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ARTICLE

Metal based gel as versatile precursor to synthesize stiff and integrated MOF/polymer composite membrane

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Great progresses have been made in metal-organic framework membrane recently. However, preparation of stiff and integrated MOF/polymer membrane still remains a big issue. Herein, metal based gel as versatile precursor was first employed to prepare continuous and integrated MOF/polymer hollow fiber membranes. The metal based gel was put in/on various polymer substrates adequately, which can be transformed into pure MOF crystals and lead to formation of continuous MOF crystals on the surface and in the pore of hollow fiber easily. By using this method, we can not only fabricate continuous MOF membranes without conventional activation step but also greatly enhance the stiffness of membrane through mutual support of MOFs and substrates. The strategy also has appropriate level of generality which can be used for preparation of inter-grown MOF membranes on different kinds of substrates. The prepared membranes exhibited excellent gas separation performance with H₂/N₂ separation factor as high as 22.7.

Introduction

Since metal-organic frameworks (MOFs) possess many extraordinary properties such as large surface areas, controlled pore structure and tunable sorption behaviour,¹⁻³ MOF based membranes prepared by in situ growth, secondary seeding growth, chemical modification, counter diffusion and other methods have been developed successfully in recent five years.⁴⁻¹⁰ Compared with most traditional separation processes, MOF membrane separation techniques prove to be economical and environmentally friendly, and present great potential in H₂ energy, CO₂ capture and other various applications.^{4,11-15}

According to the difference in substrates, MOF membranes can be mainly classified into three categories as follows: (1) Free-standing MOF membranes.¹⁶⁻¹⁷ They are formed without the substrates. Because of that, these membranes will display the risk in long-term separation application.¹⁸ (2) MOF membranes supported by inorganic substrates, the substrates are usually inorganic materials such as alumina, titanium dioxide and metal net.^{7,19-24} For these membranes, the relatively high price, fragility in materials and difficulties in the fabrication of inorganic substrates might hinder their further development. (3) MOF membranes supported by polymer substrates. Compared with the inorganic substrates, polymer membranes show the low cost, large membrane area and considerable ease of fabrication.²⁵⁻²⁶ Therefore, polymer supported MOF membranes have received extensive attentions for gas separation.²⁵⁻²⁸

However, MOF/polymer composite membranes usually have obvious structural weakness due to the flexibility of polymer substrates. Under hydrostatic compression, if deformation of polymer substrate happens, the crack in MOF layer will be produced. Therefore, the stiffness of MOF/polymer composite membranes is

desired to improve urgently. In our recent study, we have developed a practical method to improve the stiffness of MOF membranes supported by polymer substrates. Based on special cyclization and crosslinking reaction of polyacrylonitrile (PAN) molecules, stiff Cu₃(BTC)₂/PAN hollow fiber composite membranes were fabricated successfully.²⁸ But this method was limited for MOF/PAN composite membranes. Considering the natural rigidity of MOF crystals, we envisage that, if the crystals can be impregnated into the flexible polymer substrate, the rigid particles and substrate will support each other by mutual supporting, and therefore can greatly improve the mechanical stability of MOF/polymer composite membrane.^{10,29-30}

On the basis of the above assumption, we go forward to design different metal based gels to grow MOF particles in the pores of the substrate and apply the mutual support for preparation of highly stiff MOF/polymer composite membranes. Our method may have the following features. First, sol-gel method is straightforward and has been widely used in the fabrication of coating layers and polymer membranes,³¹⁻³² thus the synthesis process of using the sol-gel to fabricate MOF membrane can be greatly simplified, omitting the complex preparation and deposition process of the MOF seeds.³³⁻³⁴ Second, deposition of metal based gel on the substrate does not rely on the chemical properties of substrate, the metal based gel can be used for different kinds of substrates.³⁵⁻³⁶ Third, in comparison with some metal oxide precursors in solid state,^{6,37-38} which can also be used to prepare MOF membranes after complex activation steps, yet, the instability of gel state and the containing active groups may make it easier to transform into the MOF crystals without any activations.^{31,39-40} Fourth, most importantly, different from the conventional methods by growing the MOF layers only at the surface of polymer substrate, which possibly endow the poor stability of MOF layers due to the distortion of elastic substrate

under high pressure, the metal based gel can be impregnated into the polymer substrate adequately and contribute to the growth of the MOF particles in the pore simultaneously. By combining with the MOF layer on the surface, the stiffness of MOF/polymer composite membranes can be greatly increased.

