparation of novel and more favorable fillers to achieve high-performance UF membranes is highly critical and desirable.

⁎ Corresponding author.
E-mail address: peiyiwu@fudan.edu.cn (P. Wu).

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Recently, metal-organic frameworks (MOFs), which are composed of metal ions and bridging organic ligands, have emerged as promising fillers for fabricating MOF/polymer hybrid membranes [22,23]. Compared with those traditional inorganic materials, the main advantage of MOFs lies in their better compatibility with the soft polymer matrices due to the presence of organic ligands. Furthermore, the pore size/shape, surface properties, and particle size of MOFs can be readily tailored to suit the requirements for membrane fabrication and applications [24]. Zeolitic imidazolate framework-8 (ZIF-8) as a representative of MOFs has attracted the largest scientific interests due to its high porosity, and exceptional chemical and thermal stabilities [25,26]. These intrinsic advantages have led to its utilization in a broad range of applications, such as proton conduction [27], catalysis [28], gas separation [29], and drug delivery [30]. Water treatment is now considered as a new functionality of ZIF-8 benefiting from its porous structure which provides additional flow paths for water permeation [31]. For example, many independent researches show that the thin film nanocomposite (TFN) membranes incorporated with ZIF-8 for nanofiltration (NF) process presented a permeation increase [32–34]. These exciting developments show the significant advantages of ZIF-8 as fillers over traditional inorganic nanoparticles. Nevertheless, the development of hybrid UF membranes containing ZIF-8 lags behind in spite of the aforementioned advantages. This probably results from the hydrophobic nature of ZIF-8. The incorporation of ZIF-8 may do no help to membrane hydrophilicity and even compromises the phase inversion process, which adversely affects the permeation and antifouling properties of the obtained UF membranes. Besides, the operation pressure of UF membranes (0.1–0.3 MPa) usually is much lower than that of NF membranes, and at such a low operation pressure water molecules may hardly pass through the hydrophobic pores of ZIF-8 [35,36]. Therefore, although neat ZIF-8 possesses some good inherent physical and chemical properties, it may be unfavorable to be directly merged into polymers to fabricate UF membranes. Rationally modulating the compositional and morphological properties of ZIF-8 is highly desirable to truly unlock its potential for fabricating high-performance MOF/polymer hybrid UF membranes for water treatment.

In this study, hydrophilic hollow ZIF-8 (hZIF-8) was meticulously synthesized via the surface functionalization-assisted etching process by using tannic acid. Then, the obtained hZIF-8 was incorporated into PSf to prepare hybrid UF membranes via phase inversion. TA, a natural polyphenol consisting of large multiples of phenolic structural units, has been applied as a coating material for membranes by utilizing its hydrophilicity [37,38]. Most recently, TA has been proven to be an effective agent to create voids in MOFs with simultaneous surface modification because of its ability to coordinate with metal ions and weak acid property [39]. Meanwhile, the etching process did not alter the intrinsic frameworks when the process was carefully controlled. Thus, hZIF-8 may act as an outstanding filler for UF polymeric membranes and it is expected to possess several major advantages described as follows. First, the presence of TA on the surface of hZIF-8 could efficiently suppress the aggregation tendency of raw ZIF-8 and thus lead to a uniform structure of the hybrid membranes, which provides the basis for good performance. Second, the hydrophobic surface of ZIF-8 accordingly changed to hydrophilic. The high hydrophilicity of hZIF-8 benefited the hybrid membrane’s hydrophilicity and the formation of more porous structure as well. Third, the enhanced hydrophilic porous structure of hZIF-8 and the void created inside it were also essential for the high flux, which provided additional and preferential flow paths for water molecules. As a result, the permeability and antifouling performance of PSf/hZIF hybrid membranes were significantly improved without the serious sacrifice of rejection.

2. Experimental section

2.1. Materials

Commercial PSf polymer (Udel P3500) was supplied by Boji Co., Ltd. Zn(NO₃)₂·6H₂O, 2-methylimidazole (Hmim), TA were purchased from Aladdin. Methanol, N-Methyl-2-pyrrolidone (NMP), and bovine serum albumin (BSA) were provided by Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of ZIF-8 and hZIF-8

ZIF-8 nanoparticles were prepared according to the previously reported work [40]. In brief, Zn(NO₃)₂·6H₂O (2.97 g) and Hmim (2.46 g) were each dissolved in methanol (200 mL). Then the two solutions were mixed under vigorous stirring, followed by gently stirring at room temperature for 15 h. After that, white precipitates were collected and washed with methanol and dried for use. The obtained ZIF-8 nanoparticles were placed into TA solution (3 mg/mL) under stirring and aged for 7 min. The modified ZIF-8 was then collected by centrifugation and washed with water and methanol for several times. Finally, the product was lyophilized and stored in a desiccator. The typical synthesis procedure of hZIF-8 is demonstrated in Fig. 1.

