Review

Engineering covalent organic framework membranes for efficient ionic/molecular separations

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SUMMARY

Covalent organic frameworks (COFs) based on reticular and dynamic covalent chemistry are porous materials with uniform and modifiable pore size, high specific surface area, and structural designability, which have attracted widespread burgeoning in membrane separations for the less mass transport resistance and precision sieving. This critical review focuses on recent advances in COFs topology design (two-dimensional (2D) and three-dimensional (3D) COFs) towards membrane building, crucial physicochemical properties of COFs-based membranes, synthesis/fabrication methods for COFs-based membranes, and state-of-the-art applications of COFs-based membranes in sustainable ionic/molecular separations. The perspectives in this fascinating field are discussed in terms of opportunities and challenges for next-generation COFs-based membranes for sustainable development.

INTRODUCTION

With the gradual deterioration of the global climate and depletion of fossil resources, the concept of sustainable development is becoming increasingly important and has been included in regulations by an increasing number of countries and organizations. Advanced membrane separation technology has shown great potential in energy utilization and environmental protection, and has received widespread attention and research.[1] In the past few decades, membrane technology industries have grown rapidly owing to their advantages, including energy conservation, high separation efficiency, and easy operation.[2-4] However, owing to the lack of orderliness and adjustability in the pores, traditional polymer membranes are no longer able to meet the current separation requirements. Compared with traditional polymer membranes, new porous materials have significant theoretical advantages and can compensate for these shortcomings. For example, zeolites, metal organic frameworks (MOFs), porous aromatic frameworks (PAFs), polymers of intrinsic microporosity (PIM) and COFs are all considered promising membrane materials, and researchers have conducted many studies in different membrane fields.

COFs are a new type of porous material with periodic arrangements of monomers linked through covalent bonds and designed by reticular chemistry.[5] The emergence of COFs filled the synthesis gaps in two- or three-dimensional structures.[6] Owing to the significant properties of COFs, including structural designability, controllable synthesis and functional

PROGRESS AND POTENTIAL

Membrane separation technology is expected to solve global water resource problems, but traditional polymer membrane materials are increasingly unable to meet current separation needs. The emergence of new porous materials has led to the development of future membrane separation technologies, including COFs being one of them. COFs have received increasing research attention in the field of membrane separation owing to their uniform pore size, high porosity, and structural designability. This article discusses the designability of COFs based on their nanoscale morphology and structure. A further summary was made of the key COFs characteristics that affect membrane separation. Different synthesis methods for COFs composite membranes have been introduced, and a comprehensive explanation was given on the different applications of COFs in the field of membrane separation.

regulation,[7,8] they have attracted widespread interest in gas storage,[9,10] separation,[11,12] adsorption,[13,14] catalysis,[15,16] sensing,[17-19] electroactive materials,[20-22] and energy storage.[23-25]

In the field of membrane separations, COFs are also considered a highly promising material due to its various advantages.[26] Firstly, COFs are created by reversible covalent bond formation from organic linkers and possess an orderly pore distribution, uniform pore size and high porosity due to their regular periodic arrangement of covalent bonds.[27,28] Moreover, the chemical geometry of COFs depends on the geometry, size and connectivity of monomers. Therefore, molecules with different sizes can be separated by changing the chemical geometry of COFs to control the pore sizes of COFs-based membranes.[29] Furthermore, different functional groups can be introduced into the COFs structure because of their covalent bond connection pattern. COFs with different functional groups allow the membranes to exhibit different functions, such as surface charge and hydrophilicity, and further control the separation process.[30] The comparison of characteristics between COFs and other porous materials applied to membrane is shown in Table 1. Due to these advantages of COFs-based membrane, it has been widely used in gas separation,[31] water treatment (desalination and dye removal[32]), organic solvent nanofiltration (OSN),[33] fuel cells,[34] heavy metal separation,[35] and lithium extraction.[36] Several excellent review articles on COFs-based membranes have been published in recent years.

Table 1 Comparison of Characteristics of Different Porous Materials

Material	Pore	stability	Diversity	Designability	Compatibility with polymer
COFs	Uniform narrow distribution	Generally, have good stability	Excellent	Excellent	Excellent
MOFs	Uniform narrow distribution	Poor to good stability	Excellent	Excellent	Fair
zeolites	Uniform narrow distribution	Thermal stability but acid/base sensitive	Good	Good	Poor
PAFs	Disorder wide distribution	Highly chemical and thermal stability	Fair	Fair	Good
PIMs	Disorder wide distribution	Aging	Good	Good	Good

Herein, we have provided a contemporary review on COFs separation membranes for a specialized view of membrane scientists as shown in Figure 1. We first introduced the nanomorphic design of COFs towards membrane building, including symmetric and asymmetric two-dimensional structures and three-dimensional structures. Then, we discussed crucial properties of COFs in the membrane separation process. Furthermore, we summarized the synthesis/fabrication methods of COFs-based membranes and its applications. The future directions in this field are proposed in terms of next-generation COFs-based membranes fabrication and applications.

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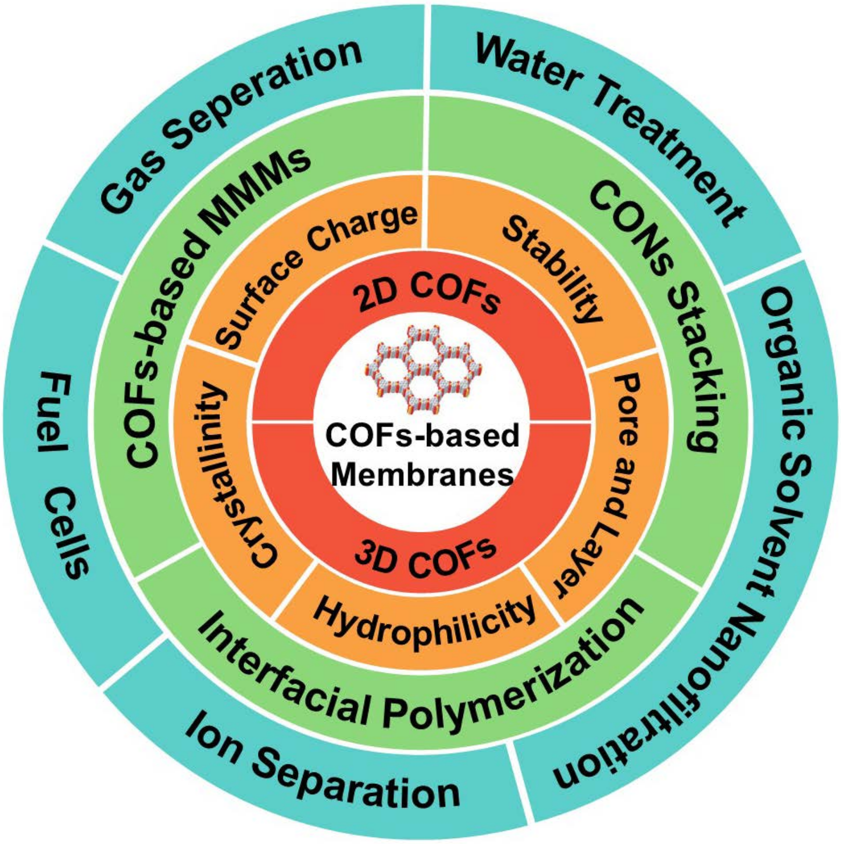

Figure 1. COFs-based membranes for sustainable ionic/molecular separations

DESIGN OF COFS NANOMORPHOLOGIES

The separation processes and applications of COFs are closely related to their nanomorphologies. For example, 2D COFs with significant electron delocalization are promising for electron conduction for ion sieving, while 3D COFs with large BET surface areas have considerable potential in gas storage.[37] The pore size, dimension, porosity, and crosslinking degree of COFs crystals can be adjusted through their nanomorphologies, further affecting the membrane separation performance.

Two-dimensional COFs

2D COFs is a planar structure with uniform pore size, similar to graphene, which form COFs structures with large specific surface areas through layered stacking.[38] Classification from the perspective of structural regularity, 2D COFs including symmetric and asymmetric polygon skeletons. The lattice structure is well organized in each case, and the pores are discrete. Behind each topology are numerous COFs with various monomers with different geometric structures.

Symmetric Topologies

The resulting COFs topology and pore structure are determined by the knot and linker structures.[39,40] The monomers used for synthesizing COFs typically have benzene rings, and the substituents on them are often in para - and meta positions due to steric hindrance and reaction activity, resulting in common COFs structures including triangles, quadrilaterals, and hexagons.[7] COFs were first reported and possessed a hexagonal pore structure. They reported that COFs had two structures: 1). COF-1 was made of terephthalboronic ($C_6H_4[B(OH)_2]_2$) acid by a self-condensation reaction with a pore size of 15 Å (Figure 2A).

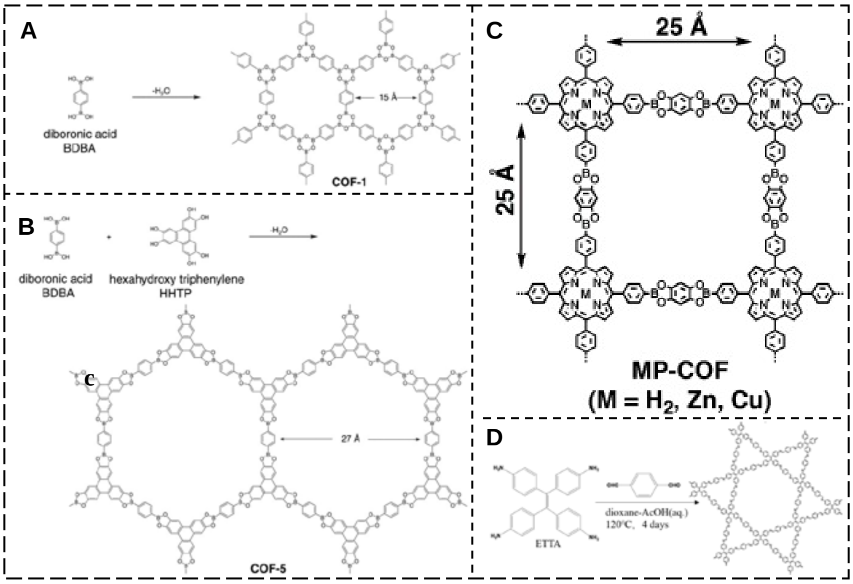

Figure 2. Different COFs pore structures synthesized through symmetric topologies.
(A, B) hexagonal COF-1 and COF-5. Copyright 2005 Science.[5]
(C) quadrilateral COFs.[42] Copyright 2012 Wiley-VCH
(D) dual-pore COFs.[44] Copyright 2014 American Chemical Society.

2).COF-5 was made by polymerization of terephthalboronic acid and hexahydroxy triphenylene ([$C_{18}H_6(OH)_6$]) with a pore size of 27 Å (Figure 2B).[5] There have been few reports on quadrilateral COFs.[41] Feng et al. reported three high-rate charge carrier conducting COFs with a quadrilateral structure (Figure 2C),[42] and Chen et al. reported a highly chemically stable quadrilateral COFs that can be used for heterogeneous photocatalytic oxidation of amines to imines under aerobic conditions.[43] Another unique COFs pore structure was reported by Zhou et al,[44] it have a structure with two geometric shapes at the same time, which is a central hexagonal structure wrapped in six triangles and similar to a star structure (Figure 2D). Terephthalaldehyde and 4,4′,4′′,4′′′-(ethene-1,1,2,2-tetrayl)-tetraaniline (ETTA) were reacted under solvothermal conditions to ultimately prepare COFs with micropores and mesopores. It features hexagonal holes and triangular pores that were alternately and randomly dispersed across the 2D sheets. This improved version of COF's remarkable dual-pore feature could introduce several novel capabilities, including multiple selectivity, and possess great theoretical advantages in the field of adsorption and separation.

At present, research on COFs-based membranes mainly focus on hexagonal COFs. Yuan et al. summarized that nearly 20 types of 2D COFs used for membrane separation are all hexagonal structures.[45] In fact, not only in the field of membrane separation, but also in the past decade, the strategy for designing new two-dimensional COFs structures has been limited to regular hexagonal shapes, and the potential relationship between their structures and electrons is still unclear.[46] Monomers in non-hexagonal COFs often require the structure of multiple benzene rings, as one or two benzene rings typically only exhibit a planar structure of 120° or 180°, and the number of multi benzene ring monomers is relatively small, resulting in a limited number of reported non hexagonal COFs, among which only a very small number of COFs are considered to have a certain possibility of application in catalysis[47] and conductivity.[42] Looking forward to further in-depth research on non-hexagonal COFs.

