

Ultrathin Metal-organic Framework Membranes Used for Industrial Separation

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Abstract. Recently, separation and purification identified as a huge and stringent challenge in industrial processes and environmental protection. Being high efficient and advanced technology, metal-organic framework (MOF) membranes and membrane processes have presented tremendous potentials in application of gas separation. Compared with conventional bulk MOF membranes, the dense and polycrystalline MOF ultrathin membranes with nanometre-thick layers have shown outstanding gas separation performances due to minimized mass-transfer barrier. In this paper, three typical synthetic strategies of MOF ultrathin molecule-sieving membranes are introduced, and their performances in gas separation are compared.

1. Introduction

Separation of mixtures is one of the most important processes in modern industry and environmental protection, consuming more than 45% of the total energy consumption in the chemical production. Among various the mixtures components, gas mixtures separation would be indispensable for industrial processes, including hydrogen purification, natural gas sweetening and hydrocarbon separation [1]. Compared with traditional separation technologies, membrane-based separation is one of the most promising techniques due to lower energy consumption, easy operation and eco-friendliness [2,3]. So far, porous materials including zeolites, carbon and metal-organic frameworks (MOFs) have been utilized to fabricate molecular sieving membranes [4-7]. Among them, MOF membranes have received considerable attention for mixture gas separation and air purification owing to their controllable pores and chemical properties [8-12].

In order to achieve high gas selectivity, MOF membranes always have a thick layer from little micrometers to tens of micrometers. It's noteworthy that increasing the thickness of MOF layer will decrease its permeability sharply. Therefore, to break through the shortcomings of bulk MOF membrane in gas separation, reducing the thickness of MOF film will be of great significance. MOF ultrathin molecular sieving membranes which have nanometre-thick dense layers can minimize mass-transfer barrier, resulting in a better gas permeation flux and selectivity. However, there still remain big challenges to prepare the ultrathin MOF membrane due to complex reactant transport and nucleation



kinetics [13]. For example, thinner MOF membranes would have more defects and weaker stability, and heterogeneous nuclear reactions in synthetic solutions also might limit the thickness of MOF dense layers. Although only a few researches are reported in the last decade, excitingly, all the prepared ultrathin MOF membranes have interesting structures and show outstanding properties in gas separation, which predict a promising future in application.

2. Fabrication of MOF ultrathin membranes

2.1. Soft-physical exfoliation

The two-dimensional nanosheet layers of some layered MOF particles, such as $\text{Zn}_2(\text{bim})_4$ and $\text{Zn}_2(\text{Bim})_3$, show a regular c-oriented stacking and connected together by weak van der Waals force. Hence, the stacked MOF crystals can be easily exfoliated into single nanosheets and assembled into membrane. As shown in Figure 1, Yang and co-workers exploited a soft-physical exfoliation method to prepare $\text{Zn}_2(\text{bim})_4$ nanosheets that retain the primary integrity of morphologies and structures. The nanometre-thick $\text{Zn}_2(\text{bim})_4$ sheets were then used as building blocks to construct an ultrathin MOF layer on the ceramic substrate. In detail, the researchers utilized wet ball milled with a low speed to separate layered $\text{Zn}_2(\text{bim})_4$ particles, and a methanol and propanol mixture solution was used as soft condition to obtain their nanosheets via continuous ultrasonication which formed a colloid suspension. After that, the nanometre-thick $\text{Zn}_2(\text{bim})_4$ sheets were used as building blocks to construct an ultrathin MOF layer on the ceramic substrate by a diluent colloid solvent evaporation. The thickness of the as-synthesized $\text{Zn}_2(\text{bim})_4$ nanosheets ultrathin membranes was about 1-10nm and exhibited an excellent gas separation selectivity [14]. Similar work has been done to exfoliate $\text{Zn}_2(\text{Bim})_3$ crystals to single nanosheets, and the ultrathin $\text{Zn}_2(\text{Bim})_3$ membranes can be prepared [15].

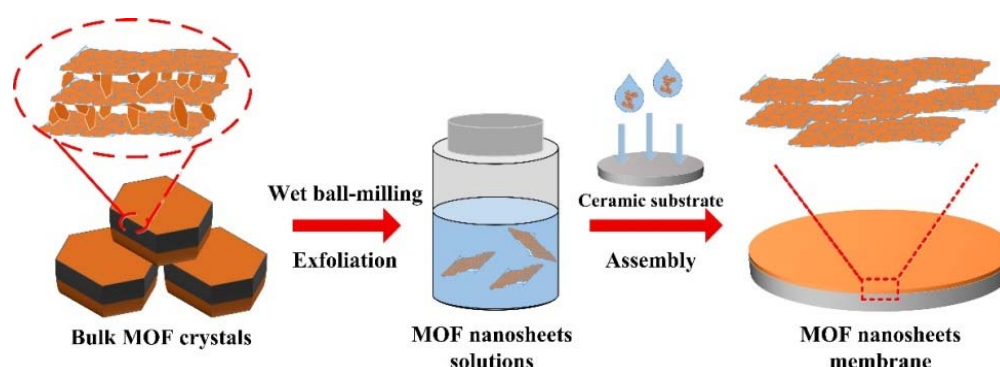


Figure 1. Schematic diagram of constructing the ultrathin nanosheets membrane via soft-physical exfoliation method.

