Solution processing of crystalline porous material based membranes for CO₂ separation

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The carbon emission problem is a significant challenge in today’s society, which has led to severe global climate issues. Membrane-based separation technology has gained considerable interest in CO₂ separation due to its simplicity, environmental friendliness, and energy efficiency. Crystalline porous materials (CPMs), such as zeolites, metal–organic frameworks, covalent organic frameworks, hydrogen-bonded organic frameworks, and porous organic cages, hold great promise for advanced CO₂ separation membranes because of their ordered and customizable pore structures. However, the preparation of defect-free and large-area crystalline porous material (CPM)-based membranes remains challenging, limiting their practical use in CO₂ separation. To address this challenge, the solution-processing method, commonly employed in commercial polymer preparation, has been adapted for CPM membranes in recent years. Nanosheets, spheres, molecular cages, and even organic monomers, depending on the CPM type, are dissolved in suitable solvents and processed into continuous membranes for CO₂ separation. This feature article provides an overview of the recent advancements in the solution processing of CPM membranes. It summarizes the differences among the solution-processing methods used for forming various CPM membranes, highlighting the key factors for achieving continuous membranes. The article also summarizes and discusses the CO₂ separation performance of these membranes. Furthermore, it addresses the current issues and proposes future research directions in this field. Overall, this feature article aims to shed light on the development of solution-processing techniques for CPM membranes, facilitating their practical application in CO₂ separation.

1 Introduction

Global warming and climate change are common environmental issues that humankind faces worldwide, and carbon dioxide emissions are responsible for 66% of global warming.¹ The latest CO₂ emission data show that the current concentration of CO₂ in the atmosphere has exceeded 420.54 parts per million (ppm), surpassing the maximum safe concentration of 350 ppm.² Unfortunately, the current energy system is still heavily reliant on fossil fuel burning, which is accompanied by massive carbon dioxide emissions. As a result, it can be foreseen that the atmospheric CO₂ level will inevitably continue to increase. The current global CO₂ emission budget is only 115 billion tons, and global CO₂ emissions between 2019 and 2020 account for about one-third of this budget.³ In situations where it is unrealistic to eliminate the use of fossil fuels, carbon capture, utilization, and storage (CCUS) technology, as an indispensable portfolio, is a crucial technical means and a backup technical guarantee to achieve carbon neutralization. CO₂ separation is the first stage of CCUS technology.

The most common CO₂ capture technology encompasses cryogenic distillation, absorption, adsorption, and membrane separation technology. The dominant CO₂ separation technology, amine absorption,⁴ is limited by its toxicity and large plant sizes. Membrane-based carbon capture is effective for capturing emissions from big stationary sources. To achieve a 90% reduction in CO₂ emissions from coal-fired power plants, the membrane process used only about 20% of the electricity it generated.⁵ CO₂ separation occurs on vast occasions, including CO₂ capture from flue gas (CO₂/N₂), CO₂ removal from blast-furnace gas (CO₂/N₂), production of landfill gas (CO₂/CH₄), sweetening of natural gas (CO₂/CH₄) and production of steam-methane re-former off-gas (H₂/CO₂).⁶⁻⁹ As for flue gas feed streams, membranes with high CO₂ permeance of 1000–5000 GPU and a selectivity of 30–50 are required to be economically competitive with amine absorption.¹⁰ The development of high-performance membrane materials is critical for efficient membrane-based CO₂ separation.

Polymer membranes dominate the field of actual membrane gas separation due to low-cost and scalable solution-casting processes.¹¹,¹² The current commercial membrane materials for natural gas treatment, such as cellulose acetate and polyimides, occupy an approximate market size of $300 million annually.¹⁰ Nonetheless, these membranes have a limitation of
the “trade-off” effect between gas permeability and selectivity. Besides, it is well known that high-pressure CO2 will exert pronounced swelling and plasticization effects on traditional polymer membranes with random pathways. As a result, materials with properties of intrinsic microporosity and regular transport channels are highly desired for the construction of next-generation high-performance membranes. Crystalline porous materials (CPMs), including zeolites, metal-organic frameworks (MOFs), hydrogen-bonded organic frameworks (HOFs), and porous organic cages (POCs), have attracted burgeoning interest in recent years due to their ordered pore structures and varied functionality. To date, with ongoing endeavors in material engineering, various types of methods such as solvothermal synthesis have emerged to manufacture crystalline porous material (CPM) membranes for precise molecular sieving. Unfortunately, the poor processability precludes the expeditious development of these CPMs. With regard to their more extensive application, the pursuit of a convenient processing strategy adapted from polymer membranes has sparked tremendous research interest.

Solution processing, with its characteristic attributes, has come to light in CPM membrane manufacturing lately. The solution-processing method is a simple and low-cost strategy widely applied for producing polymer membranes or films. To be specific, solution-processing is a strategy that assembles the precursor solution into a solid membrane. According to the features of CPMs, solution-processing can be classified into three conditions (Fig. 1). First, POCs and HOFs, as a relatively novel class of CPMs, can easily dissolve in common organic solvents, which renders them a potential material to be solution-cast into membranes. Besides, regulating the morphology of nanosheets or nanospheres is also a practical approach to improve the solution-processability. Nanosheets and nanospheres are solution-processable, allowing a defect-free and thickness-adjustable selective layer to be readily fabricated by the solution-assembly method. This morphology-regulation strategy offers a great opportunity for insoluble CPMs. At last, with the aid of other solution-processable materials, such as polymer and graphene oxide (GO) nanosheets, the CPMs with poor processability are capable of assembling into composite membranes via a solution-processing method.

The solution processing of CPMs overcomes the complexity of the traditional solvothermal method and shows great potential in scalable fabrication. This review summarizes different CPM membranes based on solution-processing and compares the merits and demerits of distinct solution-processing strategies, emphasizing the influential factors for constructing continuous membranes. The CO2 separation performance of these membranes is also categorized and discussed. In the end, the opportunities and challenges of solution-processed CPM membranes for CO2 capture are prospected.

2 Categorization of solution-processing methods for CPM-based membranes

2.1 Solution-casting

The solution-casting method is the typical strategy in solution-processing, including drop-casting, dip-casting, spin-casting, and spray-casting, which is simple to operate and low-cost. In the simplest solution-casting procedure, which refers to drop-casting, a certain amount of the precursor is dissolved in the solvent completely, and then the homogeneous solution is drop-cast flat on a glass plate. After the evaporation of the solvent, a continuous membrane will be obtained. Several factors need to be considered during the casting process, which makes a massive contribution to the membrane performance. First and foremost, the solubility determines dissolution which is the initial step in the solution-casting process for soluble CPMs. Solubility depends on the properties of both precursor and solvent, and influences the concentration and viscosity of the precursor solution. The solvent with suitable solubility of the precursor is required for continuous membrane formation. As we concluded in the previous report, the insufficient nucleation density resulting from low concentration leads to the growth of discrete crystals. The solvent with a low boiling point leads to rapid precipitation of amorphous aggregates or scattered crystals. The conditions of fabricating membranes are generally different from growing CPM single crystals, which implies that the solvent for single crystal growth is not necessarily fit for membrane solution processing. Similarly, the operation conditions, including temperature, time, solution amount, etc., significantly affect the final membrane quality, especially for polycrystalline membranes, which undergo a recrystallization process. Solvent

Fig. 1 Various solution-processing methods for CPM-based membrane preparation.
evaporation is the kinetically driven force for the nucleation and growth of CPM membranes. As a result, adjusting the parameters to provide sufficient nucleation density and matched growth rate is the key.