2.3. Preparation of membranes

The UF membranes were prepared by a phase-inversion method as described in our previous works [41,42]. First, a given content of hZIF-8 based on the weight of PSf was dispersed in NMP and sonicated for 30 min. Second, PSf (12 wt%) was added into the above solution to form a homogeneous solution by stirring. The compositions of casting solutions for all membranes are listed in Table S1. Third, the mixture was further sonicated for 30 min and stirred for 5 h. After removing air bubbles, this solution was cast onto a glass plate. Then, the glass plate

![Fig. 1. Illustration of the synthesis process of hZIF-8.](image-url)
was immersed in deionized water bath at 30 °C immediately. After primary phase separation and membrane solidification, the membrane was transferred to a fresh water bath for 24 h to accomplish phase inversion. The resultant membranes were designated as PSf/hZ-X, where X (X = 1, 2 or 3) was the weight ratio of the hZIF-8 to PSf. For comparison, the recast PSf membrane and the hybrid membranes with 2 wt % ZIF-8 (PSf/Z-2) were also prepared via the same procedures.

2.4. Characterization of nanoparticles

The morphologies of as-prepared nanoparticles were observed using a transmission electron microscopy (TEM, JEOL JEM2100). Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 470) was used to analyze their chemical composition. X-ray diffraction (XRD) was conducted on a PANalytical X’Pert diffractometer. Thermogravimetric analysis (TGA) was carried out under N₂ atmosphere with a PerkinElmer thermal analyzer at a heating rate of 20 °C/min. The N₂ adsorption-desorption, BET surface areas and pore volumes of them were obtained by Micromeritics ASAP-2020 analyzer at 77 K. The Zeta potential of nanoparticles were characterized by Zetasizer Nano ZS90.

2.5. Characterisation of membranes

The surface composition of membranes was determined by X-ray photoelectron spectroscopy (XPS, PHI 5000 C). The viscosity of the casting solutions was measured using a rotational viscometer (NDJ-8S) at the shear rate of 10 S⁻¹ at the constant temperature of 25 °C. The surface morphology was observed with both field-emission scanning electron microscope (FESEM, Hitachi, S-4800) and atomic force microscopy (AFM, Multimode Nano 4, tapping mode) techniques. Surface pore size and pore size distribution of the membranes were calculated from their corresponding FESEM images at a larger magnification. The cross-sectional morphology was observed by FESEM mentioned above and the corresponding skin layer thickness was obtained from the magnified cross sections. Element analysis was measured by an energy-dispersive spectrometer (EDS) equipped by the aforementioned FESEM. The static water contact angles of the membranes were measured by OCA15 (Datapysics CO). The porosity of the membranes was determined by the classic gravimetric method described in other work [43]. The mechanical properties of the dry membranes were investigated using MTS mechanical tester (E43.104) at an extension rate of 2 mm/min.

2.6. Permeation and rejection measurements

The pure water flux and BSA rejection of membrane were measured using a cross-flow membrane module, as shown in Fig. S1. The efficient filtration area of the tested membrane (A) is about 26.2 cm². For the permeation test, each membrane was operated at 0.2 MPa for 20 min to achieve a steady flux. Then, the volume of the permeated pure water (V) and the operation time (t) were recorded at least three times. The pure water flux (F) could be calculated via the following Eq. (1):

\[ F = \frac{V}{A \times t} \]  

The rejection to BSA (R) was measured using 0.5 g/L BSA solution (pH = 7.4) at the same conditions. And the results can be calculated by the Eq. (2):

\[ R = 1 - \frac{C_f}{C_j} \]  

where, \( C_f \) and \( C_j \) were the concentrations of the permeation and feed solutions, respectively. They were determined by an ultraviolet-visible spectrophotometer (Lambda 35, PerkinElmer, USA) at 280 nm.