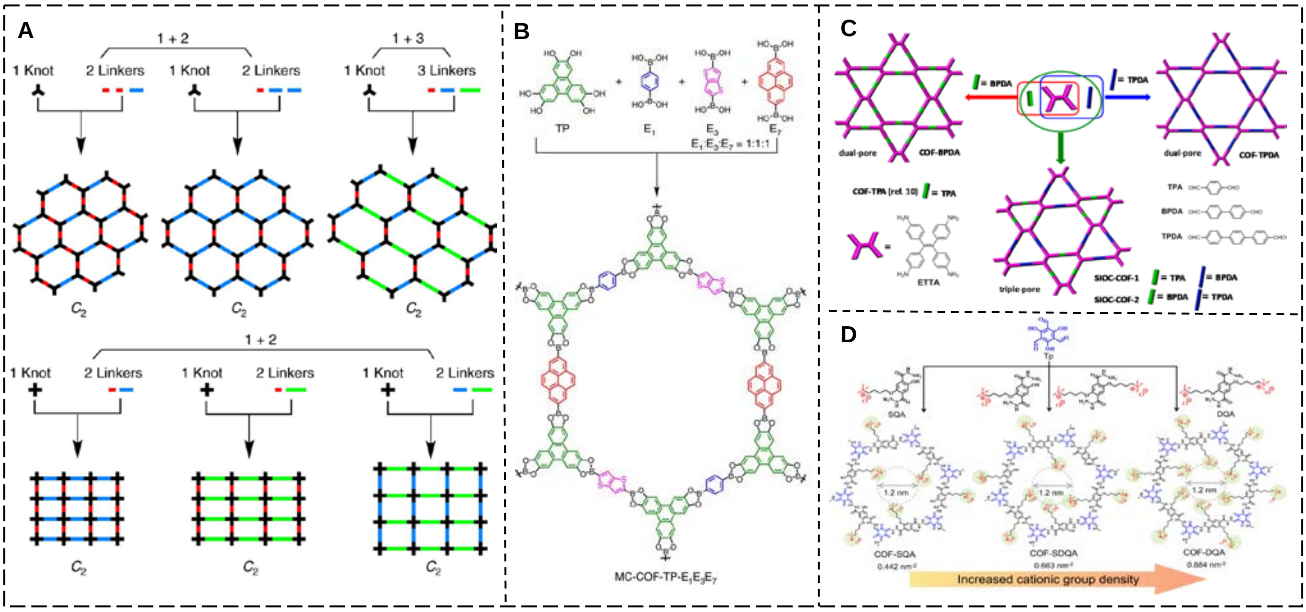

Figure 3. Different COFs pore structures synthesized through symmetric topologies.

(A) Multicomponent strategy design and synthesis of asymmetric topology COFs: three or four-component strategy.[48] Copyright 2016 Nature Portfolio.

(B) Schematic of the synthesis of multicomponent-COFs-TP-$E_1E_3E_7$ by the four-component strategy.[48] Copyright 2016 Nature Portfolio.

(C) Multiple pore structures COFs by three-component strategy.[49] Copyright 2016 American Chemical Society.

(D) Anion exchange COFs-based membranes based on asymmetric strategy.[50] Copyright 2023 American Chemical Society.

Asymmetric Topologies

The topology described above is implemented based on two monomers, one as a knot and the other as a linker. Although this connection method can form a COFs structure with excellent symmetry, it also limits the diversity of COFs types. The multi-component strategy overcomes this limitation by using two or three linkers to react with a knot to form a COFs skeleton. Huang et al. presented a generic technique based on multiple-component and condensation systems that allows the synthesis of hexagonal and tetragonal multiple-component COFs with multiple linker units (Figure 3A).[48] Their extended multi-component strategy includes four monomers, including three linkers and one knot (Figure 3B). There have also been many reports on the multicomponent COFs of the [1+2] strategy; (4,4′,4′′,4′′′-(ethene-1,1,2,2-tetrayl)tetraaniline (ETTA) was used as a knot, and three dialdehydes (terephthalaldehyde (TPA), [1,1′-biphenyl]-4,4′-dicarbaldehyde (BPDA) and [1,1′:4′,1′′-terphenyl]-4,4′′-dicarbaldehyde (TPDA)) were used as linkers of different lengths and prepared COFs with different pore structures by changing the amount of addition between different linkers. (Figure 3C).[49]

The pore structure of multicomponent COFs is an asymmetric structure different from that of two-component COFs, and this preparation method enhances the diversity and complexity of COFs structure. In theory, the different pore structures of asymmetric COFs can achieve precise separation of multi-component pollutants, achieving multifunctional sieving that symmetric COFs do not possess, but its nonuniform pore structure and uncontrollable synthesis process hamper its practical application in the field of membrane separations.[37] Therefore, there are few reports on the design of multi-component COFs-based membranes based on asymmetric strategies. Jiang et al. prepared an anionic COFs-based membranes by integrating flexible ether-bonded alkyl side chains into COFs.[50]

They found that ion conductivity is determined by both ion group density and side chain mobility, rather than simply being positively correlated with ion group density. Due to the poor effective movement space of side chains, the mobility of side chains decreases with the increase of ion group density, and the coupling relationship between the two jointly determines the ion conductivity. The COFs-based membrane with the highest ionic conductivity reported by them is an asymmetric structure COFs (COF-SDQA) with moderate ion group density and side chain mobility (Figure 3D).

Three-dimensional COFs

The planar layer structure of 2D COFs is composed of covalent bond links, but there is a weak mutual force between layers (such as π-π stacking, hydrogen bonds, and van der Waals forces). However, in 3D COFs, covalent bonds connect the entire 3D skeleton.[51] In the structure of 3D COFs, there must be a nonplanar monomer that forms covalent bonds with other monomers and eventually extends into 3D structures through a regular and orderly arrangement.[52,53] Compared with 2D COFs, 3D COFs have internal interacting pores, which gives them a higher specific surface area, lower density, and more easily accessible active sites.[54]

Since Yaghi and colleagues published the first 3D COFs in 2007[55], there have only been a few tens of different topologies in 3D COFs in the initial period of time (Figure 4A). The earliest 3D COFs had ctn (C_3N_4) (COF-102, COF-103 and COF-105) or bor (boracite) (COF-108) topological structures formed through self-polycondensation reactions. The dia (diamond) network reported later is also the most common topology in 3D COFs, which was built with tetrahedral nodes and a linear linker.[54,56] Since then, reports on 3D COFs have gradually increased, and some new model prediction methods have been proposed to predict the COFs of some possible 3D topological structures at the same time.[57-59] Although 3D COFs are regard as a promising material for gas absorption and energy storage, there are relatively few studies in the field of membrane separations.

Lu et al. first prepared 3D COF-320 membranes on a surface-modified porous α-Al_2O_3 substrate. They modified the surface of an α-Al_2O_3 substrate with 3-aminopropyltriethoxysilane (APTES) and further obtained a 3D COF-320 membrane via an imine condensation reaction between 4,4′ -biphenyldicarboxaldehyde (BPDA) and tetra-(4-anilyl)methane (TAM) under solvothermal conditions.[60] Mixed matrix membranes (MMMs) containing 3D COF-300 were successfully prepared for gas separation. Due to the good interfacial compatibility between COF-300 and two polymer matrixes, the obtained MMMs further improved gas permeation flux and selectivity (Figure 4B).[61] Shi et al. synthesized two 3D COFs membranes for the separation of different molecules and ions. They grew 3D COFs in situ on silicon wafers, prepared 3D-OH-COF membranes, and further converted 3D-OH-COF to 3D-COOH-COF through a carboxylation reaction for ion sieving (Figure 4C).[62]

To date, compared to 2D COFs, there is relatively little research on 3D COFs. The main limitation on the development differences between these two types of COFs is the issue of crystallization. In fact, the reaction sites between 2D COFs are easier to access, and the additional driving force provided by π-π stacking makes it easier to form long-range ordered crystal structures, while 3D COFs have larger monomer volumes, more pronounced steric hindrance effects, and more difficult to correct reversible covalent bonds, making them more prone to generate amorphous frameworks, which puts forward stricter and more

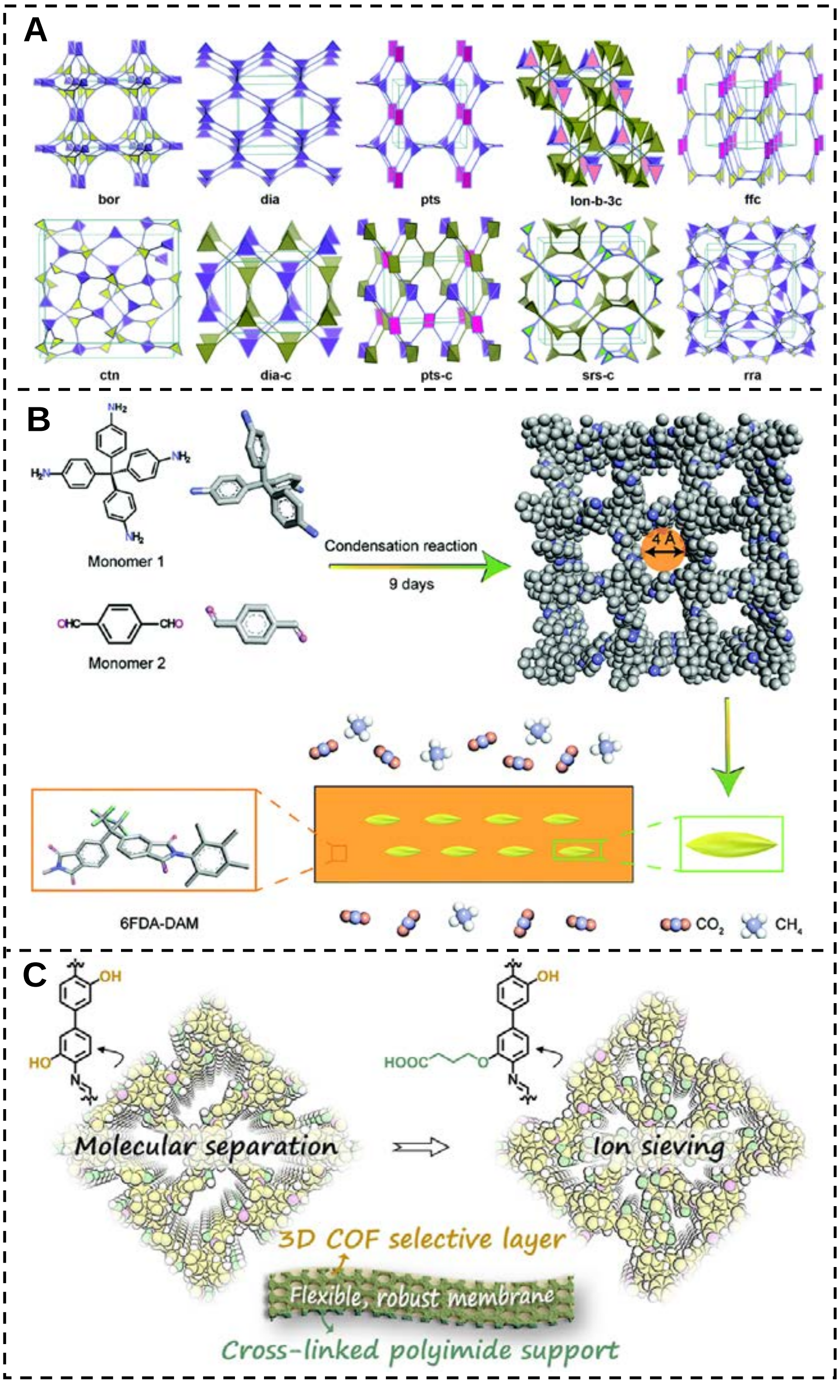

Figure 4. Related Structures and Applications of 3D COFs

(A) Nanomorphic structures in 3D COFs.[51] Copyright 2020 Royal Society of Chemistry.

(B) Preparation process of 3D COF-300 MMMs for CO_2/CH_4 separation.[61] Copyright 2019 Royal Society of Chemistry.

(C) 3D-OH-COF membranes and 3D-COOH-COF membranes for molecular separation and ion sieving.[62] Copyright 2021 American Chemical Society.

precise requirements for synthesis conditions.[63] At present, the main method to improve the crystallinity of 3D COFs is high-temperature heating.[64] Providing additional energy for covalent bond rearrangement correction through solvent thermal methods is essentially a barbaric approach. The method of achieving 3D COFs crystallization under mild conditions and unleashing its potential in widespread applications. In addition, there are relatively few types of 3D COFs, and their porous hollow structure reduces their mechanical stability.[65] The determination of the complex interpenetrating topological structure inside is also a challenging problem. Especially for interpenetrating structures and new topological structures, due to the low crystallinity of most COFs obtained as crystalline materials, powder X-ray diffraction (PXRD) detection often cannot achieve the expected results.[54] These all limit the application of 3D COFs.

CRUCIAL PROPERTIES OF COFS FOR MEMBRANE SEPARATIONS

The transport of substances across the membrane is mainly determined by the physical and chemical properties of the membrane. The pore size of COFs has a significant influence on the membrane separation performance because of its size exclusion effect. Furthermore, stability also plays a crucial role in the actual membrane separation process. Additional COFs characteristics, including crystallinity, hydrophilicity/hydrophobicity and surface charge, can significantly affect the separation performance of COFs-based membranes in various separation processes. Consequently, the design of COFs characteristics is necessary, and the main reported characteristics of COFs are summarized in this section.

