

**MXenes and Other Two-Dimensional Materials for
Membrane Gas Separation:
Progress, Challenges and Potential of MXene-based Membranes**

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Abstract

Gas-separation membranes incorporating two-dimensional (2D) materials have received considerable attention in recent years, as these membranes have shown outstanding physical, structural, thermal properties, and high permeability-selectivity. The reduced thickness and diversity of the gas transport mechanisms through in-plane pores (intrinsic defects), in-plane slit-like pores, or plane-to-plane interlayer galleries provide the membranes with a significant sieving ability for energy-efficient gas separation. The discovery of 2D transition metal carbides/nitrides materials, MXenes, has provided new opportunities in the gas separation membrane area because of their hydrophilicity, rich chemistry, high flexibility, and mechanical strength. This review puts into perspective recent advances in 2D-material-based gas separation membranes. It discusses research opportunities mainly in MXene-based gas membranes, highlights modification approaches for tuning the in-plane and plane-to-plane nanoslits, explains governing mechanisms of transport through these membranes, and compares their advantages and disadvantages with those of other 2D materials. It also discusses current challenges and provides prospects in this area.

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1. Introduction

The development of energy-efficient separation membranes is of interest in many industries to address operational and environmental challenges. Polymers have been the dominant material for the fabrication of gas and liquid membranes due to their ease of processability. They have been used in the fabrication of thin-film composite membranes for industrial applications ¹. However, their industrial applications have faced many challenges including low separation performance, severe plasticization under condensable gases and moisture, and low durability in the presence of heat, solvents, and contamination. In the recent review paper ², only a few glassy polymers with acceptable separation properties and good thermal and chemical stability (e.g., polybenzimidazole) have been suggested. At the present time, there is a need for the improvement of the stability and the performance of many polymeric membranes. Otherwise, these membranes should be replaced with more robust inorganic two-dimensional (2D) materials, which have excellent thermal stability and ultrapermeable-selective channels.

Recently developed 2D nanomaterials such as graphene oxide (GO) ³, graphene ⁴, transition metal carbides/nitrides (MXenes) ⁵, 2D transition metal borides (MBenes) ⁶, transition metal dichalcogenides, metal-organic frameworks (MOFs) ⁷, and covalent-organic frameworks (COFs) ⁸, are attractive materials for membrane separation applications. The first report on single-layer graphene films in 2004 opened a new research direction in gas and liquid separation ⁹. High surface area, size-sieving ability, abundant modifiable functional groups, and excellent thermal and chemical stability make the inorganic 2D materials an ideal candidate for use in challenging gas and liquid separation processes. Efforts have been made to improve the gas-separation performance of 2D-material-based membranes by studying how nanopores and interlayer spacing of the 2D materials affect the performance ¹⁰. The ultrafast molecular transportation through the

laminar membranes takes place between the interlayer spacing and through the pores on the layers and adjacent flakes. GOs and reduced GO (rGO) are the most investigated nanosheet materials for separation applications. They have shown exceptional transport properties due to their large surface areas, and oxygen-based functional groups (hydroxyl, carboxyl, and epoxy). However, the affinity of oxygen-based groups with water molecules diminishes the dimensional stability of GO membranes in the humidified gas flows, deteriorating the separation properties ¹¹. Additionally, the adhesion of GO on the porous support is weak, hindering the fabrication of highly selective membranes. Recently, surface modification and crosslinking of 2D nanomaterials and incorporating 2D nanomaterials into polymers have been introduced as effective methods to enhance the separation properties and chemical-mechanical stability of the membranes ^{12, 13}. Crosslinking techniques such as self-crosslinking, ion crosslinking, and molecular crosslinking can mitigate the swelling of the membranes in the presence of humidity and maintain their selectivity and permeability ¹⁴.

The fast transportation through the 2D lamellar membranes depends strongly on the continuum flow regime within the ordered channels ¹⁵. Any disturbance in the packing density and disordering of the laminates can cause a severe loss in the molecular transportation through the membranes ^{15, 16}. Therefore, high rigidity is needed to generate highly ordered nanochannels, while most current 2D materials suffer from high flexibility and the formation of irregular nanoslits ¹⁵. Also, due to the unstable d-spacing of flexible inorganic layers under different feed pressures, their separation performance varies significantly.

