Membranes



Microstructural Engineering and Architectural Design of Metal–Organic Framework Membranes

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In the past decade, a huge development in rational design, synthesis, and application of molecular sieve membranes, which typically included zeolites, metal-organic frameworks (MOFs), and graphene oxides, has been witnessed. Owing to high flexibility in both pore apertures and functionality, MOFs in the form of membranes have offered unprecedented opportunities for energy-efficient gas separations. Reports on the fabrication of wellintergrown MOF membranes first appeared in 2009. Since then there has been tremendous growth in this area along with an exponential increase of MOF-membrane-related publications. In order to compete with other separation and purification technologies, like cryogenic distillation, pressure swing adsorption, and chemical absorption, separation performance (including permeability, selectivity, and long-term stability) of molecular sieve membranes must be further improved in an attempt to reach an economically attractive region. Therefore, microstructural engineering and architectural design of MOF membranes at mesoscopic and microscopic levels become indispensable. This review summarizes some intriguing research that may potentially contribute to large-scale applications of MOF membranes in the future.

1. Introduction

At the present time, separation processes account for 45–55% of global energy consumption of the chemical industry.^[1] In the case of commercial gas separation, cryogenic distillation, pressure swing adsorption, and chemical absorption processes remain dominant in separation technologies.^[2] Membrane-based separation is a relatively new concept, but developed quickly due to low energy consumption, high efficiency, eco-friendliness, and easy operation. By now, membrane-based separation has been successfully applied in refinery gas purification, ammonia purge gas recovery, nitrogen enrichment, and dehydration. Currently, the membrane market is dominated by

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D The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.201606949.

DOI: 10.1002/adma.201606949

polymeric membranes. Nevertheless, several intrinsic limitations, like permeability/ selectivity trade-off, plasticization, and vulnerability to harsh operation conditions, have severely hindered its widespread application in industry. Molecular-sieve membranes may provide an alternative solution to the abovementioned problems, due to their permanent porosity, framework robustness, and ability to separate molecules based on their size and shape.^[3]

Metal–organic frameworks (MOFs) are a new class of molecular-sieve materials composed of metal ions or metal-oxide clusters coordinated by organic linkers to form highly regular porous networks.^[4] MOFs first came to our attention due to their permanent porosities and ultrahigh surface areas, which were considered to be advantageous for high-capacity gas storage.^[5] Owing to their adjustability in both pore apertures and functionality, MOFs in the form of membranes have offered unprecedented

opportunities for efficient gas separations. A number of MOF membranes have therefore been fabricated and shown superior performance in H₂ purification, CO₂ capture, and C₃H₆/C₃H₈ separation. Moreover, in comparison with other candidates like zeolites, graphene oxides (GOs), and carbon molecular sieves, the presence of coordinatively unsaturated metal sites, guest-induced gate-opening phenomenon and framework flexibility in some MOF materials further endows them with infinite possibilities for efficient separation of a series of gas mixtures with similar kinetic diameters (like CO/N₂,^[6] C₂H₂/CO₂,^[7] and C₂H₄/C₂H₆^[8] separation), which is otherwise quite challenging.

Unceasing pursuit of materials with superior selectivity, permeability, and long-term operation stability remains the permanent themes in the field of membrane science and technology. In the case of MOF membranes, pore aperture (selectivity), functionality (selectivity), grain boundary defects (selectivity), thickness (permeability), and binding strength (operation stability) represent the most critical factors influencing their performance. Therefore, microstructural engineering, which typically includes orientation manipulation, interfacial synthesis, and construction of mixed-phase membranes at a mesoscopic level, and architectural design, which typically contains aperture size adjustment, cage modification, and post-decoration at a microscopic level, have become indispensable for performance improvement of MOF membranes (Figure 1). Several excellent review articles on MOF membranes have been published in recent years.^[9] In this context, we will summarize the updated progress in fabrication of high performance MOF membranes, with particular concerns





over methods developed for exerting precise control over their microstructures and architectures at both mesoscopic and microscopic levels. In particular, the research frontier in the field of MOF membranes will be highlighted.

2. Microstructural Engineering of MOF Membranes at a Mesoscopic Level

This section deals with microstructural engineering of MOF membranes on a micrometer scale. Among related studies, manipulation of the preferred orientation of MOF membranes is particularly interesting. Especially for MOFs with anisotropic pore systems, preferred orientation may maximize the exposure of desired pore apertures and minimize the generation of grain boundary defects so that the gas selectivity may be reasonably enhanced. Interfacial synthesis represents a highly controllable heterogeneous nucleation method for synthesizing MOF membranes with minimized grain boundary defects and reinforced mechanical stability. In the process of interfacial synthesis, metal-ion and ligand solutions are brought into contact from different sides of substrates and readily react at their contact interface. Since diffusion is the rate-determining step, nucleation and growth of MOF membranes mainly occur at the contact interface, so that excessive bulk nucleation can be effectively avoided. Moreover, growing MOF membranes themselves could serve as barriers, and thus confine both metal-ion and ligand precursor solutions in void regions (like gaps and interstices between the MOF crystals), leading to final formation of more continuous MOF membranes. It should be emphasized that since MOFs are composed of both inorganic ions and organic ligands, high compatibility with both inorganic and organic compounds makes them easier to form MOF-containing mixed-phase membranes. Combined with the introduction of a second selective phase, the overall selectivity is anticipated to be enhanced compared with MOF membranes in a pure form.

2.1. Orientation Manipulation

Diverse methods have been employed for production of wellintergrown MOF membranes. In general, in situ solvothermal methods prefer to synthesize randomly oriented MOF membranes rather than oriented ones. This is because MOF nucleation and crystallization occur simultaneously in the bulk solution and at the solution-substrate interface, thus making precise orientation control over MOF membranes particularly challenging, except on rare occasions. In one case, Caro et al. reported that Mn(HCO₂)₂ crystal layers with a reasonable onedimensional pore system tilted 34° to the substrate surface could be in situ grown on oxidized carbon substrates by the use of sodium formate instead of formic acid.^[10] A highly controllable layer-by-layer (LBL) assembly method is intrinsically beneficial to achieve accurate control over the preferred orientation of MOF layers. For instance, Fischer et al. successfully prepared highly oriented Zn₃(btc)₂ films on COOH-terminated organic surfaces with a smooth surface morphology, by alternately dip-coating into metal- and ligand-containing precursor solutions.^[11] When it comes to porous substrates, however, the LBL strategy will



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not be so effective for oriented deposition of MOF membranes due to partial penetration and crystallization of MOF nutrients within the pore system, as has been confirmed by Fischer et al. in preparation of pillared-layered Cu_2L_2P membranes.^[12]

In contrast, secondary growth remains the most reliable approach for exerting precise control over the preferred





Figure 1. Illustration of architectural design and microstructural engineering of MOF membranes at microscopic and mesoscopic levels. Tailoring the framework dimension further provides unprecedented opportunities for significant performance enhancement of MOF membranes. Top-left image: reproduced with permission.^[17] Copyright 2011, American Chemical Society. Top-middle image: reproduced with permission.^[29] Copyright 2014, American Association for the Advancement of Science. Top-right image: reproduced with permission.^[21] Copyright 2014, American Association for the Advancement of Science. Top-right image: reproduced with permission.^[22a] Copyright 2016, American Chemical Society. Middle-left image: reproduced with permission.^[26] Copyright 2014, American Association for the Advancement of Science. Bottom-left image: reproduced with permission.^[19] Copyright 2014, American Chemical Society. 2014, American Chemical Society. Bottom-middle image: reproduced with permission.^[91] Bottom-right image: reproduced with permission.^[70] Copyright 2013, The Royal Society of Chemistry.

orientation of MOF membranes, which could be realized by predeposition of oriented MOF seed layers or optimization of epitaxial growth conditions. of polyethyleneimine. Prepared ZIF-L membranes exhibited considerable ideal selectivity for H_2/N_2 (8.1) and H_2/CO_2 (24.3) gas pairs.^[14]