The structure of a substance determines its properties, so we analyzed the properties of COFs from a structural perspective. COFs are mainly composed of monomer and covalent bond between monomers. The type of monomer largely determines the pore size of COFs and the functional groups on the monomers endow COFs with different surface charge and hydrophilicity. The covalent bond between monomers determines the crystallinity and stability of COFs. Certainly, the corresponding relationship between the structure of this COFs and its properties is not absolute, because the selection of monomers also affects the bonding method, thereby affecting crystallinity and stability and the following is a specific analysis.

Properties determined by monomers

Pore and layer

An important principle of membrane separation is the size exclusion effect. As a result, the average pore size of COFs-based membranes depends on the pore size of COFs, defining the application of COFs-based membranes. The main factors affecting the pore size of COFs are the size, geometric structure and functional group of organic monomer molecules.[40,45]

In addition to selecting COFs that have already been reported, there are two main methods for obtaining desired aperture COFs. The first method involves altering the organic linker and knots length and structure to affect pore size and geometry. Through this strategy. Chen et al. synthesized four COFs with different pore sizes by changing linker (Figure 5A).[66] Similarly, the knot of the junction can also alter the pore size of COFs. Using p-phenylenediamine as a linker, four different knots (1,3,5-triformylbenzene (TFB)[67], tris(4-formylphenyl)-amine (TFPA)[68] , 1,3,5-tris(4-formyl-phenyl)benzene (TFPB)[69], 3,8,11-tri(4-formylphenyl)-5,5,10,10,15,15-hexamethyltruxene (TFPHMT)[70]) also achieved the regulation of COFs pore size (Figure 5B). By designing the COFs pore size, precise separation of molecules of different volumes can be achieved, but this method is limited by the types of reactive monomers.

Another method to adjust the pore size is to introduce different functional groups. This synthesis method breaks the limitation of the types of COFs monomers, increases the diversity of COFs, and at the same time has a more precise adjustment of COFs pore size.

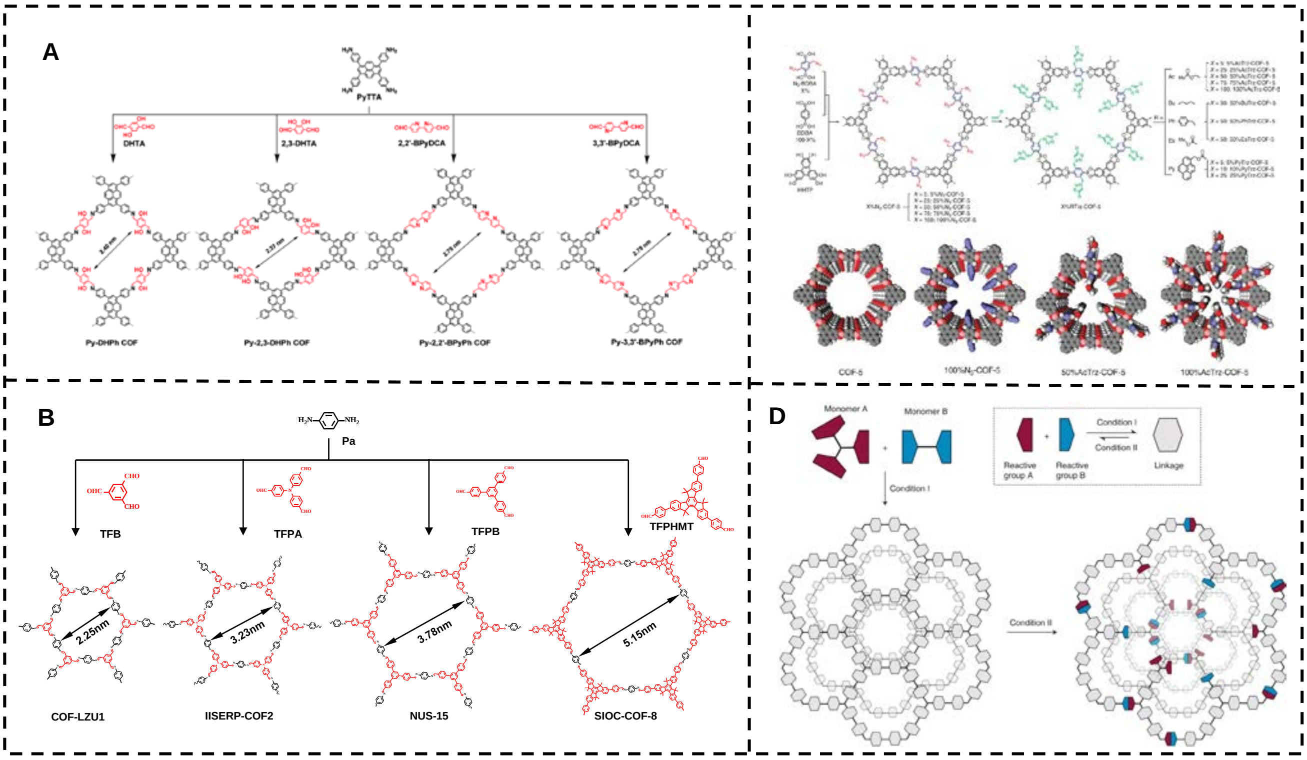

Figure 5. Different pore sizes of COFs.

(A) formed by different aldehyde monomers and PyTTA.[66] Copyright 2014 Royal Society of Chemistry.

(B) formed by different aldehyde monomers and Pa.[67-70]

(C) Postsynthetic modification of COF-5 with different functional groups.[71] Copyright 2011 Nature Portfolio.

(D) Engineering functionality gradient in COFs created by competitive reversible covalent bonding.[73] Copyright 2021 Nature Portfolio.

Jiang et al. introduced different functional groups after synthesizing COFs through postsynthetic modification (Figure 5C).[71] Through the reaction between alkynes and azide units, they prepared COFs with different pore sizes. According to these findings, postsynthetic modification is an excellent strategy for precisely modifying the pore size of COFs. They synthesized various COFs with different functional groups inside through this click reaction click reaction, including ethyl, ester, hydroxyl, carboxyl, and amino groups.[72] These substituent groups significantly alter the microenvironment of COFs pores from hydrophilicity to hydrophobicity, and from acidity to alkalinity, playing an important role in molecular transport. Although their research only focuses on the pore structure engineering of COFs and has not been applied in the field of membrane separation, it undoubtedly provides important inspiration for researchers. Liu et al. used this postsynthetic modification strategy to functionalize COFs with carboxyl groups.[74] They successfully introduced carboxyl groups into the internal pores of COFs by conducting ring opening reactions between free hydroxyl groups in COFs and acid anhydrides. They believe that carboxylated COFs can first shrink the pore size, preventing the entry of larger molecules. Secondly, covalent post-functionalization can reduce non-selective transport through invisible intergranular defects, thereby improving separation performance. The deprotonation of carboxyl groups in aqueous solutions also helps to enhance ion exclusion reactions.

Due to the difficulty in implementing single-layer COFs, the stacking method between COFs layers is another common structure, mainly consisting of two types: AA stacking and AB stacking. Different stacking modes can affect the performance of the membrane. AA stacking is an overlapping structure between COFs layers, while AB stacking is an interleaved structure. The structure of COFs is often determined under dry conditions, but for membrane separation processes, the influence of solvents must be investigated. Kang et al. studied the layer structure of four types of COFs in common solvents and found that the COFs in the solvents exhibited significant interlayer displacement, transitioning from the AA stacking mode in the dry state to the AB stacking mode after solvation. They attributed this phenomenon to the weakening of interlayer interactions between COFs and solvent molecules, resulting in interlayer displacement. They also proposed that the reversibility of this interlayer displacement process mainly depends on the strength of the interaction between the COFs layers. This study is very important for the application of COFs-based membranes in the separation process involving organic solvents. The transformation of the COFs selective layer structure will undoubtedly have a significant impact on the separation performance.[75] In addition, an increase in COFs thickness will undoubtedly increase rejection and reduce permeance. This means that there is a balance between membrane thickness and COFs pore size to achieve separation while ensuring high interception and flux. Designing a larger COFs aperture and a thicker COFs layer may suffice for this task, while a thicker COFs selection layer is also necessary for mechanical strength and stability.[76]

Hydrophilicity

The hydrophilicity of the membrane surface is another important factor affecting membrane separation performance, especially in specific applications of oil water separation. For example, in water treatment processes, hydrophilic membrane surfaces are beneficial for improving membrane flux and anti-pollution performance. Therefore, how to construct hydrophilic membrane surfaces is another important issue in the field of membrane separations.

From a chemical point of view, when there are abundant polar groups (amino, carboxyl, hydroxyl and sulfonic groups) in the inherent pore wall of COFs, the COFs materials obtained often have certain hydrophilic properties. A computational chemistry study showed that under the same aperture size conditions, TpPa-COFs-based membranes with hydrophilic functions (amino, hydroxyl, carboxyl) exhibited greater flux than membranes containing hydrophobic groups, owing to the presence of hydrogen bonds.[77] Meanwhile, experimental research also confirmed the above calculation results. Adding amine-rich COFs to PA greatly improves the hydrophilicity of the membrane. In the desalination test, compared to the COFs-based membranes without amine, the water flux increased by 92%.[78] Zhao et al. hydrolyzed the COFs linked by imine bonds through a solution of sodium hydroxide. The two sides of the membrane are first hydrolyzed, with imine bonds hydrolyzing into hydrophilic amino and aldehyde groups, while the interior of the membrane remains hydrophobic imine bonds. By controlling the hydrolysis time, channels with vertically arranged hydrophilic gradients and varying pore sizes with depth are obtained. The results revealed that the flow of COFs-based membranes was almost three times that of the most advanced desalination distillation membrane (600 $L \cdot m^{-2} \cdot h^{-1}$) (Figure 5D).[73]

Hydrophilic COFs-based membranes also provide benefits in removing dye and pervaporation. Kuehl et al. condensed f hexaketocyclohexane and benzenetetramine through microwave induction, followed by bromination. The brominated product can achieve metal catalyzed coupling reactions. Previous studies have shown that many functional groups can replace this bromine and that can be incorporated into the pores of the COFs. Unlike other COFs, these COFs can be functionalized with almost any required functional group before and after synthesis. The results showed that the COFs-based membranes with a carboxylated pore wall had high hydrophilicity. The high-density hydrophilic nanopores in the COFs-based membranes had low water transport resistance, showing an excellent water permeability far higher than that of the graphene oxide (GO) membrane.[79]

Surface charge

Surface charge is another important characteristic in membrane separation processes such as OSN and desalination. These procedures involve the rejection of solutes through physical size screening as well as electrostatic interactions. When the solution and the membrane surface have the same charge, due to the mutual repulsion of the electrostatic force, the membrane exhibits a rejection effect and anti-pollution ability. Similar to the process used to create hydrophilic COFs-based membranes, introducing different functional groups into the pores can also change the surface charge of COFs-based membranes. Li-Oakey et al. created new 2D carboxyl-functionalized COFs and added them to a PAN polymer matrix to create a variety of negatively charged ultrafiltration (UF) MMMs. Through the electrostatic repulsion between negatively charged bovine serum proteins and negatively charged carboxylic groups hydrolyzed in the COFs pores, the rejection rate of BSA increases from 3.5% to 81.9% as the COFs content gradually increases.[80] In addition to carboxyl groups, other functional groups, such as hydroxyl, amino, sulfonic acid groups and quaternary ammonium groups, can also give COFs charge characteristics. By introducing different functional groups, not only the hydrophilicity of the membrane surface is affected but also the charge on the membrane surface is changed. However, there are relatively few studies on the relationship between the hydrophilicity and electric charge of the membrane surface.

Properties determined by linkage

Crystallinity

The degree of long-range order in the atomic organization and the regularity of the pore structure in COFs is shown by crystallinity, which is critical for increasing selectivity and decreasing the mass transfer barrier in practical applications.[81] The crystallization of covalent organic frameworks mainly relies on dynamic covalent chemistry, which simultaneously controls the formation of covalent bonds and the phase transition from amorphous to crystalline to ensure the healing of structural defects.[82] Although the strength of covalent bonds helps significantly improve stability, the general irreversibility of kinetics controlled reactions hinders the molecular rearrangement necessary to form crystal structures. If the reaction can utilize reversible covalent bonds to rapidly form and break under appropriate conditions, thermodynamically stable products can be obtained instead of dynamically stable ones, providing an error correction mechanism.[53] COFs crystals with uniform size and few defects are usually achieved by reducing the degree of conformations free and controlling the nucleation process.[29]

Under the assumption of dynamic covalent chemistry, it was once considered that COFs stability and crystallinity are mutually limiting, which means that implying high crystallinity is typically associated with low stability, which is apparently extremely unfavorable in practical applications. For example, boronate ester-linked COFs exhibit a high crystallinity but completely hydrolyze in water. Similarly, imine-based COFs have a high crystallinity but are degradable in strong acids and bases. Covalent triazine frameworks may withstand harsh acidic and basic conditions, but they have substantially poorer crystallinity due to the less reversible formation process. However, as COFs have been explored more, their crystallinity and stability have been shown to be compatible[52], and there are three main methods to improve the crystallinity of COFs.