2.7. Antifouling measurements

Anti-fouling experiments were conducted via a method described in previous work [44]. The operation pressure here was 0.2 MPa during the whole process. First, deionized water was passed through the membranes for 60 min to obtain the pure water flux (\( J_1 \)). Second, 0.5 g/L BSA solution (pH = 7.4, PBS buffer solution) was used as the feed solution and filtrated for 60 min, and the flux for BSA solution (\( J_2 \)) was recorded. After this, the fouled membranes were washed with deionized water for 10 min. The pure water flux of cleaned membranes (\( J_f \)) was measured again. The flux recovery ratio (FRR), total fouling ratio (Rt), irreversible fouling ratio (Rr), and reversible fouling ratio (Rr) were calculated using the following Eqs. (3)-(6):

\[ \text{FRR} = \frac{J_2}{J_1} \]  
\[ \text{Rt} = \frac{J_1 - J_p}{J_1} \]  
\[ \text{Rr} = \frac{J_1 - J_2}{J_1} \]  
\[ \text{Rr} = \frac{J_2 - J_p}{J_1} \]  

3. Results and discussion

3.1. Characterizations of hZIF-8

The morphology of ZIF-8 and hZIF-8 was observed by TEM as shown in Fig. 2. In terms of the as-prepared ZIF-8, it shows the typical polyhedral shape with an average diameter of ca. 400 nm (Fig. 2a). The hollow structures in these ZIF-8 nanoparticles were created simply by mixing ZIF-8 and TA aqueous solution. As shown in Fig. 2b, the obtained hZIF-8 has the similar shapes and sizes to the raw ZIF-8 crystals, whereas the low contrast inside the nanoparticles indicates the success creation of voids inside each crystal, forming a hollow structure. A TEM image (Fig. 2c) at greater magnification reveals that the average shell thickness is ca. 25 nm. The formation of such a hollow structure can be explained by the proposed mechanism [39]. In principle, TA molecules can attach to the surface of ZIF-8 because of its ability to

![Fig. 2. TEM images of ZIF-8 (a) and hZIF-8 (b-c).](image-url)
coordinate with metal ions and change the surface of ZIF-8 from hydrophobic to hydrophilic. As a kind of weak organic acid, TA can release free H\(^+\), which is then able to penetrate into ZIF-8 and destroy its framework inside. While, the attached TA molecules with large molecular size can block the exposed surface of ZIF-8, thus protecting the outer parts of ZIF-8 from further etching. Finally, hollow MOF crystals with intrinsic crystalline frameworks can be obtained. The following characterization results of hZIF-8 can also certify such a mechanism to a certain extent.

The FTIR spectra of ZIF-8 and hZIF-8 are shown in Fig. 3a. In terms of ZIF-8, its FTIR spectrum exhibits the characteristic absorption peaks at 755 and 421 cm\(^{-1}\), which are assigned to the stretching vibration of Zn-O and Zn-N, respectively. The peak at 1177 cm\(^{-1}\) assigned to the C-N stretching vibration in the imidazole rings emerges in the spectrum of ZIF-8 as well\(^45\). The intensity of these peaks shows a little decrease in the spectrum of hZIF-8. Meanwhile, new peaks at 1701 and 3340 cm\(^{-1}\), most likely due to the C=O stretching of the carbonyl group and the O-H stretching, respectively, appear in the FTIR spectra of hZIF-8\(^46\). This result indicates the presence of TA on the surface of as-prepared hZIF-8.

TGA results of ZIF-8 and hZIF-8 are shown in Fig. 3b. Different from ZIF-8 which shows one decomposition stage, hZIF-8 consists of two weight loss stages. In addition to the decomposition of pure ZIF-8 phase from 450 °C, the first stage over the temperature from 250 to 400°C should be assigned to the removal of TA\(^47\). Since the catechol group has strong coordination capability with metal ions, it can be expected that the rich catechol moieties on TA molecule would act as anchoring sites to combine with Zn\(^{2+}\), which results in the coating of TA on the surface of ZIF-8. As a result, the characteristic peaks of TA energy in the FTIR spectrum of hZIF-8 and TGA results show the decomposition stage of TA. Fig. 3c illustrates the change of the zeta potential of ZIF-8 before and after etching. It is found that the zeta potential of ZIF-8 varies from positive to negative after etching. The significant zeta potential changes further confirm the existence of TA on the surface of hZIF-8. The presence of TA on the surface of hZIF-8 can also be manifested by a colour change from white for ZIF-8 to yellow-brown for hZIF-8 (Fig. S2). What's more, the adsorbed TA is expected to change the surface of ZIF-8 from hydrophobic to hydrophilic. As shown in Fig. S2, water droplets can be sustained on the ZIF-8 powder, whereas the water droplets could not reside on the hZIF-8 powder. It indicates the high hydrophilicity of hZIF-8, which is beneficial to the permeation of water molecules. The phase of the as-prepared ZIF-8 and hZIF-8 were determined by XRD. As shown in Fig. 3d, the typical diffraction peaks of ZIF-8 crystals are all found in the XRD pattern of hZIF-8, which means the intrinsic crystal framework of ZIF-8 is well maintained\(^48\). No impurities are observed after the formation of the hollow structure. However, these peaks become slightly broader, indicating partial amorphization caused by etching.

