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MOFs meet membrane: application in water treatment and separation

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Metal–organic frameworks (MOFs) are a class of solid crystalline materials formed by the self-assembly of organic ligands and metal ions or clusters through coordination bonds. Owing to their intrinsic rich chemical composition, large specific surface area, diverse topology, tunable pore channels and good thermal stability, MOFs are favored in many applications. In particular, MOFs are considered to be viable membrane-based separation materials based on their unique advantages in the adsorption of specific chemicals. Research into MOF-based membrane-preparation methods and separation applications is flourishing, and MOF-based membranes have achieved marvellous achievements in the field of gas separation and liquid separation. This review first introduces the general criteria for selecting MOFs for separation applications. Then, we specifically describe how to prepare MOF-based membranes as well as the specific classification of MOF hybrid membranes, and finally describe the application of MOF-based membranes in water treatment. Most of all, the opportunities and challenges of MOF membranes in industrial applications are outlined.

1. Introduction

Separation is widely used and plays a significant role in our daily life and industrial applications. However, traditional separation techniques such as distillation, filtration, *etc.*, are not easy to operate and are expensive when completing separation operations, hindering their practical application.[1] Recently, membrane technology has been proved to be an excellent alternative to traditional separation technologies in applications due to its high separation efficiency, low secondary pollution, and environmental friendliness. Selective separation at the molecular level can be achieved when mixtures of molecules of different particle sizes pass through a semi-permeable membrane.[2] However, the efficiency of membrane separation technologies is often affected by the interplay between the membrane permeability and selectivity. To the best of our knowledge, rubbery polymers have been demonstrated to be more permeable, whereas glassy polymers exhibit better selectivity.[3] In order to achieve simultaneously high permeability and selectivity in membrane separation, it is particularly important to develop new types of separation membrane. In most cases, good separation cannot be achieved due to harsh operating conditions. Inorganic membranes have attracted a lot of attention as ideal membrane separation materials that have stable chemical properties and an excellent separation performance. Currently, materials processed into inorganic membranes include metals, ceramics, silicon, carbon, zeolites, metal–organic frameworks (MOFs), *etc.* In various separation applications, various kinds of inorganic membrane have been utilized, depending on the properties of the materials. Among them, MOFs are of great interest because of their large surface area, rich chemical functionality, tunable pore system, and good thermal stability.[4]

Metal–organic frameworks (MOFs), a class of materials containing pores made of metal ions or ionic clusters bonded to organic ligands, are also known as porous coordination polymers (PCPs).[5,6] Unlike other materials, MOFs are preferred because of their rich chemical composition, large specific surface area, diverse topology, adjustable pore channels, and thermal stability.[7] Based on these advantages, MOF scaffolds have been applied to enhance the adsorption of specific chemicals for precise and rapid separation.[8,9] MOFs are considered to be viable membrane-based separation materials and are typically grown on substrates to construct continuous membranes or are used as fillers to form mixed matrix membranes (MMMs). The organic nature of the MOF framework can enable interactions with polymers, resulting in good compatibility.[10] Combining the benefits of MOF materials and polymeric fillers, such produced MOF-based membranes demonstrate increased permeability and perhaps selectivity compared with virgin membranes.

In past studies, MOF-based membranes have displayed extraordinary possibilities in many applications, particularly in gas separation and purification. In gas separation, advances in MOF membrane applications have been summarized in many articles. In contrast, few review articles are available on

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the synthesis and application of MOF membranes in liquid separation, particularly in water treatment. Herein, the preparation standards and methods of MOF-based membranes, as well as the classification of the various types of MOF hybrid membrane, are systematically reviewed in this paper. Then, MOF-based membranes are highlighted for the treatment of heavy metal ions, organic pollutants, and radionuclides in wastewater as well as oil–water separation and seawater desalination. Finally, the prospects of MOF-based membranes in industrial applications are discussed, and possible opportunities and challenges in the fabrication and application of MOF-based membranes are outlined in the hope of facilitating the realization of these membranes in practical applications.

2. Design criteria for MOF-based membranes

2.1 Selection criteria for MOFs

As a porous crystalline material, MOFs, with their flexible structure, high specific surface area and abundant adsorption sites, largely determine the separation ability of MOF-based membranes.[11] And in recent years, polymeric materials have become popular in the field of membrane separation because of their advantageous mechanical strength, plasticity and high elasticity.[12] In order to prepare MOF membranes with an excellent performance, researchers considered combining MOF and polymeric materials to combine the tunable pore structure and high specific surface area of the MOF with the strong mechanical strength of the polymeric material to achieve a more stable and efficient membrane separation performance. Combining MOFs and polymers, while retaining the advantages of the MOF material with its high specific surface area, can also avoid the excessive agglomeration of MOF crystals, making them more evenly dispersed in the polymer, which can better exploit their advantages. As for the polymer, the addition of MOFs makes it more flexible and improves the separation performance of polymer material in membrane separation. Therefore, combining the two would be a good choice for membrane separation. How to prepare MOF-based membranes that show an excellent performance will be the key consideration. High-efficiency MOF-based membranes should have excellent separation capabilities, high recyclability and stability, and be environmentally friendly. According to these criteria, MOFs should be homogeneously dispersed in the polymer, providing strong hydrothermal stability, hydrophilicity,[13] suitable pore sizes, and small particle sizes.[14]

Uniform dispersion. Interfacial defects are largely influenced by the dispersion of MOFs in the polymer, and an inhomogeneous dispersion of MOFs leads to the inability to form a complete laminar structure and defect-free membranes, thus degrading the performance of the MMMs. The successful preparation of MOF-based membranes with an excellent separation efficiency requires both a maximum loading and a uniform dispersion of the MOFs. Researchers have proposed several strategies to homogeneously disperse MOFs in hybrid membranes. (i) Pre-dispersion: MOFs will be poorly distributed if they are dispersed directly in the polymer during preparation; thus, as a typical example, zeolitic imidazolate framework (ZIF) particles (ZIF-8) were dispersed in isooctane, followed by treatment in an ice bath and heating to room temperature, and then the isooctane solution of ZIF-8 was mixed with the rest of the mixture to produce a homogeneously dispersed mixture.[15] In addition, it has been shown that in the preparation of chitosan (CS)/ZIF-8 MMMs, 10% of the desired CS was first added to the ZIF-8 suspension to achieve a uniform dispersion and maintain good adhesion, after which the remaining CS was added to obtain the desired concentration of CS solution.[16] (ii) Surface modification of MOFs: a general modification method is to enhance the dispersion properties of MOFs by introducing other functional groups. For example, Ma *et al.* prepared MOF/chitosan nanofiltration (NF) membranes *via* the amino modification of a Matériaux de l'Institut Lavoisier (MIL) framework (MIL-101) which was then combined with chitosan. MOF particles were evenly distributed in the chitosan polymeric matrix, significantly enhancing the flux and repulsion of the NF membrane cations.[17] (iii) Self-assembly technology: MOF particles are grown within the polymer *in situ*, while metal ions coordinate simultaneously with both MOF ligands and the functionalized organic polymer. As a result, the membrane is highly compatible and the MOFs are uniformly distributed. Adopting this method, an ultrathin ZIF-8/poly(sodium 4-styrene-sulfonate) (PSS) membrane that can effectively separate dyes was prepared.[18] Shahid and co-workers[19] optimized the MOF–polymer interactions using self-assembly and the controlled fusion of MOF and polymer particles to obtain well-dispersed ZIF-8.

Strong water stability. Considering the instability of the ligand–metal bonds of MOFs, they are extremely sensitive to water and are not suitable for use in aqueous environments. Only MOFs with strongly coordinated bonds or notable steric hindrance in the structure show good water stability.[20] In 2015, Liu *et al.* prepared the first highly water-stable UiO-66 membrane.[21] This study demonstrated that the UiO-66 MOF material can be a good choice as a membrane material for water treatment. According to the current studies, water-stable MOFs (such as MIL-100, MIL-101, ZIF-8 and UiO-66) are mainly metal carboxylate frameworks that consist of high-valence metal ions, metal azole frameworks that contain nitrogen donor ligands, and MOFs functionalized with hydrophobic pore surfaces or with clogged metal ions.[22–25] Composite membranes prepared from water-stable MOFs have a relatively high separation performance. Considering that some MOFs with poor water stability still exist, some post-synthesis modifications such as ligand modification,[26] metal and ligand exchange[27] have also been designed to improve the hydrothermal stability of MOFs.

Rational choice of hydrophilicity/hydrophobicity. Ligands and the availability of unoccupied metal sites in MOFs determine their hydrophilicity/hydrophobicity. When applying MOFs to water pollution remediation, appropriate MOF materials must be selected for target compounds with different properties. Hydrophobic MOFs usually have a remarkable ability to adsorb organic matter in water during full evaporation, for example ZIF-71, which can selectively adsorb alcohol in alcohol–water mixtures.[28] In contrast, hydrophilic MOFs show a better ability when treating dyes with MOF-based membranes. To enhance the hydrophilicity of MOFs, Zhu *et al.* fabricated thin film nanocomposite (TFN) membranes containing poly(sodium

4-styrenesulfonate) (PSS)-modified ZIF-8 in a polyamide (PA) layer using the interfacial polymerization (IP) technique.[29] Such ZIF-8 TFN membranes have a much higher hydrophilicity and water flux, and can remove >99.0% of dyes.

Suitable pore size. MOFs are preferred for membrane separation applications due to their adaptability and designability. A crucial factor determined membrane separation technology is the pore size of the MOFs. By increasing the chain length, introducing functional groups, and using the right linkers, the pore size can be changed. For example, ZIF-8 possesses a pore aperture diameter of 3.4 Å and a gate-opening diameter of 4.2 Å, and is able to separate water with a kinetic radius of 2.6 Å from ethanol with a kinetic radius of 4.5 Å.[30] Therefore, the selection of MOF materials with suitable pore diameters when performing separations can well achieve the screening of different pore size separation materials for separation purposes.

2.2 Impact factors related to polymer membrane performance

MOF polymer hybrid membranes are the most widely used class of MOF-based membranes. Combining organic and inorganic materials creates a membrane with the properties of both and a performance that is superior to that of the two phases alone. The primary requirements when choosing polymer substrates include strong chemical stability, excellent separation properties, and excellent mechanical strength. In addition, the swelling properties, solubility, and processability of the polymer should not be neglected. The molecular weight, glass transition temperature, melting point, crystallinity, and polarity are the main factors that affect the performance of polymer membranes.[31] The molecular weight is a true reflection of the degree of polymerization of organic matter and determines the viscosity, mechanical strength, and chemical stability of the polymer. Typically, the polymer viscosity, mechanical strength, and chemical stability increase with the molecular weight. In addition, the temperature affects the properties of the polymer and how it changes physically. When heated, an amorphous nucleated thermoplastic polymer transitions from a glassy state to a rubbery or pliable plastic state at a temperature known as the "glass transition temperature" (T_g). The T_g value can reflect the rigidity and flexibility of polymer chains,[32] where a low T_g increases the chain flexibility and activity. During the heat treatment of crystalline polymers, crystalline polymers's upper temperature-melting point should be considered. For rubber-based polymers, the operating temperature should be sited between the glass transition temperature and the melting point. Another significant factor in determining the performance of polymer membrane separations is the degree of crystallinity. High crystalline polymer levels reduce the permeability of the guest molecule and inhibit the membrane-separation performance.[33] An uneven charge distribution in polymers can lead to polarity. The charge density, dipole moment, and hydrogen bonding of the functional groups contained in the polymer cause the polymer to be polarized. A greater polymer polarity requires more hydrogen bonds to absorb electrons. According to the principle of "like dissolves like", polymers with polar solubility exhibit a stronger adsorption-solubilization effect on polar compounds and can achieve improved separation. Therefore, when selecting a polymer, it is necessary to consider not only its mechanical strength and water stability but also the nature of the object to be treated.[34] Polymers with a low T_g are more flexible and mobile, forming continuous dynamic channels inside the polymer molecules, and a higher permeability to liquid molecules; polymers with a high hydrophobicity are more suitable for organic separation, and the higher the T_g, the more rigid and chemically stable they are.[35,36] Many polymers have been used to be laminated with MOFs to form membranes, but not all are suitable, and the choice of polymer type should be made wisely. As for the synthesis of polymers, since MOF polymer hybrids are prepared using already synthesized polymer materials, there are no special requirements for the synthesis conditions, which will not be described in detail herein.

3. Synthesis of MOF-based membranes

Manufacturing completely continuous, complete and defect-free membranes is key to creating MOF-based membranes. Through the tireless efforts of researchers, significant advances have been made in the development of a variety of membrane fabrication techniques over the past decade (Table 1). Next, we will detail the more commonly used synthesis methods (Fig. 1).

3.1 *In situ* growth method

As a classical MOF membrane synthesis method, the *in situ* growth method has been used extensively (Fig. 2). The substrate is submerged directly in the reaction solution containing the metal solution and the linker, allowing them to diffuse in the same direction, thus enabling the MOF membranes to grow through the crystallization reaction. In this process, two steps, which include ion adsorption and crystal nucleation, must be completed. Remarkably, a wide variety of MOF membranes can be obtained through *in situ* growth. According to the nature of the substrate, three approaches – direct synthesis, modified substrate synthesis, and the "same metal source" method – have been developed to prepare continuous MOF membranes.[37]

The direct synthesis method is defined herein as the direct *in situ* formation of membranes on substrates without modification. In 2009, Liu *et al.* successfully prepared the first continuous and well-intergrown MOF-5 membrane *via* an *in situ* solvothermal method using α-Al_2O_3 as a porous scaffold.[38] The resulting membrane had a thickness of about 25 μm, was free of defects, and had a high specific surface area. Meanwhile, the membrane was strongly bonded to the carrier and could withstand high temperatures, with the MOF-5 structure remaining stable up to 400 °C. Although this method is easy to operate, the surface of the unmodified substrate fails to offer adequate nucleation sites. In addition, MOFs tend to nucleate and grow in solution under normal operating conditions, resulting in uneven membrane formation and easy detachment from the substrate, which cannot be widely applied. According to the reported studies, this synthesis method was more often used for the synthesis of ZIF-type MOF membranes, such as ZIF-8 membranes[39] and ZIF-69 membranes.[40]

An excellent way to improve the problem of poor substrate bonding is *via* chemical modification of the support. Following

Table 1 Summary of the characteristics of common synthetic methods for MOF membranes