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2.1.2. Orientation Control by Optimization of Epitaxial Growth Conditions

Besides preferred-orientation control of MOF seeds, it is also possible to fabricate oriented MOF membranes from randomly oriented seed lavers by proper optimization of epitaxial growth conditions, which involves an evolution-selection growth mechanism developed by Van der Drift in interpretation of the preferred orientation of a vapor-deposited PbO layer.^[15] For MOF crystals with anisotropic morphology, in the early stage, all MOF seeds evolved in all possible crystallographic axes. Nevertheless, in case the growth rate along one direction was much faster than that along others, when two MOF crystals met, the more steeply growing crystal would prevent the further growth of the less steeply growing crystal. Eventually, MOF crystals tended to arrange along the crystallographic axis, with the fastest growth rates perpendicular to the substrate. This principle has been successfully employed to synthesize preferentially oriented ZIF-7,[16] ZIF-8 (Figure 3),^[17] ZIF-69,^[18] ZIF-L,^[14] HKUST-1,^[19] and [Co₃(HCOO)₆] membranes.^[20]

It should be emphasized that very recently we proposed a novel "heterogeneous seeding" method for fabrication

2.1.1. Orientation Control by Predeposition of Oriented MOF Seed Layers

As in the case of zeolite membranes, predeposition of oriented MOF seed layers on substrates could induce subsequent epitaxial growth along the same direction, and ultimately lead to formation of oriented MOF membranes. Oriented MOF seed layers can be introduced on substrates by in situ or ex situ seeding. Lai et al. reported in situ deposition of preferentially (10-2) oriented MOF-5 seed layers on α -Al₂O₃ substrates using a microwave-induced thermal deposition (MITD) method.^[13] MOF-5 seed layers were then solvothermally treated and resulted in formation of continuous and oriented MOF-5 membranes (**Figure 2**).

Wang et al. prepared continuous ZIF-L membranes with a high degree of *c*-out-of-plane orientation from *c*-oriented ZIF-L seed layers, which were attached to substrates through vacuum filtration in the presence



Figure 2. SEM images of top views (upper) and cross-sections (lower) of a) an oriented MOF-5 seed layer and b) an oriented MOF-5 membrane after secondary growth. Reproduced with permission.^[13] Copyright 2009, Elsevier.



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Figure 3. a) TEM of the cross-section of the supported ZIF-8 membrane after secondary growth, and b) with traced grain boundaries for improved visibility of the columnar growth and denoted <100> direction. Reproduced with permission.^[17] Copyright 2011, American Chemical Society.

of oriented dual-ligand ZIF-78 (Zn(2-nitroimidazolate) (5-nitrobenzylimidazolate)) films on hierarchically ordered stainless-steel-mesh (HOSSM) substrates from mono-ligand ZIF-108 ((Zn(2-nitroimidazolate)2) seed layers,^[21] where ZIF-108 provided sufficient active coordination sites and secondary building blocks for epitaxial growth of ZIF-78 membranes.

2.1.3. The Influence of Preferred Orientation on Separation Performance

A detailed comparison of MOF membranes with different preferred orientation was listed in **Table 1**.

Based on the above-mentioned results, we come to the conclusion that compared with randomly oriented MOF membranes, oriented MOF membranes generally exhibit higher gas selectivity. This is reasonable since regular arrangement of MOF crystals is beneficial for reducing nonselective intercyrstalline diffusion of gas molecules through grain boundaries,

 Table 1. Comparison of gas separation performances of MOF membranes with diverse preferred orientation.

MOF-type	Preferred orientation	Gas pair	Gas permeance [10 ⁻⁸ mol m ⁻² s ⁻¹ Pa ⁻¹]	Gas selectivity
ZIF-8 ^[22]	random	H_2/CH_4	5	11.2
ZIF-8 ^[17]	<i>a</i> -oriented	H_2/CH_4	10	15
ZIF-7 ^[23]	random	H_2/CO_2	8	6.7
ZIF-7 ^[16]	<i>c</i> -oriented	H_2/CO_2	0.9	8.5
ZIF-69 ^[24]	random	CO ₂ /CO	3.6	3.5
ZIF-69 ^[18]	<i>c</i> -oriented	CO ₂ /CO	10.3	5.0
HKUST-1 ^[19]	001	CO_2/SF_6	1.9	38
HKUST-1 ^[19]	111	CO_2/SF_6	13.1	34
ZIF-L ^[14]	<i>b</i> -oriented	H ₂ /CO ₂	6.3	4.9
ZIF-L ^[14]	<i>c</i> -oriented	H_2/CO_2	7.6	15.2

and improving the uniformity of pore size distribution.^[13] Nevertheless, in some cases, gas permeability on oriented MOF membranes decreases perhaps due to reduced pore apertures and elimination of gas diffusion through grain boundary defects. In addition, regular arrangement of MOF crystals does not necessarily lead to enhanced facilitated intracrystalline diffusion of gas molecules, as in the case of *b*-oriented MIF-type zeolite membranes.^[3a,b,25] It is anticipated that this side effect can be alleviated through further microstructural engineering MOF membranes.

2.2. Interfacial Synthesis

Interfacial synthesis has been successfully employed in facile fabrication of MOF membranes due to following reasons: First, nucleation and epitaxial growth of MOF membranes could occur simultaneously under ambient conditions; Second, precursor solutions containing metal ions and organic ligands could be supplied independently. Based on fluidic properties of precursor solutions, well-intergrown MOF membranes could be fabricated with static and dynamic interfacial synthesis methods, respectively.

2.2.1. Static Interfacial Synthesis

Static interfacial synthesis involves introduction of metal-ion and ligand precursor solutions from different sides of substrates under static conditions. For example, Wang et al.^[26a] prepared continuous ZIF-8 membranes on flexible nylon substrates (**Figure 4**). Metal ions and ligands were dissolved in methanol, respectively. After crystallization under ambient conditions, 16-µm-thick ZIF-8 membranes were in situ generated on the zinc nitrate side and exhibited a H_2/N_2 ideal selectivity of 4.3. This method was also employed by Jin et al. for the synthesis of well-intergrown ZIF-71 membranes on tubular α -Al₂O₃ substrates.^[26b]

Jeong et al. further developed this method and prepared well-intergrown ZIF-8 membranes on porous α -Al₂O₃ substrates (**Figure 5**).^[27] In this process, substrates were first soaked with metal-ion solutions, and then subject to solvothermal growth in ligand-containing solutions. The concentration gradients enabled maintenance of high concentrations of metal ions and ligands in the vicinity of substrates. Owing to the optimized microstructure, prepared ZIF-8 membranes exhibited exceptional C₃H₆/C₃H₈ selectivity (~50). Moreover, a fraction of ZIF-8 crystals further penetrated into substrate pores, which significantly strengthened their mechanical stability. Validity of this method and excellent molecular-sieving behaviors of prepared MOF membranes were further verified by Hara et al.^[28]

It should be emphasized, however, that it may be a challenging task to further extend this approach to capillary substrates or hollow fibers due to severe capillary effect or concentration polarization. Moreover, nutrients on the inner side may be insufficient to sustain the formation of continuous MOF membranes due to the limited pore space. Alternatively, a dynamic interfacial method was further developed to meet this challenge. SCIENCE NEWS _____ www.advancedsciencenews.com



Figure 4. a) Diffusion cell for ZIF-8 film preparation and b) the schematic formation of ZIF-8 films on both sides of the nylon support via static contra-diffusion of Zn^{2+} and 2-mlm through pores of the nylon support. Reproduced with permission.^[26a] Copyright 2011, The Royal Society of Chemistry.