HOFs are a budding class of crystalline porous materials connected by highly reversible hydrogen-bonding interactions and other non-covalent interactions. The reversible bonds make HOFs soluble in common solvents and well-suited for solution-based membrane fabrication. Our previous work reported the first HOF membrane via a facile solution-processing method on a common α-Al₂O₃ substrate (Fig. 2a). The monomers were dissolved in dimethyl sulfoxide (DMSO) and cast on the support. A highly polycrystalline HOF membrane was prepared due to the ease of recrystallization of HOFs. A series of control experiments have revealed that the evaporation temperature and monomer concentration are crucial factors in crystal nucleation and growth, allowing for the creation of continuous and crystalline membranes. The prepared UPC-HOF-6 membrane shows an interesting pressure-responsive gas permeation due to the flexible network structure. The permeability of H₂ increased more dramatically with pressure than that of N₂, thus presenting an improved H₂/N₂ selectivity from 11.9 to 19.5. Furthermore, the reversibility of linking bonds gives the HOF membrane excellent self-healing ability. The scratched HOF membrane can be healed after being treated in the solvent vapor for 15 minutes, and the gas separation property can be recovered. The excellent solution-processability promotes the application of HOFs as membrane materials. To further investigate the effect of nucleation and growth, we regulated the orientation of the HOF membrane via a simple GO-modified strategy (Fig. 2b). Reduced substrate roughness and lower monomer concentration contribute to a decrease in nucleation sites. The arrangement of HOF precursors is governed by hydrogen bonding and electrostatic interactions. Reduced nucleation sites and controlled precursor arrangement facilitate the oriented growth of HOF membranes. When it comes to solution-cast HOF membranes, porosity, crystallinity, and membrane continuity of the HOF membrane are intricately linked. The porosity of HOFs is closely tied to the construction of an ordered framework structure. A certain type of HOF loses its ordered molecular arrangement upon activation, resulting in a non-porous amorphous phase. Considering the high crystallinity of CPMs, both order and continuity need to be considered during the membrane fabrication process. This process tends to be more complicated compared to the preparation of polymer membranes.

As another solution-processable CPM, POCs are comprised of discrete molecular cages with intrinsic and extrinsic porosity...
and show great potential in membrane manufacturing. Strikingly, crystallinity is not always responsible for the membrane separation property, but the ordered pore is. Even the amorphous POC membrane, possessing intrinsic porosity, displays precise molecular sieving due to the uniform pore size of every single cage. As elucidated by Cooper et al., the amorphous ASPOC membrane displays favorable adsorption of CO$_2$, achieving a high ideal selectivity of CO$_2$/N$_2$ (25–30). POCs can be regarded as organic molecular monomers capable of polymerizing with organic monomers without disturbing the intrinsic porosity. After the first spin-cast POC membrane for gas separation reported by Cooper in 2016 (Fig. 3a), the POC membrane has shined in various molecular separation fields. These POCs are usually dissolved in a co-solvent to realize continuous membranes. Different from the HOF cases, the solution processing of POC membranes is a rearrangement process of discrete cage molecules with uniform pores, and the solvent fraction and spin rate strongly influence the packing mode of the cage rather than the continuity of the membrane. Therefore, achieving continuity is of paramount importance in the solution-processing of POC membranes. Recently, Cooper's group reported a POC membrane with a switchable pore structure. The ordered crystalline POC membranes exhibit a switchable phase transition between two crystalline forms, CC3z-PAN and CC3y-PAN, allowing a smart responsive membrane to separate the mixtures of three organic dyes (Fig. 3b). Besides, Xu et al. reported a POC membrane applied for ion separation (Fig. 3c). The subnanometer windows of the CC3 POC can effectively sievo mono/divalent ions, while the nano-cavities provide fast delivery pathways for monovalent ions. Additionally, the ion channels with a discrete frame structure can reduce the energy consumed by ion collisions with the frame walls and promote the enhancement of ion permeation selectivity.

Applying the solution-casting method to \textit{in situ} fabricate CPM membranes is convenient and efficient. However, due to the interrelated processing factors, a systematic investigation of manufacturing conditions is required to attain a defect-free CPM membrane. The continuity and order of membranes should be balanced for efficient separation during the crystallization process of CPMs. Solution-processing is mainly applicable to soluble CPMs and nanosheets with high aspect ratio. Besides, as the CPM precursor dissolves in polar solvents generally, the substrate should be stable and resistant to polar solvents. Intrusion of precursor solution into the substrate is a severe problem that should be tackled. Excessive intrusion gives rise to a vague thickness and reduced permeance, while slight intrusion is conducive to the interlock of the membrane and substrate avoiding interfacial defects. A precursor solution with high viscosity can alleviate excessive intrusion to a certain extent. Peter and Peinemann fabricated a PAN-Matrimid composite membrane with relatively high flux by dip-coating the PAN hollow fiber in a partially cross-linked Matrimid solution. The high viscosity of the Matrimid coating solution prevented it from penetrating into the PAN substrate. Filling up the pores with a pre-wetting material before coating can also hold the coating solution on the substrate surface. Due to the high bond energy, it is challenging to dissolve zeolite materials with strong covalent bonding in common solvents. Therefore, fabricating a zeolite membrane by direct solution-casting is difficult.

### 2.2 Solution-assembly

Nanomaterials have received intense attention from various fields and show great potential in advanced applications. Nanosheets with atomic thickness, a typical two-dimensional (2D) material, have lamellar morphology and a high aspect ratio. Due to their unique morphology, nanosheets with solution-processability can be assembled into membranes in solution. Compared to non-porous 2D nanosheets, such as GO, nanomaterials with intrinsic porosity, like MOF nanosheets and COF nanosheets, can provide gas molecules with well-defined micropores to pass through, thereby reducing the resistance of mass transfer. Simultaneously, ultrathin membranes based on nanosheets can enhance gas permeability by shortening the transmission path.

Developing a rational synthetic strategy is critical to obtain porous nanosheets with high quality. The synthetic methodologies of 2D nanosheets mainly include top-down and bottom-up methods. The top-down strategy refers to the exfoliation of layered bulk materials into single layers or multi-layers using the methods of sonication exfoliation, mechanical exfoliation, and chemical exfoliation. The bottom-up methods involve the synthesis of nanosheets from building blocks. Interfaces, modulators, or soft templates are introduced to control the growth direction. Simultaneously, dispersion stability has a significant influence on membrane processing and membrane quality. The surface functionalization of nanosheets, making the interaction between nanosheets weaker than that of nanosheets and solvent, can improve the dispersity of nanosheets in the solvent. GO nanosheets chemically modified with ethanolamine, ethylene glycol, and sulfanilic acid demonstrate superior dispersion stability in organic solvents. Covene et al. investigated the influence of the degree of oxidation of GO sheets on the self-assembly behavior of GO in the polymer. GO in a high oxidation state can keep dispersion stability in PEG due to the strong hydrogen-bond interaction, whereas it tends to aggregate in a low oxidation state.

Solution-assembly always utilizes as-prepared CPM materials as building blocks. The formation of an ordered structure is not involved in the membrane fabrication process. Hence, the crystallinity and porosity can be independent of the membrane formation process. Solution assembly can be further divided into three assembly methods, including filtration, layer-by-layer assembly, and interface assembly of nanoparticles. Filtration is suited for depositing various CPM nanosheets. Layer-by-layer assembly requires strong interaction between two distinct materials, such as electrostatic interaction between ionic COFs. When dealing with nanoparticles that have poor inter-particle adhesion, utilizing polymers to assist interfacial assembly is more effective.