Method		Brief description	Advantages	Disadvantages	Ref.
In situ growth		Substrate directly immersed in growth solution, isotropic diffusion	Simple manipulation, easy to operate Low manufacturing cost Wide range of applications	MOF membranes are not tightly bound to each other, and thickness cannot be adjusted	38 and 41–45
Secondary growth		Seed crystals need to be grown on the substrate, and then placed in the MOF reaction solution for secondary growth	High crystallinity Wide range of applications Good control of the thickness and direction of membrane growth More stability	Complex operation Higher requirements for seed crystals	52–54
Layer-by-layer (LBL) growth/liquid-phase epitaxy (LPE)		The substrate is immersed in metal-only and ligand-only solutions for repeated crystal growth	Mild preparation conditions Suitable for large-scale production Precise control of membrane thickness	Time-consuming High cost Cannot produce a defect-free membrane layer	57 and 108
Electrochemical deposition (ECD)		MOFs are grown only on the conducting part of the substrate, and the membrane thickness can be controlled by tuning the voltage and electrolyte	Adjustable external conditions Mild reaction conditions Low solvent consumption	N_2 environment required Slow membrane formation speed Generation of by-products	69
Chemical vapor deposition (CVD)		Consists of two steps: adsorption and reaction	High crystallinity, no chemical contamination and corrosion	High operating temperature Product transfer difficulties	74
Atomic layer deposition (ALD)		Different gas-phase precursors are alternately passed through the reactor to complete the corresponding physical and chemical reactions to produce the MOF membranes	No solvent consumption possible Self-terminating, the thickness can be controlled down to the subnanometer level	High cost Slow deposition rate	80 and 81
Blending		MOF particles and polymers are mixed directly without any modification to form a stable solution and then coated on the substrate surface	Without the limitation of the substrate Easy to use Substrate independent Wide range of MOFs to choose from	Poor compatibility of MOFs with organic polymers, membrane-formation difficulties	83 and 84
Post-modification polymerization	Interfacial polymerization (IP)	Membrane formation *via* reverse diffusion after the polymerization of two incompatible solvents at the intersecting interface	Simple preparation process Does not alter the mechanical flexibility of the membranes, excellent scalability	Small application range	89 and 90
	Post-synthetic polymerization (PSP)	Covalent linking of MOFs crystals *via* flexible polymer chains	Improved MOF particle agglomeration and compatibility	Complicated operation	95 and 96
	Electrospinning	Microfibers of micron and submicron diameters are used to synthesize polymer films *via* certain methods	Large porosity and specific surface area Good structural and chemical adjustability Avoids corrosion or oxidation Mild reaction conditions	Easy to aggregate Difficult to operate	103–107

this idea, modified substrate synthesis was proposed. First, the substrate was modified with organic compounds (such as polydopamine) or inorganic compounds (such as hydroxide and metal oxide/sulfide, *etc.*). Then the modified substrate is self-grown into a membrane in the precursor reaction solution. For example, Hermes and co-workers selected COOH/CF_3 groups to modify Au(111) substrates to achieve the selective nucleation and growth of MOF-5 membranes.[41] The resulting membranes represented the creation of a new organic–inorganic, hierarchical nanocomposite functional material, where the MOF-5 membranes not only reached a thickness of 500 nm but also adhered well to the surface of the substrate. Inspired by this research concept, Huang *et al.* developed a range of continuously grown ZIF membranes (such as ZIF-22, ZIF-8 and ZIF-7 membranes) using 3-aminopropyltriethoxysilane (APTES) as a covalent linker to modify porous ceramic supports (such as TiO_2, Al_2O_3).[42] Similarly, under mild conditions, stainless-steel-nets (SSNs) were functionalized with polydopamine, and then added to the precursor solution. Covalent bonds of Zn–N and Zn–O were formed between the growing ZIF-8 layer and the carrier, which contributed to the nucleation and growth of the ZIF-8 membrane (Fig. 3).[43] Not only did this method synthesize dense and continuous ZIF-8 membranes, which had an excellent membrane performance, it also had a low manufacturing cost, making it suitable for mass production.

In both of these methods, the substrate plays only a supporting role. Unlike the above two methods, in the "same metal source" synthesis method, the substrate contains the same metal as the grown MOFs, enabling the reaction process to proceed without the addition of additional metal ions, while enhancing the bonding between the membrane layer and the substrate. Initially, the "twin copper source" method was proposed by Guo *et al.*[44] The copper mesh that generated green copper oxide on the surface after heat treatment was mixed with a solution containing copper nitrate and trimeric acid for a specific period of time, and the HKUST-1 ([$Cu_3(BTC)_2$]) membrane was generated on the surface of the copper mesh. In this reaction, the metal source for crystal growth is Cu^{2+} on both the copper net and in the reaction

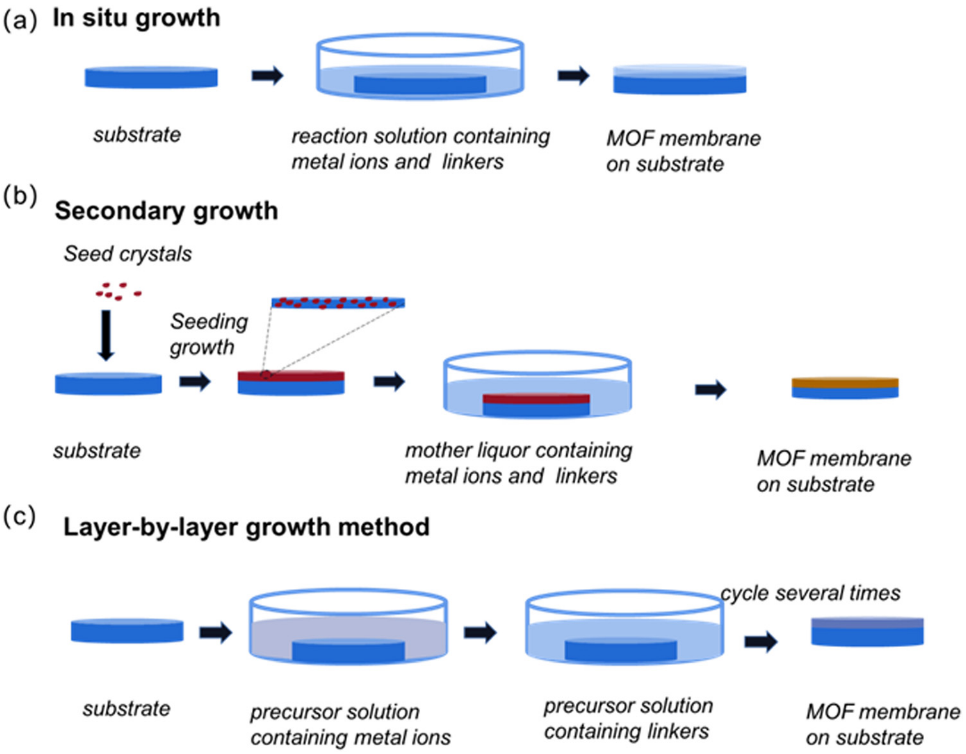

Fig. 1 Schematic illustration of three commonly used MOF-based membrane preparation routes.

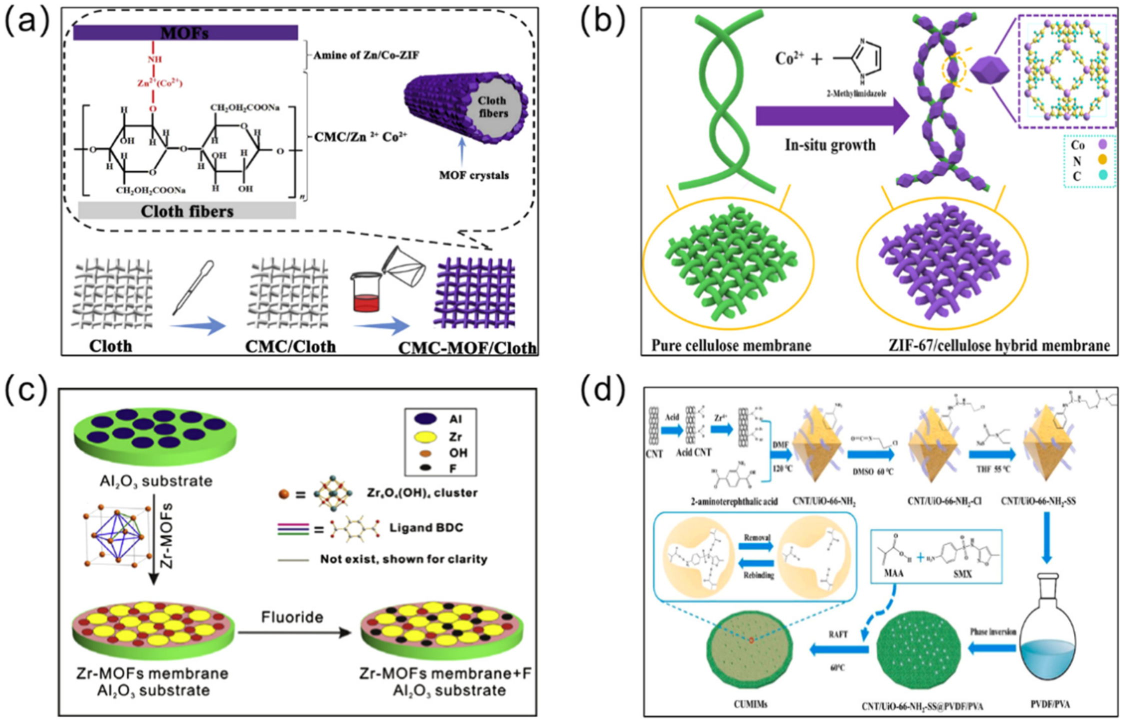

Fig. 2 Schematic diagrams of *in situ* synthesized MOF membranes. (a) Rapid *in situ* synthesis of CMC/cloth and CMC-MOF/cloth composite membranes. Reprinted with permission from ref. 46. Copyright 2018 Elsevier. (b) *In situ* synthesis of a ZIF-67/cellulose hybrid membrane. Reprinted with permission from ref. 47. Copyright 2021 Springer. (c) Preparation of a Zr-MOF membrane using the *in situ* solvent thermal method. Reprinted with permission from ref. 48. Copyright 2016 Elsevier. (d) *In situ* synthesis of CNT/UiO-66-NH_2-based molecularly imprinted nanocomposite membranes. Reprinted with permission from ref. 49. Copyright 2022 Elsevier.

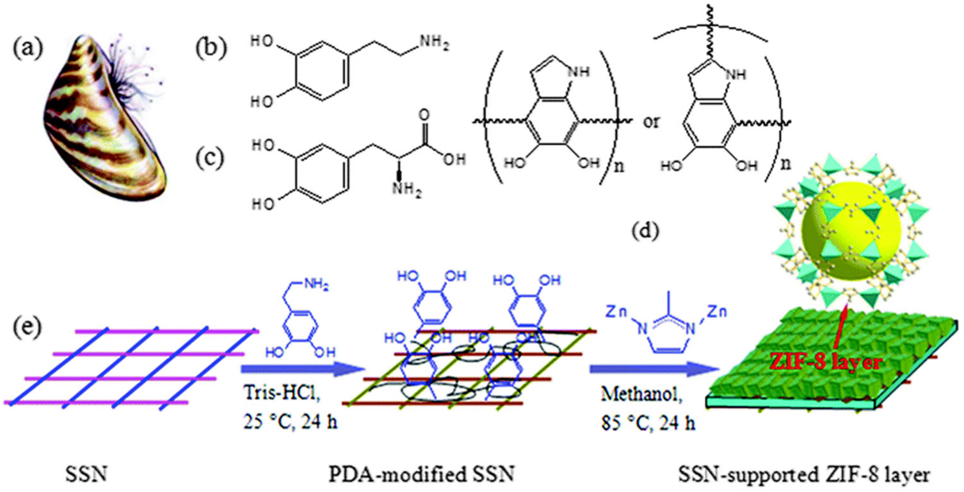

Fig. 3 Mussel with byssus threads (a); chemical structures of DPA (b), DOPA (c), and PDA (d); and schematic of the preparation of a ZIF-8 molecular sieve membrane on a PDA-functionalized SSN (e). Reprinted with permission from ref. 43. Copyright 2014 Royal Society of Chemistry.

solution, which provided the crystal with a sufficient metal source to form uniform nucleation sites for continuous membrane growth. Unlike other MOF membranes based on Al_2O_3 and ceramics, this MOF membrane contained a larger void volume and a higher permeability. In view of the advantages of the bimetallic source synthesis method, Neelakanda *et al.* used the double-zinc-source method to prepare ZIF-8 membranes.[45] ZIF-8 membranes were prepared using the *in situ* method. First, a thin ZnO layer was deposited on a polyacrylonitrile (PAN) support membrane *via* magnetron sputtering, followed by nucleation and crystal growth to form a continuous ZIF-8 membrane. The main advantages of the double-zinc-source method are the rapid synthesis speed and the simple synthesis conditions.

3.2 Secondary growth method

The secondary growth method (or seeded-assisted growth method) also has wide applicability, and achieves the generation of MOF membranes by first attaching the seed crystals to the substrate and then subjecting them to solvent heat treatment by immersing them in the mother liquor.[50] Unlike *in situ* growth, which usually results in an unsatisfactory membrane thickness, secondary growth enables easier control over the membrane thickness and direction. An important component of the secondary growth method is the seed layer. The seed size, seed layer thickness, and the bond between the seed layer and substrate all affect the separation efficiency of the resulting MOF membranes. Currently, rub-coating, dip-coating, the wiping method, spin-coating, thermal seeding and step-by-step seeding methods have been used to prepare seed layers.[51] The secondary growth method is a relatively mature method for preparing MOF membranes. For instance, Yuan *et al.* obtained a ZIF-300 membrane *via* the secondary growth method.[52] Firstly, they added ZIF-300 seeds on an α-Al_2O_3 substrate and then immersed them in a mixed solution for the solvothermal preparation of a pure ZIF-300 membrane (Fig. 4). From this, a ZIF-300 membrane about 10 μm thick was formed, which can remove 99.21% of heavy metal ions, showing good water stability and high-water permeability.

For the secondary growth method, the preparation of the seed layer is crucial, and both spin coating and dip coating are the most commonly used methods for preparing the seed layer. Gascon *et al.* coated a $Cu_3(BTC)_2$ seed solution on an α-Al_2O_3 membrane using the spin-coating method, and a $Cu_3(BTC)_2$ membrane of about 2 μm thick was prepared *via* secondary growth.[53] Fang *et al.* prepared UiO-66 and UiO-66-NH_2 membranes with thicknesses of 1.6 μm and 1.3 μm, respectively, by dip-coating UiO-66 NPs and UiO-66-NH_2 NPs onto α-Al_2O_3 tubular scaffolds.[54] Both the UiO-66 and UiO-66-NH_2 membranes exhibited a high rhodamine B (RB) removal rate ($>80\%$), and exhibited high permeability, good dye selectivity and reusability. Secondary growth can not only achieve uniform nucleation and control over the growth thickness of the membrane, but can also be used to obtain the ideal thickness of the membrane materials. One major issue that hinders the further development and large-scale application of this approach is that the operating conditions are complicated.

3.3 Layer-by-layer (LBL) growth method

The layer-by-layer (LBL) growth method, also known as liquid-phase epitaxy (LPE), begins with the repeated immersion of the substrate into respective solutions containing metal ions and organic ligands, where the layer is deposited continuously over several cycles after rinsing off the excess precursor solution, forming a continuous MOF layer[55] (Fig. 5). The most important feature of the LBL method is the ability to form a continuous MOF layer of precisely controlled thickness under mild conditions, and due to the unique advantages of LBL technology, an important class of MOF membranes, *i.e.*, surface-attached metal–organic frameworks (SURMOFs) can be produced.[56] Three types of SURMOF, namely HUKST-1, laminated MOF and hybrid MOF (MOF-on-MOF), have been reported so far, all of which have shown great potential and wide applications in water treatment. Taking inspiration from the LBL method, Shekhah *et al.* constructed the first ZIF-8 membranes *via* LBL deposition on an α-Al_2O_3 support.[57] After 150 cycles, extremely thin (0.5–1 μm) and uninterrupted ZIF-8 membranes were obtained for the separation of H_2–CO_2, H_2–N_2,

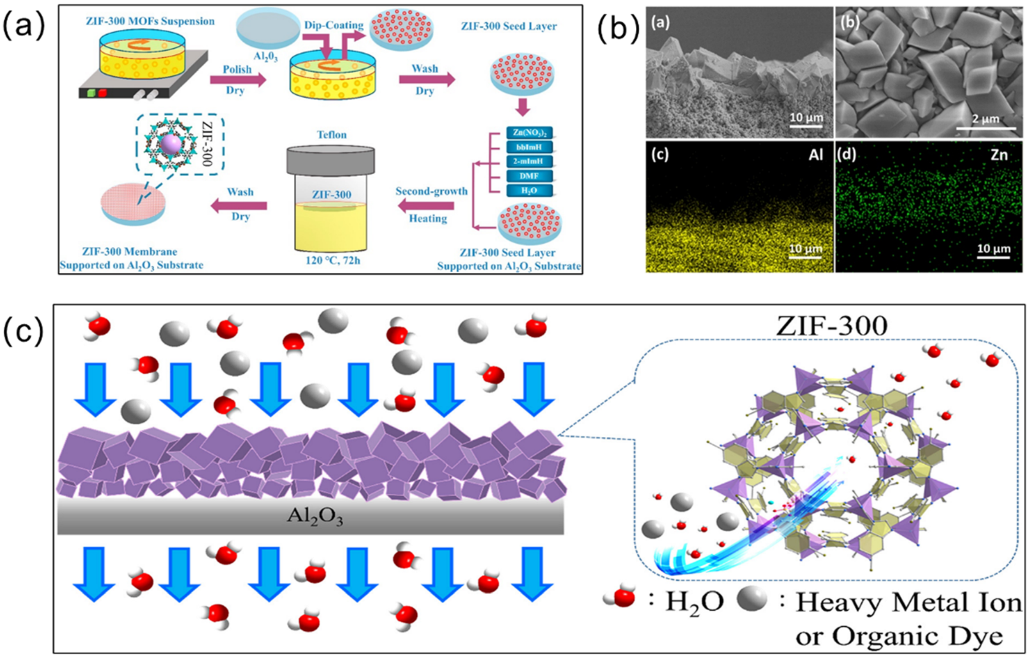

Fig. 4 (a) Preparation of a ZIF-300 membrane using the secondary growth method. (b) SEM images (a, cross-section; b, surface) and EDXS mapping images (for Al (c, yellow) and Zn (d, green), corresponding to a) of the defect-free ZIF-300 membrane supported on the Al_2O_3 substrate (120 °C, 72 h). (c) Schematic of the process of removing heavy metal ions from water on the basis of the size-exclusion mechanism for a novel asymmetric ZIF-300 membrane. Reprinted with permission from ref. 52. Copyright 2019 Elsevier.