2.2.2. Dynamic Interfacial Synthesis

Nair and Jones et al. proposed the so-called interfacial microfluic membrane processing (IMMP) for growing continuous ZIF-8 membranes with controlled locations on Torlon hollow fibers (Figure 6).^[29] A $Zn^{2+}/1$ -octanol solution was flown through the bore of the hollow fiber, while a 2-mIm/H₂O solution maintained static on the shell side. Owing to the relatively fast diffusion of Zn²⁺ to the water-oil interface, a well-intergrown and thin ZIF-8 ($\approx 2 \mu m$) membrane was thus formed on the bore side of hollow fibers. In contrast, under static conditions, noncontinuous ZIF-8 layers were generated due to the insufficient supply of Zn²⁺ ions after the initial nucleation and growth of ZIF-8 crystals. It was assumed that the miscibility of the two solvents (H₂O/1-octane) likely served as a barrier retarding the transport rate of Zn²⁺ reactant toward the shell side, thus effectively prevented excessive penetration of prepared ZIF-8 layer into the substrate pores. Prepared ZIF-8 membranes could efficiently distinguish H₂ from C₃H₈ (selectivity \approx 370) and C₃H₆ from C_3H_8 (selectivity ${\approx}12)$ based on strict size exclusion.

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Similar to the IMMP concept, Coronas et al. further prepared ZIF-8 membranes with superior H_2/N_2 and H_2/CH_4 selectivity (18.3 and 17.2 respectively) on the inner-side of polymeric hollow fibers by feeding both metal-ion and ligand precursor solutions inside hollow fibers with micropumps.^[30] Compared with ZIF-8 membranes fabricated by conventional in situ or secondary growth, 69.89% savings in metal-salt and organicligand reagents were achieved. Similarly, Qiu et al. also successfully fabricated well-intergrown ZIF-8 tubular membranes in a continuous flow system.^[31]

2.3. Construction of MOF-Based Pure and Mixed-Phase Membranes

Besides in a pure form, MOF crystals could easily integrate with both inorganic and organic materials to form highly compatible MOF-based mixed-phase membranes relying on mutual physical or chemical interactions. Based on the continuity of MOF phase, MOF-containing mixed-phase membranes can be further categorized into MOF-based composite membranes (MOF phase is continuous) and MOF-based mixed-matrix membranes (MMMs, MOF phase is sparsely distributed), which will be addressed in the following context.

2.3.1. Fabrication of Pure MOF Membranes

Caro et al. first reported microwave-assisted in situ synthesis of H_2 selective ZIF-8 membranes on bare TiO₂ substrate.^[22]



Figure 5. Schematic illustration of the membrane synthesis with the dynamic counter-diffusion method: a) A porous α -Al₂O₃ support saturated with a metal precursor solution is placed in a ligand solution containing sodium formate; b) the diffusion of metal ions and ligand molecules cause the formation of a "reaction zone" at the interface; and c) rapid heterogeneous nucleation/crystal growth in the vicinity at the interface leads to the continuous well-intergrown ZIF-8 membranes. Reproduced with permission.^[27] Copyright 2013, American Chemical Society.







Figure 6. Scheme depicting the IMMP approach for ZIF-8 membranes in hollow fibers. a) Side view of a series of fibers mounted in the IMMP reactor. b) The Zn²⁺ ions are supplied in a 1-octanol solution (light red) flowing through the bore of the fiber, whereas the methylimidazole linkers are supplied on the outer (shell) side of the fiber in an aqueous solution (light blue). c) Magnified view of fiber support during synthesis. Reproduced with permission.^[29] Copyright 2014, American Association for the Advancement of Science.

MOF-5 membranes were also demonstrated to be able to successfully in situ grow on bare α -Al₂O₃ substrates.^[32] Nevertheless, in most cases it remains a challenging task for in situ fabrication of well-intergrown MOF membranes on bare substrates. It is assumed that intrinsic low affinity interactions between the substrate and MOF crystals may inevitably give rise to a low heterogeneous nucleation density and high grain boundary defect density. Therefore, surface modification of the substrate with reactive organic functional groups becomes indispensable in the case of in situ MOF crystallization. For instance, through the coordination effect between 3-aminopropylsilyl groups of 3-aminopropyltriethoxysilane and the free Zn²⁺ centers of MOF crystals, a series of H₂-selective

MOF membranes like ZIF-22,^[33] ZIF-90,^[34] and ZIF-95,^[35] have been successfully in situ synthesized on α -Al₂O₃ substrates. Jeong et al. developed a facile organic ligand covalent functionalization method enabling in situ fabrication of ZIF-8 membranes with controlled microstructures.^[36] Besides, polymer-based surface modification (such as polydopamine and PMMA) was proven to be a powerful platform for facile synthesis of well-intergrown MOF membranes.^[37]

In contrast to organic compounds, recently significant attention has been devoted to inorganic surface modifiers, which possessed unique advantages, such as high affinity with the substrate, high thermal stability, no swelling, eco-friendly, and easy fabrication. For instance, Jeong et al. discovered that nucleation and growth of MOF-5 crystals were remarkably enhanced on graphite-coated anodized aluminum oxide (AAO) or α -Al₂O₃ substrates under microwave

irradiation, owing to the specific electric and dielectric properties.^[13,38] Zhang et al. fabricated H₂-selective ZIF-8 membranes on α -Al₂O₃ tubular substrates premodified with ZnO in the form of nanorods or ultrathin layers.^[39] In addition, some metal (such as Ni^[40] and Cu nets)^[41] and metal oxide substrates themselves (such as Al₂O₃^[42] and ZnO)^[43] could also serve as metal ion sources of MOF membranes in case they contain identical metal elements. Under certain conditions an additional "reactive seeding" step has to be employed in case substrates are too chemically inert (**Figure** 7).^[42] In this study, hydrothermal treatment of α -Al₂O₃ substrates with 1,4-benzenedicarboxylic acid aqueous solutions was first carried out and resulted in formation of uniformly distributed MIL-53 seed layers.^[42]



Figure 7. Schematic diagram of preparation of the MIL-53 membrane on porous α -Al₂O₃ substrate via the reactive seeding method. Reproduced with permission.^[42a] Copyright 2011, The Royal Society of Chemistry.





Figure 8. Schematic illustration of in situ solvothermal growth of ZIF-8 membrane on a ZnAl-LDH buffer layer-modified γ -Al₂O₃ substrate. Reproduced with permission.^[45] Copyright 2014, American Chemical Society.

After secondary growth, well-intergrown MIL-53 membranes showing excellent pervaporation performance in dehydration of the azeotrope of ethyl acetate aqueous solution were fabricated.

Since a majority of inorganic compounds employed for substrate modification are not reactive enough to direct in situ crystallization of continuous MOF membranes, it is highly desirable to introduce inorganic buffer layers with a high affinity to MOF crystals. LDHs are representative of layered compounds featuring a general formula $[M_{1-x}^{2+}M_{x}^{3+}(OH)_{2}]$ $[A^{n-}]_{x/n} \cdot zH_2O$ (M²⁺, M³⁺, and Aⁿ⁻ represent *di*-, *tri*-valent metal ions and *n*-valent anions).^[44] Our study demonstrated that surface modification of porous α -Al₂O₃ substrates with ZnAl-CO₃ LDH buffer layers enabled to significantly promote the heterogeneous nucleation of ZIF-8 crystals and result in the formation of well-intergrown ZIF-8 membranes (Figure 8).^[45] Besides LDH buffer layers, Zhang et al. further fabricated highly active ZnO buffer layers on PVDF hollow fiber substrates.^[46] Since 2-mIm was involved in preparation of ZnO buffer layers, crack-free and uniform ZIF-8 layers could be in situ fabricated without any activation procedure.