#### 2.2.1 Filtration

Due to the ultra-high specific surface area and aspect ratio of 2D materials, nanosheets are readily assembled into compact and interlocked ultrathin membranes \textit{via} a filtration approach (Fig. 4). Filtration is a typical means.
to separate solid materials and solvent which is applied to deposit the nanosheets on the substrate to form an ultrathin membrane. According to the driving force, the filtration process can be divided into pressure filtration and vacuum filtration. It is crucial to maintain a stable driving force during the filtration process to achieve a uniform and continuous membrane.\(^5\) For vacuum filtration, the force decreases as the thickness of the filtrate cake increases, which makes the membrane packing uneven in the vertical direction. The filtration method presents numerous advantages, such as simple and controlled operation, low cost, and diverse material selection. It is possible to achieve ultrathin membrane thickness through precise control of concentration and volume in the filtration-assisted method. Jiang et al.\(^5\) fabricated NCOFM-50 membranes with missing-linker nanosheets through the vacuum-filtration method (Fig. 4a). The thickness can be easily tailored from 200 nm to 57 nm by varying the volume of the filtrate, resulting in an increase in CO\(_2\) permeance from 336 GPU to 1068 GPU. Solution-assembly by vacuum filtration requires a high dispersity of nanosheets. Due to the constant shear force, the nanosheets with a high aspect ratio tend to curl and agglomerate in solution during the long-term filtration process.

It should be noted that the weak interactions between the substrate and nanosheets will give rise to cracks in the thick nanosheet-based membranes, especially for pure CPM nanosheet deposition. Incorporating a small amount of GO nanosheets (Fig. 4b)\(^5\) or condensation (Fig. 4c)\(^5\) of end functional groups at the edge can effectively avoid the formation of defects. The high aspect ratio of nanosheets enables the development of an interlocked and continuous ultrathin membrane even in the case of bending. It is important to consider that unstable nanosheets can form an impermeable layer or restack to become bulk materials during excessive filtration.\(^5\) Therefore, intercalating fillers to shore up the layers is an effective strategy to solve the restacking challenges. In addition, it is convenient to manipulate the properties of the membrane through filtration with other functional materials. A variety of molecules and ions can be inserted into the layer spacing to change the microenvironment of channels, such as metal ions,\(^5\) piperazine,\(^5\) and poly(ethylene glycol)diamines.\(^5\) For example, borate carriers were introduced within the confined nanochannels of GO to regulate layer spacing and facilitate the rapid transport of CO\(_2\).\(^6\) Using the same idea, the functional molecules or CPM particles can also be intercalated into the CPM nanosheet membranes to offer an external permeate pathway and fix the layer structure.

**2.2.2 Layer-by-layer assembly.** Layer-by-layer (LbL) assembly of hierarchical thin films is of great interest due to its nanometer control over thickness and wide material selection.\(^6\) The use of different materials with distinct structures and variable deposition sequences can result in hybrid nanostructures that possess improved functional properties, making them ideal for specific applications. Normally, due to the interaction (electrostatic interactions, hydrogen bonding, metal–organic coordination, and molecular interactions) between adjacent layers, the LbL-assembled membrane can be modified exactly as desired. A customized membrane was prepared with much less investment in manufacturing infrastructure and energy. Zhao and colleagues\(^6\) fabricated an ultrathin COF membrane (TpEBr@TpPa-SO\(_3\)Na) via LbL assembly of two distinct ionic COF nanosheets with different pore sizes and opposite charges (Fig. 4d). Under strong interlayer electrostatic interactions, two kinds of nanosheets compact staggered stacking, resulting in composite membranes with reduced apertures and ultrathin thickness (41 nm). As a consequence, the membrane shows a H\(_2\) permeance of 2566 GPU and a H\(_2\)/CO\(_2\) selectivity of 22.6 at 423 K.

**2.2.3 Interface assembly of nanoparticles.** Besides nanosheets, nanoparticles can also be well-dispersed in the solvents and assembled into membranes at the interface. Due to weak interparticle adhesion, it is unrealistic to assemble

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**Fig. 4** (a) COF nanosheet membrane, (b) MOF@GO composite membrane, (c) zeolite nanosheet membrane fabricated by filtration assembly, and (d) ultrathin COF membrane fabricated by layer-by-layer assembly. (Reproduced from ref. 53–55 and 63 with permission. Copyright 2022, Wiley-VCH; Copyright 2019, American Chemical Society; Copyright 2021, Springer Nature; Copyright 2020, American Chemical Society.)
nanoparticles into continuous films directly by filtration or LbL assembly. Banerjee\textsuperscript{64} synthesized dispersible crystalline porous nanospheres through a direct nucleation and growth approach (Fig. 5a). With the help of an interfacial assembly strategy, the solution-processable imine-based COF nanospheres were covalently self-assembled into films at the liquid–liquid interface. Besides, the direct nucleation approach enables nanoparticles to be processed into a continuous COF film via conventional techniques. Through surface modification with the polymer that produces favorable interactions between particles, Cohen\textsuperscript{65} fabricated a self-assembled porous monolayer composed of ZIF-8 nanoparticles with the aid of poly(methyl methacrylate) at a liquid–air interface (Fig. 5b). The monolayers could be layer-by-layer stacked to obtain MOF multilayers, including alternating MOF/polymer heterostructures. Later, they fabricated oriented MIL-96 and UiO-66 films at the solvent–water interface with the assistance of polydimethylsiloxane (PDMS) cure (Fig. 5c).\textsuperscript{66} The solution containing MOF particles and PDMS spreads over the water surface, and the suspended MOF particles are assembled with a preferred alignment at the water–solvent interface. With the evaporation of the solvent, PDMS is cured and holds the aligned MOF particles in place.

Choosing a suitable assembly method based on material properties is significant for membrane formation. The comparison of different solution-casting and solution-assembly methods is presented in Fig. 6. The assembly method not only determines the processing condition but also directly affects the quality and properties of membranes, such as thickness, homogeneity, and inter- and intra-layer membrane organization, with both quality and properties linked to the performance. The solution-assembly method is commonly suited for CPM membranes’ fabrication, especially for those materials with rigid structures and strong bonding, such as zeolites, MOFs, and COFs.