The porosity of hZIF-8 was investigated by a N\(_2\) sorption test and the results are shown in Fig. 4. It is found that the main microporosity of ZIF-8 is well maintained after etching since steady N\(_2\) adsorption can be observed at low relative pressure. Interestingly, an adsorption-desorption hysteresis loop emerges at high relative pressure, which suggests the generation of mesoporosity after etching (Fig. 4a). Pore size distribution analysis shown in Fig. 4b demonstrates the existence of mesopores with the pore size about 0.86 nm, which is bigger that of water molecules (0.28 nm). The parent ZIF-8 has a Brunauer-Emmett-Teller (BET) surface area of 1368 m\(^2\) g\(^{-1}\) derived from the N\(_2\) adsorption isotherms, while hZIF-8 exhibits a BET surface area of 957 m\(^2\) g\(^{-1}\), which is smaller than that of ZIF-8. This phenomenon should be attributed to the inevitably partial amorphization of ZIF-8 by etching, but well-controlled etching process here maintains most of its BET surface area\(^49\). In other words, the as-prepared hZIF-8 here not only obtains the hollow structure in its crystal but also inherits the initial porous framework of ZIF-8.
was well synthesized, and its hydrophilic surface and unique hollow porous structure make it an ideal filler for fabricating MOF/polymer hybrid UF membranes. It is believed that the unique properties of hZIF-8 can be transferred to the hybrid membranes, which will be of great benefit to the overall performance of the as-prepared PSf/hZ hybrid membranes.

### 3.2. Characterizations of PSf/hZ hybrid membranes

#### 3.2.1. Dispersion of hZIF-8 in the membrane matrix

One of the greatest challenges during the development of high-performance organic/inorganic hybrid membranes is the compatibility between inorganic fillers and polymer matrices. It is usually difficult to obtain homogeneous ZIF-8 dispersion by direct incorporation of raw ZIF-8 nanoparticles in a polymer solution due to its hydrophobic nature and/or strong interparticle interactions. Many pioneering studies have attempted to improve the dispersion of ZIF-8 in polymer membranes through various approaches \[50–53\]. Herein, XPS and EDS spectra were performed to determine the dispersion of fillers in the membranes. XPS spectra of PSf, PSf/hZ-2, and PSf/Z-2 membrane surfaces are given in Fig. 5. It is found that all the membranes have peaks for C 1s, O 1s, S 2p derived from the PSf polymer matrix. In comparison with PSf membrane, new characteristic peaks correspond to Zn 2p3 and N 1s show up in the XPS spectrum of PSf/hZ-2 and PSf/Z-2 membranes. It demonstrates the existence of fillers on the surface or in the skin layer of membranes. The chemical composition and the atomic percentage of the membrane surface calculated from XPS spectra are listed in Table 1. Interestingly, although the Zn content of hZIF-8 is lower than that of ZIF-8 after etching and functionalized process, it is observed that the Zn content of PSf/hZ-2 membrane (0.87%) is much higher than that of PSf/Z-2 membrane (0.41%), indicating more hZIF-8 located in the skin layer. It has been proven that the hydrophilic nanoparticles in the casting solution tend to migrate spontaneously towards the surface of corresponding hybrid membranes during the phase inversion process \[54,55\]. Hence, the hydrophilic hZIF-8 prefers to migrate to the top surface of the membrane and is more likely to be located in the top skin layer, which is advantageous to the amelioration of membrane hydrophilicity, permeability and antifouling properties. EDS was further applied to determine the elemental composition and characterize the dispersion of hZIF-8 in the cross section of membranes. The EDS mapping images of PSf/hZ-2 hybrid membrane (Fig. 6) illustrate that Zn and N elements originated from hZIF-8 are dispersed uniformly in the whole PSf matrix without obvious aggregation or gathering. Since TA molecules are attached to the surface of hZIF-8 and change the surface of ZIF-8 from hydrophobic to hydrophilic, the aggregation tendency of raw ZIF-8 is significantly reduced \[56\]. As a result, hZIF-8 presents a good distribution in the membrane matrix without apparent segregation or agglomeration.