MXenes have remarkable mechanical stiffness and are promising for the fabrication of membranes with rigid ordered stacking channels without curling or failure under gas or liquid high

pressure^{15,17}. In addition to the uniform size distribution of nanochannels and excellent selectivity that MXenes membranes have shown in water purification, their stability and robustness in the presence of water have made them promising for industrial applications, compared to other 2D inorganic materials. Relatively constant rejection and water flux of MXene membranes after 28h testing indicated the high stability of the membranes¹⁸⁻²⁰.

2. Background on MXenes

MXenes are a relatively young family of 2D materials with the general formula of $M_{n+1}X_nT_x$ ($n = 1-4$), where M represents a transitional metal (such as Ti, V, Mo, and Cr), X is carbon and/or nitrogen, and T stands for functional groups (e.g., O, F, OH, and Cl). Typically, the parent of a MXene is a MAX phase, $M_{n+1}AX_n$, where A is an element from group 13 or 14 of the periodic table. The selective etching of the A element from a MAX phase by using strong etchants such as hydrofluoric acid (HF) can produce layered MXenes with rich functional groups on the surface²¹. The layered MXenes with distributed functional groups, excellent hydrophilicity, a negative surface charge, and special structures like GO are attractive for the fabrication of molecular separation membranes.

Figure 1a shows the number of publications on GO- and MXene-based membranes since 2015, indicating that research on MXene gas membranes (about 160 publications in total) is still in its infancy stage, and compared to research on GO-based membranes, the interest in this area is growing rapidly. The number of publications on MXenes-based membranes has increased rapidly in the last few years, and as of February 2022, the term “MXene” has appeared in more than 52 titles and abstracts of published articles on membranes in 2022, based on Scopus database. As the pie chart indicates, about 12% of the publications on MXene membranes are review articles, based