In the present work, the metal based gel was impregnated in/on the polymer hollow fibers and transformed into pure MOF crystals to form stiff composite hollow fiber membranes (Fig. 1). To the best of our knowledge, there is no report about using metal based gel to prepare continuous and well-intergrown MOF membranes. Moreover, according to the mechanism of this method, we can prepare the intergrown MOF membranes on different substrates such as polyethersulfone (PES), polyvinylidene fluoride (PVDF), polysulfone (PSF) and polyacrylonitrile (PAN) hollow fibers. Further, the prepared stiff ZIF-8/PES composite membranes showed an excellent gas separation performance.

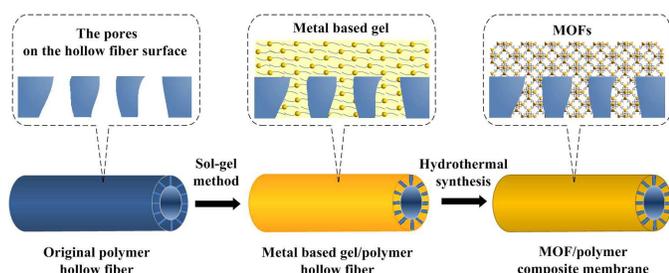


Fig. 1 Scheme of preparation of the MOF/polymer composite membrane by metal based gel.

Results and discussion

Characterization of zinc based gel/PES hollow fiber and ZIF-8/PES composite membrane

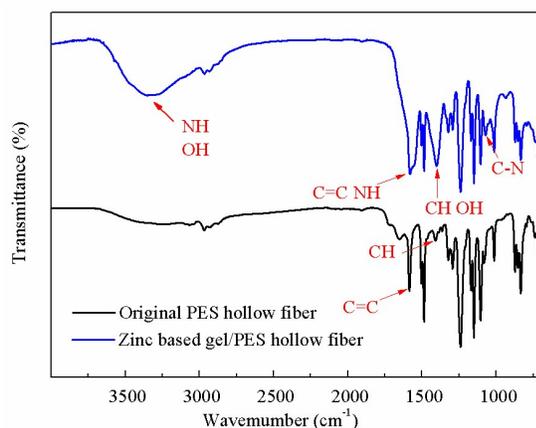


Fig. 2 FTIR spectras of the original PES and zinc based gel/PES hollow fiber.

ZIF-8 was used as the target due to their excellent thermal and chemical stability. First, the zinc based gel was prepared through the sol-gel procedures. The synthetic reactions of the zinc based gel are shown in the Electronic Supplementary Information.⁴¹ The zinc based gel not only consists of the zinc and polymer chains, but also contains the active amino groups (-NH-). The XRD patterns demonstrate that the prepared zinc based gel is amorphous (Fig. S1, ESI†). Since the hydroxyl groups of zinc based gel in the molecular chain can weakly change the average intersegmental spacing of the

PES polymer chains,⁴² the prominent peak shows a shift from $2\theta = 17.8$ to 22.5 after the zinc based gel impregnation. The FTIR spectra analysis of the zinc based gel/PES hollow fiber was also conducted and the results are shown in Fig. 2. After gel-filling, it can be noted that the peaks at around 1402 , 1580 and 3349 cm^{-1} increase distinctly due to the -OH or -NH- bands in the zinc based gel. Concomitantly, another characteristic peak of the zinc based gel appears at 1071 cm^{-1} from the C-N band. These evidences imply that the zinc based gel has been prepared in/on the PES hollow fiber. From the SEM images, we can find that a corrugated and continuous zinc based gel layer covers on the PES hollow fiber surface (Fig. 3a and c). The cross section images show that the spongy layer of PES hollow fiber is totally filled by the zinc based gel (Fig. 3b and d), and the thickness of the gel/polymer composite layer is about $40\mu\text{m}$.