#### 3.2.2. Morphology and structure of membranes

The cross-sectional FESEM images of the recast PSf membrane and hybrid membranes incorporated with hZIF-8 (with the content of 1, 2, 3 wt%) or ZIF-8 (with the content of 2 wt%) are shown in Fig. 7. All the membranes prepared by phase inversion possess a typical asymmetric structure, consisting a dense skin layer and a porous sublayer \[57\]. This structure arises from the higher mutual diffusivities of water and NMP during phase separation. The permeation and rejection of membranes are determined by the skin layer, whereas the sublayer mainly acts as mechanical support. According to Fig. 7(a–e), it is observed that the finger-like pores in the sublayer of PSf/hZ membranes turn to run through the cross-sectional structure and become wider, compared to those of the recast PSf and PSf/Z-2 membranes. Fig. 7(a1–e1) present magnified cross-sectional images of all prepared membranes. The thickness of the skin layer of PSf, PSf/hZ-1, PSf/hZ-2 and PSf/hZ-3 membranes marked in this figure (summarized in Table 2) is ca. 262, 219, 156 and 187 nm, respectively. This tendency of the thickness affected by mixing with nanocomposites was also reported by other work.

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**Table 1**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Atomic percent (at%)</th>
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<tr>
<td></td>
<td>C 1s</td>
</tr>
<tr>
<td>PSf</td>
<td>78.71</td>
</tr>
<tr>
<td>PSf/hZ-2</td>
<td>76.09</td>
</tr>
<tr>
<td>PSf/Z-2</td>
<td>74.79</td>
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![Fig. 4. N2 adsorption-desorption isotherms (a) and pore-size distribution (b) of ZIF-8 and hZIF-8.](image)

![Fig. 5. XPS spectra of PSf, PSf/hZ-2 and PSf/Z-2 membranes.](image)
These results are well consistent with the porosity of the membranes shown in Table 2. And PSf/hZ-2 hybrid membrane exhibits the highest porosity up to 71.4%. It is well-known that the incorporation of hydrophilic nanoparticles into casting solution can accelerate the water (non-solvent) inflow during phase inversion, resulting in a more porous structure [59]. Due to the presence of TA on its surface, hZIF-8 exhibits high hydrophilicity. Therefore, the incorporation of hZIF-8 leads to the fully developed finger-like pores in sublayer and the decline in the skin layer thickness. Nonetheless, the viscosity of the casting solution significantly increases when the loading of hZIF-8 is beyond 2 wt% (Table S1), which decreases the mass transfer rate of non-solvent, thus giving rise to an enhanced thickness of the skin layer in PSf/hZ-3 hybrid membrane. Conversely, the incorporation of raw ZIF-8 kind of suppresses the exchange rate during the coagulation process due to its hydrophobic nature, thus forming a poorly developed finger-like sublayer and a relatively thicker skin layer in comparison with the other membranes.

Membrane surface morphology also plays an important role in determining the flux. A rough surface commonly leads to an increase in efficient filtration area, thereby benefitting the improvement of the permeability [60,61]. AFM is used to investigate the roughness of the membrane surface, as demonstrated in Fig. 8(a2-e2). According to the AFM images and the corresponding roughness parameters presented in Table 2, the surface roughness of all the hybrid membranes, employing Rq and Ra, displays a slightly increasing trend compared with that of the recast PSf membrane. The PSf/hZ-2 membrane shows the roughest surface. The increased roughness of hybrid membranes probably is due to the fast exchange rate between NMP and water during the coagulation process and the existence of hZIF-8 in the skin layer of the membrane. Nevertheless, the PSf/hZ membrane at the filler loading of 3 wt% exhibits relatively smoother surface in comparison with PSf/hZ-2 membrane due to the slow phase inversion process. As expected, the roughness of PSf/Z-2 membrane is lower than that of PSf/hZ-2 membrane but higher than that of recast PSf membrane because of the hydrophobic property of raw ZIF-8. These results are consistent with the morphologies by FESEM images, as shown in Fig. 8(a1-e1). Although the rough surface may potentially increase the fouling propensity, the enhanced surface area induced by incorporating hZIF-8 is beneficial for a higher water flux.

The surface pore diameter distribution calculated from the FESEM images at the larger magnification (Fig. 8(a3-e3)) for each membrane is shown in Fig. 8(a4-e4). It can be seen that all membranes have average porosity, mean pore size, skin layer thickness, and the surface roughness of the membranes.