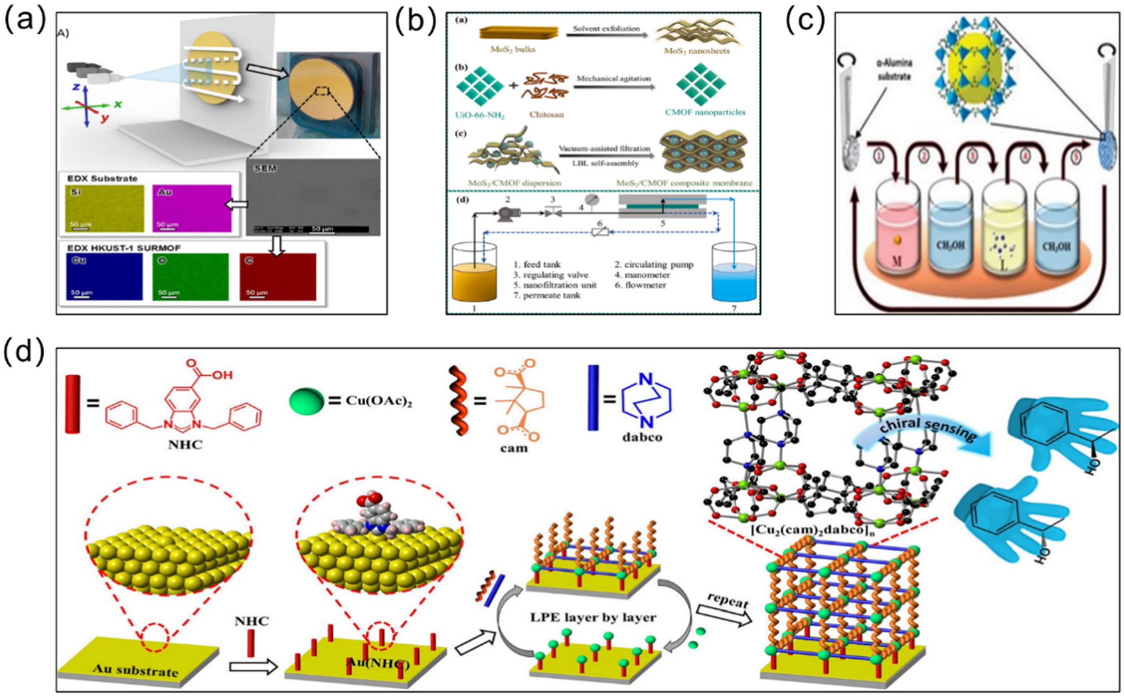

Fig. 5 (a) Synthesis of HKUST-1-based membranes using a stepwise spray method. Reprinted with permission from ref. 60. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Electrostatic LBL self-assembly strategy for constructing the MoS_2/CMOF composite membrane. Reprinted with permission from ref. 61. Copyright 2022 Elsevier. (c) Schematic representation of the LBL method used for growth of the ZIF-8 membrane. Reprinted with permission from ref. 57. Copyright 2014 Royal Society of Chemistry. (d) Preparation of $[Cu_2(cam)_2dabco]_n$ thin films *via* the liquid phase epitaxial LBL method. Reprinted with permission from ref. 62. Copyright 2020 American Chemical Society.

H_2–CH_4 and C_2H_4–C_2H_6 in gas mixtures (Fig. 5c). Gao *et al.* also applied the LBL method to prepare UiO-66-NH_2 separation membranes with good hydrophobicity and lipophilicity.[58] On a polymer substrate pretreated with high-energy γ-irradiation, the metal and organic ligand layers were incubated separately in progressive layers. Nanothickness MOF coatings (NTMCs) of ∼44 nm thick were achieved through constant repetition. Using this method, chemical bonds formed between the substrate and NTMCs and between the MOF layers, enhancing adhesion with the substrate. As a typical MOF membrane synthesis route, the LBL approach enables the use of automated machines to complete the entire membrane growth process under mild preparation conditions. Although the LBL method enables height control over the thickness, the process is cycled several times and consumes large amounts of organic solvents, which undoubtedly increases the cost of membrane production and the manufacturing time to some extent. In addition, Wang *et al.* carefully selected ceramic substrates with exceptional resistance to high temperatures, mechanical strength, and good antiswelling properties.[59] They then used an *in situ* LBL technique to create hybrid membranes made of ZIF-8 and poly(sodium 4-styrenesulfonate) (PSS). The *in situ* LBL method resulted in a greatly enhanced dispersion of the ZIF-8 particles and compatibility with PSS. The ZIF-8/PSS composite membrane was used for the nanofiltration removal of the methyl blue (MB) dye from water. On the one hand, because the pore size of the ZIF-8 particles is smaller than that of the MB molecules but larger than that of water molecules, both can be sieved. On the other hand, the anionic polyelectrolyte PSS can repel the MB anionic dye with the same charge through the charge repulsion effect. Therefore, the composite membrane can remove 98.6% MB in water. And the stability of the membrane was improved because of the good compatibility, and the dye removal rate and flux of the membrane remained at a constant level under 20 h of continuous operation. Due to their excellent mechanical properties, ceramic substrates show great potential for MOF-based membrane preparation.

3.4 Deposition

Deposition refers to the continuous settling of solid particles suspended in a liquid. The settled material forms layers without natural accumulation. MOF membrane preparation methods derived *via* deposition are relatively widely used. Three deposition methods for preparing MOF membranes are summarized as follows: electrochemical deposition (ECD), chemical vapor deposition (CVD), and atomic layer deposition (ALD).[63]

In order to shorten the synthesis time and reduce the thickness of the MOF membranes, another strategy, known as the ECD method, has been developed to fabricate MOF membranes (Fig. 6). To obtain MOF membranes with the desired thickness, the voltage and electrolyte can be regulated so that the growth of MOF crystals, which occurs only on the conductive portion of the substrate, is automatically stopped. After four stages, which include initial nucleation, island growth, mutual growth and detachment, a continuous MOF membrane is ultimately formed *via* ECD. In addition, the metal source in ECD originates from oxidation of the anode, so there is no interference of anions (*e.g.*, nitrate, sulfate, chloride, or chloride) with the metal source without the addition of metal salts.[64] Depending on the deposition method, three types of ECD, *i.e.*, anodic electrode deposition (AED), cathodic electro deposition (CED), and electrophoretic deposition (EPD), have been reported.[65]

During the AED synthesis process, the metal anode undergoes an electrochemical reaction and gradually dissolves under high positive voltage conditions. Subsequently, the metallic ions in solution combine with organic ligands to create membranes. The crystal size and thickness of the MOF membranes synthesized *via* the AED method are determined by the applied voltage.[66] The AED synthesis process is relatively flexible, and it is more often combined with other methods to jointly prepare MOF membranes with a better performance. During AED, the temperature has no effect on the solubility of the linker, the conductivity of the electrolyte, the kinetics of MOF formation and the resulting morphology.[67]

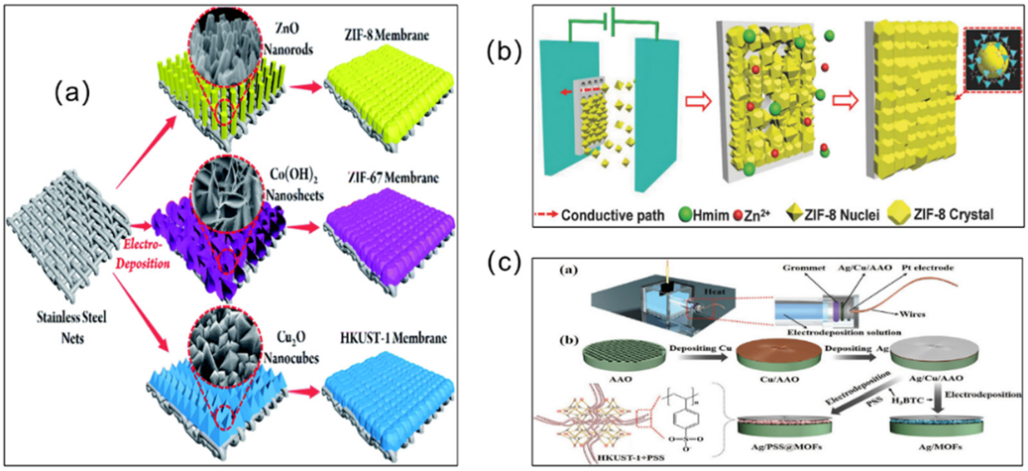

Fig. 6 (a) Schematic illustration of the *in situ* growth of three different MOF membranes on supports modified *via* electrodeposition. Reprinted with permission from ref. 70. Copyright 2017 Royal Society of Chemistry. (b) Synthesis of MOF films on various substrates *via* electrophoretic deposition. Reprinted with permission from ref. 71. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Electrochemical deposition to form an Ag/MOF membrane and the Ag/PSS@MOF composite membrane. Reprinted with permission from ref. 72. Copyright 2023 Wiley-VCH GmbH.

CED occurs through the deprotonation of organic ligands, enabling the membrane to be formed *via* cathodic precipitation. When an electrochemical reaction is performed, hydroxide ions are generated in the alkaline region near the cathode, and the OH^- react with the linker to induce deprotonation of the linker, and the deprotonated linker reacts with the metal precursor solution to produce a MOF membrane on the cathode surface. Compared with AED where the MOF layer and substrate are firmly bonded, CED also has the advantage of a flexible substrate.[68] The application potential, deposition time, supporting electrolyte, substrate and additives all influence the synthesis of MOF membranes. In particular, the deposition time controls the thickness and mass loading of the MOF membranes.

Unlike the first two methods where MOFs are deposited *in situ* on the substrate, MOFs deposited using EPD are grown in reverse order to create a membrane. By applying an external electric field to two conductive electrodes immersed in a solution containing MOFs, the MOF particles move towards the electrode with the opposite charge to deposit the membrane. ECD is used widely because of its simple operation, short time consumption and the ability to the control membrane thickness. For example, Hod *et al.* selected four representative MOFs (NU-1000, UiO-66, HKUST-1, and MIL-53) to test the broad applicability of preparing MOF membranes using the EPD method.[69] Their experimental results indicated that these four MOFs can be successfully deposited into membranes. This is further evidence that ECD is applicable to a wide range of MOF components.

As a basic technology for micro component manufacturing, CVD has a wide range of applications. CVD is carried out by evaporating the substances involved in the reaction to the gaseous state, followed by a two-step chemical reaction of adsorption and reaction, which results in a uniform and high-quality membrane after deposition.[73] A significant advantage of CVD is that because the organic linker is vaporized into gaseous form, the substrate is not contaminated and corroded by the solution. Stassen and co-workers[74] demonstrated a MOF-CVD method, which prepared ZIF-8 membranes with homogeneous and high quality properties (Fig. 7b). First, the precursor solution was vapor processed and deposited onto the substrate using atomic layer deposition to form a dense metal oxide layer. Subsequently, a continuous vapour–solid reaction was carried out. After a two-step reaction, a 500-nm-thick continuous ZIF-8 membrane was successfully prepared. Considering that CVD can achieve the solvent-free synthesis of MOF membranes, it has great potential for the preparation of green and pollution-free MOF membranes.[75]

ALD (or molecular layer deposition (MLD)) is a special CVD technique.[76] Similar to CVD, ALD can also achieve the solvent-free formation of uniform membranes,[77] and a unique advantage of ALD is that the ''self-limiting'' surface reactions can achieve nanometer-thick membranes.[78] Gas phase precursors are deposited on the substrate *via* adsorption or surface reactions to form atomic layers, where the thickness of the generated MOF membrane can be controlled precisely through continuous cycles.[79] In recent years, ALD has become the preferred deposition method for depositing high-quality thin membranes. Khaletskaya and co-workers used ALD to produce ZnO precursor membranes that could be used for nucleation and growth of

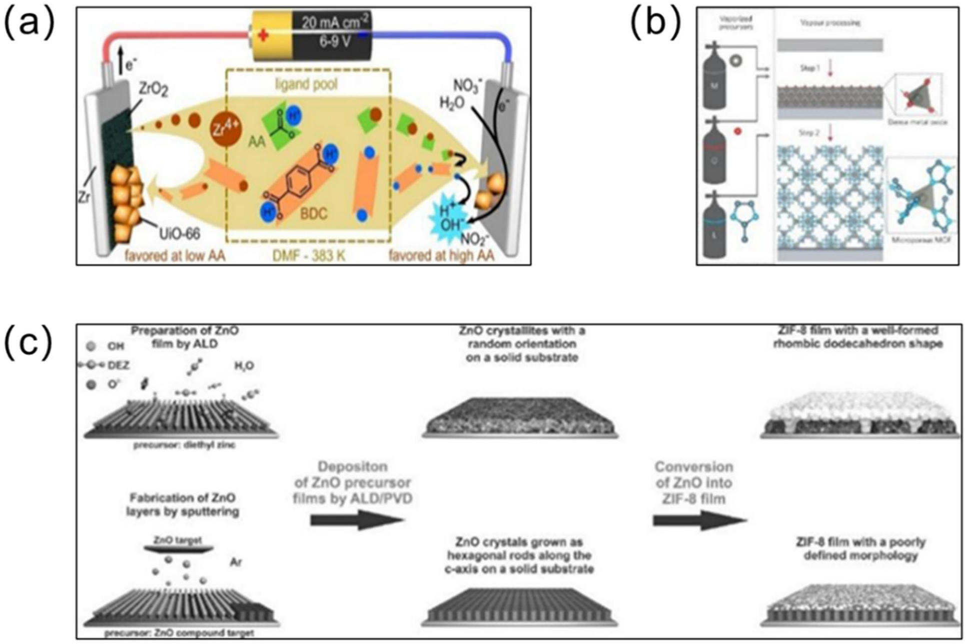

Fig. 7 (a) Schematic illustration of the anodic and cathodic electrochemical deposition mechanisms for UiO-66 membranes. Reprinted with permission from ref. 82. Copyright 2015 American Chemical Society. (b) Chemical vapor deposition of ZIF-8 thin films. Atom colors: zinc (grey) oxygen (red), nitrogen (light blue) and carbon (dark blue); hydrogen atoms are omitted for clarity. Reprinted with permission from ref. 74. Copyright 2016 Nature Materials. (c) Schematic illustration of the synthesis of ZIF-8 membranes from ZnO precursor films deposited on solid substrates. Reprinted with permission from ref. 80. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

ZIF-8 membranes, marking the first known instance of such a methodology (Fig. 7c).[80] Subsequently, to improve the problem of the poor conformation that results when MOF crystals are integrated onto fibers, Al_2O_3 substrates were obtained after 50 ALD cycles on polymeric fiber substrates, and then the HKUST-1 MOF was grown on the resulting core@shell (fiber@Al_2O_3) substrate layer by layer.[81] The addition of ALD-Al_2O_3 enhanced the wettability of the hydrophobic polymer while providing more sites to promote the MOF growth. Furthermore, the successful preparation of HKUST-1 MOF membranes demonstrated the potential applicability of this method for combining other polymer materials and MOFs.