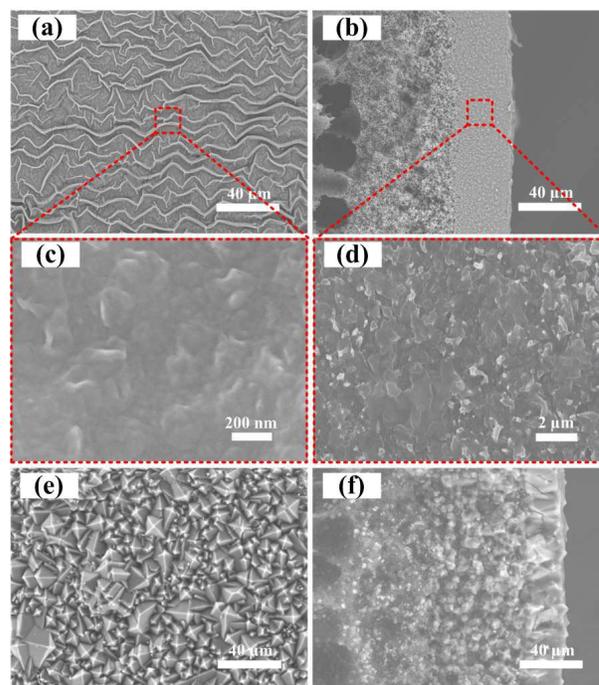


Fig. 3 (a,c,e) Top and (b,d,f) cross section view SEM images of (a-d) Zinc based gel/PES hollow fiber and (e,f) ZIF-8/PES composite membrane.

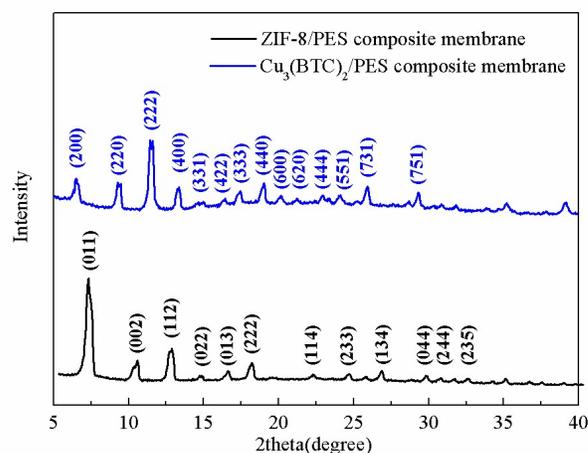


Fig. 4 XRD patterns of the ZIF-8/PES composite membrane and $\text{Cu}_3(\text{BTC})_2/\text{PES}$ composite membrane.

After preparation of the zinc based gel/PES hollow fiber successfully, the ZIF-8/PES composite membrane was prepared. The peak positions of XRD pattern reveals the pure ZIF-8 crystalline structure and proves the successful preparation of ZIF-8 membrane (Fig. 4). As shown in Fig. 3e, the ZIF-8 layer can be observed obviously without any visible gaps or cracks. Fig. 3f reveals that ZIF-8 crystals connect with the hollow fiber surface uniformly and tightly, and the thickness of continuous ZIF-8 membrane is about 20 μm . It should be noted, that a large quantity of ZIF-8 crystals are produced inside the spongy layer of hollow fiber, which simultaneously construct an integrated ZIF-8 composite hollow fiber membrane and improve the mechanical property of the membrane.¹⁰

The roles of zinc based gel

We attempted to investigate the permeation property of the zinc based gel/PES hollow fiber. It was found that no gas can go through the dense zinc based gel. In contrast, the ZIF-8/PES composite membrane showed a high hydrogen permeance. This result combining with the phenomenon that vast ZIF-8 particles formed at spongy layer indicated that the zinc based gel was fully transformed into ZIF-8 crystals after solvothermal treatment (Fig. 3 and Fig. S2, ESI[†]). This feature can be explained by the following several aspects. First, as an instable state between sol and solid particle, zinc based gel could directly coordinate to 2-methylimidazole and transform into ZIF-8 crystals, promoting the continuous MOF layer growth. Moreover, the active amino groups (-NH-) in the zinc based gel could interact with the free metal cations, which would further react with the organic links in the synthesis solution and thus facilitate the formation of well-inter-grown crystals.⁴³ To demonstrate the importance of the zinc based gel directly, we attempted to synthesize the ZIF-8/PES composite membrane without zinc based gel under same condition. As expected, the ZIF-8 crystals were non-continuous since there were no abundant heterogeneous nucleation sites on the substrate (Fig. S4, ESI[†]).