![Fig. 6. FESEM and corresponding element mapping images of PSf/hZ-2 hybrid membrane and EDS showing the presence of C, O, S, Zn and N elements.](image)

![Fig. 7. The cross-sectional FESEM images of PSf (a, a1), PSf/hZ-1 (b, b1), PSf/hZ-2 (c, c1), PSf/hZ-3 (d, d1) and PSf/Z-2 (e, e1) membranes.](image)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Porosity (%)</th>
<th>Mean pore size (nm)</th>
<th>Skin layer thickness (nm)</th>
<th>Rq (nm)</th>
<th>Ra (nm)</th>
</tr>
</thead>
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<tr>
<td>PSf</td>
<td>61.2 ± 2.3</td>
<td>7.94 ± 0.3</td>
<td>262 ± 13</td>
<td>12.6</td>
<td>10.2</td>
</tr>
<tr>
<td>PSf/hZ-1</td>
<td>66.5 ± 1.6</td>
<td>8.93 ± 0.4</td>
<td>219 ± 13</td>
<td>15.0</td>
<td>12.3</td>
</tr>
<tr>
<td>PSf/hZ-2</td>
<td>71.4 ± 2.1</td>
<td>10.11 ± 0.6</td>
<td>156 ± 1</td>
<td>17.8</td>
<td>14.3</td>
</tr>
<tr>
<td>PSf/hZ-3</td>
<td>68.8 ± 1.5</td>
<td>9.39 ± 0.4</td>
<td>187 ± 19</td>
<td>16.8</td>
<td>13.1</td>
</tr>
<tr>
<td>PSf/Z-2</td>
<td>59.2 ± 1.8</td>
<td>7.80 ± 0.9</td>
<td>295 ± 8</td>
<td>13.7</td>
<td>11.1</td>
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surface pore sizes in the range of 3.5–17.5 nm. The surface pore diameter distributions of the PSf/hZ-1 and PSf/hZ-2 membranes are shifted toward larger pore diameter values compared with that of PSf membrane. Quantitatively calculation results of average surface pore size are shown in Table 2. It is found that the average pore diameter is increased from 7.94 nm for PSf membrane to 10.11 nm for PSf/hZ-2 membrane. During the phase inversion process, hydrophilic hZIF-8 nanoparticles, with higher affinity to water than the PSf matrix, increase the diffusion velocity of the non-solvent near to the membrane, thereby facilitating the formation of large pores[61]. Nevertheless, the surface average pore size falls down when the content of hZIF-8 is up to 3 wt%. This should be attributed to the increased viscosity of the casting solution with the addition of hZIF-8 (Table S1). To be specific, the formation of hydrogen bonding between the abundant exposed hydroxyl groups on the surface of hZIF-8 nanoparticles and the sulfonyl and ether groups of the PSf chain hinders the mobility of polymer chains, thus hindering the formation of membrane pore [62]. In terms of the PSf/Z-2 membrane, the introduction of raw ZIF-8 doesn’t result in the increment of pore size, which should be attributed to the hydrophobic nature of raw ZIF-8.

3.2.3. Hydrophilicity and filtration properties of membranes

Although ZIF-8 shows obvious advantages over traditional inorganic nanoparticles due to its high porosity, it isn’t advisable to directly hybrid raw ZIF-8 with polymers to prepare membranes for water treatment due to its hydrophobic nature which may adversely affect the overall performance of as-prepared hybrid membranes [63,64]. Therefore, the study of the influence of hZIF-8 on the surface hydrophilicity of as-obtained membranes is of paramount importance for water treatment. In order to accurately verify the hydrophilicity of the obtained membranes, the water contact angle of membranes is measured and shown in Fig. 9. It is found that the PSf/Z-2 hybrid membrane shows the highest contact angle of 79.8°, which is slightly higher than that (78.6°) of the pristine PSf membrane. This indicates that the incorporation raw ZIF-8 does have a negative influence on the amelioration of membrane hydrophilicity. Interestingly, the improved hydrophilicity of membranes is easily realized after the incorporation of hZIF-8 according to the water contact angle of PSf/hZ hybrid membranes. It is found that the incorporation of hZIF-8 leads to an obvious decrease of the water contact angle to 70.1°, 62.4° and 60.7°, respectively, when 1, 2 and 3 wt% hZIF-8, is embedded. It demonstrates the great promotion effect of hZIF-8 on membrane hydrophilicity due to the presence of TA on its surface. Consequently, the improved hydrophilicity undoubtedly will benefit the water permeation and antifouling performance (discussed later).