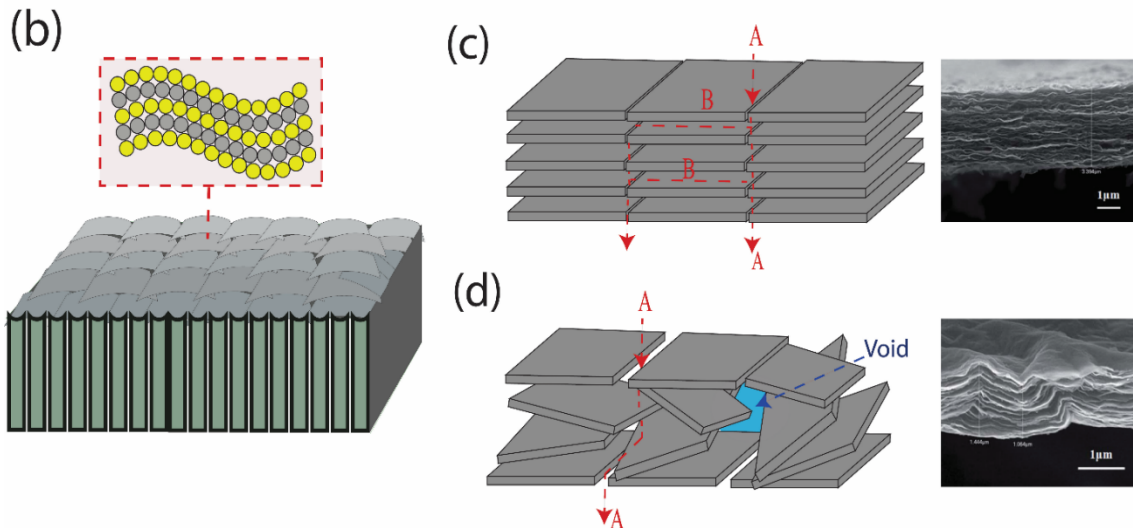
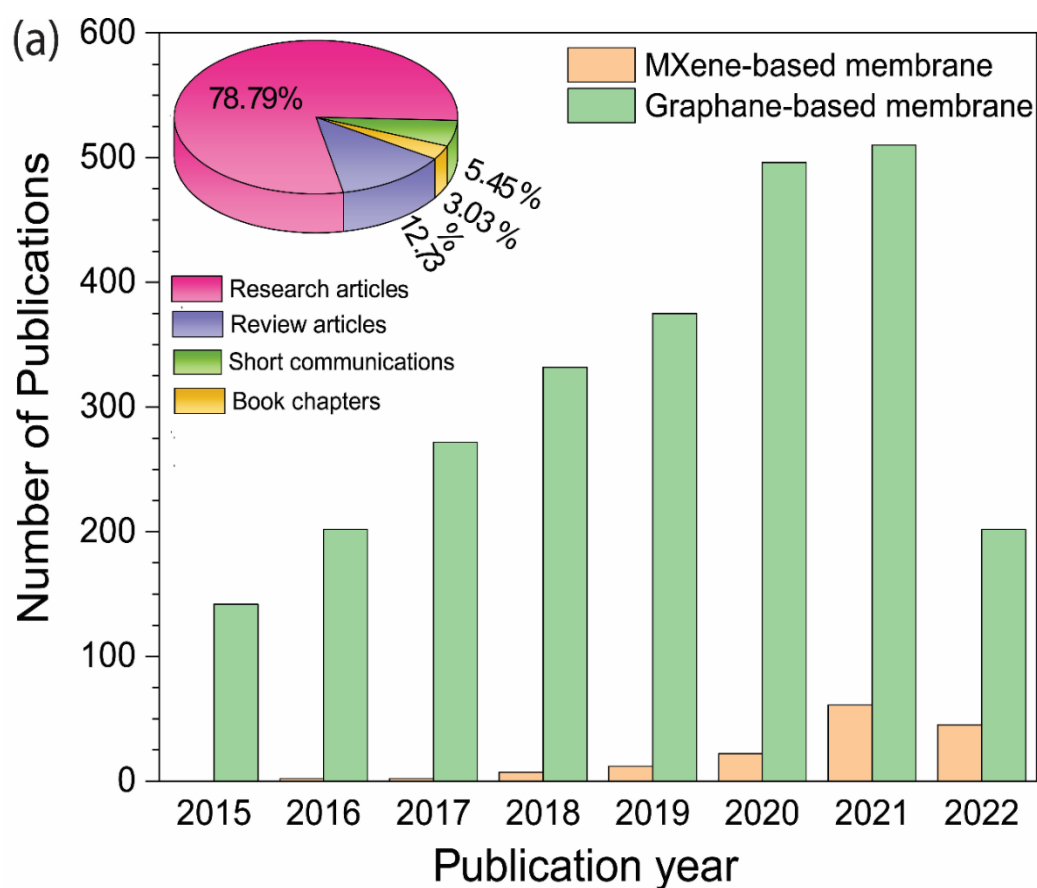


Figure 1. (a) Studies on MXene-based and graphene-based membranes as of February 2022. (b) a nanolaminated MXene membrane on a porous support. (c,d) Schematic representation of two types of mechanisms for mass transport through the in-plane slit-like pores (A), interlayer channels (B) and voids formed between the less ordered MXene nanosheets.

on Scopus database. As expected, there are many reviews on MXene synthesis, modification, purification and characterization for different applications such as energy storage^{22, 23}, catalysis

and sensors ^{22, 24}, and biomedical applications ²⁵ and separation ²⁶.

Due to the large variety of MAX phase structures and different etching processes and termination groups, a large number of MXenes has been synthesized and used in different applications. The research on MXenes membrane has been mostly limited to the separation of metal ions ²⁷, dyes ¹⁸, and solvents ^{15, 28}. The water flux of the $\text{Ti}_3\text{C}_2\text{T}_x$ membrane with a thickness of 230 nm was 9 times higher ($\sim 2300 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) than that of GO membranes with the same thickness ¹⁵. The larger d-spacing and ordered nanochannels of MXene laminates were responsible for the extremely larger water flux. Although the first article on MXene-based membranes for gas separation was published in 2018 ¹⁷, the gas separation performance of MXene membranes and the governing mechanisms of gas permeation through the membranes have not been fully explored.

There are numerous unanswered research questions in the area of MXene-based membranes. While several existing reviews have put MXene-based membranes into perspective, only a few have focused solely on MXene-based gas separation membranes. Furthermore, these reviews have not been of adequate depth to adequately focus on fundamental key issues such as the transport mechanism, stability improvement, and transport performance improvement via tuning the stacking structure and flake alignments. Moreover, compared to GO gas separation membranes, MXene membranes are in their fancy stage. This review aims to put into perspective recent advances in MXene-based gas separation membranes and point to research opportunities and gaps in field, catalyzing the determination of the gas-separation mechanisms and the improvement of the transport properties of these membranes.