3.5 Blending methods

3.5.1 Direct blending. Mixing MOF crystals and other materials to form a membrane can solve the problems encountered with a single inorganic membrane, such as low elasticity, low stretchability and high preparation costs. The blending method is a relatively simple method for preparing MOF hybrid membranes. Two methods, direct blending and post-modification polymerization, have been developed. The direct mixing method coats the substrate surface with a suspension formed by mixing the original MOFs and other materials to form a membrane. After a period of curing and drying, a complete MOF membrane can be obtained. Interestingly, based on this strategy, Fan *et al.* reported a spray self-assembly technique to prepare MOF membranes.[83] A ZIF-8-polydimethylsiloxane (PDMS) suspension and a solution of the tetraethyl orthosilicate (TEOS) cross-linking agent and the dibutyltin dilaurate (DBTDL) catalyst were poured into two self-stirring pressure drums, respectively. Then, they were simultaneously sprayed onto the polysulfone (PS) substrate. Using the mechanical atomization method, the ZIF-8 nanoparticles were uniformly dispersed on the PS surface, and an ultrathin uniform ZIF-8 membrane with high loading was achieved. In addition, the direct mixing method allows the MOF membrane to be separated from the substrate, making it more convenient to use. For example, the aromatic poly(*m*-phenylene isophthalamide) (PMIA) polymer substrate solution and MIL-53(Al) particles were mixed and stirred continuously to obtain a homogeneous polymer solution, and, after removing the air bubbles, the polymer solution was cast onto a clean glass plate and then underwent an inverse rotation to prepare substrate-free MIL-53(Al) membranes.[84] In mixed Na_2SO_4/dye solutions, the membrane was able to achieve over 80% removal of the nitroso-R salt, xylenol orange, and ponceau S, showing a broad application in dye desalination.

3.5.2 Post-modification polymerization. Direct mixing between MOF crystals and polymers to form membranes can lead to the agglomeration of MOF particles during the synthesis process due to the difference in quality and interfacial compatibility between them, resulting in a large number of void defects after membrane formation, further reducing the membrane separation performance. Therefore, researchers have used the post-modification polymerization method to address the incompatibility of MOFs and polymers. First, the surface modification of MOF particles is carried out, and then they are combined with the polymer to form membranes. This strategy is mainly achieved *via* the chemical modification of MOFs after synthesis, such as through cation exchange, linker exchange, and post-synthesis metallization. Considering the high efficiency applications of MOF-based membranes, derived from the post-modification polymerization design concept, many MOF membrane preparation strategies have been generated.

Interfacial polymerization. Unlike simple physical blending methods, interfacial polymerization (IP) synthesis is based on the reverse diffusion of two insoluble solvent molecules on the substrate (Fig. 8).[85] In this method, an interfacial reaction occurs between the aqueous and organic phases, and the MOFs crystallize at the interface to form a membrane. A large portion of MOF-based membranes are thin-film nanocomposite (TFN) membranes supported by polymers, where most TFN membranes are synthesized *via* IP methods.[86] Therefore, IP dominates in the synthesis of MOF-based membranes.[87] Zirehpour *et al.* prepared a thin PA layer on a polyethersulfone (PES) substrate *via* the IP method and then inserted MOF nanosheets into it for the first time.[88] Organic linkers in the MOF provide better compatibility between the MOF and organic polymers through covalent or non-covalent bonding. The resulting thin film composite (TFC) forward osmosis (FO) membranes have improved permeability to pure water and show great potential for desalination applications. In recent years, MOF-based TFN membranes have been widely prepared. For example, on a porous poly(phenylsulfone) (PPSU) substrate, Shukla *et al.* prepared highly permeable and salt-resistant TFN membranes *via* the IP reaction of porous Zn-MOF and polyamide.[89] Adding Zn-MOF with its intrinsic nanopore structure gives the membrane more water channels, increases the surface hydrophilicity, and improves the water permeability. Moreover, the combination of the spatial repulsion effect and the electrostatic repulsion effect produces the Donnan effect, which enabled up to 99% removal of Na_2SO_4 by the MOF TFN membrane. The IP method enabled the coordination of hydrogen and amide bonds between the Zn-MOF and polyamide, which enhanced the binding of the filler and polyamide layers, providing the Zn-MOF TFN membranes with long-term water resistance and stability. However, the chlorine concentration can affect conventional TFC membranes and reduce the membrane selectivity. The chlorine resistance of MOF TFN membranes was also investigated in this experiment. Due to the protective amide bonds produced by Zn-MOFs during IP and the good hydrogen bonding and hydrophilicity between the MOF material and the polyamide, damage to the composite membrane by chlorine was avoided. After 264 hours of chlorine immersion and 72 hours of filtration, the MOF TFN membrane performance remained stable. In addition, Liu *et al.* treated UiO-66-NH_2 nanoparticles with palmitoyl chloride to prevent agglomeration by introducing long alkyl chains. Then the modified UiO-66-NH_2 nanoparticles and a TMC/cyclohexane organic solution were subjected to the IP reaction to prepare TFN membranes.[90] Dispersing the palmitoyl chloride-modified UiO-66-NH_2 nanoparticles in organic solvents, on the one hand, reduced the agglomeration of MOF particles, and, on the other hand, the –COOH generated by the ionization in the organic phase adsorbs the positively charged amine monomer, making the substrate more hydrophilic. Besides, ZIF-8/GO TFN membranes

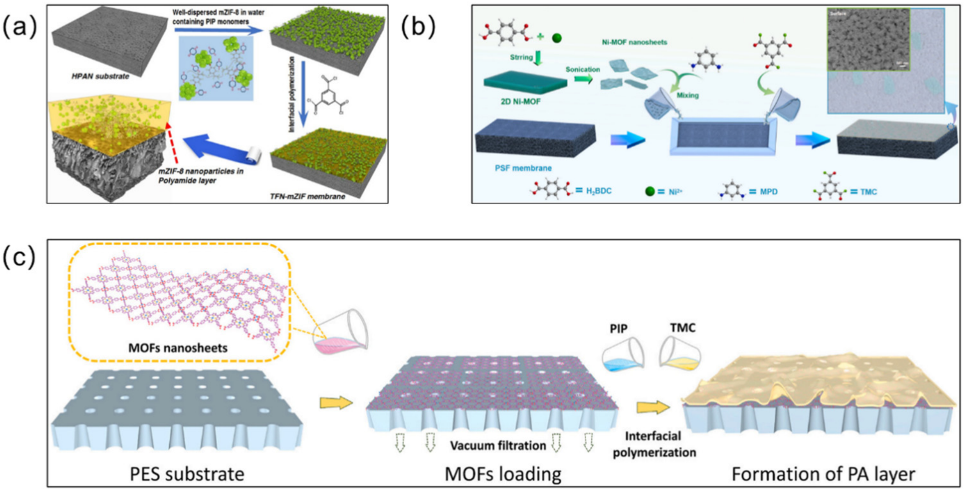

Fig. 8 (a) Preparation process of a TFN containing PSS-modified ZIF-8 nanoparticles *via* IP. Reprinted with permission from ref. 29. Copyright 2016 American Chemical Society. (b) Schematic illustration for the fabrication of a 2D-MOF-modified TFN membrane *via* the IP reaction. Reprinted with permission from ref. 97. Copyright 2022 Elsevier. (c) Fabrication process for the MOF-interlayered TFN membrane. Reprinted with permission from ref. 98. Copyright 2022 Elsevier.

with effective antibacterial and desalination properties[91] and Ag@HKUST-1/PA TFN membranes, which have antibacterial properties and the ability to degrade pesticides,[92] were also synthesized *via* the IP method. Although IP technology is currently widely used for the fabrication of PA layers in many commercial TFC membranes and for the preparation of MOF TFN or TFC membranes in laboratory-scale studies, it is not perfect. It is still a challenge to prepare extremely thin PA layers and requires more organic solvents to be consumed, which are more expensive and difficult for large-scale generation.[93] It is hoped that the existing IP technology can be modified in the future so that these disadvantages can be overcome and it can be better applied to the preparation of MOF membranes.

Post-synthetic polymerization. Inspired by IP, a new post-synthetic modification method for post-synthetic polymerization (PSP) has been proposed.[94] In this method, MOF crystals are covalently linked by flexible polymer chains in an orderly manner, achieving the copolymerization of MOFs with polymerizable functional groups and organic monomers to improve the separation performance. Yao *et al.* used the PSP method to polymerize UiO-66-NH_2 nanoparticles and polyurethane low polyester oligomers for the preparation of membranes that can selectively adsorb hydrophilic dyes (*e.g.*, eosin Y (EY), RB, malachite green (MG), and methylene blue (MB)).[95] The resulting membranes were substrate-independent, defect-free, and stable, enabling the separation of individual dyes (EY and RB) and mixed dyes in aqueous solutions. In another study, Min *et al.* used PSP to realize a luminescent membrane comprised of a MOF, polymers and lanthanide ions.[96] Specifically, through copolymerization of the MOF and ethyl methacrylate doped with lanthanide ions (Eu^{3+} or Tb^{3+}), a uniform MOF membrane with a good structure and excellent luminescence properties was successfully prepared.

Electrospinning. Another effective strategy for improving the efficiency of MOF membrane separation is electrospinning (Fig. 9). As a relatively new technology, it is widely used to polymerize microfiber materials of micron and submicron diameters. Electrospun fiber membranes have been widely used as ideal carriers for MOFs due to their large porosity, specific surface area and adjustable structure.[102] Recently, combining functional nanoparticles with electrostatic spinning fibers has become a hot topic in the current research field. More scholars are also working on the preparation of MOF/polymer hybrid membranes *via* electrospinning. Wang *et al.* prepared nanocomposite membranes by introducing ZIF-8 into green biodegradable poly(lactic acid) using the electrospinning method.[103] To enhance the nanofiber substrate adhesion, Yang *et al.* used the "solvent basing" method to pretreat the poly(vinylidene fluoride) substrate, and then performed electrospinning with the MOF materials.[104] Using this method, the water contact angle of the membrane was increased and the NaCl removal rate was 99.99% with a high cycling stability. MOF membranes produced *via* electrospinning are effective in removing heavy metal ions from solution. For example, Liu *et al.* synthesized polyurethane (PU)/UiO-66-NH_2 and PAN/UiO-66-NH_2 fiber membranes using electrospinning.[105] The composite membrane can adsorb precious metal Pd(II) and Pt(IV) from strongly acidic solutions with a good regeneration performance. Efome *et al.* selected the PAN nanofiber with hydrophilic properties and Zr-based MOF-808 materials to prepare composite PAN membranes *via* electrospinning.[106] The loading of the MOF on the composite membrane was up to 20%, which can adsorb and separate Cd^{2+} and Zn^{2+} effectively. Guo *et al.* prepared UiO-66 membranes *via* electrospinning using PAN as the substrate and uniformly mixing it with the Zr-based MOF (UiO-66).[107] This Zr-based MOF composite membrane maintains the original adsorption performance of the MOF for As(III) and As(V), and exhibits a stable performance and easy recovery. As introduced above, MOF membranes prepared *via* electrospinning can achieve "zero loss of material", which is beneficial for environmental safety.

In addition to the methods mentioned above, there are many methods for the synthesis of MOF membranes. Several

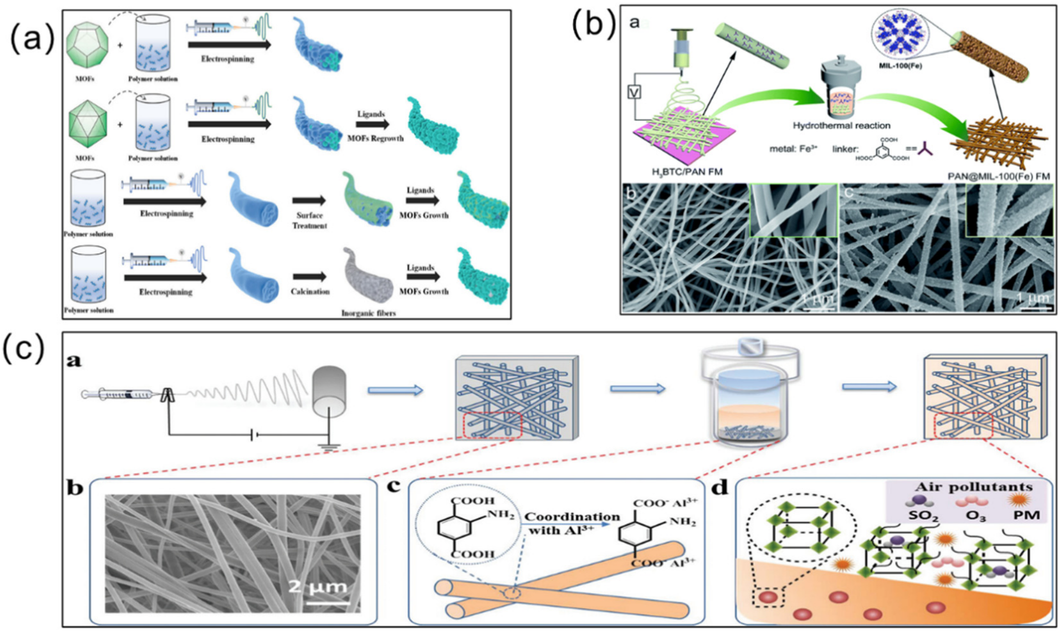

Fig. 9 (a) Schematic diagram of electrospinning for the manufacture of MOF nanofibers (NFs). Reprinted with permission from ref. 99. Copyright 2022 Elsevier. (b) Preparation of the PAN@MIL-100(Fe) fiber membrane *via* electrospinning. Reprinted with permission from ref. 100. Copyright 2019 Royal Society of Chemistry. (c) Preparation and adsorption process of a MOF-based fiber membrane prepared *via* electrospinning. Reprinted with permission from ref. 101. Copyright 2019 Royal Society of Chemistry.

innovative strategies have been shown to be useful in the production of MOF membranes, such as pressure-assisted self-assembly (PASA) filtration technology, the contra-diffusion method, and so on (Table 2). To further enhance the membrane separation efficiency, researchers are developing new methods to enable MOF membranes to be more widely used.