The results of membrane filtration performance concerning the pure water flux and BSA rejection are summarized in Fig. 10. It is found that the pure water flux of PSf/hZ membranes gradually increases from 210 L m⁻² h⁻¹ for the pristine PSf membrane to a maximum (597 L m⁻² h⁻¹) for PSf/hZ-2 membrane with the increased loading of
hZIF-8 at the range of 0–2 wt%. The rejection rates of these PSf/hZ hybrid membranes decrease slightly with the incorporation of fillers derived from the larger mean pore size and more porous structure, still staying at a relatively high level (> 98%). The water permeability along with the BSA rejection of PSf/hZ-2 membranes demonstrates significant advantages over most of hybrid UF membranes reported in the previous works (Table S3). The improvement of PSf/hZ hybrid membranes in water flux should be attributed to the well-tailored chemical composition and nanostructure of hZIF-8. On the basis of above discussion about the various properties of membranes, we postulate that the following main factors jointly contribute to the enhanced water permeability. First, the coated TA on the surface of hZIF-8 could efficiently suppress the aggregation tendency of raw ZIF-8, which leads to an even dispersion of hZIF-8 particles in PSf casting solution and thus a uniform structure of PSf/hZ hybrid membranes. This is the crucial precondition of obtaining a high-performance MOF/polymer hybrid UF membranes. Second, the high hydrophilicity of hZIF-8 not only accelerates the phase inversion of PSf/hZ hybrid membrane during the coagulation process, endowing the hybrid membrane with highly porous structures and larger surface pore size but also helps to enhance the hydrophilicity of membranes. These greatly reduce the flow resistance, thus being beneficial to the water permeation. Third, the hydrophilic porous and hollow structure of hZIF-8, as well as the tiny interspaces, provide additional and preferential flow paths for water molecules to easily pass through. Last but not least, the rougher surface is also beneficial for a higher water flux. Hence, the enhanced hydrophilicity, together with the more porous structures, the rougher surfaces, and the additional flow passageways, enable the PSf/hZ membranes to present superior water flux than the other controlled membranes. However, when the loading of hZIF-8 reaches 3 wt%, the flux of PSf/hZ hybrid membranes no longer increases, which should be attributed to the increased viscosity of the casting solution (Table S1). The formation of hydrogen bonding between the abundant exposed hydroxyl groups on the surface of hZIF-8 nanoparticles and the sulfonyl and other groups of the PSf chain hinders the mobility of polymer chains, thus suppressing the exchange between solvent and non-solvent, and the hybrid membrane turns out to present a smoother surface and a less porous structure, which results in a decrease in water flux [65,66].

According to these results of PSf/Z-2 membrane, it is found that the incorporation of raw ZIF-8 almost does no help to the permeation improvement, which is accorded with the above discussion about its surface morphology, surface hydrophilicity properties, overall porosity, and mean pore size, along with a worst BSA rejection. As is well known, the compatibility of fillers in polymer matrices plays an important role in the selectivity of separation membranes. Due to the strong agglomeration tendency of raw ZIF-8 that comes from the hydrophobic nature and/or strong interparticle interactions, the dispersion of raw ZIF-8 in PSf matrix is not good enough, thus resulting in the formation of non-selective voids [34,49]. Ultimately, the rejection of PSf/Z-2 membrane declines obviously. After being etched and modified with TA, the surface of ZIF-8 transfers to hydrophilicity and the interactions are reduced, and a better dispersion of MOF in PSf can be obtained. However, it should not be ignored that the resultant PSf/hZ membranes show relatively larger mean pore sizes. As a result, the BSA rejection of PSf/hZ hybrid membrane slightly decreases, but still stay at a relatively high level.

In the practical industrial application of the membranes, the operational stability is an essential parameter for the composite membranes [67]. As shown in Fig. S2, the pure water flux of PSf/hZ-2 membrane first decreases slightly and then stabilizes at 0.2 operation pressure in the 7-day duration, clearly indicating that the prepared composite membranes possess great potential for long-time operation. This also indicates that the hZIF-8 possesses good stability during the UF process for water treatment. Conclusively, these results demonstrate that the reasonably designed and synthesized hZIF-8 is an ideal and favorable filler for fabricating hybrid UF membranes and the water permeability and rejection of the hybrid membranes could be effectively tailored through the incorporation of hZIF-8.

3.2.4. Antifouling performance of membranes

Antifouling performance is another important factor for evaluating the application potential of membranes in water treatment [68]. The process of membrane fouling is very complicated and is primarily caused by the protein adsorption derived from the combination of electrostatic interaction, hydrogen bonding, hydrophobic impact and van der Waals forces. Membrane fouling is harmful to the membrane permeability, filtration stability, and maintenance cost [69]. Great efforts have been devoted to enhancing the antifouling ability of membranes [70]. Therefore, the fouling behavior of the as-prepared membranes here (with 2 wt% fillers) is investigated using dynamic filtration experiments and a BSA solution (pH = 7.4) is chosen as a model protein. Fig. 11a shows the typical time-dependent fluxes of different membranes in the three cycles of BSA solution filtration. It is found that the permeation flux of all the tested membranes declines sharply when deionized water is replaced by the BSA solution. This phenomenon mainly results from the membrane fouling and concentration polarization. Even after rinsing with pure water, the permeation flux of all the membranes can’t recover to their initial values due to the obstinate fouling.