2.3 Solution-processing with the assistance of additional materials

2.3.1 Different CPMs as fillers. Mixed-matrix membranes (MMMs) are prepared dominantly using the solution-casting method, which combines the porosity of porous materials with the solution-processability of polymers to enhance the CO\textsubscript{2} separation performance. Since the pioneering study by Kulprathipanja \textit{et al.}\textsuperscript{67} that assessed the potential of MMMs, a number of important research studies have been reported. Various CPMs act as performance boosters to break the “trade-off” between selectivity and permeance. Many important reviews have provided systematic summaries of MMMs.\textsuperscript{19,68–70} Here we only give a brief overview of CPM-based MMMs for CO\textsubscript{2} separation. To prepare high-performance MMMs, some of the most significant factors to consider are the dispersion of CPM fillers in the casting solution and interactions between the filler and polymer. From the aspect of CPMs, choosing high-performance and dispersible fillers is a key consideration for developing MMMs. Zeolite, as the typical inorganic filler in MMMs, is low-cost and highly stable due to the rigid...
frameworks. However, the zeolite-based MMMs may suffer from the compatibility problem between the fillers and matrix, and surface modification of zeolite fillers can improve this problem. An important development in MMM research has been the replacement of traditional zeolite fillers with CPMs containing organic linkers, which are more chemically similar to polymers than inorganic fillers. A filler that is more easily “dissolved” in the polymer matrix is favored to construct MMMs without interface defects. The zeolitic imidazolate framework (ZIF) series of MOFs have a similar structure to zeolites but contain imidazolate linkers that can better interact with the polymer matrix. High ratios of ZIF-7, ZIF-8, ZIF-11 and ZIF-90 were incorporated into polybenzimidazoles (PBI), achieving improvements in gas permeability and selectivity. The specific functional groups on an organic MOF linker can be used to enhance compatibility. For example, -NH2 groups are commonly incorporated into multiple MOFs such as MIL-101(Al)-NH2, MIL-53(Al)-NH2 and UiO-66-NH2 to optimize the membrane performance. The functional group modification strategy not only leads to improved compatibility but also brings additional affinity with target CO2, resulting in excellent separation performance. COFs, HOFs, and POCs with all-organic frameworks can render a more favorable interaction with the polymer matrix. Especially POCs, which are soluble in common organic solvents, facilitate intimate mixing with the polymer at the molecular level. Cooper’s group demonstrated a novel MMM in which the CC3 cages as the dispersed phase are polymerized at the molecular level. Cooper’s group demonstrated a novel MMM in which the CC3 cages as the dispersed phase are polymerized at the molecular level. Cooper’s group demonstrated a novel MMM in which the CC3 cages as the dispersed phase are polymerized at the molecular level.

In MMMs’ preparation, nano-sized particles and nanosheets are utilized as fillers to enhance polymer–filler surface interaction by maximizing their surface-area-to-volume ratios, thereby reducing nonselective interfacial defects. For a systematic comparison, Japip et al. prepared a series of 6FDA-durene/ZIF-71 MMMs with filler sizes ranging from 30 to 600 nm to illustrate the effects of particle size. In recent work, Jiang et al. prepared different MMMs containing nano-sized HOF-21 and micro-sized HOF-21. The membranes with micro-sized HOF-21 were nonselective due to numerous defects, while the membranes with nano-sized HOF-21 showed much superior performance. In addition to particle size, the morphology of the filler is also an important parameter. In 2014, Rodenas et al. used FIB-SEM to study the internal structure of the MMMs containing CuBDC nanosheets (ns-CuBDC) or bulk CuBDC (b-CuBDC) crystals (Fig. 7b). At the same loading ratio, b-CuBDC particles are agglomerated, whereas the ns-CuBDC present more uniform dispersion in the matrix which results in a higher CO2/CH4 selectivity. Considering another aspect, while regulating the morphology of nanosheets, exposing the more stable crystal orientation is of significance for membrane application. Our group prepared oriented [211] ZIF-67 nanosheets for the fabrication of MMMs. ZIF-67 with the exposed [211] crystal face exhibits enhanced stability due to a lower proportion of the Co–N bond and higher surface atomic density.

Modifying the filler with a polymer brush or fragment is an effective strategy to mitigate the formation of non-selective defects. The similar chemical composition of the “core–shell” structure as that of the polymer matrix, realizing good interfacial compatibility. Li et al. proposed a strategy to covalently graft polyimide (PI) brushes on the UiO-66-NH2 surface to improve the interfacial affinity with the PI matrix. The improved MOF-loadings can be up to 88 wt% due to the significantly enhanced compatibility (Fig. 7c). For COFs, the surface of the COF-LZU-1 particle was covalently modified with the segments of poly(vinylamine) (PVAm) in Wang’s work. The modified COFs were highly compatible with the PVAm matrix due to their similar chemical surface, and the incorporated COFs effectively restricted the mobility of the PVAm chains boosting the pressure resistance for high-pressure CO2/H2 separation. Besides, directly covalently linking the matrix and filler using a specific chemical reaction is a strong approach to enhance the interface.

### 2.3.2 Different materials as the matrix

Polymers are the traditional matrix materials used to prepare composite membranes with CPMs, owing to the low-cost and solution-processability feature. The Maxwell model is usually used to
predict the performance of MMMs with different composites. The trends showed that adding CPMs to the polymer with high selectivity but low permeability will result in slightly enhanced permeability with no change in selectivity. When using a permeable but non-selective polymer as a matrix, the identity of the fillers plays a critical role. A permeable but unselective MOF leads to a MMM with lower selectivity. Therefore, an excellent match between fillers and matrix is necessary to optimize the performance. Gascon et al. selected various polymers with different properties, including Matrimid (low permeance-mid selectivity), Polyactive (mid permeance-high selectivity), and 6FDA:DAM (high permeance-low selectivity), as a matrix for blending with ACOF-1 (Fig. 8a). The results demonstrated that MMMs composed of Polyactive have reduced permeability attributed to the plugged pores by more flexible polymer chains.

In addition to polymers, taking advantage of the water-dispersible property, GO is easily assembled on substrates to fabricate lamellar GO membranes. Due to the limited layer spacing, the gas permeance is relatively low and decreases gradually with time, and thus the strategy for modifying the environment of the layer space is developed. Studies about GO membranes with fillers to improve CO₂ separation performance have been reported. For example, Jiang et al. intercalated polyethylene glycol diacrylate (PEGDA) into GO membrane nanochannels to construct heterogeneous CO₂-philic and non-CO₂-philic nanodomains, promoting the fast dissolution and diffusion of CO₂. Compared to nonporous fillers, intercalating the CPMs into GO layer spacing is a promising strategy for high-efficiency CO₂ separation, which can introduce additional functional pathways for permeating and separation. Zeolites, MOFs, and COFs are intercalated into the GO layer spacing to improve CO₂ separation. Direct mixing of the CPMs with GO and then filtration onto the substrate is a simple and convenient strategy for preparing nanosheet-based membranes. A series of TpPa COFs, synthesized via mechanical grinding, were integrated with GO to form lamellar membranes through vacuum filtration (Fig. 8b). The thickness of the COF/GO composite membrane can be regulated by adjusting the amount of GO, indicating a simple and applicable regulation strategy. To confirm the uniform and order alignment of nanosheets and nanoparticles, the in situ conversion process was also applied to fabricate composite membranes.

Moreover, there have been reports attempting to substitute the polymer matrix with CPMs to fabricate an all-nanoporous composite membrane. For the first time, Nair’s group introduced MFI particles into Zn gel, which converted into a ZIF-8-MFI composite membrane. Using a similar concept, Jiang et al. applied COF nanosheets as a dispersion phase and in situ prepared ZIF-8 as a matrix to construct an “alloy” membrane (Fig. 8c), exhibiting a record-high propylene/propane separation. Li et al. fabricated a UiO-66-NH₂ (filler)/ZIF-8 (matrix) membrane via a solution-casting method similar to the traditional MMM preparation. Compared to the above-mentioned CPMs, the most intriguing interest of HOFs and POCs is that they are soluble and easy to regenerate in organic solvents, and thus it is easy to process a membrane with POCs or HOFs as the matrix via a solution-casting method, simplifying the manufacturing procedure. The perfect re-match between nucleation and growth of the soluble CPM matrix is required to regulate the membrane formation.