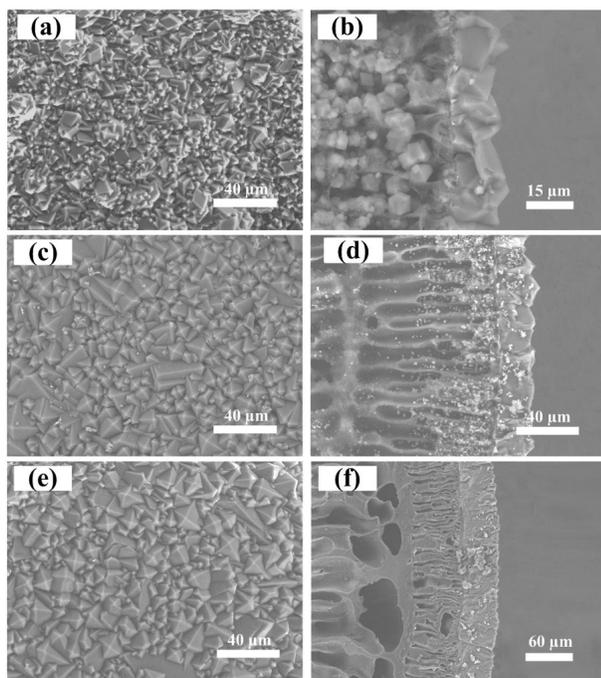


Fig. 5 SEM images of the ZIF-8/polymer composite membranes: (a,b) ZIF-8/PVDF, (c,d) ZIF-8/PSF and (e,f) ZIF-8/PAN.

In order to demonstrate the general applicability of our methods, some other polymer hollow fiber substrates, such as PVDF, PSF and PAN, were also exploited to prepare ZIF-8/polymer composite membranes. From the SEM images (Fig. 5), we can find, no matter what the substrate is, the compact and intergrown ZIF-8 layer can always be obtained. However, there are also some differences between these membranes. The ZIF-8/PAN composite membrane possesses the thickest MOF layer, about 40 μm . This can be attributed to the strongly polar (-CN) groups of PAN molecules exhibits a good adsorption for the 2-methylimidazole.⁴⁴ We also find that the formed ZIF-8 crystals in the pore of the PVDF and PES are much more than the PSF and PAN hollow fibers. The reasons for this phenomenon are described as follows. Different from the finger-like structure of PSF and PAN hollow fibers, PES hollow fiber has the spongy layer near to the outer surface. This spongy structure, with larger specific surface area, can adsorb more zinc based gel in the sol-gel process and promote the formation of ZIF-8 crystals in the pores. The PVDF hollow fiber does not possess the spongy structure, but it is the microfiltration membrane, which has the larger aperture and will also soak up more gel in the pores. Meanwhile, we also investigated the growth of ZIF-8 membranes without zinc based gel on these substrates. And the result is similar to the PES that the poorly continuous ZIF-8 crystals were dispersed on the fiber surfaces (Fig. S5, ESI[†]). It should be noted that our method was not only limited to the ZIF-8 membrane synthesis. Besides the zinc based gel, we also attempted to fabricate the copper based gel and then apply it to fabricate $\text{Cu}_3(\text{BTC})_2$ membrane. The results demonstrated that a well inter-grown $\text{Cu}_3(\text{BTC})_2$ membrane can be obtained (Fig. S1, S6 and S7, ESI[†]).