Table 2 Comparison of the performance of MOF membranes synthesized using different methods

	Membrane type			
Method	MOF	Support	Membrane performance	Ref.
In situ growth	MOF-5	α-Al_2O_3	Langmuir surface area of 2259 m g^{-1}; membrane thickness is around 25 μm, can withstand 400 °C high temperatures	38
	ZIF-8	Polydopamine (PDA)-modified stainless steel nets	High selectivity and high permeability	43
	UiO-66-NH_2	Polyvinylidene fluoride (PVDF)/polyvinyl alcohol (PVA)	The adsorption capacity of SMX was 2.11 mg g^{-1}, and after 8 cycles, the adsorption capacity of CUMIMs for SMX remained relatively stable, still reaching 87.1% of the maximum adsorption capacity	49
	UiO-66-NH_2	Polyvinyl alcohol (PVA)	The water permeability was 130.9 ± 2.9 L m^{-2} h^{-1} MPa^{-1} with significant removal of Congo red, methyl blue, active black 5 and direct red 23 (99.89–100%)	109
Secondary growth	ZIF-300	α-Al_2O_3	Thickness of 10 μm; high water permeance (39.2 L m^{-2} h^{-1} bar^{-1}); the removal rate of dyes (RhB, MB, MO) was higher than 98% and the removal rate of heavy metal ions was 99.21%	52
	UiO-66 and UiO-66-NH_2	α-Al_2O_3	Thicknesses of 1.6 μm and 1.3 μm, respectively, and the removal efficiency of RB was greater than 80%	54
Layer-by-layer (LBL) growth/liquid-phase epitaxy (LPE)	UiO-66-NH_2	PP films	Thickness of 44 nm, good hydrophobicity and lipophilicity, can be used for oil–water separation	58
	ZIF-8	Poly(sodium 4-styrenesulfonate) (PSS)	Water flux was 210 L m^{-2} h^{-1} bar^{-1}, with a 98.6% nanofiltration removal toward MB from water	59
	UiO-66-NH_2	PVDF	Water permeance was 78.98 ± 1.45 L m^{-2} h^{-1} bar^{-1}, with superior antibiotic removal (98.01 ± 1.12% for ciprofloxacin and 94.31 ± 0.68% for ofloxacin)	61
Electrochemical deposition (ECD)	HKUST-1	Anodic aluminum oxide (AAO) membrane	Excellent ion selectivity and ultrahigh permeability, showed an ultra-high energy conversion efficiency of 48.76% at a 100-fold salinity gradient	72
Chemical vapor deposition (CVD)	ZIF-8	Titanium-based layers	Thickness of 500 nm, green and pollution-free	74
Atomic layer deposition (ALD)	HKUST-1	Non-woven polypropylene (PP), polyethylene terephthalate (PET), cotton fiber mats	Good uniformity and high fiber coverage of MOF membranes with a specific surface area of ~535 m^2 g_{MOF}^{-1}	81

Blending		MIL-53(Al)	Poly(*m*-phenylene isophthalamide) (PMIA)	Water permeates above 45 L m^{-2} h^{-1} under a 1.0 MPa operating pressure, and the removal rate of paraxylene xylenol orange was about 99%	84
Post-modification polymerization	Interfacial polymerization (IP)	MOF nanocrystals, consisting of silver(I) and 1,3,5-benzenetricarboxylic acid (3HBTC)	14 wt% polyethersulfone (PES) and 1 wt% polyvinylpyrrolidone (PVP)	Water flux was 82 L m^{-2} h^{-1}, seawater fluxes of above 34 L m^{-2} h^{-1}	88
		Zn-MOFs	Poly(phenylsulfone) (PPSU)	Water permeability of 2.46 ± 0.12 LMH bar^{-1}, removal of NaCl (>90%) and Na_2SO_4 (>95%), showed excellent water stability during 72 h of filtration and showed resistance to chlorine after 264 h of a chlorine immersion test	89
		UiO-66-NH_2	Polyacrylonitrile (PAN)	When the UiO-66-NH_2-PC loading amount was within 0.10% w/v, the $MgSO_4$ removal was about 100% and NaCl removal was above 30%	90
		ZIF-8	Poly(ether sulfone) (PES)	Water permeability was 40.63 L m^{-2} h^{-1} MPa^{-1}, Na_2SO_4 and $MgSO_4$ removal rates were 100% and 77%, respectively; anti-microbial activity was 84.3%	91
		Ag@HKUST-1	Ultra-filtration (UF) poly(sulfone) supporting membranes	Complete degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) within 17 min, high salt removal values of up to 90%, and the water flux was 27 kg m^{-2} h^{-1}	92
	Post-synthetic polymerization (PSP)	UiO-66-NH_2	Free-standing membrane	Thickness of about 100 μm, effective removal of aqueous solutions of eosin Y (EY), and RB	95
	Electrospinning	MOF (iron 1,3,5-benzenetricarboxylate)	Non-woven substrate	Water vapor flux was 2.87 kg m^{-2} h^{-1}, the removal rate of NaCl at 35 g L^{-1} was 99.99%, no Fe^{2+} ion leaching	104
		UiO-66 and UiO-66-NH_2	Aluminum foil, Teflon paper, or filtration paper	Adsorption of precious metals Pd(II) and Pt(IV) from strongly acidic solutions	105
		MOF-808	Poly(vinylidene difluoride) (PVDF)	The maximum adsorption capacities were 225.05 and 287.06 mg g^{-1} for Cd^{2+} and Zn^{2+}, respectively	106
		UiO-66	Polyacrylonitrile (PAN)	The maximal adsorption capacities of the hybrid membrane for As(V) and As(III) were 42.17 mg g^{-1} and 32.90 mg g^{-1}, respectively	107

4. Types of MOF hybrid membrane

In order to achieve excellent separation performance, more scholars have combined MOFs with other functional membranes to form MOF hybrid membranes (Fig. 10). MOF hybrid membranes can simultaneously combine the molecular transport channels of two or even more materials with special morphological microstructures, and integrate the excellent properties of multiple materials. MOF–carbon based hybrid membranes, MOF–LDH hybrid membranes, MOF–zeolite molecular sieve hybrid membranes, MOF-other skeletal material hybrid membranes (such as MOF–MOF and MOF–COF hybrid membranes), MOF–ionic liquid hybrid membranes, and MOF–organic polymer hybrid membranes are the main types of MOF hybrid membrane at present.[110] Next, we will introduce these different types of MOF hybrid membrane in detail.

4.1 MOF–carbon-based hybrid membranes

In order to achieve a better separation effect, researchers have chosen to combine carbon-based materials and MOFs to form MOF–carbon-based material hybrid membranes. As typical carbon nanomaterials, graphene oxide (GO) and carbon nanotubes (CNTs) have promising applications in the fields of energy storage, catalysis, separation, and sensing.[115–117] At present, MOF–carbon-based hybrid membranes mainly include MOF–GO hybrid membranes and MOF–CNT hybrid membranes. GO is an important type of graphene derivative. It is a two-dimensional (2D) carbon material with a single atomic layer. In contrast to graphene, GO is considered to be a more economically viable option[118] due to the oxygen-containing functional groups on the thin GO layers,[119] which enable GO to exhibit good hydrophilicity and be easily dispersed in water. When GO is dispersed in water, the carboxyl groups are hydrolyzed into negatively charged carboxylic acid and hydrogen ions, thus a stable water-dispersible solution is formed. Subsequently, a separation membrane made of single-layer GO sheets stacked in parallel can be prepared *via* spraying, spin coating and vacuum filtration. Due to the excellent properties of GO, researchers have considered hybridizing and combining it with MOF materials to form a membrane. Li *et al.* proposed a novel environmentally friendly one-step etching-assisted cross-linking strategy to synthesize hollow MOF/GO composite membranes with good antifouling and desalination properties.[120] Due to the inclusion of ZIF-8 in the hollow structure, the interlayer spacing of the GO nanosheets was expanded, providing more water channels. Meanwhile, ZIF-8 crystals

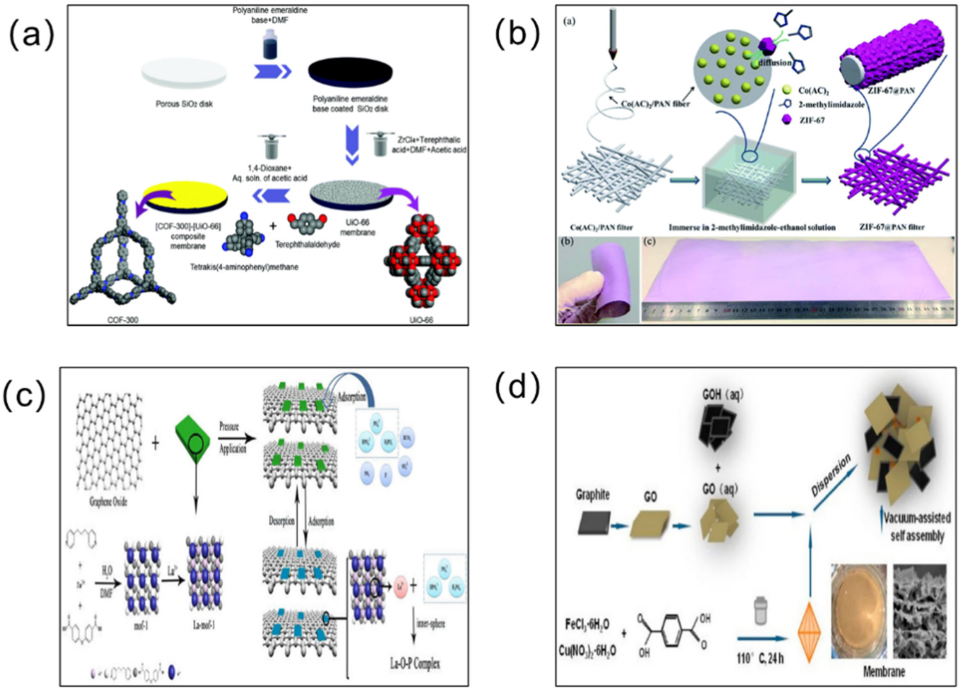

Fig. 10 (a) Strategy for the fabrication of the [COF-300]–[UiO-66] composite membrane. Zirconium, carbon, nitrogen, and oxygen atoms are shown as cyan, gray, blue, and red, respectively. Hydrogen atoms are omitted for clarity. Reprinted with permission from ref. 111. Copyright 2018 Royal Society of Chemistry. (b) Schematic representation of the fabrication procedure for ZIF-67@PAN filters. Reprinted with permission from ref. 112. Copyright 2018 Royal Society of Chemistry. (c) Schematic diagram of the construction of the lanthanum-modified MOF–graphene oxide composite membrane. Reprinted with permission from ref. 113. Copyright 2020 Elsevier. (d) Preparation of the GO/GOH/FeCuBDC ternary blend membrane. Reprinted with permission from ref. 114. Copyright 2022 Elsevier.

modified with tannic acid cross-linked with the adjacent GO nanosheets through π–π interfacial interactions and the abundant –OH groups on their surfaces increased the permeability of the membranes, resulting in a more stable structure and a much higher antifouling performance of the composite membrane. The modified MOF/GO composite membrane with its stable 3D/2D structure can achieve a higher than 99% removal of Congo red (CR) and an 86.3% removal of Na_2SO_4 using an optimal MOF loading. Qu *et al.* embedded 3D ZIF-8 into graphene oxide membranes to prepare ZIF-8/GO membranes with a high water permeability.[121] By adding positively charged ZIF-8 to neutralize the negative charge in GO, the defects presented in the single-layer GO could be masked, further enhancing the electrostatic stability of the GO membrane (GOM) and improving the structure of the separation membrane.[122] Compared with the pure GOM, the composite nanofiltration membrane showed a 6-fold higher water permeability and removed more than 99% of MB and RB. Meanwhile, dopamine-modified prGO@cHKUST-1 composite membranes were prepared.[122] GO was partially reduced by the addition of polydopamine (PDA), and the interlayer spacing of GO was increased by the insertion of cubic HKUST-1. These changes to the stacking pattern of GO were beneficial to form more active sites on the membrane surface. The prGO@cHKUST-1 membrane permeability was significantly increased, demonstrating an admirable separation capability in oil–water emulsions.

Recently, nanostructured carbon materials have become increasingly popular because of their unique atomic structure and excellent physical and mechanical properties. CNTs, as a typical one-dimensional nanomaterial, are seamless tubular structures curled around the central axis of 2D graphene sheets. Considering the high specific surface area and special mechanical properties, separation membranes constructed from CNTs with a high permeability are ideal materials for separation and filtration.[123] For example, researchers seeded ZIF-8 nanocrystals on CNT bucky-paper supports and synthesized ZIF-8/CNT membranes *via* the secondary growth method. Carbon nanotubes were fully embedded within the ZIF-8 matrix, resulting in a novel CNT–ZIF-8 hybrid membrane boasting excellent selectivity and hydrothermal stability.[124] The new CNT–ZIF-8 hybrid membranes were also an ideal material for the separation of complex gases and liquids. An alternative preparation strategy is that carbon nanotubes covered with MOF particles were successfully prepared using NH_2-MIL-101(Al) for *in situ* growth on carbon nanotubes.[125] Subsequently, the synthesized composites were applied to the preparation of polyimide-based MMMs. These synthesized MMMs showed much improved permeability and gas selectivity, which also provided a more efficient way to modify the MOFs on the filler.

4.2 MOF–LDHs hybrid membranes

Layered double hydroxides (LDHs), consisting of interlayer anions and positively charged laminates stacked on top of each other, are a typical representative of ionic layered compounds, and include hydrotalcite and hydrotalcite-like compounds (HTlcs). Their general formula is $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2](A^{n-})_{x/n}\cdot zH_2O$ (where M^{2+} and M^{3+} represent di- and tri-valent metal ions, respectively, and A^{n-} denotes inorganic or organic anions).[126] As an important class of inorganic separation membrane materials, LDHs consisting of positively charged layers and charge-balanced anions exhibit highly tunable interlayer voids, making them attractive for the separation of gas or liquid mixtures.[127] A characteristic feature of LDHs is their very uniform gallery height that can be adjusted by inserting different anions. However, the LDH membranes often include a large number of water molecules between the layers, which will prevent the diffusion and transmission of other gases and liquids molecules. So, LDH membranes need to be activated by heating to remove the interlayer water molecules.[128] Using this strategy, Liu *et al.* successfully synthesized ZIF-8–ZnAl-NO_3 LDH composite membranes through the partial self-conversion of MOFs by laminated membranes. Firstly, ZnAl-NO_3 LDH membranes were grown *in situ* on a γ-Al_2O_3 substrate, which can provide a zinc source for ZIF-8 growth. Then, the LDH membranes were partially dissolved *via* the solvothermal method in methanol solution, leading to the synthesis of the ZIF-8–ZnAl-NO_3 LDH membranes.[129] Due to the specific affinity of LDHs for CO_2 and the partial dissolution of the ZnAl-NO_3 LDH membrane, the diffusion barrier was lowered and the membrane thickness was reduced. Moreover, the addition of ZIF-8 achieved charge compensation for the LDH interlayer channel, further enhancing the separation performance of the membrane.

4.3 MOF–zeolite molecular sieve hybrid membranes

Zeolite molecular sieves are microporous crystalline materials formed by crystalline alum inosilicate metal salts. Common zeolite molecular sieves are NaA (LTA-type structure), ZSM-5 (MFI-type structure), X or Y (FAU-type structure), AIPO-5 (AFI-type structure) molecular sieves and so on.[130] MOF–zeolite molecular sieve hybrid membranes are formed mainly *via* the distributed assembly method. Currently, the hybrid membranes prepared are assembled mainly from ZIF-8 with an LTA-type or T-type molecular sieve distribution. For instance, Zhang *et al.* first introduced the NaA zeolite membrane as a modified layer *via* the secondary growth of microchannels. Then, a catalyst layer consisting of a ZIF-8 membrane was grown on top of the NaA zeolite layer using a ZnO-induced synthesis method, resulting in the successful synthesis of the stable ZIF-8/NaA composite membrane.[131] Furthermore, Yeo *et al.* synthesized the ZIF-8–zeolite-T hybrid membrane with high CO_2/CH_4 selectivity.[132] Firstly, the ZIF-8 continuous layer was prepared through novel vacuum thermal seeding with α-Al_2O_3 as the carrier, and then zeolite T was deposited in the crystal interstices of the ZIF-8 layer, supplemented by secondary growth to obtain the ZIF-8–zeolite-T hybrid membrane. After the double screening of ZIF-8 and zeolite T, the separation performance of the hybrid membrane was significantly improved and showed both good stability and high activity after 50 h. By adding ZIF-8, the zeolite T hybrid membrane achieved a good balance of permeability and selectivity.