2.2. Interfacial synthesis

Interfacial synthesis, known as a contra-diffusion method, has been developed for construct MOF ultrathin membranes [16-21]. Because the metal ion part and organic molecular are separated by a solid substrate, it can eliminate the heterogeneous reaction around MOF precursor. Wang et al. pre-prepared ZIF-8/GO mixture nanosheets as seeds to promote ZIF-8 dense membrane preparation, and form ultrathin ZIF-8 membrane via contra-diffusion method (Figure 2). The thickness of ZIF-8/GO membrane was 100nm [22]. Furthermore, different thickness of ZIF-8 dense layer can be obtained only by changing ZIF-8/GO nanosheets to ZIF-8/mesoporous GO nanosheets. All ultrathin ZIF-8 membranes exhibited surprising gas separation properties [23].

Besides, interfacial synthesis can also be used to construct MOF ultrathin membranes without nanosheets as seeds. Peinemann and co-workers selected a specific polymer support polythiosemicarbazide (PTSC) that chelated metal ions via thiosemicarbazide group, and the ultrathin and dense ZIF-8 membrane was prepared by an interfacial synthesis strategy on the PTSC substrate [24].

Only through metal chelating on the polymer surface, ZIF-8 crystals were formed with a several nanometer size, and the thickness of ZIF-8 dense membrane was only about 10-20nm. In order to further improve gas separation performance, 0.5 wt% PTMSP solution were coated on ultrathin ZIF-8/PTSC membrane, and the selectivity of prepared membrane increased dramatically.

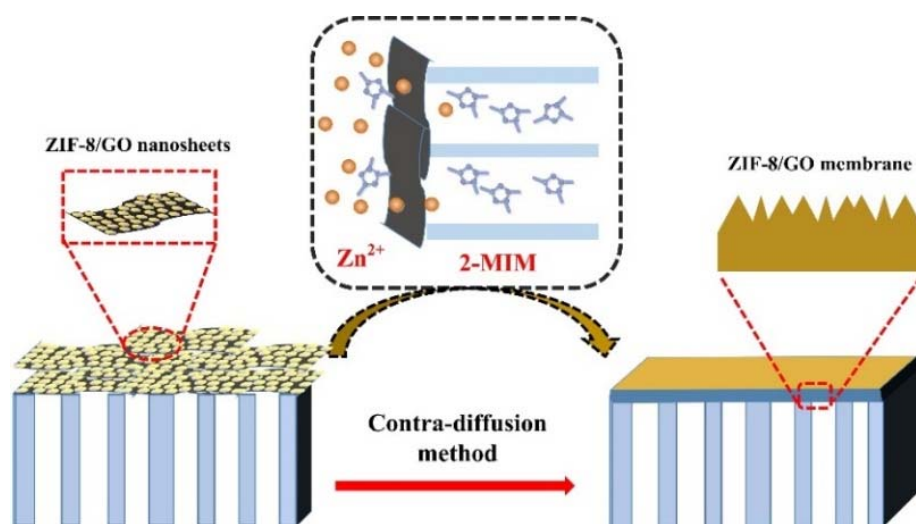


Figure 2. Schematic diagram of preparing the ultrathin ZIF-8/GO membrane through contra-diffusion method.

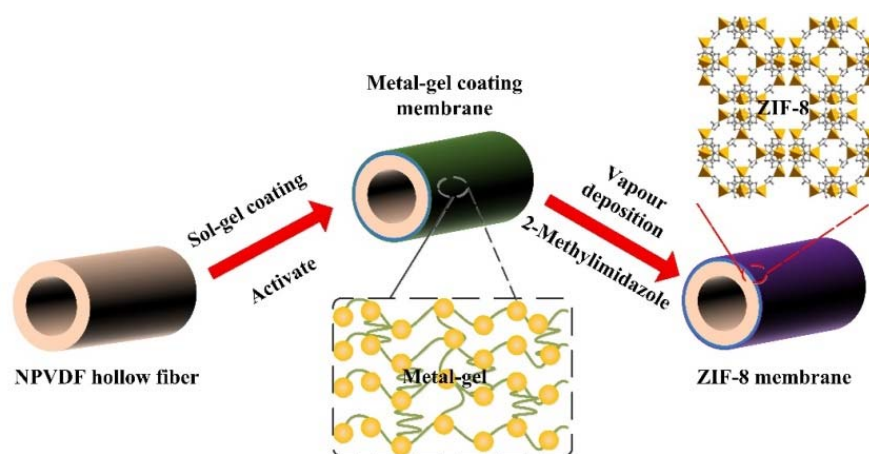


Figure 3. Schematic of ultrathin ZIF-8 membrane formation process by gel-vapour deposition method.