The compressive property of the ZIF-8/PES composite membrane

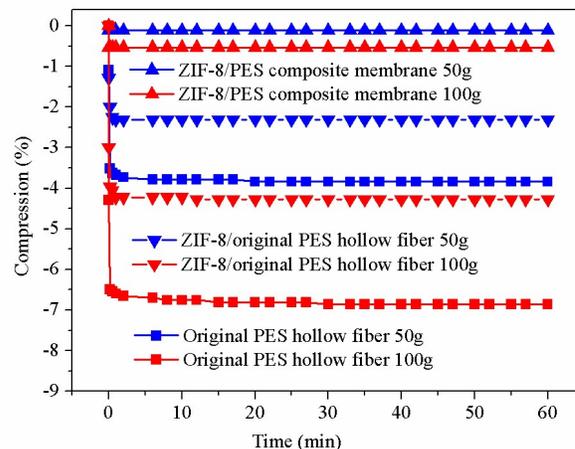


Fig. 6 The compression of the ZIF-8/PES composite membrane, ZIF-8/original PES hollow fiber (ZIF-8 membrane grown on the original PES hollow fiber) and the original PES hollow fiber at different pressures as time increases.

As mentioned above, the stiffness of MOF membranes is very important for the practical application. The most MOF crystals display a big hardness value in the range of 0.1 to 2 GPa, however, they usually exhibit low stability against shear stress, especially for the continuous MOF layers.³⁰ Therefore, the polymer supported MOF membranes should have large hardness to prevent the deformation of MOF layers. In order to test the stiffness of the synthesized composite membrane, as our previous report,²⁸ the

membranes were placed between the sheet steels under a constant pressure to obtain the change amount of the diameter with times. Fig. 6 displays that the diameter variations of the ZIF-8/PES composite membrane were much smaller than those of the original PES hollow fiber and ZIF-8 membrane grown on the original PES hollow fiber. When the pressure was 50 g, the original PES hollow fiber rapidly compressed, and the diameter compression was 3.84%. As the pressure added up to 100 g, the diameter compression further increased to 6.86%. For the ZIF-8 membrane grown on the original PES hollow fiber, the diameter compression slightly reduced to 2.31% and 4.27%, respectively. However, the diameter of the ZIF-8/PES composite membrane had almost no change. This experiment strongly demonstrates that the produced MOF crystals in the pores of the fiber could enhance the stiffness and compression strength of the MOF/polymer composite membrane.

Gas permeation of the ZIF-8/PES composite membrane

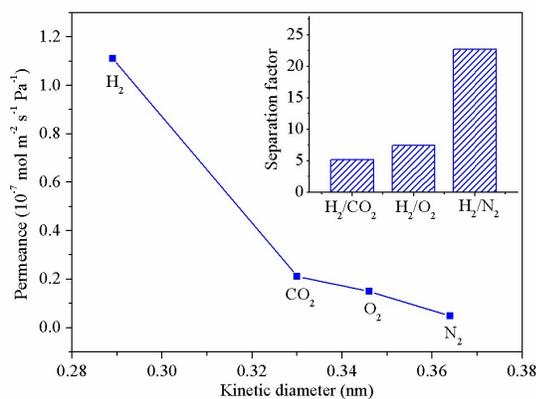


Fig. 7 Single gas permeances of the ZIF-8/PES composite membrane as a function of kinetic diameter at 20 °C. The insert shows the separation factors for H₂ over other gases.

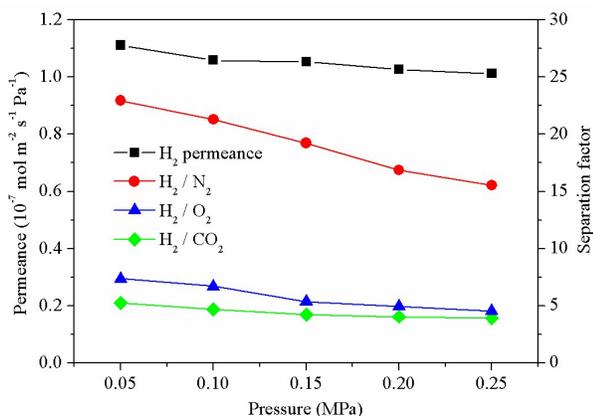


Fig. 8 H₂ permeance and separation factors of the ZIF-8/PES composite membrane as a function of pressure at 20 °C.