Monomer selection

The structure and properties of the monomers used to construct COFs greatly affect the crystallinity of COFs. For example, substances containing aromatic rings affect the crystallinity of COFs by balancing the electron thickness or polarization of the π-cloud. The investigations have illustrated that altering fluorines[83,84] or methoxy bunches[85] to aldehyde moieties accomplishes the high crystallinity of COFs. Higher fluorine concentrations in COFs result in an increase in charge transfer interactions between structures, which increase π-cloud polarization. Compared with COFs without introducing fluorine, the crystallinity and BET area of COFs containing fluorine are both improved.

Hydrogen bonds

Noncovalent interactions are effective in maintaining the planar structure and reducing defects during the COF formation process. The presence of hydrogen bonds can effectively inhibit the movement between molecular chains, thereby reducing defects in the formation of COFs and improving crystallinity. In 2013, Sharath et al. proposed this strategy by converting ether bonds (-OMe) near the imine bond center into hydroxyl (-OH), thereby introducing hydrogen bonds (OH--N=C) into porphyrin COFs (Figure 6A). Intramolecular hydrogen bonds enhance the rigid structure of porphyrin COFs, while improving their long-range ordering and crystallinity.[84]

Slowing the rate of nucleation and growth

Reducing nucleation and growth rates can effectively avoid defects in the formation of COFs, further improving crystallinity. There are many factors that affect the nucleation and growth rate of COFs formation, including various reaction conditions and the addition of nucleation inhibitors. Liu et al. dissolved the alcohol in dimethyl sulfoxide (DMSO), and the alcohol gradually oxidized to aldehydes, which then reacted with amines to form COFs via Schiff base reaction. Their research found that alcohols were slowly oxidized to aldehydes, and the oxidation reaction runed through the entire polymerization process. The initial low concentration of aldehyde monomers delayed and controlled the reaction rate, slowing down the nucleation rate of COFs. Later, increasing the reaction temperature promoted crystal growth. Therefore, they believed that controlling the reaction temperature during the nucleation and growth stages is crucial for improving the crystallinity of COFs.[86] They also improved the preparation method by controlling the feed rate of aldehyde monomers to adjust the monomer concentration, further controlling the nucleation and growth rate of crystals, and ultimately producing highly crystalline COFs (Figure 6B).[87] Calik et al. added an appropriate amount of nucleation inhibitors during the preparation of COFs, which reacted with the construction monomer, inhibiting the formation rate nucleation and growth,

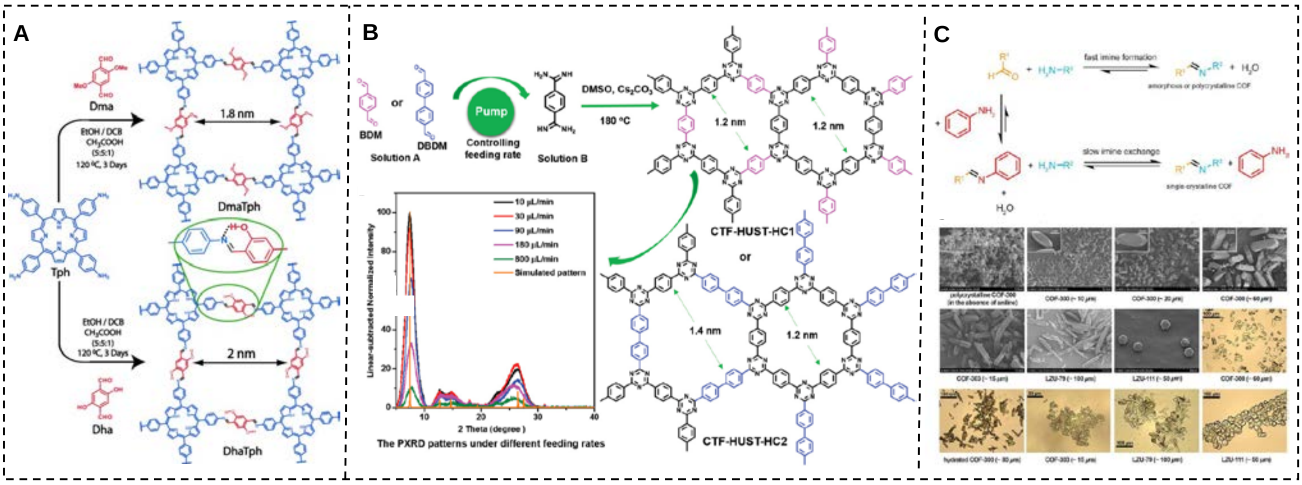

Figure 6. Factors affecting the crystallinity and stability of COFs.

(A) Synthesis of COFs containing hydrogen bonds by the condensation reaction.[84] Copyright 2013 Wiley-VCH.

(B) Synthesis of high crystallinity COFs by controlling nucleation and growth rate through low feed rate.[87] Copyright 2019 Wiley-VCH.

(C) Formation mechanism and images of crystal growth of imine-based COFs modulated by aniline.[88] Copyright 2018 American Association for the Advancement of Science.

facilitating the repair of defects, and ultimately forming COFs with high crystallinity.[89] Similarly, Ma et al. added aniline to the system of imine-linked COFs, using aniline as an inhibitor to compete with the amino monomers that form COFs, slowing down the growth rate of imine-linked COFs, allowing COFs to obtain a longer time for self-repair, and ultimately preparing high crystallinity imine COFs (Figure 6C).[88]

Stability

The chemical and thermal stability of COFs is the foundation for ensuring the long-term and stable separation capacity of COFs-based membranes, which determines whether COFs-based membranes can be used in actual environmental systems such as organic solvents, high humidity, strong acid/alkali, and other harsh systems. Typically, COFs synthesis is based on reversible reactions, but it has a significant negative impact on their chemical stability. In the reversible reaction of the preparation of COFs, water as a product will promote the reverse reaction, leading to the decomposition of the structure of COFs. However, in the process of membrane separations, aqueous solution is the most commonly used system, which greatly limits the application of COFs in the field of membrane separations. Initially reported COFs are extremely unstable in water and prone to hydrolysis.[90] To design and synthesize COFs with strong stability, different researchers have performed many different studies.[84,85] Currently, there are two main methods: using stable organic monomers to synthesize COFs and introducing hydrogen bonds between molecules.

The first strategy to improve the stability of COFs is to use stable monomers and covalent bonds. The basic framework of COFs is prepared by covalent bonding between atoms such as carbon, oxygen, phosphorus, and nitrogen, and its stability greatly depends on the stability of the covalent bonds generated between monomers. The earliest COF-1 and COF-5 are extremely unstable and easily decomposed in water because the electrons in the outer layer of the boron atom are very prone to nucleophilic reactions.[65] After that, COFs for other connection methods were gradually developed, including condensation of aldehydes and amines, hydrazones, azines, and imides, among which the imine bond connection COFs were the most stable. This is because imine-based COFs are prepared under acidic conditions, which means that imine-based COFs are very stable in neutral solutions or some organic solvents.[45] However, the imine-bond COFs are not alkali resistant. As mentioned earlier, Zhao et al. hydrolyzed the imine-bond COFs using alkaline solution.[73] The second method for increasing COFs stability involves increasing intramolecular and interlayer hydrogen bonds. Hydrogen bonds are mainly caused by functional groups in organic monomers. Liu and colleagues demonstrated the exist of hydrogen bonding in azine-linked COF-JLU3 intramolecular (OH--N=C).[91] The COFs have extremely high stability, not only maintaining stability at 400℃ but also resisting acid, alkali, and common organic solvents.

SYNTHESIS OF COFS-BASED MEMBRANES

Applying COFs materials to membrane separations and improving the performance of the separation process is the most important. Compared with other materials, the most important issue in applying COFs to membrane separations is how to fully exploit the potential of an orderly arrangement of COFs pore structures. Initially, COFs were prepared as a porous filler to prepare MMMs, but the COF structure was discontinuous, and the pore structure of the matrix membrane remained the main mass transfer channel and did not fully exert the performance of COFs. With the progress of membrane preparation technology and COFs synthesis methods, in situ growth, layer-by-layer stacking, Interfacial polymerization (IP), and other methods have been proposed to prepare continuous COFs-based membranes. The following section is a detailed introduction to these preparation methods.

COFs-based MMMs

The MMMs combines the advantages of porous materials and polymer matrices and has been widely studied. However, the interface compatibility between organic and inorganic materials hinders its large-scale application. The emergence of COFs that are fully covalently bonded and have good compatibility with polymer matrices effectively solves this problem.[92]

The main method of blending COFs into the membrane is nonsolvent-induced phase separation (NIPS). In a typical NIPS process, polymer and COFs are uniformly mixed in organic solvent to form a homogeneous solution. Subsequently, the solution is poured onto the surface of a glass plate or nonwoven fabric, and a scraper is used to form a liquid membrane of a specific thickness. Finally, the liquid membrane is introduced into water, where the organic solvent is miscible with water, while the polymer containing COFs is insoluble in water and is converted into a solid membrane to complete the phase conversion process. Immerse the resulting membrane containing COFs in deionized water to remove solvent residues, completely complete the phase conversion process, and store it in deionized water. The UF MMMs prepared by Phuoc H et al. used the typical NIPS process (Figure 7A).[80] This membrane that directly mixes COFs with polymers is also known as a MMMs. MMMs have attracted widespread attention due to their ability to balance organic and inorganic properties. In recent years, research has mainly focused on adding porous materials to them to meet separation performance requirements.

In recent years, researchers have synthesized MMMs using a variety of COFs[93-96], such as SNW-1, COF-1, TpPa-1, TpBD, LZU1, TpHZ, TpPa-2, NUS-10 and COF-300. SNW-1 has received widespread attention due to its low synthesis cost and high hydrophilicity. Yang et al. added SNW-1 to sodium alginate (SA) to prepare a hybrid membrane. The addition of SNW-1 increases the water permeation flux while also improving thermodynamic stability and mechanical properties.[97] Cheng et al. reported MMMs for carbon dioxide separation based on COF-300. The addition of 3D COF-300 increases the free volume inside the membrane, further improving gas permeation flux. Ultra-small voids of COF-300 fillers and the rigid polymer chains on their surfaces can improve gas selectivity.[61] Yang et al. synthesized a mixed matrix membrane based on H-TpBD. They mixed the synthesized hollow H-TpBD nanospheres into the sodium alginate (SA) matrix. Due to the introduction of a large number of hydrophilic groups, MMMs have rapid water permeability. In addition, excellent interfacial compatibility between TpBD and SA can avoid the formation of interfacial defects and maintain long-term application (Figure 7B).[98]

Another method to fabricate COFs-based MMMs is solvent evaporation phase conversion. This method directly evaporates the solvent in the prepared liquid membrane to achieve phase conversion and prepare a solid membrane material. Through this method, Duan et al. prepared MMMs containing COF-5 for gas separation. They ultrasonically dispersed the prepared COF-5 powder into a Pebax-1657 matrix, evaporated the solvent in a PTFE dish, and dried it to obtain a membrane (Figure 7C). Due to its unique structure, COF-5 exhibits a high absorption capacity for carbon dioxide, with the highest CO_2 permeability reaching 493 Barrers, while enhancing the selectivity of CO_2/N_2 (from 31.3 to 49.3).[99]

The preparation of MMMs by surface modification of COFs is also another hot research topic. Zhao et al. proposed a strategy of modifying COF-300 with ionic liquids (IL).[100] They soaked the synthesized COF-300 in [bmim] [Tf_2N] and then used IL@COF-300 as a filler to prepare of MMMs for gas separation. The addition of IL reduces the pore size of COF-300 from 1.28 nm to 1.09 nm, improving the diffusion coefficient difference ($DCO2/DCH_4$) between CO_2 and CH_4. On the other hand, IL has high CO_2 solubility, thereby increasing the solubility difference (SCO_2/SCH_4). Due to the dual function of IL, the optimal membrane has a selectivity of 39 for CO_2/CH_4, and a high CO_2 permeability of about 1601 Barrer. Liu et al. prepared MMMs using polyethylene glycol monomethyl ether (PEG) modified COF-DhaTab as filler and Pebax as matrix.[12] PEG introduces an ethylene oxide groups with higher affinity for CO2, which improves solubility selectivity and diffusion selectivity. In addition, PEG has the same structure with PEO chain segments of Pebax, improving the interfacial compatibility between COFs fillers and Pebax matrix.