4.4 MOF–MOF/MOF–COF hybrid membranes

MMMs can be constructed using MOFs because of their excellent physicochemical properties.[133] Combining two or even more MOFs to prepare hybrid membranes has been reported. For example, to avoid the issue of difficulty in controlling the operation during the solvent heat reaction, Knebel *et al.* prepared 180 nm ZIF-8 membranes through layer-by-layer growth on ZIF-67 membranes *via* the self-assembly method.[134] These ZIF-8-on-ZIF-67 membranes were defect-free and showed a stronger adsorption effect, thus improving their selectivity. Xiao *et al.* prepared a novel MOF-on-MOF membrane, *i.e.*, constructed from double-layered UiO-66-based (–$(COOH)_2$ and –NH_2) membranes *via* a seed-assisted *in situ* growth method.[135] The experimental results showed that, compared with the double-layered UiO-66-NH_2 membrane, the UiO-66-based membranes with –COOH were more selective for monovalent ions (Li^+) than divalent ions (Mg^{2+}) because the monovalent ions were more easily trapped or attracted by the negatively charged –$(COOH)_2$ under electric-field-driven conditions. In addition to the composite of structurally similar MOF materials, some composite membranes of MOF materials with completely different structures have been prepared.[136] Inspired by this, Xu *et al.* designed a heterogeneous layered UiO-66-NH_2@ZIF-8 membrane[137] using a simple layer-by-layer assembly method. The UiO-66-NH_2@ZIF-8 membrane retained the large pores of the UiO-66-NH_2 material and the molecular-sieving pores of ZIF-8, which promoted the transport of water and intercepted the dye with a $>97\%$ dye removal rate. Through such simple preparation method, the advantages of the respective MOF materials were well preserved, which will undoubtedly be a good alternative for designing other advanced methods.

Covalent-organic frameworks (COFs) are a new class of porous skeletal materials in which light elements (such as C, B, N, O, Si, *etc.*) are connected by reversible strong covalent bonds.[138] Similar to MOFs, COF materials have a tunable pore size, a large specific surface area, and high crystallinity. The pure organic component in COF materials makes them less dense and well compatible with other materials.[139] Combining the excellent properties both materials, Fu *et al.* firstly reported the generation of COF–MOF composite membranes in 2016, which were assembled from COF-300 and ZIF-8 in a distributed manner.[140] The preparation method is relatively simple, and the chemicals used are inexpensive, and easy to mass produce. COF crystals form chemical bonds through the interaction of imine groups with the polyaniline layer, while HN-Zn-imidazole bonds close the interface between the COF and ZIF materials to form an amorphous MOF layer. This amorphous MOF layer is beneficial for membrane selectivity, and this unique preparation method also means that the COF–MOF composite membrane has a better separation performance. Very recently, COF–MOF hybrid membranes have also received increasing attention.[141,142] Thanks to the synergistic effect of hybrid membranes, Das *et al.* prepared UiO-66/COF-300 composite membranes *via* the continuous and uniform growth of COF-300 on UiO-66 membranes. The synergistic effect of COF-300 and UiO-66 led to a significant improvement in the permeability and selectivity.[111] Inspired by the alloying effect of the aluminum alloy, Liu *et al.* demonstrated the formation of MOF–COF "alloy" membranes (AMs).[143] By adding quaternary ammonium salt (QA)-functionalized COFs to the ZIF-8 matrix and adjusting the loading of the COFs, composite membranes with a specific rigidity were obtained through a one-step electro-driven co-deposition method. The addition of different amounts of QA enabled good control over the molecular screening ability of the AMs, whereas the addition of COFs promoted the epitaxial growth of ZIF-8 and reduced the thickness of the membranes, resulting in a better separation performance of the composite membrane. In the future, MOF membranes laminated with COF materials will also be a good choice for the mass production of high-quality MOF membranes.

4.5 MOF–ionic liquid hybrid membranes

Ionic liquids (ILs) are type of ionic compound with a melting point below 100 °C.[144] ILs are green solvents for chemical synthesis with strong solubility, non-combustibility, high thermal and chemical stability.[145] As a new type of membrane separation material, ILs can form ionic liquid membranes (ILMs) with various forms and structures. Over the past few years, important gas-purification and wastewater-treatment developments of composite membranes that combine the advantages of ILs and MOFs have been accomplished.[146] The most applied are supported ionic liquid membranes (SILMs).[147] Compared with conventional ionic liquid adsorbents, SILMs have a larger contact area between the gas and liquid phases, and show a higher adjustability, separation efficiency and stability.[148] For example, Tzialla *et al.* prepared ZIF-69 membranes on porous α-Al_2O_3 substrates using the secondary growth method.[149] Then, ZIF-69-functionalized membranes with tricyanomethanide anion/alkylmethylimidazolium cation-based ionic liquid were used to synthesize the ZIF-69–IL hybrid membranes. After the functionalization of ZIF-69 by the ionic liquid, the intergranular boundaries and defects of the ZIF crystals were repaired, and the gaps between the ZIF crystals were plugged, allowing the framework pores to open. This composite material exhibited a higher selectivity and permeability, and can be used widely for membrane separation. To further enhance the separation efficiency of the hybrid membrane, Hao *et al.* prepared a MOF–polymerized ionic liquid–ionic liquid three-phase hybrid membrane.[150] First, they prepared ZIF-8, a polymerizable room temperature ionic liquid (poly(RTIL), *i.e.*, 1-vinyl-3-butylimidazolium-bis(trifluoromethylsulfonyl)imidate ([vbim][NTf_2]),) and a "free" room temperature ionic liquid (RTIL), which was (i) 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]), (ii) 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([emim]-[NTf_2]) or (iii) 1-ethyl-3-methylimidazolium tetracyanoborate ([emim][$B(CN)_4$]), and then synthesized the poly(RTIL)/RTIL/ZIF-8 membranes *via* UV polymerization. In the three-phase hybrid membrane, the ZIF-8 particles were homogeneously dispersed. The combined advantages of each component meant that the permeability of the hybrid membrane was significantly improved and showed good separation. More studies have reported the use of ILs to functionalize MOF materials and then combining them with polymers to prepare MMMs.[151,152] Strong electrostatic interactions between the ionic polymers and the MOFs can enhance their compatibility and enable the preparation of defect-free MMMs without additional treatment.

4.6 MOF–organic polymer hybrid membranes

MOF–organic polymer hybrid membranes are formed by hybridizing MOF grains with organic polymers. According to the binding pathway between the MOF and the polymer, these hybrid membranes can be classified into three types: surface-grown, organic phase-filled and mixed-matrix membranes. Among these, MMMs are a kind of bi-directional hybrid membrane formed using an organic polymer as the matrix in which the MOF grains are embedded. MMMs are the most common and widely used type of MOF–organic polymer hybrid membrane.[12,153] In MMMs, polymer materials are commonly used as separation membranes, and include polysulfone (PSF), polyaniline (PA), polyarylate (PAR), polycarbonate (PC), polyimide (PI), polyetherimide (PEI), and so on.[154] For instance, Liu *et al.* synthesized ZIF-8–PMPS composite membranes that can selectively adsorb furfural molecules by filling the silicone rubber matrix with ZIF-8 particles.[155] A hierarchically ordered stainless steel mesh (HOSSM) was used as the skeleton matrix. Then, the holes in the top layer of the HOSSM were plugged with ZIF-8 nanoparticles. Finally, the space between the nanoparticles and the mesh filaments was filled with polymethylphenylsiloxane (PMPS) silicone rubber. Influenced by the unique adsorption selectivity of ZIF-8 on furfural molecules and the space restriction and physical cross-linking of the HOSSM, the ZIF-8–PMPS composite membrane demonstrated a superior permeation performance in comparison with the other membranes reported, and still maintained good stability after 120 h of operation at 80 °C. Li *et al.* prepared MMMs of amine-functionalized MOFs combined with PI.[156] Compared with the pure PI membrane, the amine-functionalized MOFs showed enhanced hydrogen bonding with PI, improved MOF dispersion in PI solution, and a 1.5-fold increased permeability of the composite membrane. A novel MOF hybrid membrane with excellent antifouling properties was prepared using zwitterionic MOF polymerized PA.[157] Featuring superior thermal properties, an exceptional resistance to harsh chemicals, and an outstanding mechanical strength, polyvinylidene fluoride (PVDF) has emerged as a highly popular choice for porous polymer membranes.[158] For instance, Tan *et al.* prepared MOF–polymer hybrid membranes by incorporating functionalized NH_2-MIL-101 (Cr) into porous PVDF using a co-blending method.[159] The $-NH_2$ groups in the CR dye and NH_2-MIL-101 (Cr) undergo chemisorption through hydrogen bonding. Incorporating the MOF particles improves the membrane's hydrophilicity and porosity, achieving good adsorption separation of dye wastewater. Other than that, a series of MOF–PVDF hybrid membranes were also prepared, such as PVDF/NH_2-MIL-88B(Fe) membranes,[160] and MIL-101/PVDF membranes.[161] Experimental results showed that the MOF–PVDF hybrid membranes will provide a new route for the design of antifouling membranes. Benefitting from the promotion of 2D materials for the fabrication of a thin separation layer and better compatibility with polymers, Shu *et al.* chose PEI, which has good solubility in water/ethanol, as the polymer substrate and combined it with a new 2D MOF material, BUT-203, to prepare the BUT-203/PEI-HPAN(x) composite membrane (where x represents the MOF nanosheet loading).[162] The best performance was shown by the BUT-203/PEI-HPAN$_{(73)}$ membrane, which had a thickness of 70 nm and a MOF loading of 73%. The removal rate of anionic dyes with a molecular weight greater than 461 was 97.9%, and the water permeability of 870 L m^{-2} h^{-1} MPa^{-1} was one order of magnitude higher than that of commercial filtration membranes. In addition, the membrane showed a good desalination performance for dye solutions within 30 h, as well as a good antifouling performance for bovine serum albumin (BSA) and humic acid (HA). This is due mainly to the higher electrostatic repulsion and anti-scaling properties of the negatively charged BUT-203 nanosheets against anionic dyes.

5. Applications in water separation and treatment

Water pollution is escalating as a significant ecological concern, presenting a critical danger to the well-being of humanity, animals, and plants.[163] In order to achieve effective treatment of the water environment, MOF materials have been applied to the treatment of water pollution due to their adjustable structure and excellent performance. In particular, MOF membranes, with notable benefits in separation and adsorption, have been used increasingly in wastewater treatment, seawater desalination, and oil–water separation in recent years (Fig. 11).

5.1 Removal of heavy metal ions

Heavy metal ions that are not biodegraded are enriched through the food chain and gradually increase in concentration, eventually entering the organism and causing chronic toxicity,[168] even at trace levels.[169,170]

In recent years, to further improve the treatment efficiency, more researchers have chosen MOF–organic polymer hybrid membranes to treat heavy metal ions in wastewater.[171–173] For example, Efome and co-workers prepared Zr-based MOF-808–PAN electrospun nanofiber composite membranes through electrospinning.[106] After "hydractivation", the composite membrane maintained the original hydrophilic nature of PAN. During hydractivation, the pore space was occupied by water, the lattice was stretched, and the MOF structure was deformed, resulting in expansion of the pores, resulting in enhanced adsorption capacity. Compared with the conventional vacuum-activated composite, the PAN/MOF-808 hydractivated composite membrane showed an enhanced ability to treat Cd with maximum adsorption capacities of 225.05 and 287.06 mg g^{-1} for Cd^{2+} and Zn^{2+}, respectively. In another example, Li *et al.* prepared hybrid membranes with highly loaded MOFs *via* electrostatic spinning on an electrospun-silk-nanofiber (ESF) membrane substrate.[174] The ESF@MOF (ZIF-8 or ZIF-67) showed the highest loading content among other common polymer membranes and reported analogs, with both ZIF-8 and ZIF-67 being above a 30% loading. This enabled the ESF@MOF composite membrane to have a homogeneous dispersion of MOFs and obtain the maximum number of active adsorption sites. The acid–base sites of the hydrogen and

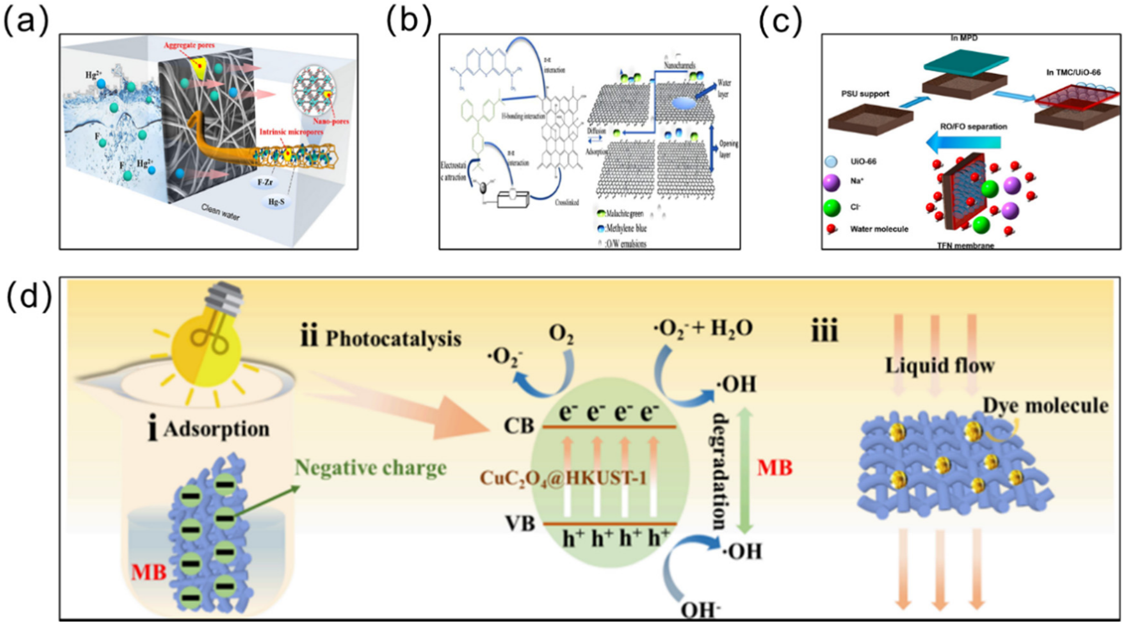

Fig. 11 (a) Schematic of the Zr-based MOFs@PIM nanofiber membrane containing multi-stage pores for the effective removal of Hg(II) ions from water. Reprinted with permission from ref. 164. Copyright 2023 Elsevier. (b) Schematic of the PDA/RGO/MOFs&SiO$_2$-COOH membrane separation of dyes. Reprinted with permission from ref. 165. Copyright 2022 Elsevier. (c) Schematic of thin film nanocomposite (TFN) membrane desalination combined with the super-hydrophilic metal–organic framework (MOF) UiO-66. Reprinted with permission from ref. 166. Copyright 2017 American Chemical Society. (d) Schematic of the rational mechanism and complex emulsion separation of CM@CuC$_2$O$_4$@HKUST-1 for dye removal *via* adsorption and photocatalysis. Reprinted with permission from ref. 167 Copyright 2022 Elsevier.

amino groups formed on the surface of the ZIF-8 crystals tightly bonded with the As(V) ions, while Cr(VI) was adsorbed by the activated site Co^{2+} on the surface of ZIF-67 through electrostatic interactions. Nearly 100% of Cr(VI) and As(V) ions can be removed by the hybrid membrane. Furthermore, Wang *et al.* prepared a range of MOFs@PIM-W membranes to remove Hg(II) from water by hybridizing UiO-66 functionalized with porous nanofiber membranes.[164] Due to the hydrophobic group in UiO-66-SH (Ui-S), in which S^{2-} will coordinate well with Hg(II), the Ui-S@PIM-W nanofiber membrane can effectively remove Hg(II) from water in a wide pH range (pH = 2–10) with a 99% removal efficiency, and no significant loss of adsorption capacity after 3 cycles.