After the membrane was fabricated successfully, the H₂, CO₂, O₂ and N₂ gas permeation properties of the ZIF-8/PES composite membrane were investigated. Fig. 7 displays single gas permeances of the ZIF-8/PES composite membrane as a function of kinetic diameter at 20 °C and 0.05 MPa. As shown in Fig. 7, the membrane possesses remarkable higher H₂ permeance of $1.11 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ compared with other

gases of CO₂, O₂ and N₂, and the order of gas permeances is clearly decided by their kinetic diameter, H₂ (0.289 nm) > CO₂ (0.33 nm) > O₂ (0.346 nm) > N₂ (0.364 nm). As reported, the theoretical pore size of ZIF-8 membrane is 0.34 nm, the real pore size for gas penetration is measured about 0.40–0.42 nm because of the well-known lattice flexibility, so the O₂ and N₂ can also pass through the membrane.^{4,45} The separation factors of H₂/CO₂, H₂/O₂ and H₂/N₂ are 5.2, 7.4 and 22.7, respectively, which are much larger than the corresponding Knudsen constant (4.7, 4.0 and 3.7, respectively), indicating that the membranes are well-intergrown and free of cracks. Additionally, in comparison with other polymer supported MOF membranes in the literatures (Table S2, ESI[†]), the ZIF-8/PES composite membrane prepared in this work shows excellent gas separation performance which obviously surpasses the Robeson upper bounds (Fig. S8, ESI[†]). Moreover, the Cu₃(BTC)₂/PES, ZIF-8/PVDF, ZIF-8/PSF and ZIF-8/PAN composite membranes also show the acceptable performances (Table S3, ESI[†]).

High stiffness is crucial for the polymer supported MOF membranes applied in high feed pressure.²⁸ To further investigate the mechanical stability of the synthesized MOF membrane, the permeation test under different pressures were carried out. With the feed pressure increasing from 0.05 to 0.25 MPa, the H₂ permeance decreased slightly, and that of other gases increased, leading to the separation factors drop with elevated pressure (Fig. 8). As reported in other literatures, ZIF-8 crystals filled by adsorbed hydrogen molecular could generate high occupancy-dependent diffusion resistance at higher pressure.⁴⁶ Hence, the slight decrease of hydrogen permeance was appeared in our research when the feed pressure was increased. Even so, the membrane still shows the excellent separation performance under high feed pressure, with H₂ permeance of $1.01 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and H₂/CO₂, H₂/O₂ and H₂/N₂ separation factor of 3.9, 4.5 and 15.5, respectively. This indicates that the membrane has the great mechanical stability.

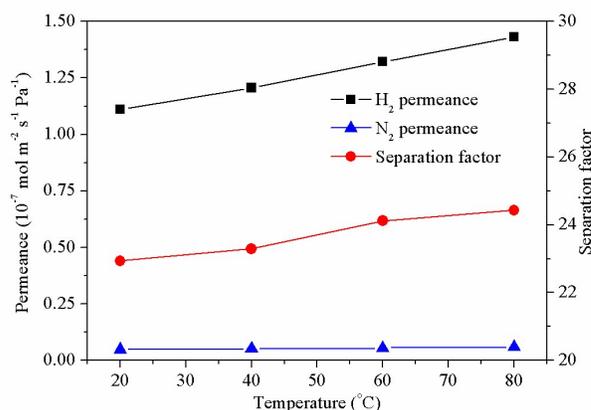


Fig. 9 Gas permeances and separation factor of the ZIF-8/PES composite membrane as a function of temperature at 0.05 MPa.

Besides the pressure, the thermal variation can also lead to the transformation of polymer membranes. To investigate the thermal stability of the ZIF-8/PES composite membrane, the gas permeances at different temperatures were also collected. When the temperature rose from 20 to 80 °C, the permeance of H₂ continuously increased from 1.11×10^{-7} to $1.43 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, and the N₂ permeance improved in the range of 4.9×10^{-9} to $5.9 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, leading to the increment of the H₂/N₂ separation factor from 22.7 at 20 °C to 24.4 at 80 °C (Fig. 9). This suggests that the ZIF-

8/PES composite membrane has good thermal stability, and the rupture of MOF layer does not happen during the temperature changes.