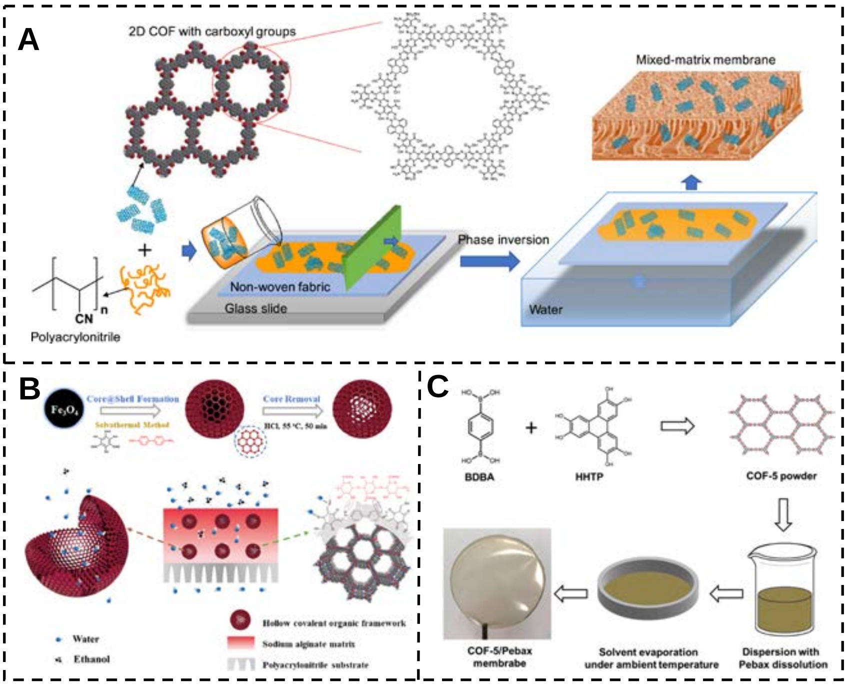

Figure 7. Different methods for preparing MMMs

(A) The process of preparing COFs MMMs using the NIPS method.[80] Copyright 2019 Elsevier.

(B) Hollow COFs preparation process and molecular transport through SA-H-TpBD MMMs.[98] Copyright 2018 Elsevier.

(C) Synthesis processes of COF-5 MMMs via solvent evaporation phase conversion.[99] Copyright 2019 Elsevier.

Covalent organic nanosheet stacking

The preparation of graphene and GO membrane inspired the method of covalent organic nanosheets stacking to prepare COFs-based membranes.[101] The COFs blocks are stripped by solvent-assisted exfoliation,[102] mechanical delamination,[103] chemical exfoliation[104] and self-exfoliation[105] to prepare covalent organic nanosheets (CONs). Afterwards, the CONs are uniformly attached to the membrane surface through spin coating,[106] drop-casting[103] or vacuum assisted filtration.[107] Currently, most reported COFs have a 2D structure, and by breaking the van der Waals interaction between Molecular interlayer, single-layer COFs nanosheets can be obtained. Tang et al. provided a specific summary of stripping methods for different COFs.[108] David et al. reported chemical stripping of COFs by adding acid. They demonstrated that adding acid to the imide-linked COFs powder can weaken the interaction between layers through electrostatic repulsion, thereby achieving dispersion of the COFs layer and obtaining a COFs nanosheet structure.[104] After that, the obtained nanosheet can be stacked on a porous substrate in various ways, such as vacuum-assisted filtration and dip coating. The thickness of the selected layer of the COFs-based membranes synthesized by this method is thinner than that of the in suit growth preparation, and the thickness can be adjusted by changing the number of COFs nanometers. However, the binding between the COFs selective layer and substrate is weak.

Li et al. subjected COF-1 to ultrasound in dichloromethane to produce a sheet-like structure and then coated COF-1 nanosheet solution to prepare COFs-based membranes. The resulting COFs have high permeability and thermal stability[103]. The composite membrane of

COFs and GO prepared by this method can be used for the separation of

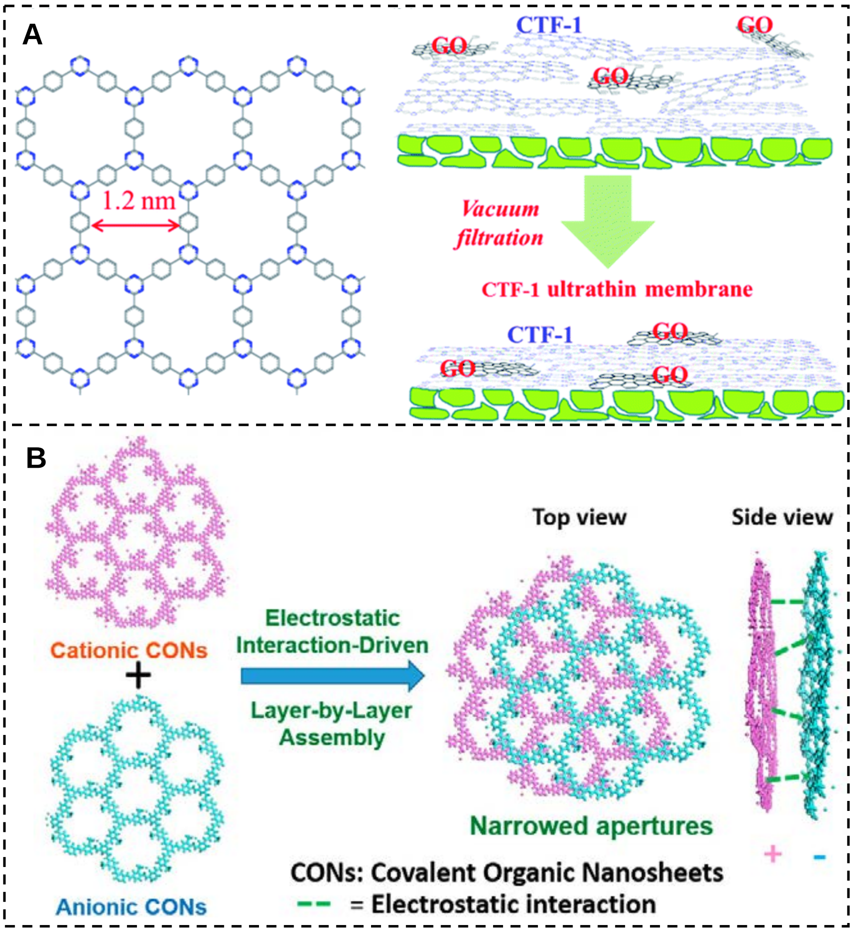

Figure 8. Preparation of COFs-based membrane by layer-by-layer stacking method.

(A) Preparation process of the composite membrane of COFs and GO by layer-by-layer stacking.[109] Copyright 2016 Royal Society of Chemistry.

(B) Layer-by-layer stacking of two COFs with different charges to prepare ultrathin membranes with narrow pore sizes.[110] Copyright 2020 American Chemical Society.

carbon dioxide, hydrogen and ion separation (Figure 8A).[79,109] Ying et al. used the interaction of the electrostatic force to prepare ultrathin 2D membrane materials by stacking two kinds of COFs (TpEBr@TpPa-SO_3Na) with opposite charges and different apertures. Due to the staggered stacking of CONs with strong electrostatic interactions, the synthesized membrane has the characteristics of reduced pore size and dense and compact structure, exhibiting higher permeability to hydrogen than most reported similar membranes while breaking the Robson upper bound (Figure 8B).[110]

Interfacial polymerization

Liquid-liquid interface

IP technology refers to two monomers with high reaction performance dissolved in two immiscible solvents, and an irreversible polycondensation reaction is carried out at the interface of the two phases. The starting monomer is usually dispersed in two different solutions, and the reaction occurs only at the interface[111]. Commonly used monomers include polyamine, polyols, polyphenol and polyacid chloride. Polyamines, polyols and polyphenols can be dissolved in water, while polyacid chloride need to be dissolved in an organic solvent.[112-114] Commonly used organic solvents include n-hexane and dichloromethane.

Diamine is the most commonly used monomer in the IP process. It is an aliphatic or aromatic compound, and its activity is sufficient to form a layer of polyamide. Generally, IP also requires a microfiltration membrane or UF membrane as the substrate, such as polyethersulfone (PES) and polysulfone (PSF). The separation effect of using pure monomer polycondensation IP to prepare composite membranes is often not ideal, so the addition of various additives in the reaction process has become a research hotspot. Common additive types include surfactants, nanofiller additives, cosolvents, amine diffusion inhibitors, etc.[115]

The first reported IP membranes were reported in 2017[116]. Kaushik et al. dissolved 1,3,5-triformylphloroglucinol (Tp) in dichloromethane and dissolved amine monomers in water. Due to the immiscibility of dichloromethane and water, Tp and the amine monomer underwent a Schiff base reaction at the interface, which formed a thin active layer through condensation polymerization (Figure 9A). Wang et al. prepared a TpPa selective layer over a PSF UF substrate by an IP process, which two phases of organic solvent and water are dichloromethane and water, respectively Under the condition of acetic acid as a catalyst, the TpPa layer formed throughout the PSF UF support in just 10 s (Figure 9B). The reaction time played a crucial role in the IP preparation process, not only for scalability but also for determining the final features of the membrane. The obtained TFC PA membrane was washed with methanol to remove all the residual monomers, solvents, and catalysts. After heating the membrane at 60℃ for 5 minutes, the TpPa selective layer still maintained a connection with the PSF substrate. However, this method is strictly limited by reaction time and monomer solubility in the desired solvents.[32] Wang et al. proposed an IP method for single diffusion by placing an aqueous solution of Pa and an n-hexane solution of Tp on both sides of the diffusion cell. With a PVDF substrate in the middle of the diffusion cell, only Pa molecules passed through the PVDF and reached the n-hexane solution to react with Tp (Figure 9D). Due to the non-direct contact between the two phases in this method, the reaction rate of the two monomers also depends on the diffusion rate of Pa. The formation process of COFs can be controlled by reducing the concentration of the Pa solution, extending the reaction time, or other methods to reduce the defects of COFs and improve the separation efficiency of the membranes.[117]

Other interfaces

In addition to IP at the liquid-liquid interface, IP can also theoretically be carried out at the liquid-gas interface,[118] liquid-solid interface,[119,120] and gas-solid interface.[121] IP at the gas-liquid interface has been reported, while IP processes at other interfaces have rarely been reported. Zhang et al. described a simple vapor-liquid interfacial polymerization (VLIP) approach for fabricating TpHZ COFs-based membranes under mild circumstances. They placed a PAN or AAO substrate between two glass cells, a bottom cell containing ethanol

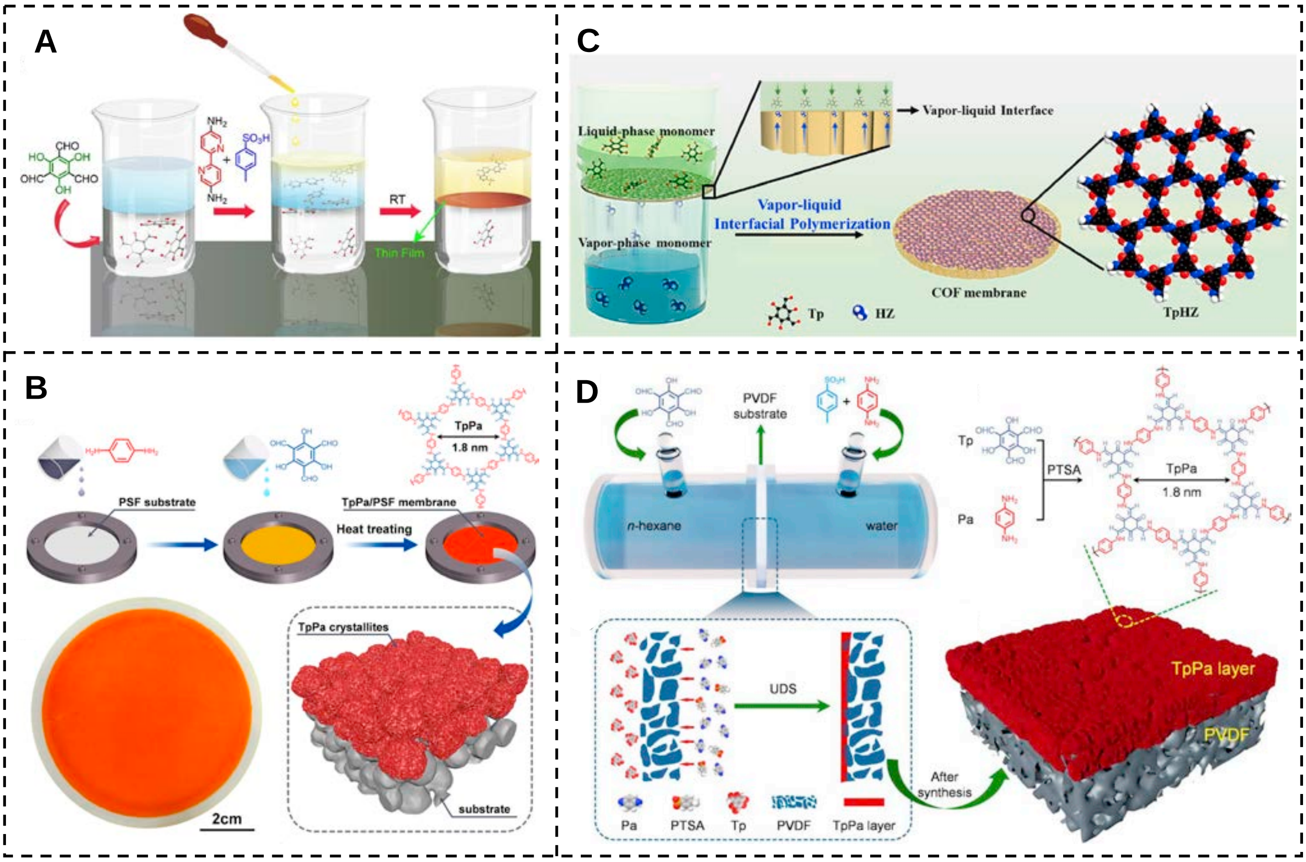

Figure 9. Polymerization reaction process at different interfaces

(A) IP used to synthesize the Tp-Bpy thin membrane.[116] Copyright 2017 American Chemical Society.