3. MXenes Synthesis

There are two approaches to synthesize MXenes, top-down and bottom-up ²⁹. A top-down approach includes selective etching and chemical transformations. Although the bottom-up methods (e.g., chemical vapor deposition) generate higher quality MXene sheets, the simplicity and scalability of top-down approaches have received significantly more attention ³⁰. As Table 1 indicates the majority of 2D nanomaterials have been prepared using top-down fabrication approaches ³¹.

Table 1. Typical 2D nanomaterials used for the fabrication of gas-separation membranes.

Material	Synthesis method	Brief description of the process	Ref.
MXene	Top-down	Synthesized by the mixture of etching agents (typically a strong acid) exfoliated by the intercalation of cations between the layers	32
Graphene	Top-down	Mechanical delamination and exfoliation	33
	Bottom-up	Chemical vapor deposition (CVD) to control the properties of porous graphene by changing the process parameters (temperature, etchant, and substitutional doping)	34
GO	Top-down	Modified Hummer method and mechanical exfoliation	35
2D-MOFs	Top-down	This strategy relies on different methods (e.g. ball milling, sonication, freeze-thaw-cycling, and microchemical sonication to exfoliate 2D MOF crystals into single or a few-layers MOF.	36-38
	Bottom-up	By selecting the appropriate ligands or surfactants, different methods such as interfacial and surfactant-assisted synthesis, three-layers synthesis and modulated synthesis were utilized to grow 2D MOFs with the minimum defects to be used as the gas separation membranes.	39, 40, 41-43
COFs	Top-down	Chemical exfoliation or delamination by a mechanical process (e.g., ball milling, sonication)	44
	Bottom-up	Interfacial synthesis (air/liquid and liquid/liquid) and self-exfoliation strategies	45

In a top-down approach, a MXene is synthesized from a MAX phase, $M_{n+1}AX_n$, where M is a transition metal, A is an element from group IIIA or IVA, and X is either carbon or nitrogen. The selective etching of the transition metal element (i.e. Al) by an appropriate etchant (mostly a strong acid) has been used. Concentrated HF, hydrochloric acid (HCl) and lithium fluoride (LiF), a mixture of HF and HCl, ammonium hydrogen difluoride (NH_4HF_2), and ammonium fluoride (NH_4F) have been used as an etchant (Figure 2a) ⁴⁶. In the selective etching methods, the properties of the MXene product including the type and density of functional groups on the surface of the MXene are affected by factors such as the type of etchant, the etchant concentration, intercalating agent, temperature, and reaction time. Studies reported in the literature indicate that the use of different delamination/etching procedures leads to the production of MXenes with different qualities. Naguib et al. ⁴⁷ conducted a comprehensive study about the impact of reaction parameters for several MAX phases. The tendency of MXenes to oxidize and degrade upon exposure to oxygen and/or water has motivated the development of different synthesis methods and MXene storage protocols ^{48, 49}. The synthesis of a MXene in an organic solvent hinders the degradation of the MXene. Natu *et al.* introduced a method to fabricate and delaminate MXenes in organic solvents using NH_4HF_2 as the etching agent. The synthesized MXenes showed an accordion-like structure with a significantly larger d-spacing compared to MXenes prepared with HF ⁵⁰.

In a top-down approach, the delamination and exfoliation of nanolayers are vital for the fabrication of high-performance gas membranes. 2D materials have strong in-plane chemical bonds and electrostatic interactions, but weak out-of-plane van-der Waals bonds, which can be

mostly overcome by mechanical shearing or intercalation processes. Typical sonication/delamination methods for 2D materials are ball milling, sonication Ball-milling, sonication in an appropriate solvent, ion and polymers intercalation and melt compounding ⁵¹. Unlike most 2D materials, MXenes cannot be delaminated using mechanical delamination (by applying shear force) due to the strong M-A metallic bonds.