Besides porous inorganic substrates, flexible polymers in the form of plates, tubes, or hollow fibers are also promising substrate candidates for MOF-based membranes. Although porous inorganic substrates are intrinsically more thermally and mechanically stable, thus allowing long-term exposure of supported MOF membranes to harsh operating conditions, polymeric substrates still exhibit superiority in terms of structural flexibility, easy processability, low production cost, and high affinity for MOF phase. In addition, some polymeric substrates themselves have shown considerable gas selectivity. As a result, most polymer-supported MOF membranes embrace excellent overall gas selectivity as well as mechanical stability. To date, a wide variety of polymeric materials like poly(amide-imide),^[47] co-polyimide,^[48] polyacrylonitrile,^[49] polybenzimidazole,^[50] polvethersulfone,^[51] polyester,^[52] polysulfone,^[53] bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide),^[54] and polyphenylsulfone^[55] have been employed as substrates for the construction of high-performance MOF membranes.

It should be emphasized that besides the chemistry of substrate surface, microstructure (like pore size and roughness) of the substrate surface also exerts significant influence on final microstructure and separation performance of MOF membranes. For instance, it is generally recognized by most researchers that the larger the pore size of the substrate, the larger the risk of generation of defects in the MOF membrane, which may severely deteriorate the separation performance.^[56] Therefore, pore size of the substrate should be properly controlled (<0.5 µm) to reduce the risk of defect generation. Yang et al. reported that through deposition of APTESmodified α -Al₂O₃ particles with a grain size of 0.5 μ m onto a coarse α -Al₂O₃ substrate with an average pore size of 3 um, pore size of the substrate was effectively reduced, and heterogeneous nucleation of ZIF-8 crystals was significantly promoted, which resulted in

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the formation of an extremely thin and defect-free ZIF-8 membrane with considerably high H_2/N_2 separation factor.^[57]

As mentioned above, in general, large-pore and rough substrate surface disfavors solvothermal synthesis of high quality MOF membranes. Nevertheless, this is not always the case. For instance, during the seeding process, some MOF seeds tend to be sucked inside the pores of the substrate in case MOF seed crystals are smaller than substrate pores. After epitaxial growth, the prepared MOF membrane may partially penetrate into the underlying substrate pores. This structural feature is quite beneficial for promoting mechanical stability of the MOF membrane due to an enhanced adhesion between the membrane and substrate.^[58]

In order to maintain a stable attachment of MOF seeds to the substrate, sometimes we even deliberately enhance the substrate roughness by surface modification with an inorganic buffer layer. For instance, relying on physical interactions, Liu and Caro et al. developed a novel seeding method to prepare high quality ZIF-8 membranes on porous α -Al₂O₃ substrates.^[59] The most critical step was to construct a network composed of vertically aligned MgAl-CO₃ LDH walls on porous α -Al₂O₃ substrates. The LDH network efficiently collected seeds in a "perch", and thus effectively prevented ZIF-8 seeds from peeling off during secondary growth.

2.3.2. MOF-Based Composite Membranes

MOFs could easily couple with zeolites,^[60] covalent organic frameworks (COFs),^[61] layered double hydroxides (LDH),^[62] carbon nanotubes (CNTs),^[63] GO,^[64] or room-temperature ionic liquids (RTIL)^[65] to form MOF-based composite separation membranes. Owing to the presence of an additional selective layer, MOF-based composite membranes are anticipated to show significantly enhanced selectivity.

A series of MOF–MOF composite membranes have been fabricated and shown impressive separation performances.^[66,67] Jeong et al. proposed a heteroepitaxial growth method to fabricate continuous and well-intergrown ZIF-8–ZIF-67 composite membranes (**Figure 9**), which were realized by first







Figure 9. Schematic illustration of the membrane synthesis via heteroepitaxial growth. Reproduced with permission.^[66] Copyright 2015, American Chemical Society.

heteroepitaxial growth of ZIF-67 membranes from nanosized ZIF-8 seed layers, followed by heteroepitaxial tertiary growth of ZIF-8 overlayers on prepared ZIF-67 membranes.^[66] Prepared composite membranes exhibited unprecedentedly high separation factors of propylene over propane (≈ 200), possibly due to an enhanced grain-boundary microstructure. Zhang et al. reported a novel route for partial transformation of HKUST-1 membranes into HKUST-1-MIL-100 composite membranes based on multivalent-cation substitution under ambient conditions.^[67] Through this approach, pore apertures could be reduced through the immobilization of amorphous FeCl₃ residues in MIL-100 cavities, and desired HKUST-1 crystal facets could be exposed to provide competitive molecular sieving ability. Compared with HKUST-1 membranes in a pure form, prepared HKUST-1-MIL-100 composite membrane exhibited significantly enhanced H₂/CO₂, H₂/O₂, H₂/N₂, and H₂/CH₄ selectivity (77.6, 170.6, 217.0, and 335.7, respectively).

A double multiplying effect of molecular sieving through a MOF–zeolite composite membrane has recently been demonstrated. Chai et al. synthesized CO₂-selective ZIF-8 membranes (CO₂/CH₄ selectivity \approx 4.1) on porous α -Al₂O₃ substrates via vacuum thermal seeding followed by coating prepared ZIF-8 membranes with continuous zeolite T top-layers.^[60] Prepared T-ZIF-8 composite membranes demonstrated an unprecedented CO₂/CH₄ selectivity (\approx 229).

COFs as an emerging class of porous materials are built by strong organic covalent bonds in a periodic arrangement entirely from light elements. COFs display several impressive characteristics, such as structural diversities, high permanent porosities, high thermal stability, and low densities, enabling them superb candidates of highperformance molecular-sieve membranes.^[68] Qiu et al. presented growth of [COF-300]-[Zn₂(bdc)₂(dabco)] composite membranes by sequentially growing individual epitaxial layers on premodified porous SiO2 substrates.^[61] Prepared COF-MOF composite membranes easily surpassed the Robeson upper bound of polymer membranes for $\mathrm{H}_{2}/\mathrm{CO}_{2}$ gas pairs, due to the synergy between two porous materials.

LDHs are composed of positively brucite-like sheets and interlayer galleries containing charge-compensating anions. Through judicious choice of metal ions and charge-compensating anions, the gallery height of LDHs can be flexibly tuned from the nanometer to sub-nanometer scale, which is comparable with most industrially important gas molecules. So it is of great importance to explore their potential as high-performance gas-separation membranes. Liu and Caro et al. first prepared H₂-selective ZnAl-NO₃ LDH membranes on porous γ Al₂O₃ substrates by in situ hydrothermal growth. Prepared LDH membranes were then subject to solvothermal treatment in a 2-mIm-containing methanol solution, and resulted in final formation of ZIF-8-ZnAl-NO₃ LDH composite membranes with both enhanced H₂/CH₄ selectivity and H₂ permeability in comparison with LDH membranes in a pure form (Figure 10).^[62]



Figure 10. SEM image (a) and EDXS mappings (b,c,d) of the cross-section of ZIF-8-ZnAl-NO₃ LDH composite membrane. Color code: blue = O (b); yellow = Al (c); red = Zn (d). Reproduced with permission.^[62] Copyright 2015, Wiley-VCH.





2.3.3. MOF-Based MMMs

MMMs represents a kind of polymer-based membranes composed of discontinuous inorganic fillers and continuous polymeric matrix. Nevertheless, the poor filler-polymer compatibility often results in the generation of nonselective interfacial defects, which in turn may severely deteriorate their separation performance. In terms of MOF fillers, surface functionality, particle size, and aspect ratio can often exert significant influence on their interfacial microstructures and the separation performance. Some typical examples are listed as follows.