(B) Fabrication process of the TpPa/PSF membranes via IP.[32] Copyright 2018 Elsevier

(C) fabrication of TpHZ/PAN membranes through the VLIP.[118] Copyright 2022 Elsevier.

(D) Preparation process of the TpPa/PVDF membranes via the UDS method.[117] Copyright 2019 Elsevier.

dissolved hydrazine hydrate (HZ), and an upper cell containing Tp and mesitylene solution. Through evaporation, HZ reacts with Tp to form TpHZ-COF on the surface of the substrate (Figure 9C). Under the most favorable conditions, the TpHZ/PAN membrane has a pure water flux of 8160 g m^{-2} h^{-1}, a separation factor of 1023 for n-butanol, and exhibits high stability.[118]

There is still an important and incomplete research area in the preparation of free-standing membranes through IP method, which is the film-forming property issue, that is, whether the final reaction product morphology is particles or thin films after monomer reaction contact reaction at the interface of the two phases. We speculate that the structure of COFs will definitely affect its film-forming ability. Relatively flexible segments (aliphatic chain) are more prone to film-forming, while COFs with a rigid structure (aromatic ring) is often more prone to particle formation. In addition, the diffusion of COFs monomers and catalysts in two-phase solutions is also an important influencing factor. Wang et al. reported the effect of different acid catalysts on the preparation of COFs-based membranes through IP.[122] They reported on various organic acid catalysts. When the diffusion coefficient of acid in solution was high, it was easy for the acid to diffuse from the organic phase to the aqueous phase, and then form salts with amine monomers, losing its catalytic effect. Almost no COFs grew on the membrane surface. When the diffusion coefficient of organic acids was small, the COFs layer on the membrane surface became thicker, looser, and more prone to detachment.

Only when the diffusion coefficient was appropriate, can a thin and dense COFs selective layer be prepared on the membrane surface. By strictly limiting the contact between monomers at the interface through physical methods, film formation can also be achieved, which was the gas-solid, gas-liquid, and liquid-solid interfaces introduced earlier.

CHARACTERIZATION METHODS OF COFS-BASED MEMBRANES

Morphology and Structure

Scanning electron microscopy (SEM) is a common technique for characterizing morphology and structure. It uses a narrow focused high-energy electron beam to scan the sample, excites various physical information through the interaction between the beam and the material, and further collects, amplifies, re-images this information to achieve the purpose of characterizing the microscopic morphology of the material. The resolution of SEM can reach 5 nm, and field emission scanning electron microscopy can even reach a resolution of 0.6-0.7 nm. By studying the surface of the COFs-based membrane through SEM, the morphology of the COFs-based membrane surface can be determined, whether there are obvious COFs particles or dense film. By observing the cross-section of the membrane, the structure of the membrane pores can be determined, whether they are finger like or sponge like, and the thickness of the selected layer can be determined (Figure 10A, B).[123]

Transmission electron microscopy (TEM) projects accelerated and aggregated electron beams onto a very thin sample, causing electrons to collide with atoms in the sample and change direction, resulting in stereo angular scattering. The size of the scattering angle is related to the density and thickness of the sample, so it can form images with different brightness and darkness. TEM can provide a clearer observation of the thickness of the COFs selection layer and the boundary between the layer and the substrate (Figure 10C).[124] Ordinary resolution TEM is mainly used to observe the microstructure of membrane materials, but high-resolution transmission electron microscopy (HRTEM) can directly observe the crystal lattice fringes of COFs. In addition to imaging, TEM can also perform selected area electron diffraction (SAED) on COFs crystals to further determine the successful preparation of COFs on the membrane surface (Figure 10D).[125]

Atomic force microscopy (AFM) is another common technique for characterizing morphology and structure, which utilizes the atomic interaction forces between the micro-force sensitive element at the probe tip and the material surface to study the structure and properties of the material surface. AFM has high resolution in the vertical direction and can calculate the surface roughness of the sample through scanning. Gadwal et al. utilized this characteristic to characterize the thickness of the COFs selection layer on the membrane surface. They believed that the cliff like descent in the vertical direction of the membrane surface was the boundary where COFs synthesized on the substrate surface, and the vertical drop height was the thickness of the COFs selection layer (Figure 11A).[125]

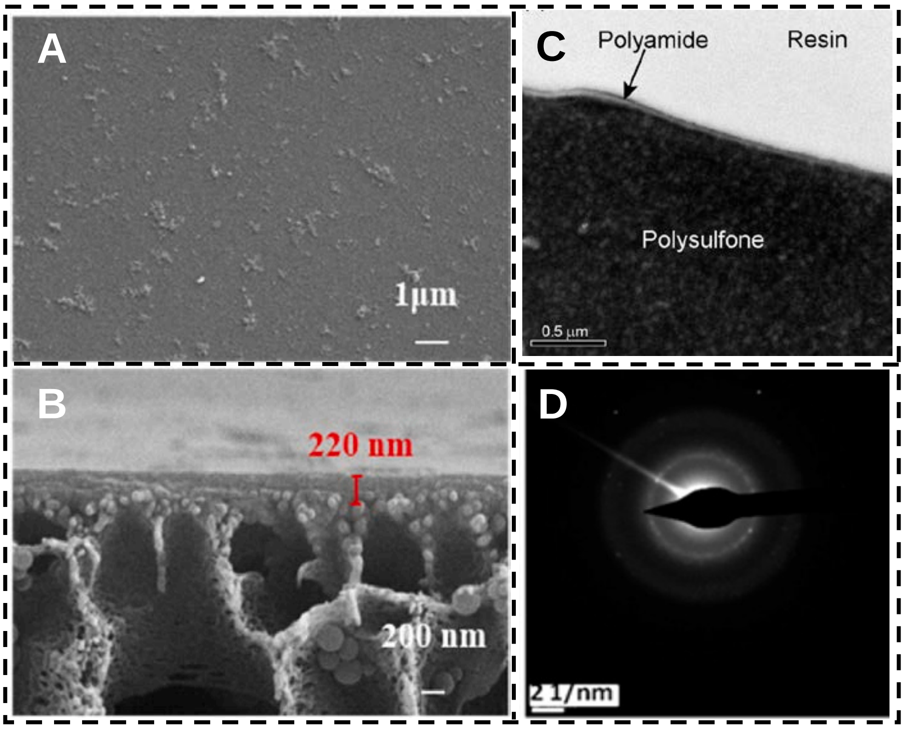

Figure 10. **SEM, TEM images of COFs-based membrane and diffraction images of COFs.**

(A,B) SEM images of membrane surface and cross-section.[123] Copyright 2022 Elsevier.

(C) Select layer and substrate cross-sectional TEM images.[124] Copyright 2010 Elsevier.

(D) selected area electron diffraction images of COFs.[125] Copyright 2018 American Chemical Society.

As a porous crystal structure, X-ray diffraction (XRD) is a necessary characterization method for COFs. The current main method is to characterize the crystallinity of COFs through PXRD. Due to the periodic arrangement of its two-dimensional or three-dimensional structure, significant strengthening peaks can be observed at specific positions. However, it is often difficult to accurately estimate the crystallinity and amorphous phase content of COFs-based membranes using XRD for characterization, as COFs-based membranes require a polymer film as support, and the crystal structure of the polymer can have a significant impact on the diffraction l peaks. In addition, the crystal facet orientation can affect the intensity of XRD diffraction peaks, so sometimes researchers may physically damage the film and thoroughly grind it to randomly distribute its crystal facet orientation. [121]

Scanning tunneling microscopy (STM) can further and more finely characterize the structure of COFs with atomic layer thickness. Liu et al. achieved the preparation of defect free SCOF by controlling temperature and adjusting the evaporation rate of steam, and observed the highly ordered crystal structure of COFs using STM (Figure 11B).[67]

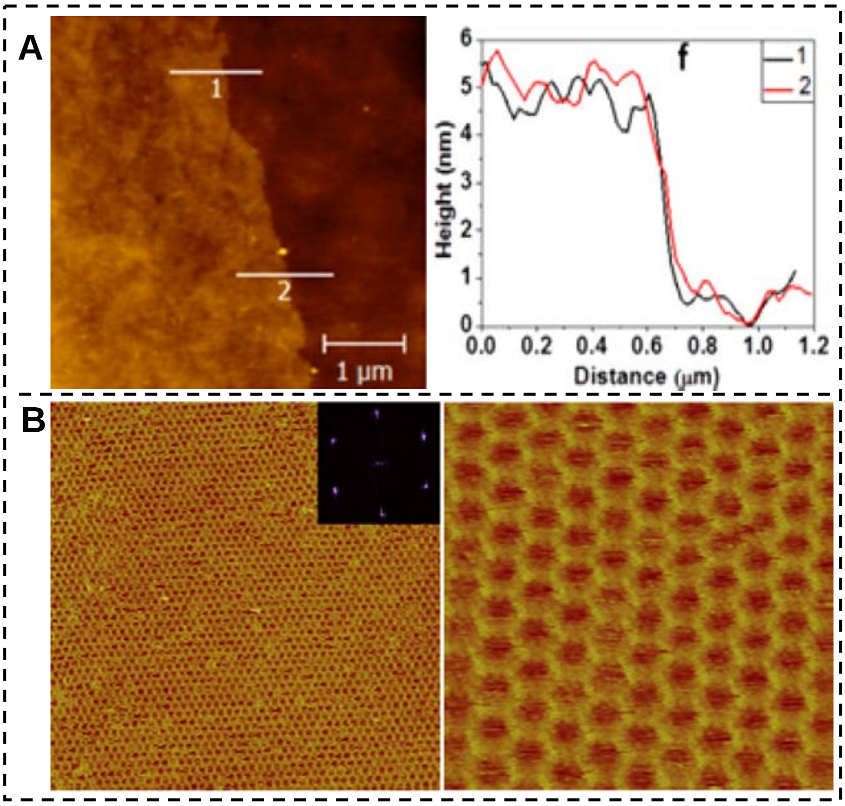

Figure 11. AFM and STM images of COFs.

(A). AFM image at the junction of COFs selection layer and polymer substrate membrane.[125] Copyright 2013 2018 American Chemical Society.

(B). STM images of regular lattice pores in COFs.[67] Copyright 2013 American Chemical Society.

Chemical Composition

In addition to characterizing the morphology and structure of COFs, it is also necessary to determine the atomic connection mode and element content of COFs. Fourier-transform infrared (FT-IR) is the most basic and common characterization method, which reflects the vibration signals of chemical bonds and functional groups. It can judge the degree of polymerization and modification based on the differences in characteristic peaks before and after.[106,126] X-ray photoelectron spectroscopy (XPS) uses X-ray irradiation to stimulate the emission of electrons or valence electrons within atoms or molecules, and then collects and analyzes them using an energy analyzer to obtain XPS spectrum.[127] XPS has high sensitivity and can achieve precise control of penetration depth, which can obtain the elemental composition and valence bond connection information of the membrane at different depths.[128] In addition to XPS, energy-dispersive spectroscopy (EDS) can also perform elemental analysis on COFs-based membranes. It emits characteristic X-rays from different elements by bombarding the surface of the sample with an electron beam. By analyzing X-rays of different wavelengths and intensities, it qualitatively and semi-quantitatively analyzes different elements. EDS is usually used in combination with SEM and TEM. Through spectral processing, the distribution of surface element phases and bulk phases can be clearly observed, and EDS has high sensitivity for the determination of trace elements in COFs-based membranes.[129]

APPLICATIONS OF COFS-BASED MEMBRANES

Due to the regular pore structure and large surface area of COFs materials, the applications of COFs were first started in gas storage. With the continuous deepening of research on COFs, multifunctional COFs that can be designed in advance have been proposed continuously. Researchers have gradually realized that the combination of COFs with membrane separation technology can help improve the flux and selectivity of separation membrane. Gradually, COFs materials have been applied to various membrane separation processes.