To further improve the separation capacity of MOF membranes, bimetallic MOF membranes are also being gradually applied for heavy metal ion removal. Sharma *et al.* first incorporated bimetallic MOFs into a TFN to synthesize hydro-stable TFN membranes.[175] Thanks to the π–π interaction between the Co–Zn mixed MOFs (mMOFs) and the 2-MIM ligand in the *m*-phenylenediamine (MPD) monomer, the nanoparticles were more uniformly dispersed in the membrane. The incorporation of the two metal centers provided more effective adsorption sites for arsenic. Due to the favorable compatibility between the MOF monomer and organic ligands, the formed PA layer was defect-free in the MOF-modified TFN membranes synthesized *via* IP. Therefore, the permeability of the modified TFN was 2.5 times higher than that of the unmodified TFN, thus showing great potential for arsenic removal, with a 94% removal efficiency for As^{5+}. Inspired by the bimetallic MOF membranes, Yang and co-workers demonstrated the rapid *in situ* method of synthesizing Zn/Co-ZIF crystals to form uniform and robust MOF membranes on readily available cloth.[46] Due to its highly hydrophilic, flexible, biocompatible, large-surface-area, and low-cost features, it was beneficial to select cloth as the substrate. By introducing sodium carboxymethyl cellulose (CMC), the chemical surface adhesion of MOF crystals was enhanced, while the agglomeration of crystals in the liquid phase was hindered. The CMC-MOF(Zn/Co-ZIF)/cloth membrane showed remarkable selectivity and an excellent adsorption capacity (862.44 mg g^{-1}) for Pb(II). After 5 cycles, the adsorption capacity of the CMC-MOF/cloth composite membrane decreased insignificantly, and the removal rate of Pb(II) still reached 79.12%, which showed potential for water purification and remediation.

5.2 Removal of organic contaminants

With the current economic and industrial development, organic pollution has become the most important source of water pollution.[176,177] The direct disposal of synthetic industrial dyes and the misuse of antibiotics and pesticides pose a huge challenge for water pollution management. Membrane materials with a microporous structure and a good adsorption capacity are ideal for the continuous removal of organic contaminants. To enable effective wastewater treatment, many researchers have also applied MOF membranes to separate organic pollutants from contaminated water bodies.

5.2.1 Dyes. Dyes are carcinogenic, teratogenic and mutagenic, and are difficult to degrade, and thus they are a threat to animal and human health.[109] Compared with traditional adsorption technology, MOF membrane separation technology enables the adsorption of dyes with different properties and easy recovery.[180–182] Taking the GO–MOF membrane as an example, Xiao *et al.* used a vacuum filtration self-assembly device to prepare composite membranes of MOFs that can efficiently remove dyes from wastewater.[178] The strong π–π conjugation between PTCDA and GO in the GO@PTCDA-UiO-66-NH_2 membrane (PTCDA = perylene-3,4,9,10-tetracarboxylic acid dianhydride) made the modified UiO-66-NH_2 bind strongly to GO. At the same time, in addition to the spherical structure formed for dye adsorption, PTCDA-UiO-66-NH_2 also achieved the secondary lateral adsorption of the dye, and the whole membrane formed a unique vertical screening and horizontal adsorption filtration structure (Fig. 12a). The π–π stacking, hydrogen bonding, and electrostatic effects work together to achieve the complete removal of the dyes. As a result, the GO@PTCDA-UiO-66-NH_2 membrane achieved nearly 100% degradation of MB, CR, crystalline violet (CV) and dispersion black 9 (DB9). What is even more surprising is that the membrane maintains a good filtration performance at a high salt concentration (9 w/v%) and under extreme pH conditions. This was due to the improved viscosity and membrane resistance of the dye at high salt concentrations, which makes it easier for the dye molecules to agglomerate and thus increases the removal rate. After the addition of PTCDA, the compatibility between PTCDA-UiO-66-NH_2 and the GO sheet increased due to the binding effect between PTCDA and GO, and the composite membrane became more compact and less susceptible to damage, which contributed to extending the membrane life. The dye removal rate remained the same after 6 cycles in the pH range of 2–8. By contrast, the ternary GO/GOH/MOF hybrid membrane constructed from GO, hydroxylated graphene (GOH) and FeCuBDC using vacuum filtration exhibited a high RB separation efficiency (99.98%).[114] The horizontal structure formed by GO, GOH and FeCuBDC, and the vertical sieve structure of the GO layer formed a laminar structure with many nanochannels. In addition, the insertion of the bimetallic MOF swelled the GO nanosheets and increased the interlayer spacing of the composite membrane, which greatly improved the membrane flux, and the water flux of the composite membrane was 9.5 times higher than that of the GO membrane. By contrast, the removal of dyes depended on the electrostatic attraction, hydrogen bonding, and size sieving between GO and FeCuBDC. Most importantly, the inclusion of GO and GOH in the ternary blend membrane accelerated the electron transfer rate during the catalytic process of the bimetallic MOF FeCuBDC, which not only brought about an efficient removal efficiency but also enhanced the self-cleaning effect of the membrane. Another membrane, *i.e.*, g-C_3N_4/NH_2-MIL-88B(Fe)/CD@GO (called M2), which was prepared by embedding a Z-type heterojunction composite photocatalyst (g-C_3N_4) into GO nanosheets, still showed a removal rate of more than 95% for CR and MB after 6 cycles at pH = 1–3 and a salt concentration of 10%.[183] Surprisingly, due to the g-C_3N_4/NH_2-MIL-88B(Fe)/CD embedded in the GO layer, the roughness of the composite membrane and the GO interlayer spacing increased, and the membrane permeation

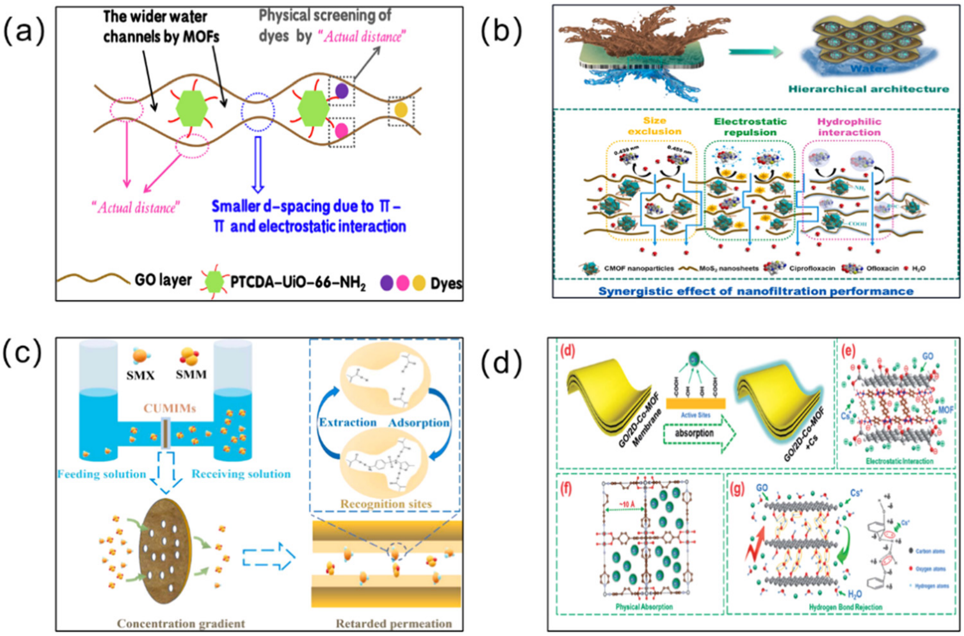

Fig. 12 (a) Adsorption schematic of the GO@PTCDA-UiO-66-NH_2 membrane. Reprinted with permission from ref. 178. Copyright 2022 Elsevier. (b) Separation mechanisms across the MoS_2/CMOF composite membrane with the synergistic effect of the molecular sieving effect (size exclusion), electrostatic repulsion, and hydrophobic–hydrophilic interactions for the removal of ciprofloxacin and ofloxacin. Reprinted with permission from ref. 61. Copyright 2022 Elsevier. (c) Schematic illustration of the selective separation mechanism in CUMIMs. Reprinted with permission from ref. 49. Copyright 2022 Elsevier. (d) Schematic diagram of the adsorption mechanism of Cs^+ by the GO/Co-MOF membrane. Reprinted with permission from ref. 179. Copyright 2018 Royal Society of Chemistry.

was improved, where the pure water permeation of M2 (253.26 L m^{-2} h^{-1} bar^{-1}) was 13 times higher than that of pristine GO (18.83 L m^{-2} h^{-1} bar^{-1}). Due to the strong size-sieving effect, π–π conjugation and electrostatic effects, M2 maintained a good separation efficiency and permeability even after 10 cycles. In the composite membrane, on the one hand, the tightly arranged structure formed by GO and the role of the capillaries and the photocatalytic process prevented catalyst agglomeration, provided transfer channels for electron transfer, avoided electron–hole pair recombination, and improved the degradation performance of the composite membrane. On the other hand, the addition of the photocatalyst not only oxidized and reduced some dye molecules, but also reduced some other pollutants, which effectively alleviated the problem of membrane pollution. Therefore, the emergence of this composite membrane provided an effective and feasible direction for the development of new environmentally friendly water-treatment membranes using MOFs.

Considering that not just a single dye is usually present in the wastewater but a mixture of binary, ternary, or even multiple dyes more often exists, Li and co-workers loaded Zr-MOFs onto polyurethane foam (PUF) and evaluated the performance of Zr-MOF–PUF membranes in binary or ternary systems for the removal of different dyes.[184] RB (neutral dye), MB (cationic dye), and CR (anionic dye) were chosen as the model contaminants to study the membrane filtration performance. The cationic form of RB, the positively charged form of MB, and CR with protonated amino/azo groups were easily attracted by the negatively charged Zr-MOF–PUF membrane through electrostatic interactions, coupled with the fact that SO_3^- in the CR molecule will interact with zirconium ions through Lewis acid–base interactions. Taken together, the composite membrane can simultaneously remove RB, MB, and CR due to electrostatic interactions, hydrogen bonding, and Lewis acid–base interactions between the membrane and the dye molecules. This makes the Zr-MOF–PUF membrane more valuable for practical applications.

5.2.2 **Antibiotics.** Misuse of antibiotics in homes, hospitals, livestock and agriculture is another major source of contaminants in water.[185] Since antibiotics are not fully absorbed by humans and animals when used, a large proportion of the antibiotics is discharged into wastewater as metabolites. Although few studies on the treatment of antibiotics using MOF-based membrane separation technology have been reported, the potential of these membrane materials in such a field has been presented in the limited literature.[186,187] For instance, Fang *et al.* prepared loosely layered composite membranes by inserting the UiO-66-NH_2 MOF (CMOF) in MoS_2 using an electrostatic layer-by-layer self-assembly method.[61] Due to the synergistic mechanism between the molecular sieving effect (size repulsion), electrostatic repulsion and hydrophilic–hydrophobic interactions, the membrane surface formed abundant specific active sites. The inserted CMOF nanoparticles provided layered nanopores to enhance the solute inhibition and the hydrophilicity of the membrane (Fig. 12b). The shape-selective function, the molecular sieving effect and the electrostatic interactions of the MoS_2/CMOF composite membrane enable the membrane to exhibit a higher removal capacity of ciprofloxacin (98.01 ± 1.12%) and ofloxacin (94.31 ± 0.68%) compared with the two monolithic membranes. Because of the addition of UiO-66-NH_2 MOFs with a rigid 3D pore structure and the hydroxy-methylation reaction of the formed polysaccharide chitosan in NaOH solution, the composite membrane can continuously maintain a good separation under alkaline and acidic environments for 72 h. In addition, Li *et al.* modified glass fibers with PVDF solutions containing hydrophilic GO hybrid NH_2-MIL-101 (Fe) particles, and successfully prepared glass fiber (FG) assisted PVDF hybrid membranes with a strong mechanical strength.[188] Due to the semiconducting nature of NH_2-MIL-101 (Fe) and its strong oxidation in the valence band, it formed a direct Z-type photocatalyst after being combined with GO, which inhibited electron–hole recombination and improved separation efficiency. The composite membrane not only degraded tetracycline (TC) up to about 93% within 90 min in the emulsion, but could also be reused dozens of times without cracking, with the degradation rate remaining higher than 90%. There is rarely just one type of antibiotic present in water, so their selective removal is relatively difficult. Recently, using the specific recognition role of molecular imprinting technology, Wang *et al.* prepared molecularly imprinted nanocomposites (CUMIMs) based on CNT/UiO-66-NH_2 that are capable of the selective removal of sulfamethoxazole (SMX) by combining molecular imprinting technology and membrane separation technology.[49] In the process of preparing the CUMIMs, an SMX imprinted layer was formed on its surface in the first step, which enables the formation of SMX selective recognition sites, followed by the removal of SMX on the surface. Through the SMX selective recognition sites on the imprinted layer, the CUMIMs in wastewater could selectively adsorb SMX (2.11 mg g^{-1}) (Fig. 12c) and remain relatively stable after eight cycles, still reaching 87.1% of their maximum adsorption capacity. This showed that the prepared CUMIMs had good stability and reusability, which is beneficial for practical applications and opened up a new pathway for the synthesis of MOF membranes.

5.2.3 Other organic contaminants. MOF-based membranes can not only achieve good removal of dyes and antibiotics from wastewater but are also applicable for some other organic pollutants (Fig. 13).[189–193] In order to continuously and effectively remove micro-pollutants from water, Xu *et al.* prepared horseradish peroxidase (HRP)@ZIF-8 membranes that can be combined with enzyme catalysis.[194] Owing to the synergistic effect between the adsorption of the MOFs, catalytic oxidation by enzymes and membrane retention, this biocatalytic composite membrane can remove 98% of Bisphenol A (BPA) *via* continuous operation, and exhibits greater stability and reusability, even in the presence of proteolysis. As for hydrocarbons and their chlorinated substitutes, Wu *et al.* prepared a ceramic hollow fiber NF membrane containing UiO-66 through the IP of UiO-66 and PA on a ceramic support,[195] achieving a greater than 96% removal of trichloroethylene (TCE) and trichlorobenzene (TCB). Benefitting from the stability of the ceramic substrate and the defect-free PA separation layer, the diffusion coefficient of water in the pores of UiO-66 is about 1.5 times higher than in PA. Among the tested membrane formulations, the membrane with 0.02% UiO-66 in the organic phase showed the best performance with a pure water flux of 30.4 L m^{-2} h^{-1} bar^{-1}. At present, there are relatively limited types of MOF-based membranes used in water treatment separations, and it is hoped that more types of MOF membrane will be used in water treatment applications in the future.

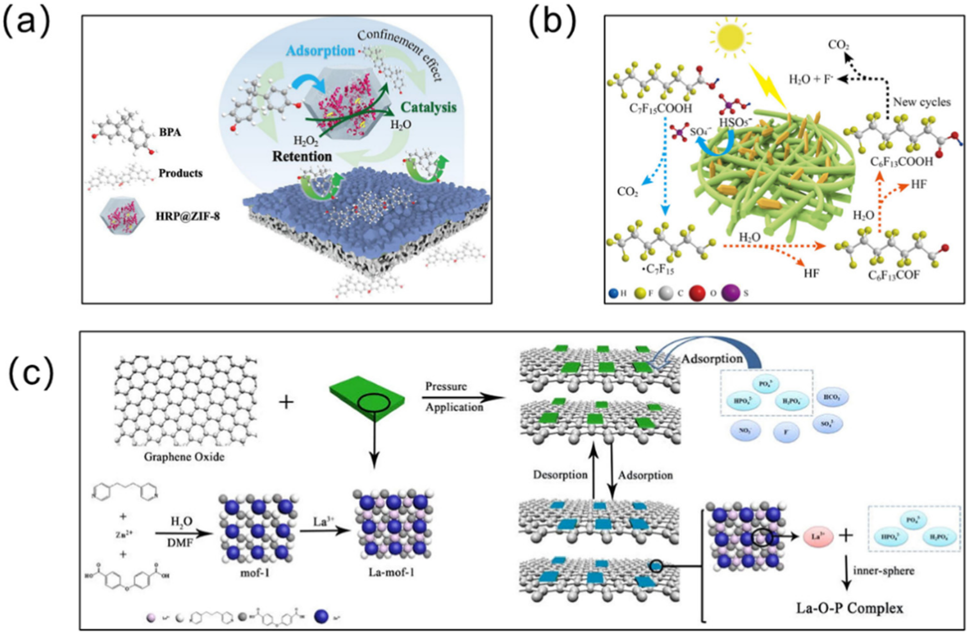

Fig. 13 MOF membranes remove other organic contaminants from water. (a) HRP@ZIF-8 on a PDA/PEI membrane for BPA removal. Reprinted with permission from ref. 194. Copyright 2021 Elsevier. (b) Degradation of perfluorooctanoic acid (PFOA) by the lignin/polyvinyl alcohol/Co/Fe MOF (lignin/PVA/bi-MOF) composite membrane. Reprinted with permission from ref. 191. Copyright 2021 Elsevier. (c) Highly selective phosphorus recovery from lanthanum-modified MOF–graphene oxide composite membranes. Reprinted with permission from ref. 113. Copyright 2020 Elsevier.