Overall, we concluded three solution-processing strategies for fabricating CPM-based composite membranes, including traditional polymer–CPM composite membrane (also called MMM), GO–CPM composite membrane, and CPM-based all-nanoporous composite membrane. The advantages and disadvantages of different strategies are compared in Table 1. Generally speaking, MMMs are a promising candidate for scalability and practical applicability due to their low-cost and simplicity. However, the performance of MMMs usually falls in the lower limit of the polymer performance. For the GO–CPM composite membrane, the application areas are mainly limited to pre-combustion capture of CO₂, showing high hydrogen permeance due to the thin thickness and porous transport pathways. The large-scale fabrication of the GO–CPM composite membrane mainly depends on the assembly strategy and suitable processing modules. The CPM-based all-nanoporous composite membrane is expected to refine the Robeson upper bound, but its development is still in infancy. A more universal preparation strategy and growth mechanism should be developed to pave the way for fabricating all-nanoporous composite membranes.
3 CO₂ separation performance of solution-processed CPM-based membranes

3.1 Pre-combustion capture

Pre-combustion capture of CO₂ is mainly applied to coal-fired integrated gasification combined cycle (IGCC) plants. The coal undergoes partial oxidation in steam and oxygen at high temperatures and pressures to form synthesis gas, which subsequently experiences a water–gas shift reaction producing a gas mixture rich in H₂ and CO₂. The concentration of CO₂ in the obtained mixture can range from 15 to 50% and the shifted synthesis gas stream is under high pressure, which allows for easier removal of CO₂ before H₂ is combusted. Under the alarming global warming scenario, efficient CO₂ capture, or more specifically, H₂/CO₂ separation is recognized as the “sweet spot” for high-purity blue H₂ production and simultaneously putting curbs on CO₂ emission. Membrane technology offers an energy-efficient approach to producing high-purity H₂. Solution-processed CPMs have shown the desired performance in the prospected economic target range (PH₂ > 200 GPU, zH₂/CO₂ > 10), as summarized in Table 2.

Although it is difficult to create a zeolite polycrystalline membrane through direct solution-casting, in situ confined growth between GO layers is a feasible approach to construct zeolite-based membranes. A SOD/GO membrane was fabricated by in situ conversion of an amorphous precursor gel inside the layer spacing of GO. The cross-linking between GO and zeolite promises the composite membrane with good H₂/CO₂ separation performance (PH₂ = 4900 GPU, zH₂/CO₂ = 56) at 200 °C.

### Table 1
The comparison of different strategies with the help of other solution-processable materials

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<th>Composition</th>
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<th>GO-CPM membrane</th>
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<td>Practical applicability</td>
<td>★★★★★</td>
<td>★★★★☆</td>
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<td>Manufacturing cost</td>
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<td>Environmental impacts</td>
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</tbody>
</table>

### Table 2
The summary of the CO₂ separation performance of different solution-processed CPM membranes

<table>
<thead>
<tr>
<th>Membrane structure</th>
<th>Methods</th>
<th>Separation of mixtures</th>
<th>Permeability (GPU)</th>
<th>Selectivity</th>
<th>Operational conditions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuBDC-GO</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>2865.67</td>
<td>95.1</td>
<td>298 K, 1 bar</td>
<td>54</td>
</tr>
<tr>
<td>CTF-1/GO</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>5074.62</td>
<td>17.4</td>
<td>298 K, 1 bar</td>
<td>92</td>
</tr>
<tr>
<td>TpPa-1/GO</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>3185.07</td>
<td>25.57</td>
<td>298 K, 1 bar</td>
<td>93</td>
</tr>
<tr>
<td>CTF-BTD/GO</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>655.6</td>
<td>43.1</td>
<td>298 K, 1 bar</td>
<td>104</td>
</tr>
<tr>
<td>ZIF-67/GO</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>5922 ± 1000</td>
<td>75 ± 4</td>
<td>298 K, 1 bar</td>
<td>90</td>
</tr>
<tr>
<td>SOD/GO</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>4900</td>
<td>56</td>
<td>473 K, 1.2 bar</td>
<td>89</td>
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<tr>
<td>Zn₂(bim)₆/GO</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>418</td>
<td>103</td>
<td>303 K, 1.6 bar</td>
<td>98</td>
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<tr>
<td>ZIF-8/GO</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>406</td>
<td>30.8</td>
<td>298 K, 2 bar</td>
<td>91</td>
</tr>
<tr>
<td>RUB-15</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>41–424</td>
<td>20–100</td>
<td>523–573 K, 1 bar</td>
<td>55</td>
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<tr>
<td>[CuBr₂(IN)₂]₆</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>&gt; 519</td>
<td>&gt; 190</td>
<td>298 K, 1 bar</td>
<td>103</td>
</tr>
<tr>
<td>ECNU-28</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>1271</td>
<td>61</td>
<td>298 K, 1 bar</td>
<td>97</td>
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<tr>
<td>Zn₂(bim)₆ MSNs</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>760–3760</td>
<td>53–291</td>
<td>298 K, 1 bar</td>
<td>99</td>
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<tr>
<td>Zn₂(bim)₆ MSNs</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>2388</td>
<td>166</td>
<td>298 K, 1 bar</td>
<td>100</td>
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<tr>
<td>TpPa-2</td>
<td>Solution-assembly</td>
<td>CO₂/CH₄</td>
<td>328</td>
<td>22</td>
<td>298 K, 1 bar</td>
<td>105</td>
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<tr>
<td>Zn₂(bim)₆ (amino groups)</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>1417</td>
<td>1158</td>
<td>298 K, 1 bar</td>
<td>102</td>
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<tr>
<td>MAMS-1</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>715</td>
<td>245</td>
<td>293 K, 1 bar</td>
<td>101</td>
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<tr>
<td>TpEBr@TpPa-SO₃Na</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>2566</td>
<td>22.6</td>
<td>423 K, 1.2 bar</td>
<td>63</td>
</tr>
<tr>
<td>TpTGCl@TpPa-SO₃Na</td>
<td>Solution-assembly</td>
<td>H₂/CO₂</td>
<td>2163</td>
<td>26</td>
<td>423 K, 1.2 bar</td>
<td>106</td>
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<tr>
<td>Cu(dihbct)(bpy) H₂O</td>
<td>Solution-assembly</td>
<td>CO₂/CH₄</td>
<td>188–1051</td>
<td>4–19.6</td>
<td>298 K, 0.1–1.4 bar</td>
<td>107</td>
</tr>
<tr>
<td>NCOFN</td>
<td>Solution-assembly</td>
<td>CO₂/CH₄</td>
<td>173.8–1076.7</td>
<td>4.1–22.8</td>
<td>(CO₂ partial pressure)</td>
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<tr>
<td>BMIMBF₄@CC3</td>
<td>Solution-assembly</td>
<td>CO₂/N₂</td>
<td>10.74</td>
<td>130</td>
<td>298 K, 2 bar</td>
<td>53</td>
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<tr>
<td>COF-316</td>
<td>Solution-assembly</td>
<td>CO₂/N₂</td>
<td>500</td>
<td>50</td>
<td>298 K, 2 bar</td>
<td>108</td>
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<tr>
<td>iCOF [TpPa-SO₃H]@PEI</td>
<td>Solution-assembly</td>
<td>CO₂/N₂</td>
<td>1371</td>
<td>33</td>
<td>298 K, 2 bar</td>
<td>110</td>
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<tr>
<td>DhaTGC₁</td>
<td>Solution-assembly</td>
<td>CO₂/CH₄</td>
<td>316</td>
<td>49</td>
<td>298 K, 1 bar</td>
<td>116</td>
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<tr>
<td>TpTGCl/GO</td>
<td>Solution-assembly</td>
<td>CO₂/CH₄</td>
<td>164.2</td>
<td>27</td>
<td>303 K, 2 bar</td>
<td>117</td>
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<tr>
<td>HCMS</td>
<td>Solution-assembly (post-pyrorolized)</td>
<td>CO₂/CH₄</td>
<td>47.64</td>
<td>128</td>
<td>298 K, 1.4 bar</td>
<td>118</td>
</tr>
</tbody>
</table>