Relying on the gate-opening effect of ZIF-8 crystals and its high affinity for iso-butanol, for the first time, we successfully prepared organophilic pervaporation ZIF-8-PMPS MMMs with a simple solution-blending dip-coating method.^[69] ZIF-8 nanocrystals were homogeneously embedded in the PMPS matrix with no interfacial voids. Under optimized conditions, i-BuOH permeance as high as 6000-7000 GPU with i-BuOH/ H₂O separation factor up to 34.9–40.1 was obtained, which had surpassed the upper limit of state-of-the-art OPV membranes and reached an economically attractive region (Figure 11). In order to improve the *i*-BuOH recovery efficiency further, a so-called shell-ligand exchange reaction (SLER) method was developed for surface modification of ZIF-8 nanocrystals with 5,6-dimethylbenzimidazole (DMBIM).^[70] i-BuOH sorption isotherms revealed an absence of a "gate-opening" effect and enhanced transport diffusivity on DMBIM-modified-ZIF-8 nanocrystals (Figure 12). Compared with ZIF-8-PMPS MMMs, prepared ZIF-8-DMBIM-PMPS MMMs exhibited superior selectivity towards iso-butanol while maintaining the iso-butanol permeance constant.

Long et al. prepared MMMs consisting of MOF-74 nanocrystals with diverse crystal size dispersed within 6FDA-DAM for efficient C_2H_4/C_2H_6 separation.^[71] It was found that the C_2H_4/C_2H_6 selectivity was sharply enhanced with the reduction in crystal size. This is because smaller particle sizes for MOF-74 nanocrystals could lead to a greater fraction of the polymer at the nanocrystal interface, thereby minimizing the number of non-selective pathways for gas permeation (**Figure 13**). In



Figure 11. Butanol/H₂O separation factor versus butanol permeance for ZIF-8-PMPS MMMs. The dashed line represents the best performance of the state-of-the-art organophilic pervaporation membranes. Reproduced with permission.^[69] Copyright 2011, Wiley-VCH.

 $[Zn(MIM)_2]_n + nx \cdot DMBIM \xrightarrow{SLER} [Zn(MIM)_{2-x}(DMBIM)_x]_n + nx \cdot MIM$



Figure 12. Schematic representation of the shell–ligand-exchange-reaction (SLER) process of ZIF-8. Reproduced with permission.^[70] Copyright 2013, The Royal Society of Chemistry.

addition, framework–polymer interactions further reduced chain mobility of the polymer, which may jointly contribute to the enhanced membrane separation performance.

Gascon et al. developed a bottom-up synthesis strategy for dispersible [Cu(1,4-bdc)]-polyimide MMMs.^[72] Incorporating MOF nanosheets as thin as 5 nm into polymer matrices endowed resultant MMMs with outstanding CO₂/CH₄ selectivity (\approx 90). This could be attributed to a superior occupation of the membrane cross-section by MOF nanosheets as compared with bulk crystals, which improved the accuracy of molecular sieving and minimized nonselective permeation pathways.

It should be emphasized that an optimization of MOF loadings should be carried out carefully, since usually much lower fractions of fillers could not alter the transportation properties of polymers, while much higher fractions of fillers may cause severe mutual aggregation, thus leading to generation of interfacial voids, which may sharply degrade separation performances of MOF-based MMMs.^[73]

A detailed comparison between MOF-based composite membranes and MMMs is listed in **Table 2**.

2.4. Case Study: Microstructure Optimization of ZIF-8 Membranes for Efficient C_3H_6/C_3H_8 Separation

 C_3H_6/C_3H_8 separation as one of the largest energy consumers in the petrochemical industry is traditionally achieved by cryogenic distillation, which is extremely energy-intensive due to the close volatilities of C_3H_6 and C_3H_8 . Membrane-based C_3H_6/C_3H_8 separation has therefore been considered as an energy-efficient and environmentally friendly alternative. In comparison with traditional polymeric and molecular-sieve membranes, unprecedented C_3H_6/C_3H_8 separation performances of ZIF-8 membranes can be attributed to the accurate molecular sieving functions, where the equivalent aperture size of ZIF-8 just falls between the kinetic diameters of C_3H_6 and C_3H_8 . In addition, robust hydrothermal and chemical stability of ZIF-8 framework further endow this material with promising long-term operation stability. C_3H_6/C_3H_8 separation performance of ZIF-8 membranes is mainly determined by their





Figure 13. Ethylene/ethane separation performance for MOF-74/6FDA-DAM membranes. a) Membrane performance relative to the upper bound for polymers. b) SEM images of $Co_2(dobdc)$ and $Mg_2(dobdc)$ membrane cross-sections and corresponding illustrations of the proposed gas transport mechanisms. Reproduced with permission.^[71] Copyright 2016, Nature Publishing Group.

microstructures. Herein, we briefly summarized how progressive microstructural improvements on ZIF-8 membranes had enabled exceptionally high C_3H_6/C_3H_8 -separation performance.

2.4.1. ZIF-8-Based Pure and Composite Membranes

Lai et al. first prepared ZIF-8 membranes with considerable C_3H_6/C_3H_8 selectivity by a facile hydrothermal seeded growth method.^[74] Prepared membranes showed a C₃H₆ permeability up to 200 bar, with the C_3H_6/C_3H_8 selectivity as high as 50, which had well surpassed the "upper-bound trade-off" lines of existing membranes and reached the economically attractive region. In order to further improve their reproducibility, ZIF-8 membranes were prepared through hydrothermal synthesis under the partial self-conversion of sputter-coated ZnO buffer layers on porous α -alumina substrates.^[75] Results showed that separation factors for C₃H₆/C₃H₈ mixtures on all ZIF-8 membranes were higher than 47, with a standard deviation of only 2. Aiming at enhancing their separation performance further, solvent exchange with methanol was employed to remove residual water located in ZIF-8 membranes to protect ZIF-8 grains from corrosion.^[76] As a result, ZIF-8 membranes with significantly enhanced C₃H₆/C₃H₈ selectivity (>90) were achieved. In addition, Pan et al. further explored the potential of zinc-substituted ZIF-67 membranes in the separation of $C_{2}H_{6}/C_{3}H_{8}$ mixtures.^[77]

Besides the hydrothermal growth method, as has been mentioned in section 2.2.2., a novel IMMP technique was recently proposed by Nair et al. for growing continuous ZIF-8 membranes with controlled locations on polyamide-imide (PAI) hollow fibers.^[29] Moreover, a detailed mechanistic study of ZIF-8 membrane growth under microfluidic conditions indicated that interfacial membrane formation in hollow fibers occurred via an initial formation of two distinct layers followed by their subsequent rearrangement into a single layer.^[78] To improve the separation performance further, PAI hollow fibers with more open and uniform surface pore structure, which permitted increased and uniform penetration of 2-mIm-containing solvents, was fabricated.^[79] Prepared ZIF-8 membranes showed unprecedented C₃H₆/C₃H₈ separation factors of 180 at 1 bar (R.T.) and 90 at 9.5 bar (R.T.), respectively. Furthermore, there was a 4-fold increase in C₃H₆ permeability at 9.5 bar as compared with operation at 1 bar. Long-term stability of hollowfiber-supported ZIF-8 membranes was further confirmed by continuous operation over one month.

By analogy to the counter-diffusion approach, Jeong et al. developed a microwave-assisted rapid seeding method enabling fast formation of uniform and close-packed ZIF-8 seed layers on porous substrates. Subsequent secondary growth of ZIF-8 seed layers led to the formation of well-intergrown ZIF-8 membranes with excellent C_3H_6/C_3H_8 selectivity (\approx 40).^[80] Further improvement of this method led to the formation of ZIF-8 membranes with optimized microstructures and exceptional C_3H_6/C_3H_8 selectivity (\approx 50), as illustrated in section 2.2.1.^[27] In addition, the influence of sodium formate to ligand ratios, the nature of zinc salts and solvothermal activation processes on final microstructures, and separation performance of ZIF-8 membranes was further investigated.^[81] The latest research progress involved development of a heteroepitaxial growth method to fabricate continuous and well-intergrown ZIF-8-ZIF-67

 Table 2. A detailed comparison between MOF-based composite membranes and MMMs.