Gas Separation

Gas membrane separation is achieved by utilizing the differences in the dissolution and diffusion properties of gas components within the membrane. Under the effect of pressure on both sides of the membrane, the gas mixture penetrates the membrane material at different permeation rates to achieve separation of the gas mixture. Compared to traditional distillation separation processes, the biggest advantage of gas separation membranes is energy savings.

As a new green energy source, the separation process of hydrogen has attracted much attention. Computational studies have shown a high separation factor at room temperature by monolayer COFs-based membranes. However, the experimental separation factors differ significantly from the calculated values.[31,130-132] The main reason is that the COFs-based membranes obtained through experiments are much thicker than the ideal single layer of continuous COFs-based membranes in the computational process. Fan et al. reported a MOF-in-COF composite membrane with a special pore structure, which greatly improved the permeability of hydrogen, and the separation of H_2/CO_2 and H_2/CH_4 far exceeded the Robeson upper bounds (Figure 12A).[11] Fan et al. prepared a double-layer COF-COF composite membrane on a porous substrate, and the prepared double-layer COF membrane exhibited higher separation selectivity for H_2/CO_2, H_2/N_2, and H_2/CH_4 gas mixtures than single-layer COFs-based membranes (Figure 12B).[130] Similarly, Ying et al. prepared multilayer COFs-based membranes through multilayer interface crystallization, which displays high H2 permeance and H_2/CO_2 selectivity (Figure 12C).[31] CO_2/N_2 separation is of great significance for research on carbon capture processes to address issues of global warming. Computational research pioneered CO_2/N_2 separation, and research has shown that changing the packing mode of covalent organic framework nanosheets can obtain high carbon dioxide permeability and excellent CO2/N2 selectivity.[133,134]

Methane is another widely studied gas and is a promising alternative to traditional fossil fuels due to its rich natural reserves and low pollution. However, CH_4 is frequently contaminated with CO_2, lowering its energy content and heat value. Therefore, it is necessary to detach CO_2 from CH_4 prior to transporting and utilizing natural gas.[27] According to computational chemistry, the interaction between CO_2 and functional sites in COFs facilitates the selective separation of CO_2, especially fluorine- and chlorine-modified COFs, which have the most significant effect on promoting the separation of CH_4 and CO_2.[135] However, there are relatively few reports on gas separation membranes containing COFs with these two functional groups. In experimental research, Meixia et al. prepared MMMs containing ACOF-1 during the separation process of CH_4 and CO_2, and MMMs loaded with 16% wt.% ACOF-1 exhibited the highest CO_2 permeability, twice as high as that of pure polymer membranes.[136]

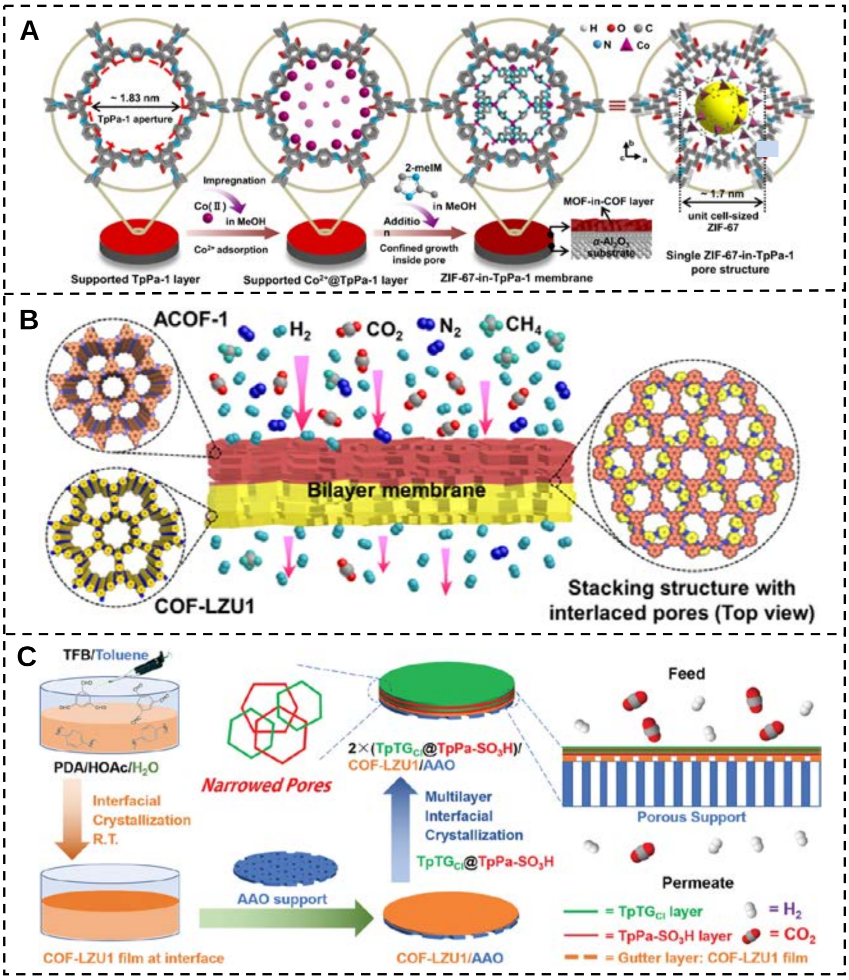

Figure 12. COFs-based membranes for gas separation.

(A) Synthesis process of ZIF-67-in-TpPa-1 membranes.[11] Copyright 2021 Nature Portfolio.

(B) Pore structures of double layer COFs-based membranes. Copyright 2018 American Chemical Society.

(C)Preparation of multilayer COFs-based membranes by multilayer interface crystallization.[31] Copyright 2022 Wiley-VCH.

Water treatment

Wastewater treatment is an important issue to be solved by membrane separations. Because of its many applications in desalination and wastewater recycling, membrane separations have been shown to be an energy-efficient and environmentally friendly method of meeting the growing need for clean water. According to the reported pore size range of COFs, it can meet the requirements of NF and UF of dyes, salts, and organic substances in water.

Ultrafiltration

UF is usually used for pretreatment of reverse osmosis (RO) to remove colloids, proteins, and other macromolecular compounds from water. Usually, it is carried out under low pressure; small molecular solutes are pushed by pressure through the UF membrane to reach the low pressure side, while large molecular substances are trapped to achieve a separation effect. Blocking and adsorption should be minimized as much as possible to extend the service life of UF membranes, which involves careful design of the UF membrane structure. Because of their structural benefits and adaptability, COFs have attracted much interest in the field of UF in recent years.

Xu et al. first prepared TpPa-2 by microwave synthesis and then prepared MMMs by mixing TpPa-2 as a nanofiller into polysulfone (PSF).[137] The results showed that MMMs effectively improved water flux and rejection, breaking the trade-off effect between membrane permeability and selectivity. Liu et al. prepared a highly hydrophilic UF membrane by constructing the imidazole-quartet water channel in COFs and using composite self-assembly technology (Figure 13A).[138]

Nanofiltration

Nanofiltration [139] is mainly used for the separation of substances with molecular size bigger than UF, and its operating pressure is between UF and RO. The main mechanism of the NF separation process is size screening and charge interaction. COFs-based membranes can intercept ions and dye molecules through NF, and the size of dye molecules is much larger than that of ions. The pore size of 2D COFs is reported to be much larger than the radius of ions. Especially for sodium chloride, the separation efficiency reported by many current research institutes still needs to be improved. Currently, research on NF COFs-based membranes mainly focus on dye separation; therefore, it is necessary to further reduce the pore size of COFs for ion separation. The typical COFs used for NF is summarized in Table 2.

Li et al. reported COFs-based membranes with subnanopores with high separation performance. By changing the stacking method of COFs, the pore size of the membrane can be reduced to the subnanometer scale. Finally, the pore size of the membranes prepared using FS-COM-1 can reach 0.6 nm, achieving efficient ion separation.[140] The NF membrane prepared using alumina as the substrate has excellent mechanical properties. The P-COF NF membrane prepared by in situ growth at room temperature exhibits excellent separation performance when using α-alumina as the substrate and exhibits excellent mechanical properties (Figure 13B).[141] Wu et al. used PDA-TpPa as the intermediate layer for IP and prepared a dense and ultrathin PA layer by controlling the IP process (Figure 13C). The prepared NF membrane achieved a permeation flux of 207.07 L m^{-2} h^{-1} MPa^{-1} for pure water and a rejection rate of 93.4% for Na_2SO_4.[142] Yang et al. reported COFs-based membranes prepared by mixing one-dimensional cellulose nanofibers with 2D COFs (Figure 13D). The pore size of the membranes was between 0.45-1 nm, and the rejection rate for Na_2SO_4 reached 96.8%, while the rejection rate for NaCl was only approximately 23%. Compared with membranes reported in other literature, they have good ion selectivity for monovalent and divalent ions.[26]

Table 2 Typical COFs for NF and their separation performance

COFs	Substra	Separation molecules	Rejection (%)	Permeability (L^{-1} m^{-2} h^{-1} bar^{-1})	Ref
TpPa	PI	Na_2SO_4	99.5	115	129
LZU1	Al_2O_3	Methyl blue	99.2	76	32
TpPa	PSF	Congo red	99.5	50	143
TpBd	PSf	Congo red	99.5	33.6	144
TpTGCl	PAN	Methylene blu	99	24	145
COF-300	Al_2O_3	Chrome black	97.4	79	146
TBDH	Nylon	Congo red	99	439.4	147
TpPa-SO_3Na	-	Methylene blu	99.5	270	116
TpBpy	-	Rhodamine B	98	211	148
Hz-TFPTZ	PSf/PVP	Basic Blue 41	92	94.7	149
TpEB	PAN	Congo red	99	32.3	150
MPD-TFB	Nylon	Congo red	98.6	94.4	151
Tp-TAPA	PAN	Congo red	99	68.1	152
Tp-TTA	mPSF	Chrome black	98.1	36.5	138

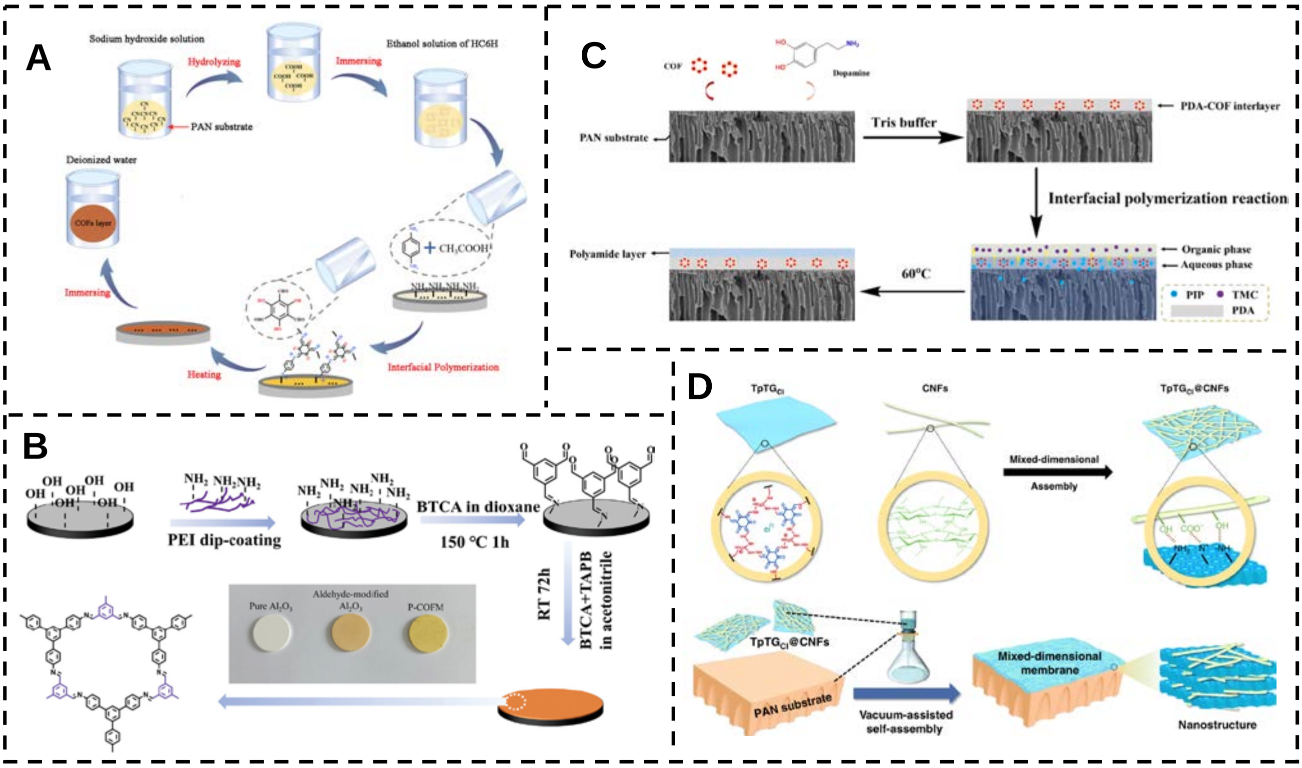

Figure 13. COFs-based membranes for water treatment.