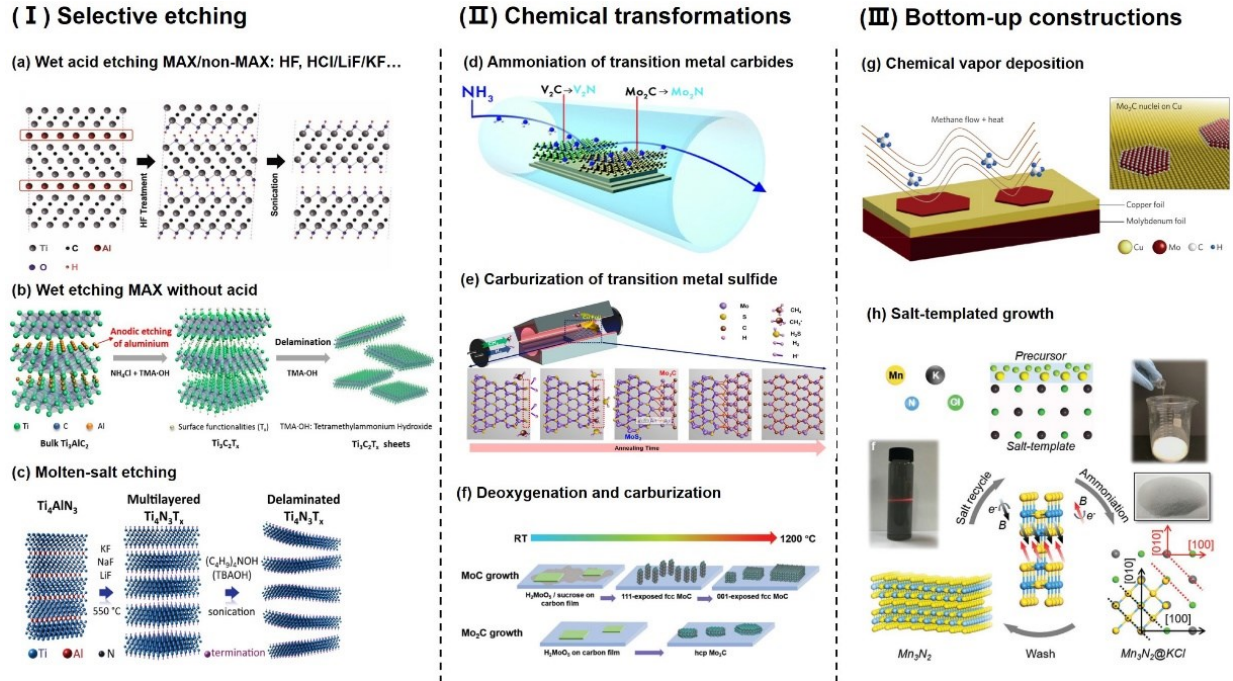


Figure 2. MXenes synthesis methods. (i) Selective etching: (a) acid etching, (b) anodic etching without using acid, and (c) molten-salt etching. (ii) Chemical transformation: (d) ammoniation transition metal carbides to achieve their transition metal nitrides at high temperatures, (e) carburization of transition metal sulfides to MXenes via thermal annealing under methane and hydrogen, and (f) de-oxygenation and carburization. Bottom-up construction: (g) chemical vapor deposition (CVD) and (h) salt-templated growth process under a flow of ammonia ⁵². Reprinted with permission from Jiang, X.; Kuklin, A. V.; Baev, A.; Ge, Y.; Ågren, H.; Zhang, H.; Prasad, P. N., Two-dimensional MXenes: From morphological to optical, electric, and magnetic properties and applications. Physics Reports 2020, 848, 1-58

In a bottom-up approach, a 2D ultrathin MXene is produced by chemical vapor deposition (CVD) or salt-templated growth, which results in the production of MXene flakes with larger lateral sizes and fewer defects. The bottom-up approaches have facilitated the tuning of surface

terminations, morphology, and size distribution ⁵³. In the CVD method, Ti_3AlC_2 MAX was synthesized by deposition of C, Al, and Ti on insulated support using direct-current magnetron sputtering (Figure 2g). Salt-templated growth has also been used for the preparation of MXenes at high temperatures (700 – 750 °C), where nitrogen was supplied by an ammonia stream ⁵⁴. Diverse transition metal nitrides (Mn_3N_2 , W_2N , and V_2N) have been produced by this approach (see Figure 2h). It should be noted that different MXene structures can be achieved due to lattice distortion caused by the salt templates (NaCl and KCl) ⁵⁵.