2.3. Gel-vapour deposition

Sol-gel coating is identified as a simple and straightforward method to modify the functional of substrate surface, promoting the fast growth of dense MOF membrane [25-27]. Our group had developed a metal-based gel to synthesis the dense ZIF-8 membrane on the varieties of polymer hollow fibers due to abundant MOF nucleation sites [28]. Based on our previous studies, we pre-coated metal-based gel on aminated PVDF membrane and stabilized at high temperatures, and then the functional substrates were placed on 2-methylimidazole vapour environment via stainless steel reactor (Figure 3) [29]. As a result, the ultrathin ZIF-8 membranes were obtained by 2-methylimidazole vapour reaction with Zn^{2+} or ZnO . By coordinating gel concentrations with coating times, the thinnest thickness of the as-resulted MOF ultrathin membrane was about 17nm at optimum condition. Moreover, the Zn gel coating method was

employed in membrane module to prepare the fascicular ultrathin MOF membranes. The vapour deposition method could provide a scalable and controllable operation in molecular sieving gas separation membrane, showing a potential value in industrial separation process.

3. Gas separation performances of ultrathin MOF membrane

Ultrathin, dense MOF membranes have shown excellent and unexpected advantages in gas separation field due to minimized mass-transfer barrier and membrane defects. Fascinating progresses appeared on ultrathin MOF membrane in most recent years. For example, Peinemann et al. developed a 10-20nm thickness of ZIF-8/PTSC membrane and had the highest levels hydrogen/propane selectivity about 8350 [24]. Yang and co-workers obtained a $\text{Zn}_2(\text{bim})_4$ nanosheets ultrathin membrane via soft-physical exfoliation method, and the composite membrane had the thinnest thick about 10nm and highest H_2/CO_2 selectivity of 291 [14]. Our group first developed the ultrathin ZIF-8 membrane by gel-vapour deposition, the membrane had a surprising gas permeances about $215.4 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and exhibited an excellent $\text{H}_2/\text{C}_3\text{H}_8$ selectivity up to 3400 [29]. As shown in Table 1, the gas separation performances of nano-meter MOF membranes coming from literature reports are summarized. According to the separation mechanism is known as molecule-sieving, the high gas selectivity's can be found. Larger gas molecules are prohibited into ultrathin MOF layer, while the gases with smaller sizes can penetrate through.

Table 1. Gas separation performances of ultrathin MOF membrane in literature.

Ultrathin MOF membrane	Thickness (nm)	Synthetic method	H_2 Permeance ($\text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ or GPU)	Separation factor			Ref.
				H_2/CO_2	$\text{H}_2/\text{C}_3\text{H}_8$	$\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$	
$\text{Zn}_2(\text{bim})_4$	<10	Soft-physical exfoliation method	2700GPU	291	-	-	[14]
$\text{Zn}_2(\text{Bim})_3$	10	Soft-physical exfoliation method	8×10^{-7}	166	-	-	[15]
ZIF-8/PTSC	10-20	Interfacial synthesis method	2.1×10^{-7}	-	8350	150	[24]
ZIF-8/NPVDF	17	gel-vapour deposition method	215.4×10^{-7}	5.5	3400	70	[29]
ZIF-8/GO	100	Interfacial synthesis method	5.46×10^{-8}	1.6	405	12	[22]
ZIF-8/CNT	100-200	Interfacial synthesis method	2.86×10^{-5}	14	52.4	18.13	[21]
IF-8/MGO	430	Interfacial synthesis method	1.17×10^{-6}	-	2409	35	[23]

4. Conclusion and outlook

Ultrathin MOF membranes with unique structures have shown unimaginably higher separation performance than those traditional massive ones. In summary, three strategies including soft-physical exfoliation, interfacial synthesis and gel-vapour deposition can be effectively used to develop MOF ultrathin molecule-sieving membranes. Despite the considerable separation performance of the MOF

ultrathin membranes at present, there are still some bottlenecks that limit the thickness of MOF layers. Therefore, necessary new methods and materials are urgent for developing ultrathin membranes in the future.

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