Note: The CO₂ separation performance of MMMs is not listed in this table.
with steam and no degradation in performance during the test of 50 h. The zeolite membrane originated from nanosheet assembly has also been widely applied for pre-combustion CO₂ capture. Agrawal et al.⁵⁵ reported the exfoliation of the sodalite precursor RUB-15, leading to a dispersed solution of crystalline 0.8 nm thick nanosheets. The synthesized nanosheets were dispersed in ethanol and then stacked into a membrane by filtration, which led to an inter-sheet gap with a molecular cut-off of 3.6 Å. The gaps can be diminished by the condensation of the terminal silanol groups, giving rise to good H₂/CO₂ selectivity (\(PH₂ = 41–424\) GPU, \(zH₂/CO₂ = 20–100\)) at 250–300 °C. Recently, Wu et al.⁹⁸ exfoliated a swollen layered zeolite ECNU-28 into nanosheets and assembled the nanosheets into membranes by vacuum filtration; these membranes showed good H₂/CO₂ selectivity (\(PH₂ > 1194\) GPU, \(zH₂/CO₂ = 61\)).

Jiang et al.⁵⁰ deposited a continuous and uniform CuBDC nanosheet membrane with the assistance of flexible GO via the vacuum-filtration method. The voids between the junctions of rigid MOF nanosheets were well-repaired by GO sheets and the interlayer interaction was strengthened by abundant hydrogen bonding and π–π interaction, resulting in remarkable separation performance (\(PH₂ = 2865\) GPU, \(zH₂/CO₂ = 95.1\)). Furthermore, our group fabricated a ZIF-67/GO sandwich membrane through an in situ conversion process.⁹⁰ The Co(OH)₂ nanosheets as a precursor were filtered with GO onto the nylon substrate, and then the precursor was transformed to a MOF through the reaction with organic linkers. The ZIF-67/GO membrane showed improved H₂/CO₂ separation performance than the pristine GO membrane (\(PH₂ = 5922 ± 1000\) GPU, \(zH₂/CO₂ = 75 ± 4\)) at 25 °C. Similarly, Zhang et al. mixed ZnEG fibers with GO and then vacuum filtered onto an alumina hollow fiber support.⁹¹ The resulting converted ZIF-8/GO composite membrane also displayed effective H₂/CO₂ separation (\(PH₂ = 406\) GPU, \(zH₂/CO₂ = 30.8\)). Zhang et al.⁹⁸ deposited a ZnO nanoparticle layer and a GO thin layer on a porous tube successively by a dip-coating method. The ZnO nanoparticles were confined and self-converted into highly oriented ZnO/[bim]₄ nanosheets in the synthesis solution. The resulting ZnO/[bim]₄/GO membrane with a thickness of 200 nm demonstrated a good H₂/CO₂ separation performance (\(PH₂ = 418\) GPU, \(zH₂/CO₂ = 106\)). Nevertheless, it should be mentioned that the filtration method is unsuitable for all 2D nanosheet membranes. The fast restacking makes the nanosheets reverse back to ordered pristine structures at elevated concentrations when the solvent is filtered out, leading to partial or total blockage of the molecular sieve pores. Addressing this problem, Yang et al.⁹⁹,¹⁰⁰ reported a hot-drop casting (HDC) method, preparing a series of membranes with excellent H₂/CO₂ separation performance based on MOF nanosheets. Using the same assembly method, Zhao et al.¹⁰¹ produced ultrathin membranes of MAMS-1 nanosheets on an AAO substrate, and the resulting 40 nm films showed the best overall performance (\(PH₂ = 800\) GPU, \(zH₂/CO₂ = 268\)). Interestingly, the gas transport pathways of these membranes exhibit a reversed thermo-switchable feature due to the intensified thermal vibration of the tert-butyl groups. Nevertheless, functionalizing nanosheet membranes is challenging due to the lack of mild conditions that avoid distortion of their structure. Recently, Yang’s group¹⁰² synthesized amino-decorated Zn₅(bim)₄ nanosheets through a bottom-up protocol. The obtained nanosheets were assembled on a porous α-Al₂O₃ substrate via a hot-drop coating method to form an amino-functionalized Nₓ-Zn₅(bim)₄ membrane. The introduction of low-dose, small-sized amino side groups was able to retard CO₂ permeation through the synergistic effect of steric hindrance and physisorption affinity. The as-prepared membranes showed very high H₂/CO₂ selectivity and good H₂ permeance (\(PH₂ = 1158\) GPU, \(zH₂/CO₂ = 1417\)) (Fig. 9a). Furthermore, Wang et al.¹⁰³ prepared an ultrathin [CuBr(IN)₃]₃ nanosheet membrane with less than 10 nm thickness by drop-casting and thoroughly studied the influence of the drop-coating temperatures on nanosheet stacking modes. The accelerated evaporation rate of the solvent causes an escalation of the AA stacking mode, resulting in a mixed stacking mode of AA and AB stacking modes, which leads to a reduction of defects but expands the molecular transport apertures. Hence, the average H₂ permeance increases from 317.4 GPU to 481.2 GPU with the drop-casting temperature increasing from 50 to 90 °C. The membranes prepared at the optimal drop coating temperature of 90 °C showed great H₂/CO₂ separation performance (\(PH₂ = 598.9\) GPU, \(zH₂/CO₂ = 192.9\)).

Zhong et al.⁹² reported a GO-assisted LBL restacking method to prepare ultrathin covalent triazine framework (CTF) membranes. CTF-1 nanosheets were able to deposit on the cellulose acetate support to form a dense membrane, showing high H₂ permeance and competitive selectivity (\(PH₂ = 5074\) GPU, \(zH₂/CO₂ = 17.4\)) with a thickness of 100 nm. Using the same strategy, our group produced a TpPa-1/GO composite membrane on a nylon substrate, with a facile mechanical ball milling method to synthesize TpPa-1. The thickness and the H₂/CO₂ selectivity of the membrane can be regulated by increasing the amount of GO. The optimal membrane (TpPa-1–30/GO-10) possessed the highest selectivity with a high H₂ permeance (\(PH₂ = 3185\) GPU, \(zH₂/CO₂ = 25.57\)) with a thickness of 0.3 μm. In common cases, the traditional vacuum filtration is conducted at room temperature to avoid the heat-driven aggregation of nanosheets. In contrast, Liu et al.¹⁰⁴ utilized heating in the vacuum filtration process to disturb the restacking mode of nanosheets. Compared to the composite membrane prepared under ambient conditions, the CTF-BTD/GO membranes showed enhanced H₂/CO₂ selectivity (\(PH₂ = 655.6\) GPU, \(zH₂/CO₂ = 43.1\)). Under heating conditions, the CTF nanosheets go through random and irregular rearrangement under the synergistic effect of vertical pulling force and horizontal turbulence. However, when the temperature of the filtration process was increased to 483 K, the ultrafast solvent evaporation resulted in decreased selectivity. Besides, COF nanosheets have also been solution-processed into membranes for pre-combustion capture of CO₂. A 2D COF nanosheet (TpPa-2) membrane was fabricated by a hot-drop casting method and it displayed an optimal CO₂/H₂ selectivity of 22 and a CO₂ permeance of 328 GPU.¹⁰⁵ The pore size of the TpPa-2 membrane was reduced.
Zhao et al. used a direct layer-by-layer growth approach to construct a TpTG@TpPa-SO$_3$H hierarchical membrane with relatively large-pore COF-LZU1 as a gutter layer. The multi-interfacial engineering strategy assembles two different pore sizes to form narrowed apertures, resulting in a comparable H$_2$/CO$_2$ separation performance ($P_{H_2} = 2163$ GPU, $a_{H_2/CO_2} = 26$) at 423 K.