To investigate the antifouling performance more specifically, the flux recovery ration (FRR) and fouling resistance ratio (Rc, Rf, and Rr) are introduced and calculated, as illustrated in Fig. 11b. Generally, a higher FRR represents a better antifouling property of the membrane. As can be clearly seen in Fig. 11b, FRR of the recast PSf membrane is as
The hydrophilic nature of ZIF-8 should be responsible for this phenomenon. This result further reveals that raw ZIF-8 is not favorable enough to be directly utilized to fabricate hybrid UF membranes for water treatment membranes. However, the FRR of PSf/hZ-2 hybrid membrane is as high as 81.1%. More specifically, the $R_c$ of PSf/hZ-2 membrane considerably reduces from 36.0% for recast PSf membrane to 18.7%. In irreversible fouling, the foulants are tightly attached to the membrane and are difficult to be removed by facile washing. This result further indicates that PSf/hZ-2 membrane has an excellent antifouling property. We speculate that it results from the more hydrophilic surface of the PSf/hZ membranes which suppresses protein adsorption. In addition, the more negatively charged PSf/hZ membranes due to the incorporation of negative ZIF-8 give rise to the higher electrostatic repulsion against negative charged BSA, which also plays an ignored role in the better antifouling performance of PSf/hZ membranes [71,72]. As a result, the antifouling performance of PSf/hZ membranes is greatly improved benefited from the more hydrophilic and more negative charged membrane surface even though it exhibits relatively rougher surface. What’s more, the flux recovery of the PSf/hZ-2 composite membrane is good and stable even after the long-term antifouling tests (Fig. S4), which implies its excellent stability of the antifouling performance during the long-term operation. Collectively, these results suggest that the PSf membrane doped with hZIF-8 possesses a fairly favorable antifouling performance, showing the significant application potential in practical water purification.

3.2.5. Mechanical properties of membranes

The mechanical strength of UF membranes is a key factor to evaluate their practical application potential [73]. Thus, we examined the mechanical strength of all the as-prepared membranes by testing their tensile strength, Young’s modulus, and elongation at break. The representative stress-strain curves for the membranes are plotted in Fig. 12 and the corresponding mechanical property data are listed in Table S2. It is found that the incorporation of raw ZIF-8 nanoparticles sharply decreases the elongation of the PSf membrane from 15.0% to 7.6% with similar tensile strength, indicating that the membrane becomes fragile. This is consistent with the generally accepted conclusion that the incorporation of foreign component in UF membranes will cause the decline of the toughness of membranes [74,75]. Nevertheless, the tensile strength and elongation of the PSf/hZ-2 composite membrane increase slightly to be 1.51 MPa and 19.3% as compared to the recast PSf membrane. It indicates that the incorporation of an appropriate amount of hZIF-8 nanoparticles could contribute to the improvement of the mechanical strength of membranes. This can be attributed to the homogenous distribution of hZIF-8 in PSf membrane and the formation of hydrogen bonding between the abundant exposed hydroxyl groups on the surface of hZIF-8 nanoparticles and the sulfanyl and ether groups of the PSf chain [76].

4. Conclusions

In this work, hydrophilic hollow ZIF-8 (hZIF-8) was synthesized first, and then incorporated into PSf to prepare hybrid UF membranes via phase inversion method. As confirmed by a series of characterizations, TA used as etching agent not only endowed hZIF-8 with highly hydrophilic surface and unique hollow structure, but also did not alter the intrinsic frameworks, thus enabling the design and fabrication of high-performance UF membranes for water treatment. Thanks to the well-tailored surface property and nanostructure of hZIF-8, the obtained PSf/hZIF hybrid UF membranes exhibited significantly improved water permeation without sacrificing rejection property in comparison with the recast PSf membrane or the hybrid membrane containing raw ZIF-8. Meanwhile, the incorporation of hZIF-8 significantly enhanced the membrane’s resistance to fouling. The present study has provided a promising avenue for fabrication of high-performance membranes with the incorporation of other rationally designed MOFs for water treatment and will stimulate further development in near future.

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References


Appendix A. Supporting information

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