The delamination degree of MXenes affects the feature of MXenes. The presence of strong hydrogen bonds between MXene layers leads to irreversible restacking of those layers. Consequently, the efficiency of mechanical exfoliation techniques for providing single/few layers of MXenes is very low. To address this challenge, simultaneous ion intercalation and delamination have been employed to generate single-layer MXenes. The intercalation of cations such as Li^+ or the use of a polar solvent [e.g., dimethyl sulfoxide DMSO]) has been used successfully to increase the interlayer spacing and avoid restacking. It is believed that electrostatic interactions contribute to the introduction of cations between the layers ⁵⁶. DMSO diffuses between the $\text{Ti}_3\text{C}_2\text{T}_x$ galleries after stirring for a few hours, following up with sonication in water ⁵⁷. Most of the methods used to synthesize MXenes are time-consuming and involve the use of hazardous acids. Therefore, current studies have been on finding more environmentally friendly etchants and decreasing the synthesis time.

4. Membrane Fabrication: Methods, Properties, and Limitations

Lamellar membranes for gas separation are fabricated mostly using a top-down approach that can involve vacuum-assisted or pressure-assisted filtration, dip-coating, spraying, and vacuum spin coating.

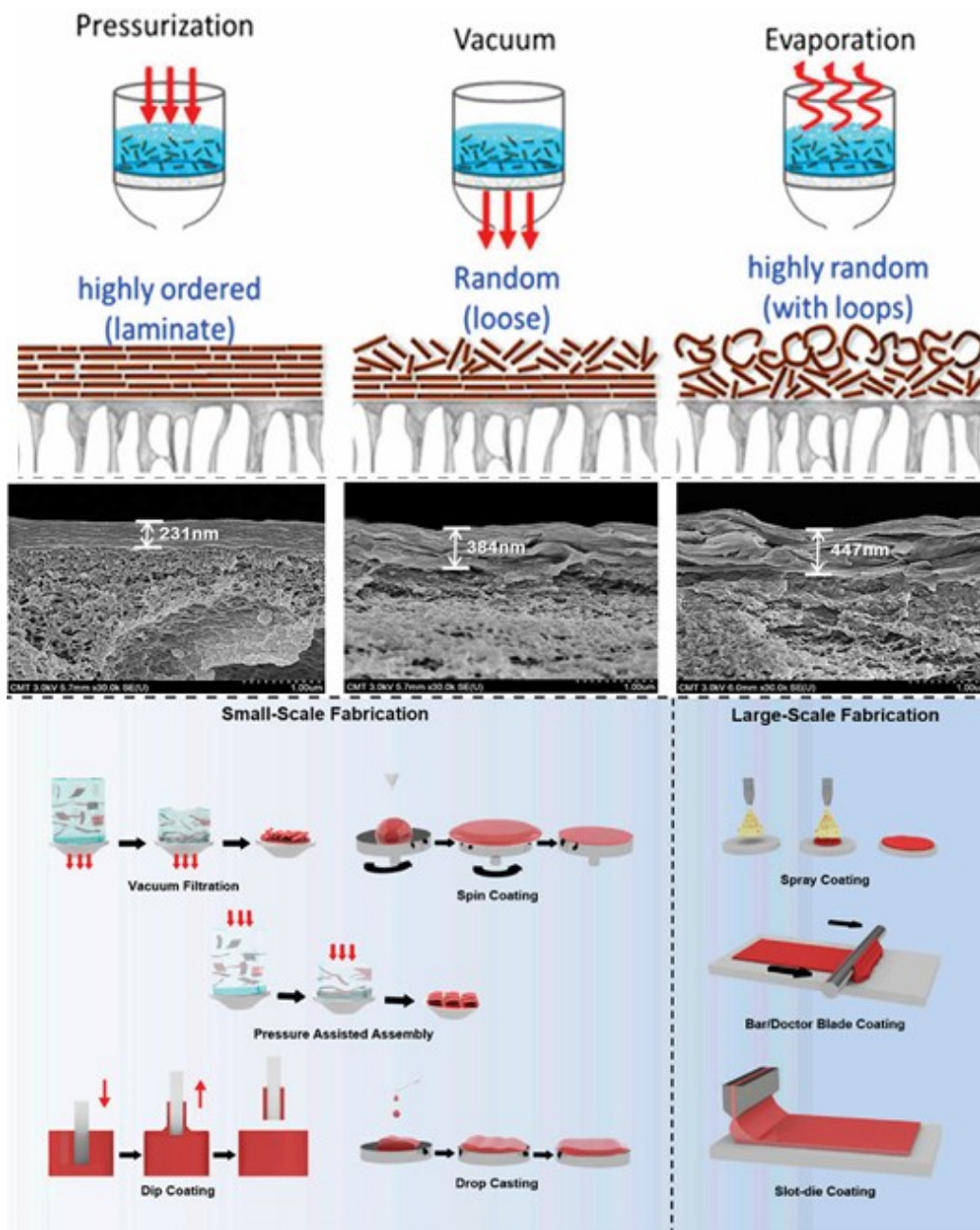


Figure 3. Top image: comparison of the structure of the membrane prepared via filtration methods. Bottom image: different types of membrane fabrication techniques⁵⁸.

Filtration. The capillary forces applied during the filtration process compete with the repulsion force between the adjacent sheets that can affect gas transport properties within the lamellar membranes. The filtration of a huge volume of a solution at low concentrations takes time, and the separation performance is very dependent on the packing density and orientation of the layers. Vacuum-assisted and pressure-assisted filtration methods are easy, scalable, controllable, and flexible. They provide a large degree of flexibility in the material selection, supports, and membrane thickness. Vacuum filtration involves the application of a vertical force from the bottom to deposit a suspension on top of a support, which has mostly been used method to fabricate aligned and high-packed 2D MXene membranes^{31,46}. The vacuum driving force decreases with increased thickness, which causes more packing near the support and a looser structure for the top layers (shown in the cross-sectional SEM images in Figure 3). However, the level of randomness is lower than in the solvent evaporation method, creating more compact membranes (with lower thicknesses). On the other hand, pressure filtration produces a denser, more uniform, and ordered structure due to stable driving forces evidenced by the cross sectional SEMs and the membranes thickness (Figure 3, top image)⁵⁹.