Membrane-based separation technology is a strong route for pre-combustion CO$_2$ capture. Solution-processed CPM membranes for pre-combustion CO$_2$ capture mainly concentrate on the membranes based on CPM nanosheets, including zeolite nanosheets, MOF nanosheets, and COF nanosheets. Hence, the preparation of nanosheets with high efficiency and high yield is required for the pursuit of scalable fabrication. Inspired by the scalable GO membrane, large-scale manufacturing methods and modules of CPM nanosheet membranes should be developed.

### 3.2 Post-combustion capture

Post-combustion CO$_2$ capture involves the separation of CO$_2$ from the exhaust gas (mainly composed of 15% CO$_2$ and 75% N$_2$) originating from fossil fuel power plants. It is primarily applicable to conventional coal-fired, oil-fired, or gas-fired power plants, but could also be applicable to integrated gasification combined cycle (IGCC) and natural gas combined cycle (NGCC) flue gas capture. Compared to the pre-combustion capture, post-combustion capture technology is more mature and applicable in the industrial demonstration stage. It has been estimated that an economically viable membrane for post-combustion carbon capture from exhaust gas should have $P_{CO_2}$ > 1000 and $a_{CO_2/N_2}$ > 30. For effective CO$_2$/N$_2$ separation through a membrane, a functional membrane with adsorption selectivity and diffusion selectivity is desired due to the similarity in the kinetic diameters of CO$_2$ (3.3 Å) and N$_2$ (3.64 Å).

Previously, Zhao et al. fabricated a pressure-responsive ultrathin membrane by compositing flexible Cu(dhbc)$_2$(bpy)$_2$H$_2$O nanosheets with GO via a pressure-assisted self-assembly strategy. The well-assembled membrane presented unprecedented CO$_2$-responsive gas separation performance with a dramatic increase of CO$_2$ permeance and selectivity ($P_{CO_2} = 173.8$ to $1144$ GPU, $a_{CO_2/N_2} = 4.1$ to $22.8$) under increased CO$_2$ partial pressure from 0.1 to 1.4 bar, which can be attributed to the CO$_2$-responsive “gate-opening/closing” properties of the few-layer MOF nanosheets.

For COF materials, Jiang et al. proposed a two-step method to synthesize functionalized COF nanosheets, COF-316-COOH (carboxyl groups) and COF-316-AO (amidoxime groups), which were then fabricated into COF membranes via a vacuum-assisted self-assembly method. The optimized COF-316-AO membrane exhibited excellent separation performance ($P_{CO_2} > 500$ GPU, $a_{CO_2/N_2} > 50$). Defect engineering has provided an efficient strategy to enhance membrane separation, and it has been widely exploited in MOF-based membranes.

Recently, missing-linker defects have been created in the COF nanosheet membrane to promote efficient CO$_2$ separation. The amino-functionalized COF nanosheets (NCOPN) were fabricated via the reactive assembly of amine monomers and mixed aldehyde monomers by Jiang et al., where the monoaldehyde was a...
branes, the ideal selectivity of CO₂/N₂ is surprisingly high under a humidified state (PCO₂ = 3713 GPU, τCO₂/N₂ = 33).

Recently, Jiang et al. fabricated HOF-based MMMs for carbon capture for the first time based on a solution-casting method. A metallic-hydrogen-bonded organic framework, HOF-21 ([Cu₄(aden)(H₂O)₄][SiF₄]), was altered as a filler and combined into the Pebax™ 1657 polymer matrix. The HOF-21n@Pebax membrane with nano-sized fillers was free of defects while the HOF-21m@Pebax membrane with micro-sized fillers was discontinuous. Benefiting from the multiple synergetic effects (Cu²⁺, water, biogenic amine molecule) and the frame channel of HOF-21, the optimum separation membrane of HOF-21n@Pebax-3 displayed comparable CO₂ permeability and selectivity (PCO₂ ≈ 840 Barrer, τCO₂/N₂ ≈ 60).

POCs are discrete molecules with intrinsic cavities and free of extended covalent or coordination bonding in the solid state. As a result, POCs are soluble in common solvents and they can be processed into membranes by solution-casting. Cooper et al. synthesized a series of POCs (CC3, CC13, ASPOC) via [4+6] cycloelimination reactions for the first time. It was possible to solution-process POCs into continuous and defect-free microporous thin membranes without the need of a supporting polymer. The CC3 membrane prepared by spin-coating showed a high CO₂ permeance of 2746 GPU with CO₂/N₂ selectivity of around 19 and CO₂/CH₄ selectivity of ≈ 10. For ASPOC membranes, the ideal selectivity of CO₂/N₂ is surprisingly high (25–30) with relatively low permeability. However, these cage membranes tend to densify over time, as reflected by loss in gas permeability. The uncontrollable growth, such as rapid precipitation during the spin-coating process, could cause disorder and uneven arrangement, resulting in abundant extrinsic inter-cage spaces and sacrificed molecular discrimination ability. An electrostatic interaction-induced strategy was applied to promote in situ surface recrystallization of the POC membrane. Jin et al. used the electrostatic attraction between ionic liquid (IL) molecules (BMIMBF₄) and cage molecules to rearrange the cage molecules into an ultrathin and defect-free crystal layer. The introduced BMIMBF₄ molecules tightly anchored on the windows of the cage and effectively regulated the cage window size from 5–6 Å to 3.6 Å, aiding the preferential capture of CO₂ molecules from binary gas. The optimized BMIMBF₄@CC3 exhibited an impressive CO₂/N₂ performance (PCO₂ = 10.74 GPU, τCO₂/N₂ = 130) [Fig. 9b].

Post-combustion carbon capture by solution-processed CPM-based membranes offers an efficient technology that would have a profound impact on mitigating the impact of climate change. However, there are a lot of obstacles that should be solved for the practical demonstration, including large exhaust gas volume, relatively low CO₂ concentration, low flue gas feed pressure, contaminants of vapor, and the need for high membrane surface area. Especially for the membrane containing relatively unstable CPMs, maintaining the performance stable under actual service conditions is rather significant.

3.3 Sweetening of natural gas

Raw natural gas is a mixture of hydrocarbons, always typically containing 75–90% methane and 0.6–15% carbon dioxide. On the one hand, the existence of acidic CO₂ will corrode pipes during transportation; thus, carbon dioxide removal from natural gas is necessary to meet pipeline specifications. On the other hand, although carbon dioxide is innocuous, high concentrations of CO₂ will inevitably reduce the high calorific value and combustion efficiency of natural gas. Traditionally, CO₂ removal from natural gas has been dominated by amine absorption. In recent decades, membrane technology has competed most directly against absorption in the CO₂/CH₄ separation process. If membranes with higher performance than polymers were deployed, a significant shift from traditional amine absorption processes could be realized. For CO₂ removal from natural gas, a membrane with CO₂ permeance PCO₂ > 100 GPU and CO₂/CH₄ selectivity τCO₂/CH₄ > 20 is desired to target commercial viability. MOF-based MMMs generally possess attractive CO₂/CH₄ separation properties. Post-treatment of MMMs provides an effective pathway to further optimize the performance. A melt-quenching treatment was proposed to improve the performance of solution-processed MMMs. Inspired by the properties of MOF glass, which could convert to a molten phase at high temperatures and solidify when cooling down, our group fabricated a ZIF-62/PIM-1 mixed-matrix membrane, followed by in situ thermal treatment to form a porous MOF glass/polymer membrane (agZIF-62/PIM-1). The molten ZIF-62 during thermal treatment is helpful in eliminating interfacial voids between the filler and the polymer matrix. The optimized thermally treated membrane exhibits significantly enhanced selectivity of CO₂/CH₄ and permeability of CO₂ (PCO₂ = 5914 GPU, τCO₂/N₂ = 67). In addition, although MOFs are insoluble in organic solvents in most cases, the MOFs with outer surface functionalization can be processed into porous liquids, which can be stable in large solvent molecules and fabricated into highly loaded MMMs. This type of MOF-based porous liquid with a functionalized group may offer an advanced approach to fabricating highly filler-loaded MMMs for CO₂ separation.