Membrane type	Advantage	Disadvantage	
MOF-based composite	1. Potentially adapt to harsh operating conditions;	1. Suffer from a relatively low reproducibility;	
membranes	2. May lead to significantly enhanced gas selectivity;	2. Suffer from a relatively complicated fabrication procedure;	
	3. Possess higher mechanical strength.	3. May suffer from defect generation due to the large discrepancy in lattice parameters.	
MOF-based MMMs	1. Permit highly flexible membrane structures;	1. May be vulnerable to harsh operating conditions;	
	2. The membrane manufacturing process is relatively simple;	2. May suffer from plasticization after long-term use;	
	 Often lead to dual enhancement of permeability and selectivity. 	3. May become brittle after mixing with MOF particles.	

composite membranes^[66] showing unprecedentedly high C_3H_6/C_3H_8 selectivity (≈ 200), as discussed in section 2.3.2.

2.4.2. ZIF-8-Based MMMs

Koros et al. first fabricated ZIF-8/6FDA-DAM MMMs by simply mixing ZIF-8 nanoparticles (≈200 nm, BASF) with ZIF-8/6FDA-DAM polyimide.^[82] Good adhesion between ZIF-8 nanoparticles and 6FDA-DAM was demonstrated, and prepared MMMs exhibited 258% and 150% increases in C3H6 permeability and C₃H₆/C₃H₈ selectivity over pure 6FDA-DAM membranes with 48.0 wt.% ZIF-8 loading. In the next step, ZIF-8/6FDA-DAM MMMs showing significantly enhanced $C_{3}H_{6}/C_{3}H_{8}$ selectivity were successfully extended to scalable hollow-fiber geometry, representing a major advancement in the research area of MMMs.^[83] A recent study conducted by Chung et al. clearly indicated that the plasticization resistance and C3H6/C3H8 selectivity of ZIF-8/6FDA-DAM MMMs were strongly dependent on the amount of cross-linkable moiety and annealing temperature.^[84] Besides, ZIF-67 as an excellent substitute for the ZIF-8 counterpart was further integrated into the 6FDA-DAM polymer matrix, showing considerable C_3H_6/C_3H_8 selectivity as well as long-term operation stability.^[85]

3. Architectural Design of MOF Membranes at the Microscopic Level

Accurate architectural design of MOF membranes on a nanometer scale, which could be realized through aperture size adjustment, cage modification, and functional group post-decoration, may exert significant influence on the separation performance of MOF membranes.

Aperture size adjustment and cage modification mainly influence the diffusive selectivity of guest molecules within the MOF framework, especially in case the pore aperture and cavity size are in the range of the kinetic diameters of the guest molecules. In contrast, functional group post-decoration is employed mainly for the purpose of improving the adsorptive selectivity or eliminating intercrystalline defects within MOF membranes. In particular, as depicted below, the synergy among aperture size adjustment, cavity modification, and functional group postdecoration may jointly contribute to the performance improvement of MOF membranes.

3.1. Aperture Size Adjustment

MOF materials feature highly flexible pore apertures. In the case of MOF-based membranes, rational adjustment of their aperture size can be achieved through 1) metal ion substitution, 2) rational design and functionalization of ligands, and 3) pre-ferred orientation control.

Recently, we fabricated a series of dual-metal ZIF-108-polysulfone (PSF) MMMs showing attractive performance for separation of CO_2/N_2 and CO_2/CH_4 gas pairs due to enlarged aperture size and enhanced affinity for CO_2 after partial metal substitution of Zn^{2+} in ZIF-108 framework with Co^{2+} .^[86] In addition, Ni²⁺ partial substitution resulted in a remarkable increase in adsorption selectivity for ZIF-108 powders toward CO_2 over N₂ by a factor of up to 227. Similarly, through isomorphic substitution of Co^{2+} by Zn²⁺ in the ZIF-67 framework, Pan et al. fabricated well-intergrown ZIF-67 membranes for efficient separation of C_3H_6/C_3H_8 mixtures.^[77] Separation performances were found to increases with increasing the substituted amount of Zn²⁺, which could be attributed to the slight contraction of equivalent aperture size caused by partial Zn²⁺ substitution.

Rational design and functionalization of ligands was quite universal and effective for tailoring the aperture size of MOF membranes. Typically, a series of ZIF-based membranes with diverse aperture size, including ZIF-7 (2.9 Å),[16,23] ZIF-8 (3.4 Å),^[17,22] ZIF-22 (2.9 Å),^[33] ZIF-69 (4.4 Å),^[18,24] ZIF-71 (4.2 Å),^[43b] ZIF-78 (3.8 Å),^[43c] ZIF-90 (3.5 Å),^[34] ZIF-95 (3.7 Å),^[35] and ZIF-100 (3.4 Å),^[37b] have been prepared and exhibited diverse separation performances. These ZIF materials were constructed with identical metal ions (Zn^{2+}) but diverse organic ligands (a series of imidazole derivatives). Nair et al. further demonstrated continuous tuning of molecular sieving and adsorption behaviors of mixed-linker ZIF-8-90 frameworks, owing to the adjustability of equivalent aperture size and ratio of polar to nonpolar functional groups in the framework.^[87] Mixed-linker ZIF materials with different organic linker compositions were then served as fillers of MMMs.^[88] Gas permeation test demonstrated that inclusion of mixed-linker ZIFs yielded MMMs with better ideal CO2/CH4 selectivity than membranes containing ZIF-8, which was attributed to the enhanced diffusion selectivity associated with better control over the aperture size of mixed-linker ZIF fillers.

Zhu et al. prepared NH₂-MIL-53 membranes with 2-aminoterephthalic acid (NH₂-H₂BDC) as ligands.^[89] Owing to the unique 1D diamond shaped channels accompanied with high-affinity interactions between $-NH_2$ and CO₂, prepared membranes showed considerable permeability for H₂ together with very high H₂/CO₂ selectivity in comparison with unmodified MIL-53 membranes.^[42a] Similarly, Liu et al. further prepared UiO-66-CH₃ membranes by secondary growth with 2,5-dimethyl-terephthalic acid as ligands.^[90] It was observed that both hydrothermal stability and hydrophobicity of UiO-66 framework were strengthened by incorporating methyl groups into the organic ligand.

Preferred orientation control has proved to be efficient for realizing facet-tuned separation performance of MOF membranes. For instance, Peng et al. prepared cuboctahedron and octahedron HKUST-1 membranes with exposure of [001] facets with pore size of 0.9 nm and [111] facets with pore size of 0.46 nm, respectively.^[19] Since the window size of [111] facets (0.46 nm) was smaller than that of [001] facets (0.9 nm), HKUST-1 membranes with exposure of [001] facets demonstrated a higher CO₂ permeability but lower CO₂/SF₆ separation factor but lower CO₂ permeability (Table 1).

3.2. Cage Modification

Besides tailoring aperture size, cage modification is considered to be an alternative choice for tuning molecular sieving



behaviors of MOF membranes. Compared with aperture size adjustment, there exists substantial space for accurate manipulation of both the size and functionality of cages in MOFs. Cage modification, which can be categorized into in situ and postcage modification respectively, represents a new concept in the field of MOF membranes. In situ cage modification refers to embedding guest modifiers in cages during the synthesis of MOF materials. We have reported in situ confinement of an imidazolium-based IL [bmim][Tf2N] into ZIF-8's SOD cages via ionothermal synthesis. [Tf₂N]⁻ was considered favorable for CO2 adsorption while [bmim]+ was bulky enough for reduction of the cage size.^[91] After loading, the cage diameter had been reduced from 1.12 nm to 0.59 nm, which showed accurate molecular sieving behavior (Figure 14). In particular, IL@ ZIF-8-PSF MMMs exhibited remarkable enhancement of the CO_2/N_2 and CO_2/CH_4 selectivity without sacrificing the CO_2 permeability.