Coating. Coating a 2D inorganic suspension on porous supports is a common, easy and scalable method to fabricate membranes. The structure of the resulting membranes depends strongly on the evaporation rate, surface tension, support type, and compatibility with the support. However, the compactness, thickness, and orientation of the layers are very difficult to control. The membrane properties can be tuned by the selection of a suitable coating method such as spin coating, drop-casting, spraying, and casting. Drop casting and dip coating are the simplest methods for the fabrication of 2D inorganic membranes. In spin coating, shear forces can help to generate

a smoother membrane with a well-oriented, interlocked structure⁶⁰. Spray coating is known as a scalable method for constructing tubular membranes⁶¹. The casting technique is effective for the coating of thin-film mixed-matrix membranes (MMMs), in which the motion of a doctor blade can facilitate the continuous fabrication of uniform, aligned membranes^{58, 62}.

Layer-by-layer (LBL) assembly. This method is used mostly for materials with opposite surface charges⁶³. Due to the presence of interactions between each layer, the membranes show an extremely dense structure that can provide high selectivity⁶⁴. By controlling the material chemistry and the sequence of coating, we can prepare a large variety of membranes with desired performances⁶².

5. MXene Membranes

2D inorganic materials such as MXenes, graphene and graphene oxides with subnanometer pores and channels can differentiate gas species with similar molecular sizes. The development of 2D materials membranes is very different from the fabrication of polymeric membranes. MXene layers are willing to self-assemble due to their strong hydrogen bonding and van der Waals interactions. Due to their rich functional groups, vacuum filtration is an effective method to fabricate free-standing and thin-film MXene membranes. An ideal MXenes nanosheet with no intrinsic pores on the layer is impermeable to all gases, and the membrane's high selectivity is obtained from the tortuous gas pathway created between the plane-to-plane nanochannels (Figure 1c).

The size of nanochannels in 2D membranes varies between sub-nanometer (<0.7 nm) and microspores (0.7 nm-2nm)⁶⁵, depending on the material feature, preparation, and membrane fabrication. This can cause a very wide range of gas separation properties. For example, Lei et al.⁶⁶ prepared a 1.8 nm GO membrane via vacuum filtration technique that demonstrated a very high

H₂/CO₂ selectivity of 3400. On the other hand, Nair ⁶⁷ observed that the micrometer GO thick membranes are impermeable to all gases and vapors due to the thousands of tightly GO monolayers. However, the interlocked GO membranes can possess CO₂/N₂ selectivity under high relatively humidified streams ⁶⁰.