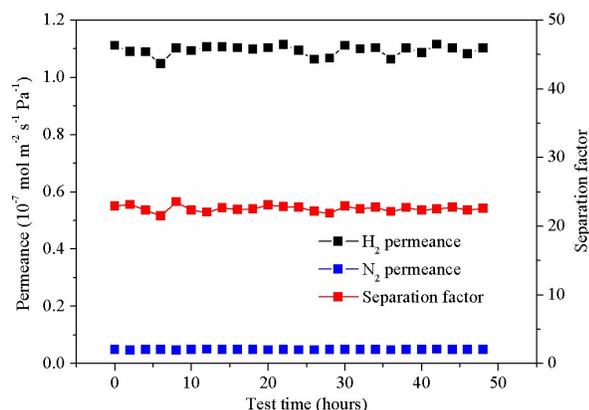


Fig. 10 Gas permeances and separation factor of the ZIF-8/PES composite membrane as a function of test time at 20 °C and 0.05 MPa.

We also tested the durability and reproducibility of the ZIF-8/PES composite membrane performances. The gas permeation of the membrane was run for 48 hours. The result shows that both the gas permeances and H₂/N₂ separation factor were almost constant in the entire test time (Fig. 10), proving the great durability of the membrane. To evaluate the reproducibility of the membrane, five additional membranes were prepared under same condition. All H₂ permeances of these membranes are similar with an average value of $1.02 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ (Table S1, ESI†). Moreover, the separation performances of H₂/CO₂, H₂/O₂ and H₂/N₂ also get consistent results, which demonstrate the great reproducibility of the new synthesis method.

The mixture gas separation performance was evaluated and displayed in the Table S4, ESI†. Compared with the single gas permeance, the H₂ permeance in the mixtures showed a slight decrease due to the competitive permeation of the large molecules (CO₂, O₂ and N₂). The separation factors of the membrane were similar to that of the single gases, far beyond the corresponding Knudsen constant, indicating the promise for hydrogen separation and purification.

Conclusions

In summary, we reported a new method to prepare the stiff, integrated and reproducible MOF/polymer composite membranes by depositing the metal based gel in and on the polymer hollow fibers. Metal based gel can effectively grow into the MOF membranes without the activation step, and the MOF crystals in the pores will enhance the stiffness and mechanical stability of the polymer supported MOF membranes through mutual support. Moreover, our strategy shows a great applicability and can be used to prepare intergrown and uniform MOF membranes on various substrates. In addition, the prepared ZIF-8/PES composite membrane possesses the excellent gas separation performance with the H₂ permeance of $1.11 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and H₂/N₂ separation factor of 22.7. All of these results demonstrated that the metal based gel was an excellent precursor to prepare stiff and integrated MOF membrane.

Experimental

Materials

Zinc acetate dihydrate, zinc chloride, copper acetate monohydrate and copper nitrate hydrate were purchased from Changzheng Chemical Reagent Co., Ltd, China. 2-methylimidazole, sodium formate, benzene-1,3,5-tricarboxylate and monoethanolamine (MEA) were supplied by Hangzhou Banghua Chemical Co., Ltd, China. The solvents of ethanol and methanol were used as purchased directly without further purification. And the water used in this study was made by a self-made RO-EDI system, in which the ion concentration was detected by IRIS Intrepid ICP and Metrohm 861 Compact IC and controlled to reach the experimental requirement of $\sigma \leq 0.5 \mu\text{S cm}^{-1}$. Polyethersulfone (PES, porosity 78%, molecular weight cutoff of 65000 Da), Polyvinylidene fluoride (PVDF, porosity 75%, 0.2 μm), Polysulfone (PSF, porosity 74%, molecular weight cutoff of 50000 Da) and Polyacrylonitrile (PAN, porosity 74%, molecular weight cutoff of 60000 Da) hollow fibers were self-made by typical wet spinning method. The hollow fibers were all cut into the length of 30 mm and cleaned with deionized water.