5.3 Removal of radioactive pollutants

Due to the gradual shortage of fossil fuels, nuclear energy has attracted intensive attention as a clean energy source. However, the rapid development of nuclear power plants has brought about many safety and environmental problems. Removing and recovering radionuclides from wastewater has become a major challenge in water treatment.[196] In order to solve the problems of low cost and high energy consumption for the removal of radionuclides using conventional treatment technologies, researchers have also applied MOF-based membrane technology for the removal of radionuclides from wastewater.[197] Back in 2018, Cheng *et al.* achieved the adsorption and removal of Cs^+ using a 2D GO/Co-MOF membrane.[179] Using vacuum filtration devices, negatively charged GO and positively charged Co-MOF were assembled into a composite GO/Co-MOF membrane with mechanical flexibility. Two groups, C–O and C=O, were generated in the 2D GO/Co-MOF composites, providing sufficient sites for bonding with Cs^+ during the reaction. In GO/Co-MOF membranes, hydrogen bonds on the GO surface are easily eliminated by the interface between Co-MOF and GO, resulting in the facilitated permeation and adsorption of Cs with oxygen-containing groups in GO. Interfacial or surface complexation and electrostatic interactions between the membrane materials promoted the chemisorption of Cs^+ by the membrane (Fig. 12d). The 2D GO/Co-MOF membrane could adsorb up to 88.4% of Cs^+, and still showed a good separation performance in strong acid/base solutions. For strontium (Sr), as one of the most dangerous radiological contaminants that threaten the environment and human beings, its separation and recovery from wastewater is a very urgent issue. In another study, GO/Ni-MOF membranes were prepared using a simple filtration method, where the oxygen-containing functional groups in GO nanosheets were combined with Sr^{2+} through electrostatic interactions.[198] As with the GO/Co-MOF composite membrane, the interface formed between Ni-MOF and GO in the GO/Ni-MOF membrane effectively eliminated hydrogen bonding on the GO surface and promoted a portion of Sr^{2+} uptake. Secondly, the electrostatic interaction between Sr^{2+} and O–C=O and C=O in the GO nanosheets, the physical adsorption of porous MOFs, and the substitution of Sr^{2+} for Ni^{2+} in the structure of MOFs synergistically promoted the removal of Sr^{2+}. Thus, the maximum effective adsorption of Sr^{2+} in a 100 mg L^{-1} Sr^{2+} aqueous solution of 32.99% could be achieved with only 2 mg of the composite membrane. For other radionuclides, Liu *et al.* prepared a composite membrane with high mechanical strength by inserting a prepared 1,3,5-benzenetricarboxylic acid (BTC)-MOF into the interlayer of GO using the intercalation method.[199] The interlayer distance within the GO membrane increased after MOF insertion. By changing the separation factor, both the prepared Cu-BTC-MOF/GO and Zn-BTC-MOF/GO membranes achieved the highly selective separation of Th^{4+} and UO_2^{2+}. More importantly, the Cu-BTC-MOFs/GO membrane can remove 100% of Ce^{3+}. In view of these above examples, GO–MOF hybrid membranes may become an ideal material for the effective treatment of radionuclide wastewater in the future.

5.4 Oil–water separation

Oil-containing wastewater from industry and daily life has seriously polluted the environment and affected all aspects of people's lives.[167] Traditional oil–water separation technology has a low separation efficiency and thus a high cost. Considering these problems, the preparation of membranes with superhydrophilic and underwater superoleophobic properties to separate oily wastewater would be a better choice.[200] In recent years, researchers have also begun to apply MOF-based membranes to the separation of oily wastewater.[165,201] For example, Cao and co-workers combined electrostatic spinning with MOF materials and prepared PVP–UiO-66-NH_2 membranes that can effectively separate oil-containing wastewater.[202] By grafting PVP chains onto UiO-66-NH_2, the pore volume and pore size of the nanoparticles were increased, enhancing the hydrophilicity of the particles. Before contact with oil, the formation of a microsphere/fine fiber structure *via* a continuous electrostatic sputtering electrospray method may form a functional layer/water biphasic distribution interface, blocking the adhesion of oil to the electrostatic sputtering nanofiber membrane (NFM) fibers. Then, on the NFM surface, the oil phase of the emulsion undergoes rolling and coalescing, increasing the diameter of the oil droplets. After reaching a certain value, the oil droplets will detach and float up into a continuous phase to achieve oil–water separation. These NFMs achieved a 99.2% oil–water separation efficiency and have a stable antifouling performance. Similarly, Samari *et al.* prepared MOF–PES composite membranes by combining modified UiO-66-NH_2 with PES *via* the phase inversion method.[203] UiO-66-NH_2, when modified with melamine, introduces more amino groups onto the surface to provide hydrogen bonds, increasing the hydrophilicity of the membrane. As the addition of MOFs improved the membrane porosity and reduced the surface roughness, the modified hybrid membrane demonstrated a higher hydrophilicity and antifouling ability, and a 99% oil–water separation efficiency. In addition to one-dimensional structured MOF membranes, 2D MOF-based membranes with ultrafast oil–water separation capabilities were prepared by He *et al.*[204] Cu-CAT-1@CM membranes with micro/nanostructures can be synthesized in just 20 min at room temperature. The MOF was grown directly on the copper mesh (CM), and the resulting layered structure will combine with polar nanocavities in the MOF crystals to endow the copper mesh membrane with superior superhydrophilic and submerged superoleophobic properties. In addition, the separated crude oil flux under gravity conditions exceeded 329 kL m^{-2} h^{-1} and the residual oil was as low as 24.6 mg L^{-1}. Most pleasingly, the flux was still maintained above 200 kL m^{-2} h^{-1} after 20 cycles, and the residual oil content was lower than 7.4 mg L^{-1}. This enables the composite membrane to operate consistently under challenging conditions.

5.5 Desalination

Although water covers 70.8% of the Earth's surface, freshwater accounts for only 2.5% of it. About one-third of the world's population faces the problem of insufficient drinking water. In order to cope with the shortage of water, seawater desalination has become the main response. Desalination includes two main processes: distillation desalination and membrane desalination.[205] Recently, membrane desalination technology has gained widespread adoption owing to its higher processing efficiency and lower cost.[98] However, the poor anti-fouling properties and short service life hinder the further development of polymer membranes.[206] Polymeric membranes combined with high-quality MOFs can improve the compatibility between the filler and the matrix, effectively reducing any resulting non-selective defects in the membrane. As a result, the composite membrane displays excellent physical and chemical properties.[207,208] Therefore, Hu *et al.* proposed a new synergistically driven *in situ* self-assembly method to prepare ZIF-8–PA TFN membranes.[209] In seawater, the different molecules and ions present have different sizes, and the intrinsic pores of ZIF-8 crystals enable the separation of water molecules with small pore sizes from Na^+ and Cl^-. Notably, the *in situ* grown ZIF-8 crystals made them more favorable for the separation of NaCl from water. This method resulted in the uniform doping of the ZIF-8 material into the membranes without agglomeration and defect generation. ZIF-8 TFN membranes show a 5-fold higher water flux than conventional TFN membranes and inhibit 99.03% of NaCl. As another example, Kachhadiya *et al.* successfully synthesized GO@CUBTC integrated PVDF membranes with high stability, selectivity and reusability.[210] By doping GO@CuBTC into the PVDF membrane, the GO@CuBTC was uniformly dispersed, which increased the porosity and hydrophilicity of the membrane, and the separation performance and stability of the membrane were enhanced. Experimental data showed that the membrane can run continuously for 260 h with a desalination rate of 99.68%. Similar to MOF membranes applied for oil–water separation, 2D MOF membranes also can be applied in seawater desalination. Liu *et al.* prepared a high-performance reverse osmosis (RO) TFN membrane by embedding a 2D nickel-based MOF into a polysulfone substrate selective layer.[97] The additional pore space of the 2D-MOF and its H-bonding with free water molecule ligands accelerated the transport of water molecules. Because the pore size of the MOFs is smaller than Na^+ and Cl^-, water molecules pass through the membrane while salt molecules are rejected. Thus, both the salt rejection and the water permeability were maintained by the modified TFN membrane (99.3% NaCl rejection). Moreover, the higher surface hydrophilicity and roughness enable the 2D-MOF membrane to maintain good antifouling properties even under a high humic acid concentration. Thus, 2D MOFs will potentially become ideal membrane separation materials in water treatment.

6. Perspective on the industrial scale up of MOF-based membranes

To sum up, MOF-based membranes are widely applied in water treatment, achieving good separation abilities for organic and inorganic compounds in water. Nonetheless, studies are still in the laboratory stage, and the industrial scale up of MOF-based membranes has not yet been realized. The biggest challenges in applying MOF-based membranes to industrial applications are hydrothermal stability and large-scale production.

First of all, the high hydrothermal stability can extend the environmental applicability of MOF membranes in industrial applications, especially at certain high temperatures and acidic/alkaline environments. As mentioned in Section 2, we can select MOF materials with water stability, such as MIL-100, MIL-101, ZIF-8 and UiO-66, for preparation of the membrane; secondly, we can also choose to modify the synthesized MOF materials to enhance their water stability, mainly through ligand modification and metal–ligand exchange to enhance the stability of the ligand–metal bonds.

Some industrial assembly line operations can achieve more complex operational processes. Indeed, large-scale production requires a relatively simple and easy preparation route, which facilitates the formation of an assembly line operation. Currently, the more commonly used methods for preparing MOF membranes can be hindered due to more complex operations, high preparation costs and the time-consuming nature of the method, so most existing methods are unable to achieve the large-scale manufacture of MOF membranes. Fortunately, as research on MOF membranes continues, innovative preparation methods have made it possible to fabricate MOF membranes on a large scale. And with more and more hydrothermally stable MOF materials being discovered, it is likely that both large-scale and high-performance MOF membranes will be produced in the future. In addition, many MOF materials currently have the problem of low yield, and only by solving the problem of low yield can mass-produced high-performance MOF materials better serve the industry. First, MOF particles in a single MOF membrane tend to agglomerate, thus affecting the membrane performance, so MOFs and functional membrane materials are combined to form hybrid membranes. Due to the limited compatibility between MOFs and other materials, MOFs are first modified and then combined to form hybrid membranes. By homogeneously dispersing MOF particles in MOF hybrid membranes through functionalization, the inherent advantages of both the MOFs and the polymers are retained, which results in high stability of the hybrid membranes. Secondly, synergistic strategies are used to engineer different synthetic pathways in the growth of MOFs and membrane preparation considering the shortcomings of a single MOF membrane preparation method. Studies have been conducted, showing the potential of MOF-based membranes for industrial applications. The modification of MOF materials or combining them with other functional materials greatly improves the hydrothermal stability of MOF membranes. And the combination of two or more synthesis methods not only reduces the preparation cost, but also enables preparation within a short time. Both ideas offer good potential for industrial-scale applications based on MOF-based membranes.

7. Conclusion and outlook

Recently, MOF-based membranes have shown great potential for practical separation applications. MOF membranes prepared from water-stabilized MOFs have been used in gas separation, adsorption, catalysis and liquid separation. This review has summarized the key factors for the preparation of MOF-based membranes, such as uniform dispersion, high water stability, and suitable hydrophobicity, which lay the foundation for the preparation of high-performance membranes. Then, the article focused on the common methods of MOF-based membrane preparation and the classification of MOF hybrid membranes. In addition, the latest advances in MOF-based membranes for water treatment were discussed in depth, which show their high superiority in the removal of heavy metal ions, dyes, antibiotics, and radionuclides from wastewater, as well as in desalination and oil–water separation, and we concluded with the prospects for industrial applications of MOF-based membranes and the challenges that may be encountered during their future development. Highly water-resistant MOFs will undoubtedly be an ideal choice for wastewater treatment, and further exploration for the effective separation of MOF-based membranes will soon emerge. However, there are still several challenges regarding the development of MOF-based membranes.

First of all, in terms of the MOF membrane materials themselves, not all reported MOF-based membranes reported so far have a high separation performance. Thus, the selection of MOFs with both chemical stability and high efficiency is crucial for expanding their application in membrane separation. (1) Most of the MOF-based membrane materials reported so far are monometallic-centered MOFs, which have good water stability. Their separation efficiency, however, needs to be improved. Firstly, given the synergistic effect between different metals, the selection of suitable bimetallic-centric MOFs would be an effective strategy. Meanwhile, three-dimensional MOF-based membrane materials with more active sites can be constructed to achieve more efficient separation, since the widely applied one-dimensional structured MOFs membranes and few two-dimensional structured MOFs membranes. In addition, it is also necessary to focus on the performance of the supported membranes. Choosing membrane materials with better compatibility or improving the membrane performance through membrane modification will greatly increase the success rate of preparing MOF membranes with a high separation efficiency. (2) The chemical stability of the membrane is a key factor in determining its separation efficiency. Current research is usually conducted under relatively mild conditions, and further research is needed to enhance the stability of MOF-based membranes in strong acid/base, high temperature, and complex composition environments. (3) Several types of MOF hybridized membranes have been prepared, but the membranes more commonly used in water treatment applications are those that are hybrids of MOFs and organic polymers. Some other types of hybrid membrane have not worked in the field of water treatment, and efforts to develop different types of hybrid membrane for water treatment may be a new way to expand the application of MOFs for membrane separation.

In addition to this, the current characterization and mechanistic analysis of membrane materials does not enable a comprehensive analysis of the possible chemical mechanisms in the system. Due to the complexity of the structure and surface chemistry of MOF membranes, more efforts should be devoted to investigating the fabrication of model MOF-based membranes, or even establishing correlations between their structures and separating abilities, with both a single contaminant type and for more complex situations. Future research needs to use more advanced characterization tools and theories to characterize materials at a smaller level and analyze the adsorption separation mechanisms in depth. A combined experimental and theoretical approach, especially one that combines advanced machine learning, will be essential to understand these structure–function relationships thoroughly and to identify the structure, mechanism, and kinetics of water separation or treatment.

From a wider perspective, the demand for the development of environmentally friendly and resource-efficient processing equipment is giving momentum to MOF-based membranes, and may contribute to their large-scale applications for liquid separation and purification. For existing membrane separation technologies, the membrane surface is easily contaminated and needs to be cleaned. In order to achieve potential large-scale applications, attempts can be made to develop MOF membrane materials that can perform self-cleaning with good water stability and solvent resistance. It is also hoped that MOF membrane materials with a wider range of applications can be developed for the removal of conventional contaminants in industrial effluents and municipal sewage, and even for the removal of nanoscale contaminants, such as microplastics, from atmospheric and aqueous environments.

All the limitations and prospects mentioned above contribute to the fact that a more economical, environmentally friendly, safe and efficient application of MOF membranes can be achieved in the future. Overall, MOF-based membranes are expected to provide an alternative for the efficient and scalable separation and treatment of water.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. There are no conflicts to declare.

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