As mentioned in section 2.3.2., based on multivalent cation substitution, HKUST-1-MIL-100 composite membranes were successfully prepared under ambient conditions by partial transformation of pure HKUST-1 membranes.^[67] The remarkably enhanced separation performance of HKUST-1-MIL-100 composite membrane was to a large extent attributed to in situ embedment of amorphous FeCl₃ species in MIL-100 cavities during the conversion process, which equivalently narrowed the effective cage size and led to remarkably enhanced diffusive selectivity.

It should be noted that due to the restriction of aperture size, in most cases it was impractical for post-modification of cages with bulky guest molecules, with the exception of ion exchange. Eddaoudi et al. prepared well-intergrown *sod-*ZMOF membranes on α -alumina substrates, which showed strict size-based molecular sieving behaviors.^[92] Interestingly, *sod-*ZMOF possessed an anionic framework, and the positively charged imidazole SDAs located in the cavity may be exchanged by various inorganic cations, which in turn may exert significant influence on their gas-separation performance.

3.3. Functional Group Post-Decoration

In contrast to accurate manipulation of both the aperture size and cage of MOF membranes, which emphasized on optimization of their diffusive selectivity, functional group postdecoration of MOF membranes enabled enhanced adsorptive selectivity and sealed grain boundary defects. Based on the nature of interactions, functional groups post-decoration could be categorized into physical and chemical post-decoration, respectively.

Physical post-decoration is based on physical interactions between MOF layers and functional groups. Therefore, surface properties of MOF layers will not exert significant influence on the choice of modifying agents. Jeong et al. coated IRMOF-3 membranes with surfactant Span 80 during the drying process, which effectively reduced the capillary stress and resulted in the final formation of crack-free IRMOF-3 membranes.^[93]

Post-modification was also proved effective for patching defects in MOF membranes. Zhong et al. employed ionicliquid-functionalized multi-walled carbon nanotubes for sealing defective sites in ZIF-9 membranes. Owing to the cooperative effects of ZIFs, CNTs, and ILs ([BMIM][Tf₂N]), prepared CNT@ IL/ZIF-9 membranes showed an impressive H_2/CO_2 selectivity as high as 40.04.^[63] Similarly, Karanikolos et al. also reported sealing of defective sites in ZIF-69 membranes with [omim] [TCM] IL.^[65] Since IL components were highly selective to CO₂, functionalized ZIF-69 membranes exhibited an excellent selectivity (64) in the separation of CO_2/N_2 gas pairs.

Chemical post-decoration relies on chemical bonding interactions between MOFs and modifying agents so that modifying agents should be deliberately designed and selected based on the functionality of MOF materials. Compared with physical post-decoration, chemical post-decoration enabled to significantly change adsorptive selectivity, aperture size, and grainboundary structures of MOF membranes simultaneously. Huang et al. reported facile covalent post-functionalization of ZIF-90 membranes with ethanolamine^[94] and 3-aminopropyltriethoxysilane^[95] by an imine condensation reaction, respec-

b) in Hindebound to the interaction respectively. Prepared MOF membranes exhibited significantly enhanced H_2/CO_2 selectivity, which was attributed to contracted aperture size of ZIF-90 as well as reduced nonselective transport through invisible intercrystal-line defects. In addition, Jeong et al. further post-modified IRMOF-3 membranes with heptatonic anhydride, which in turn changed effective aperture size and surface property of IRMOF-3 membranes.^[93] Accordingly, prepared membranes favored C₃H₈ over CO₂, which was attributed to the increased solubility of C₃H₈ in the presence of hydrocarbon moiety.

4. The Frontier: Two-Dimensional MOF Membrane

It was noted that MOF materials employed in membrane fabrication dominantly possessed



Figure 14. Illustration of the cavity-occupying concept for tailoring the molecular sieving properties of ZIF-8 by incorporation of ILs. The cut-off size shifts from the aperture size of six-membered ring to the reduced effective cage-size by confinement of [bmim][Tf₂N] in a ZIF-8's SOD cage. Reproduced with permission.^[91] Copyright 2015, Wiley-VCH.



three-dimensional (3D) framework structures. In contrast, design, fabrication and application of two-dimensional (2D) layered MOF-based membranes, however, had not appeared until the year 2014.^[96] In principle, membranes constructed from 2D layered MOFs can be only one-atom thick, thus enabling minimization of the transport resistance and maximization of the permeability. Moreover, in contrast to their 3D counterparts, guest species enable to permeate through 2D layered MOF membranes and realize precise molecular sieving relying on either pores within MOF nanosheets (if any) or interlayer passages between neighboring nanosheets, which provides us with unprecedented opportunities to tailor their pore aperture and functionality. All these advantages make 2D layered MOFs superb candidates as high-performance separation membranes. Based on the phase purity, 2D layered MOF-based membranes can be further categorized into "pure" and "mixed-phase" types.

4.1. 2D MOF Membranes in a Pure Form

For the first time, we demonstrated the use of 1-nm-thick 2D MOF nanosheets as building blocks for the construction of ultrapermeable 2D layered MOF membranes showing excellent unprecedented H_2/CO_2 separation performance.^[96] Initially, monodispersed single $Zn_2(bim)_4$ sheets were prepared by exfoliation of bulk $Zn_2(bim)_4$ microcrystals with the newly developed soft-physical process involving low-speed, wet ball-milling and ultra-sonication-assisted exfoliation (**Figure 15**). Owing to the structural flexibility of $Zn_2(bim)_4$ nanosheets, the theoretical 0.21-nm-sized pores permitted permeation of H_2 through the membrane, while other larger gas molecules (for instance CO_2) were precisely excluded. In the next step, a hot-drop

coating technique was developed for a disordered stacking of 2D Zn₂(bim)₄ nanosheet building blocks on porous α -Al₂O₃ substrates. Under optimized conditions, a H₂/CO₂ mixed selectivity around 300 with a H₂ GPU around 3000, which had by far exceeded the latest Robesons upper-bound for the H₂/CO₂ gas pair, and easily reached the economically attractive region, was achieved on the 1.8-nm-thick 2D Zn₂(bim)₄ layered membrane.

Besides in delaminated form, Wang et al. further prepared preferentially *b*- and *c*-oriented 2D bulky ZIF-L membranes with the thickness of 10 and 5 μ m, respectively. ZIF-L possessed a cushion-shaped cavity between nanosheets with a dimension of 9.4 × 7.0 × 5.3 Å. The 2D layers stacking along the *c*-direction were part of the sodalite (SOD) topology.^[14] Owing to their relatively large cavity size (>5.3 Å) and considerable thickness (>5 μ m), prepared 2D layered ZIF-L membranes did not show superior separation performance (H₂/CO₂ and H₂/N₂) over other traditional 3D MOF membranes. To overcome this issue, both pore aperture and thickness of 2D layer MOF membranes should be precisely controlled.

4.2. 2D MOF Membranes in a Mixed-Phase Form

Besides in a pure form, 2D layered MOF nanosheets can further integrate with other materials (like 3D MOFs, GO, and polymers) and form highly compatible MOF-based mixedphase membranes. Kang et al. reported a novel methodology involving the employment of 2D layered ZIF-L as seed crystals for the epitaxial growth of continuous ZIF-8 layers, which ultimately led to the formation of ZIF-L-ZIF-8 composite membranes.^[97] This approach guaranteed effective incorporation of ZIF-L within the ZIF-8 matrix with a high volume fraction of



Figure 15. a) Architecture of layered MOF precursor. b) Illustration of the grid-like structure of $Zn_2(bim)_4$ nanosheets. c) Space-filling representation of $Zn_2(bim)_4$ nanosheets. d) TEM image of $Zn_2(bim)_4$ nanosheets. e) SEM top and f) cross-sectional view of a $Zn_2(bim)_4$ layer on α -Al₂O₃ support. Reproduced with permission.^[96] Copyright 2014, American Association for the Advancement of Science.