Synthesis of zinc based gel/polymer hollow fibers

Zinc acetate dihydrate (5.2 g) was first added into ethanol (15ml) and stirred at 60 °C for 0.5 hours. Maintained the molar ratio of MEA to zinc acetate dihydrate at 1.0, the MEA was added into the above solution and produced the transparent zinc sol. The obtained zinc sol was aged for 0.5 hours to serve as a coating solution. After that, cleaned and dried PES hollow fiber was immersed into the sol for 10 min under ultrasonic treatment. When the PES hollow fiber was taken out, the nitrogen was employed to blow the redundant sol. Finally, the PES hollow fiber with zinc sol was dried at 150 °C for 2 hours to evaporate the solvent and fix zinc in/on fiber with the gel state. The PVDF, PSF and PAN hollow fibers were prepared in the same way.

Synthesis of copper based gel/PES hollow fiber

Copper acetate monohydrate (4.7 g) was first added into ethanol (15ml) and stirred at 60 °C for 0.5 hours. Maintained the molar ratio of MEA to copper acetate monohydrate at 1.0, the MEA was added into the above solution and produced the blue copper sol. The obtained copper sol was aged for 0.5 hours to serve as a coating solution. After that, cleaned and dried PES hollow fiber was immersed into the sol for 10 min under ultrasonic treatment. When the PES hollow fiber was taken out, the nitrogen was employed to blow the redundant sol. Finally, the PES hollow fiber with copper sol was dried at 150 °C for 2 hours to evaporate the solvent and fix copper in/on fiber with the gel state.

Synthesis of ZIF-8/polymer composite membranes

The solid mixtures of zinc chloride (0.542 g), 2-methyl-imidazole (0.491 g) and sodium formate (0.271 g) were dissolved in methanol (30 ml) by sonication for 10 min at room temperature. The zinc based gel/polymer hollow fibers were placed vertically in a Teflon lined stainless steel autoclave. Then the synthesis solution was poured into the autoclave followed by heating at 80 °C for 24 hours. After solvothermal synthesis, the ZIF-8/polymer composite membranes were washed by fresh methanol for several times, and then dried in air. In order to make a comparison, the ZIF-8 membrane grown without zinc based gel was also conducted under same condition.

Synthesis of Cu₃(BTC)₂/PES composite membrane

The copper nitrate hydrate (0.875 g) dissolved in 12 ml water and benzene-1,3,5-tricarboxylate (0.42 g) dissolved in 12 ml ethanol was mixed together to form the synthesis solution. The copper based gel/PES hollow fiber was placed vertically in a Teflon lined stainless steel autoclave. Then the synthesis solution was poured into the autoclave followed by heating at 110 °C for 24 hours. After solvothermal synthesis, the Cu₃(BTC)₂/PES composite membrane was washed by fresh ethanol for several times, and then dried at room temperature.

Characterization

X-ray diffraction (XRD) measurements of all samples were taken with a X'Pert PRO (PANalytical, Netherlands) diffractometer with CuK α radiation (40kV, 40mA, $\lambda=0.154056$ nm). The chemical structures of PES and zinc based gel/PES hollow fibers were studied by using FTIR spectroscopy (Nicolet 6700, Thermo Scientific, USA). The morphologies of the membranes were characterized by a scanning electron microscope (SEM, TM-1000, Hitachi, Japan). The membranes were coated with a thin platinum layer to reduce charging effects of the MOF crystals.

Permeation experiments

The epoxy glue was used to seal the ZIF-8 membrane in a permeation module for the gas permeation tests. Before each experimental test, the permeation module was swept with the gas to be studied for removing residual gas. The volumetric flow rates of the permeated gases H₂, CO₂, O₂, and N₂ through the membrane were measured by a soap film flowmeter. The feed gas was regulated at pressures of 0.05 to 0.25 MPa, while the permeated gas was open to atmosphere. The separation factor was calculated by permeated flow rates. The mixture separation factor of binary mixture permeation was defined as the quotient of the molar ratios of the components in the permeate, divided by the quotient of the molar ratio of the components in the retentate.

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† Electronic Supplementary Information (ESI) available: XRD pattern, SEM images, and the data for the gas separation. See DOI: 10.1039/b000000x/

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