Most of the COFs have frameworks extended in 2D, which can be processed into “soluble” nanosheets either by top-down exfoliation or by bottom-up growth. A large amount of COF...
nanosheets were processed into a solution and assembled into membranes by a vacuum-assisted method for diverse applications. Among COF nanosheets, ionic COF nanosheets with uniformly distributed ionic sites and exchangeable counterions endow specific affinity sites for CO2 capture. Jiang et al. proposed a novel oil–water–oil triphase method to fabricate imine-linked COF nanosheets (DhaTGCl) with an ultra-high aspect ratio of 20 000, which were vacuum-filtered onto a PAN substrate and exchanged with aspartic acid to form an ultrathin composite membrane DhaTG Asp. The amino and carboxyl groups of aspartic acid aligned in the pores facilitate selective CO2 transport, achieving a high CO2 permeance (PCO2 = 316 GPU, zCO2/CH4 = 49) in the DhaTGAsp-65 membrane, hitting the target area of commercial application (Fig. 9c). At the same time, the DhaTGAsp-150 with moderate permeance and selectivity exhibits a high-pressure stability of up to 1.5 bar of CO2 partial pressure. In the same group’s work, the borates were introduced into the cationic COF (TpTGCl) with chloride ions through a two-step ion exchange, which could facilitate CO2 transport. Subsequently, the composite of 2D TpTGp nanosheets and GO were anchored on a polyacrylonitrile substrate for forming COF membranes via a vacuum-assisted self-assembly process. The ultrathin separation layer thickness of TpTGp-GO (1) and TpTGp-GO (2) membranes was only 20 and 35 nm, which contributed to reducing gas mass transfer resistance and achieving high performance (PCO2 = 164.2 GPU, zCO2/CH4 = 27) for simulated biogas (CO2/CH4 = 30/70 vol%).

Carbon molecular sieves (CMS) membranes are ideal candidates for CO2 separation due to the rigid pore structure and high stability, and the majority of CMS membranes have originated from amorphous polymer precursors. Recently, our group reported a novel CMS membrane (HCMS) derived from a solution-cast Hof membrane (UPC-HOF-6). The crystalline UPC-HOF-6 membrane was fabricated by spin-casting and then pyrolyzed at different temperatures. Higher pyrolysis temperature caused narrower distributions of pore size and a higher ratio of graphite-N and pyrrole-N in HCMS, which are beneficial for absorbing CO2 molecules and improving the molecular sieving effect. The HCMS-600 membrane with suitable pore size and strong CO2 affinity exhibited a high CO2/CH4 selectivity (PCO2 = 49.18 GPU, zCO2/CH4 = 127.9) and good stability.

Ionic liquids, as a good CO2 adhesion agent, are widely applied to modify the inner and outer surfaces of porous materials, enhancing the sieving performance of MOF-MMMs and COF-MMMs. Recently, our group fabricated MMMs based on PIM-1 with IL-saturated CC3 cages as fillers, and the CO2/CH4 separation performance of these membranes (PCO2 = 7868 Barrer, zCO2/CH4 = 78.4) was found to be dramatically increased compared with pure PIM-1 and original CC3/PIM-1 membranes. The ionic liquid [Bmim][Tf2N] was restricted within the crystalline porous molecular fillers of CC3 to narrow the cavity size, and it exhibited excellent affinity to CO2 and hence boosted the separation performance. Besides, the soft and flexible ionic liquid improves the compatibility between the filler and the matrix, thus avoiding interfacial defects and increasing the stability.

The membrane-based gas separation system has started to penetrate into the natural gas purification market. Today, membranes account for approximately 10% of the market share for the sweetening of natural gas, which is primarily the removal of CO2 from CH4. The performance of CPM-based membranes fabricated by solution processing in CO2/CH4 separation is presented in Table 2. Various types of membranes have been investigated for this separation, but challenges still exist, including the processing of larger membrane areas and membrane stability over the full life of the membrane under real conditions.

### 4 Conclusions and outlooks

Solution processing is an excellent method for manufacturing high-performance membranes with CPs used for CO2 separation. This process is simple to operate, easy to scale-up, and allows for facile functionalization. Although tremendous progress has been made in solution-processed CPM membranes, many challenges still remain and need indispensable consideration.

For the commonly applied solution-casting method, the accumulated knowledge of polymer membranes can be used for reference to manufacture CPM membranes. Nevertheless, the crystal growth of the CPM membranes should adhere to crystal nucleation and growth rules which raises a request for seriously controlling processing conditions. A systematic investigation should be undertaken to optimize the operation conditions and eliminate inter-crystalline defects. Using an encapsulating agent to control the kinetics growth and then offering more space to “error-correcting” may be an effective strategy to regulate the balance of “order” and “continuity”, which will open a new avenue to manipulate the membrane formation for soluble materials. In situ casting of a soluble precursor usually produces polycrystalline membranes like Hof membranes and POC membranes. For this type of membrane, the stability of the membrane is a ground of concern; in addition to selecting materials with rigid structures, post-treatment by covalent-linking and casting a protection layer, such as a PDMS layer, are feasible approaches. At the same time, a noteworthy point is that HOFs and POCs can be applied as a matrix combined with other outstanding fillers to form high-performance all-microporous composite membranes. The substrate contributes to the membrane processing. For Hof or POC membranes, the substrate with smooth surface and resistance to polar solvents is required. The intrusion of the precursor solution into the substrate is a problem that needs attention. Selecting a substrate with suitable pore size, increasing the viscosity of the casting solution, and pre-wetting the substrate are feasible approaches to relieve intrusion.

Beyond solution casting, the solution assembly also puts forward a request for a support which has strong adhesion with nanosheets. These ultra-thin CPM nanosheet membranes with ordered pore structures possess high gas permeance and...
selectivity for CO₂ separation. For scalable fabrication, mass production of nanosheets and a convenient manufacturing strategy such as printing and roll to roll assembly⁶⁶,¹²² should be developed. Furthermore, the structure and separation performance stability at high pressure should also be evaluated and improved for the nanosheet-based ultra-thin membranes. Various ions, molecules, and particles can hold up the layer spacing. In most cases, the nanosheets will be prone to packing closely during long-term tests and high-pressure operations, resulting in a trade-off between membrane permeability and stability. Baking the oligomer solution of CPMs, mainly referred as zeolite, MOF and COF, also facilitates the solution-casting preparation of CPM membranes.

Although many challenges remain to be overcome to bring these new technologies from bench to market, we hope to provide a comprehensive review of the research progress in the field of CO₂ capture based on the solution processing strategy. Meanwhile, with the escalating emergence of novel materials and the rapid development in material engineering, the new concept of membranes will break the barrier between lab and industry with the help of scalable preparation methods such as solution processing.

Conflicts of interest
There are no conflicts to declare.

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Notes and references
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