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ZIF-L (\approx 28%). Compared with pure ZIF-8 membranes, ZIF-L-ZIF-8 composited membranes exhibited a three-fold enhancement in H₂ permeability, as well as a rational increase in H₂/ CO₂ selectivity (from 2.3 to 4.7). The superior separation performance of ZIF-L@ZIF-8 composite membranes was attributed to the intrinsically high diffusivity of ZIF-L for H₂.

Zhong et al. proposed a GO-assisted layer-by-layer restacking method to fabricate ultrathin GO-CTF-1 composite membranes for gas separation.^[98] Favorable functional group interactions between GO and CTF-1 nanosheets led to the formation of continuous and ultrathin GO-CTF-1 composite membranes (\approx 100 nm) with a narrow interlayer passages. Prepared membranes exhibited very high H₂ permeance (1.7 × 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹) as well as a competitive H₂/CO₂ selectivity.

In addition, as mentioned in the section 2.3.3., relying on the diffusion-mediated modulation of the MOF growth, Gascon and Kapteijn et al. developed a bottom-up synthesis strategy and kinetics, and successfully prepared Cu(1,4-bdc) nanosheets that could be readily dispersed into polyimide matrix.^[72] In comparison with bulk MOF-based MMMs, 2D layered MOF-based MMMs showed remarkably enhanced performance in CO₂/CH₄ gas separation, which was mainly attributed to a superior occupation of the membrane crosssection by ultrathin MOF nanosheets, as compared with bulk crystals.

4.3. Challenging Issues in the Construction of 2D MOF-Based Membranes

As mentioned above, 2D MOF-based membranes have shown unprecedented opportunities for energy-efficient gas separation. Nevertheless, several critical issues are still waiting to be solved before the large scale commercialization.

First, simplification of the 2D-MOF-nanosheet fabrication process. Currently, MOF nanosheets are mainly obtained through controlled top-down exfoliation of bulk MOF microcrystals. Nonetheless, it is still a challenging task to obtain MOF-nanosheet building blocks with balanced integrity, grain size, thickness, monodispersity, and productivity. Therefore, it is highly desirable that a facile and general method (in particular, a bottom-up approach) could be developed for bulk preparation of high-quality MOF nanosheets.

Second, uniform distribution of 2D MOF nanosheets on substrates with controlled microstructures (including thickness, preferred orientation, and interlayer structures). As mentioned above, microstructures of 2D MOF membranes usually exert significant influence on their separation performance. Nanosized membrane thickness (preferentially <20 nm) is beneficial for maintaining a high gas permeability; oriented arrangement of 2D MOF nanosheets is beneficial for alleviation of nonselective diffusion of gas molecules through intercrystal gaps; while interlayer structure represents an exceptionally important microstructural parameter dominating separation performance of 2D MOF membranes. It is therefore anticipated that an innovative process allowing facile deposition of 2D MOF nanosheets with controlled microstructures can be developed. Recently, Tsapatsis et al. reported a Langmuir–Schaefer deposition method for facile self-assembly of 3-nm-thick mordenite framework inverted (MFI) nanosheets on silicon wafers. Combined with layer-by-layer deposition, an accurate control on film thickness was ultimately demonstrated.^[99] The validity of this approach for controlled selfassembly of 2D MOF nanosheets, however, still requires further verification.

Third, long-term operation stability under harsh operating conditions. Owing to the fragile nature of single 2D MOF nanosheets and lack of strong interlayer interaction, prepared 2D MOF membranes may be vulnerable to harsh operating conditions (like high pressure drop and operating temperature) and, ultimately, lose their permselectivity. Strengthening of interlayer bonding interactions between neighboring 2D MOF nanosheets (like introduction of pillaring ligands or covalent post-synthetic modification), which is still largely unexplored to date, may be critical for promoting their large-scale applications in industry.

5. Conclusion

In recent years, a significant progress has been made in rational design and production of MOF membranes, along with an exponential increasing of publications discussing their potential applications in energy-efficient gas separation. In order to compete with current separation and purification technologies, not only the separation performance (including both gas permeability and selectivity) of MOF membranes should reach the economically attractive region, but also some other challenges facing practical applications of MOF membranes, such as the low mechanical stability, scale-up difficulty, high substrate costs, and poor membrane reproducibility, have to be conquered. Aiming at its practical applications in energy-efficient gas separation, it is proposed that a major breakthrough could possibly be made by 1) employing diverse 2D layered MOF nanosheets as building blocks for the construction of high performance MOF-based membranes; 2) using polymer hollow fibers as substrates; 3) developing new membrane fabrication processes, and 4) exploring MOF-based composite membranes or MMMs.

1) Construction of diverse 2D layered MOF-based ultrathin membranes. As mentioned above, 2D layered materials have been considered as superb candidates for high-performance separation membranes due to the unprecedented single-atom thickness in theory, extraordinary mechanical flexibility, and diversified mechanism for molecular sieving.^[100] Moreover, 2D layered MOFs further exhibited certain superiority over other 2D layered materials due to their highly tailorable aperture size and functionality. Besides ZIF-L and Zn₂(bim)₄, a wide range of 2D layered MOFs with attractive aperture size and functionality, like $In(OH)(C_{17}H_8F_6O_4)$, ^[101] $Zn(TPA)(H_2O) \cdot DMF$, ^[102] $Cu(bpy)_2(OTf)_{2,}^{[103]}$ $Cu(\mu-pym_2S_2)(\mu-Cl),^{[104]}$ $Mn_8(pshz)_8$ (bpea)₂(dma)₄,^[105] and CIDs^[106–108] have been successfully synthesized and well-characterized. It is anticipated that these precisely designed 2D layered ultrathin MOF membranes with optimized microstructures will provide us with





unprecedented opportunities for potential industrial applications in energy-efficient gas separation. So far, 2D layered MOF-based ultrathin membranes are to a great extent a rarely explored research field, which definitely deserves further exploration in the near future.

- 2) Expanding the use of polymeric hollow fibers as substrates. Besides the intrinsic high affinity MOF-polymer interactions, polymeric hollow fibers themselves may further offer additional selectivity so that polymeric-hollow-fiber-supported MOF membranes usually exhibit higher gas selectivity than on nonselective substrates. Additional benefits for polymeric hollow fibers include their flexibility, ease in large scale production, high pressure stability, and large membrane surface area available per unit volume. A wide range of polymerichollow-fiber-supported MOF membranes have been reported, and some of them indeed exhibited impressive separation performance. We feel optimistic that the widespread application of polymeric hollow fibers would significantly advance commercialization of MOF membranes in the near future.
- 3) Development of new process technology in MOF membrane fabrication. Besides in situ and secondary growth, emerging process technologies, which typically include IMMP, electrospray deposition, microfluidics, vacuum filtration, and LBL assembly, are very promising for large-scale production of high-performance MOF membranes due to obvious advantages like facile control over the membrane position, reinforced mechanical stability, tunable membrane thickness, significant reduction in reagent consumption, and easy implantation. It is anticipated that other facile and efficient approaches should be developed for fabrication of MOF membranes with improved microstructure and separation performance based on the unique property of MOF materials.
- 4) Exploration of the potential of MOF-based mixed-phase membranes. As mentioned above, in comparison with initial single-phase membranes, most MOF-based composite membranes and MMMs have shown significantly enhanced gas selectivity, owing to synergistic effects between MOFs and the other phase. In the near future, facile and general approaches for a simultaneous increase of both selectivity and permeability of MOF-based mixed-phase membranes should be developed, which could be a shortcut to exceeding the Robesons upper-bound for desired gas pair, and ultimately reaching the economically attractive region.

Acknowledgements

W.Y. thanks the financial support of the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17020400), National Natural Science Foundation of China. Y.L. thanks the financial support of "the Fundamental Research Funds for the Central Universities (DUT16RC(3)103)".

Conflict of Interest

The authors declare no conflict of interest.

Keywords

architectures, membranes, metal–organic frameworks, microstructures, separations

Received: December 24, 2016 Revised: March 31, 2017 Published online: June 19, 2017

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