(A) The synthesis process of composite matrix membranes by IP.[140] Copyright 2022 MDPI.

(B). Synthesis of the P-COF membrane on a porous α-Al_2O_3 substrate.[142] Copyright 2022 Wiley-VCH.

(C) Preparation process of the PA/PDA-COF/PAN NF membranes. Copyright 2019 Elsevier.

(D) Vacuum assisted self-assembly preparation TpTGCl@CNFs.[127,153] Copyright 2019 Nature Portfolio.

Organic solvents nanofiltration

Organic solvents are abundant in many industrial production processes, such as petrochemical, biopharmaceutical, and food processing. OSN is the process of using membrane separation technology to achieve the purification, recovery, and concentration of organic solvents. The pore size of the OSN membrane is approximately 1-2 nm.[33] Compared to other membrane separation processes, the most important thing about OSN membranes is their stability in organic solvents. However, most traditional polymer membranes cannot be used in organic solvents for a long time. COFs-based membranes are suitable for OSN applications due to the stability of some special covalent bond-linked COFs in organic solvents.

Gao et al. prepared hollow fiber membranes with Janus characteristics using in-suit growth method.[127] They circulated tris(4-aminophenyl)amine (TAPA) and benzene-1,3,5-tricarboxaldehyde (BTCA) solutions along the shell and tube layers of hollow fiber modules, respectively, to prepare COFs layers on cross-linked polyimide (cPI) substrates. The inner cavity of low polarity COFs connected by imines can serve as a transport channel for non-polar solvents, while the imides bonds of cPI substrates are converted into amide bonds with high hydrophilicity, which is conducive to the transport of polar solvents. Therefore, they had a Janus structure with both hydrophilic and hydrophobic pores. Due to this structure, COFs-based membranes had high flux of acetone (395.21 L m^{-2} h^{-1} bar^{-1}) and n-hexane (266.27 L m^{-2} h^{-1} bar^{-1}). Shinde et al. synthesized TFP-DHF 2D COFs-based membranes through the Langmuir Blodgett (LB) method.[154] They adjusted the pore size of COFs by changing the length of alkyl chains and achieved efficient OSN through these adjustable pore size COFs-based membranes.[155] In 2019, Li et al. reported TFN OSN membranes with excellent solvent resistance stability. Due to the interaction between COFs and PA layers, it exhibits extremely high long-term stability in DMF solutions.[156] Although the COFs-based membranes exhibit high permeation flux in the application of OSN, the molecular weight intercepted by the COFs-based membranes is much larger than that of traditional polymer membranes. Due to the adjustability of the COF structure, COFs-based membranes still have great potential to be developed in OSN.

Fuel cells

With the gradual depletion of fossil fuels and the pollution caused to the environment, hydrogen fuel cells, as a new green energy source, have received widespread attention.[157] The proton exchange membrane in fuel cells not only isolates oxygen from hydrogen but also provides a proton exchange channel to achieve the charging and discharging process. Proton conductivity has a significant impact on the functioning of a proton exchange membrane. COFs contain well-defined nanochannels that allow proton carriers to pass through, giving them controllable proton conductivity. In addition, connecting strong acid groups in COFs, such as sulfonic acid and phosphoric acid groups, helps to improve proton conductivity. As a result, COFs-based membranes have demonstrated enhanced performance as proton exchange membranes. Phosphoric acid is a typical proton carrier that is added to COFs to improve proton conductivity. The proton conductivity was improved by adding H_3PO_4 to Tp-Azo.[158] Similarly, by loading H3PO4 onto SNW-1 to prepare COFs-based membranes, under ideal conditions, the proton conductivity increased by 101.8%.[159] There are also many reports on improving the proton conductivity of COFs by introducing sulfonic groups. Himadri et al. prepared three types of COFs-based membranes loaded with different sulfonated COFs, which showed super protonic conductivity (Figure 14A).[34] Li et al. developed a proton conductive membrane with weak conductivity affected by humidity based on COFs with sulfonic acid groups.[160] At the same time, they pointed out that in this field, more effort should be invested to solve the problem of gas crossover, which can be achieved by reducing the pore size of COFs and optimizing the battery system, thereby solving practical application problems.

Ion separation

Heavy metal ion separation

The free heavy metal ions (such as cadmium, lead, mercury, copper, etc.) in industrial wastewater have a significant impact on the environment due to their non degradability. In recent years, there have been frequent reports of using COFs to remove heavy metal ions. Su et al. reported a strategy of in situ formation of a 2D COFs ultra-thin intermediate layer on the surface of polysulfone hollow fiber (HF) substrate to prepare polyamide membranes, which achieves superior metal ion interception ability. The prepared membrane has a rejection rate of over 90% for cadmium, copper, zinc, manganese.[161] Although COFs are widely used for heavy metal ion separation, most of it is based on adsorption theory, [159] and there are relatively few reports on COFs-based membranes. Therefore, further exploration of the combination of COFs and membranes is needed to achieve sustainable heavy metal ion separation.

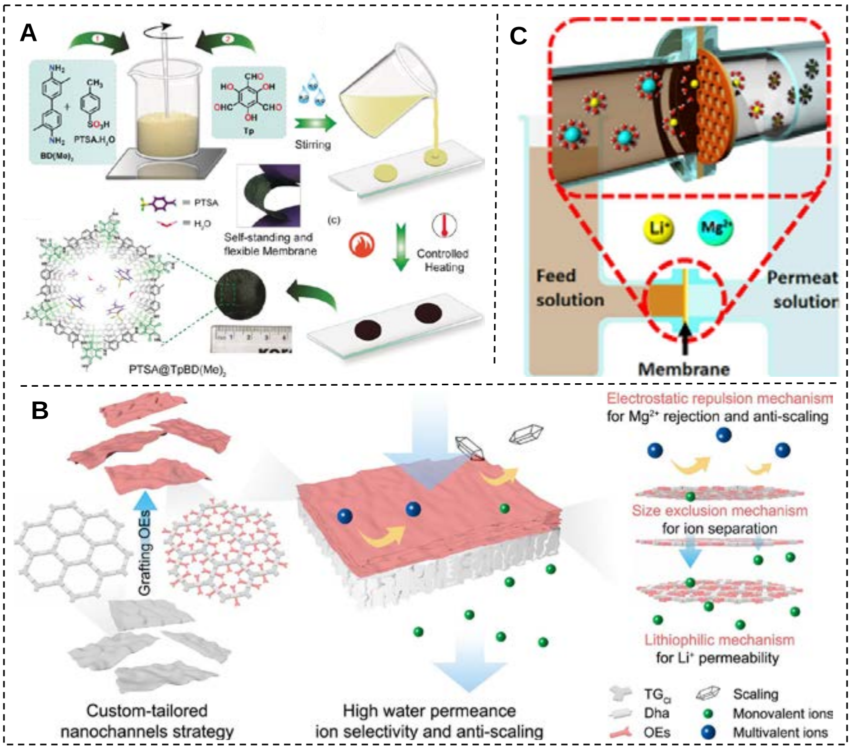

Figure 14. COFs-based membranes for fuel cell and ion separation.

(A) Preparation process of PTSA@TpBD(Me)$_2$ membranes.[162] Copyright 2018 Wiley-VCH.

(B) Preparation of COFs-based membranes with lithiophilic channels.[163] Copyright 2023 Elsevier.

(C) Ion permeation through COF-4EO-PAN in a homemade diffusion cell.[164] Copyright 2021 Elsevier.

Lithium Extraction

With the continuous development of the lithium battery industry, the demand for lithium in the market is increasing. Due to the presence of over 62% of lithium in salt lakes worldwide, the use of membranes to extract lithium from salt lakes has correspondingly received extensive research. Niu et al. achieved the selectivity of K^+/Li^+ and Mg^{2+}/Li^+ reached 31.5 and 14.7 through a mixed matrix membrane prepared by COF-300 and polystyrene (PS).[162] Ren et al. prepared a lithiophilic channels by grafting oligoethers (OEs) into COFs, which exhibited excellent water permeance of 32.1 L m^{-2} h^{-1} bar^{-1} and high Li^+/Mg^{2+} separation factor of 30.2 in simulated salt-lake brine (Figure 14B).[163] Bing et al. constructed a special Li^+ transport channel by introducing lithiophilic oligoethers into COFs (Figure 14C). Because of the interaction between lithiophilic oligoethers and Li^+, the COFs-based membranes constructed by this method exhibits high Li^+ selectivity.[165] Although COFs-based membranes have made some progress in the separation of Li^+/Mg^{2+}, there are still many challenges in the separation of Na^+ and K^+ with similar chemical properties to Li^+.

SUMMARY AND OUTLOOK

As an emerging porous crystalline material, COFs are widely applied in various fields due to their ordered pore structure, low density, and large surface area. In the field of membrane separations, by selecting and modifying monomers and the synthesized COFs, various strategies are used to synthesize COFs-based membranes with different properties. Excellent performance and enormous potential have been demonstrated in some applications. Although current research has achieved certain achievements, corresponding challenges still exist.

Firstly, the mechanism of nucleation, growth, and defect formation of COFs is still not clear enough, which makes it difficult to achieve precise control of the structure of COFs. In particular, unavoidable defects in the COFs preparation process seriously affect the separation performance of the membranes. There are no reports on the reliable large-scale preparation methods of defect-free COFs-based membranes. Predicting structure and function through computational methods may contribute to the study of COFs mechanisms. At the same time, there is an urgent need for new characterization methods to better understand the growth mechanism of COFs, and characterization methods applied to other materials may also be suitable for COFs research,

Secondly, for the structure of COFs, it is extremely challenging for COFs-based membranes for desalination, because there are still many problems in constructing COFs-based membranes with pore sizes less than 1 nm for the efficient rejection of salt. This type of COFs can potentially be achieved using monomers with smaller molecular volumes, but this method has limitations. Another method is to modify the monomers before synthesis or modify the COFs after synthesis, introducing side groups into the pore wall structure of COFs to further reduce pore size. In addition, the structure of COFs is closely related to the research of smart membranes. By modifying pH, temperature, and light sensitive chemical groups into the pores inside COFs, when the external environment changes, it will directly control the material transport pores, effectively achieving the function of intelligent response. However, there is still relatively little research on smart membranes.

Moreover, at present, the main preparation methods for COFs-based membranes are IP and direct mixing with polymers. In the IP process, the two-phase monomers must be dissolved in two incompatible solvents, and the solubility and diffusion rate of different monomers can affect the formation process of the COFs layer. For MMMs, the problem is the discontinuity of the COFs selection layer, which hinders the full potential of the selective separation of COFs. Due to some common characteristics between MOFs and COFs, some methods for preparing MOFs can also be applied to the preparation of COFs. For example, a simple surfactant assisted synthesis method has been successfully used for the preparation of MOFs-based membranes, and this method can also be attempted for the synthesis of COFs-based membranes. With the continuous development of technology, 3D printing technology is currently expected to be applied in the preparation process of COFs-based membranes. Exploring a simple and efficient method for preparing defect-free COFs-based membranes is of great significance for promoting the development of COFs-based membranes.

Last but not the least, in the field of industrial applications, the mechanical, chemical, and long-term stability of COFs-based membranes under actual separation conditions still needs to be researched although COFs-based membranes typically demonstrate the high-performance for separations. The industrial applications request the membrane module with the large membrane area and the reliable fabrication method is still challenging for the mass production of COFs-based membranes. The high cost of raw materials and preparation limits the practical large-scale application of COFs-based membranes. A significant amount of effort should be invested in developing effective synthesis methods to obtain products with high yield and no by-products, while maintaining economic benefits and ecological safety, as well as subsequent recyclability and explanation of issues.

In summary, this review summarizes the structure, key characteristics, preparation methods, and separation applications of COFs-based membranes. Compared with traditional polymer membranes, COFs-based membranes have significant theoretical advantages, but the application of COFs in membrane separation is still in its early stages. In different separation processes, it is necessary to design multifunctional COFs to improve separation performance. There is an urgent need for more detailed research on the synthesis mechanism of COFs and new preparation methods to accurately control the structure of COFs in order to achieve better separation performance and practical application results. We believe that this review can provide some guidance for the research of COFs in the field of membrane separations and inspire new creative research.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (22178076 and 22208072), the Fundamental Research Funds from the Central Universities of Ministry of Education of China (2023FRFK03047), China Postdoctoral Science Foundation (2021M690829), Special support from China Postdoctoral Science Foundation (2021TQ0088) and Open Project of State Key Laboratory of Urban Water Resource and Environment (Harbin Institute of Technology; No. QA202127).

DECLARATION OF INTERESTS

The authors declare no competing interests.

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