In addition to the pure MXene films, many studies have been devoted to making composites consisting of MXenes and other inorganic or polymeric materials ⁶⁸. In this section, we will discuss recent progress in MXene membranes and the mechanism of gas transportation and suggest approaches to improve the separation performance and stability of MXene membranes.

5.1. Recent Progress in MXene Lamellar Membranes for Gas Separation

Ti₃C₂T_x MXene with a d-spacing of 1.35 nm and an actual interlayer spacing of 0.35 nm has a good potential to separate gas molecules of different sizes. Ding et al. ¹⁷ prepared sturdy free-standing Ti₃C₂T_x MXene membranes by vacuum filtration on anodic aluminum oxide (AAO) supports (Figure 4a). The peeled-off membrane (Figure 4a) exhibited high tensile strength ~51.5 MPa and Young's modulus ~3.8 GPa. The membranes also showed H₂ permeability of 2402 Barrer and H₂/CO₂ selectivity of 238, exceeding the 2008 Robeson upper bound (Figure 4b). Molecular dynamics simulation confirmed the size sieving ability of the nanoslits in MXene membranes. It showed fast permeation through the membranes for small gases such as H₂ and He, while gas species with a molecular size > 0.35 nm permeate 100 times slower ¹⁷. Also, the interaction of CO₂ with Ti₃C₂T_x owing to its quadrupole property inhibited the CO₂ passage and caused much lower permeance. It was reported that the main pathway of gas molecules in the Ti₃C₂T_x membranes takes place through the interlayer spacing (pathway B in Figures 1c and 1d). On contrary, Yu et al. ⁶⁶ reported that gas transport takes place through the selective pores and defects of ultrathin

GO membranes (pathway A in Figures 1c) rather than the interlayer channels. Based on calculated interaction energies of CO₂ (−175 kJ/mol) and N₂ (−97.5 kJ/mol) to Ti₃C₂T_x, it has been concluded that the high affinity of CO₂ to MXenes inhibited the gas diffusivity and caused inverse CO₂/N₂ selectivity¹⁷. Although the interlayer spacing (pathway B in Figures 1c and 1d) has been discussed mostly as the main pathway of gas molecules in the Ti₃C₂T_x membranes, no conclusive evidence on the gas transport mechanism through the 2D materials membranes has been provided yet. On contrary, Yu et al.⁶⁶ reported that gas transport takes place through the selective pores and defects of ultrathin GO membranes (pathway A in Figures 1c) rather than the interlayer channels. In another study, Shen et al.¹³ reported that in-plane slit-like pores contribute more effectively to the gas permeation and sieving ability of the 20-nm MXene membranes rather than the interlayer galleries. Their finding was based on their observation of unchanged selectivity (e.g., H₂/C₃H₈ selectivity~110) of their MXene membranes after annealing and shrinkage of the d-spacing from 0.52 nm to 0.38 nm. However, Fan et al.⁶⁹ reported an opposite result; they attributed the higher selectivity of the MXene at higher temperatures to the lower interlayer spacing, which can be due to the higher H₂ diffusivity at higher temperatures.

Similar to other 2D materials, MXenes membranes are H₂-selective. The functionalization of Ti₃C₂T_x MXene with borate and polyethyleneimine (PEI) is an effective strategy to improve the CO₂ permeability and mechanical properties under humidified conditions. It was reported that the main pathway of gas molecules in the Ti₃C₂T_x membranes takes place through the interlayer spacing (pathway B in Figures 1c and 1d). On contrary, Yu et al.⁶⁶ reported that gas transport takes place through the selective pores and defects of ultrathin GO membranes (pathway A in Figures 1c) rather than the interlayer channels. (Figures 4c and 4d), confirmed by the 43% higher CO₂ adsorption compared to the pristine Ti₃C₂T_x MXene¹³ (Figures 4e).

When the feed gas was humidified, $\text{Ti}_3\text{C}_2\text{T}_x$ membranes functionalized with borate and amine groups showed improved CO_2 selectivity. It seems the surface modification changed the

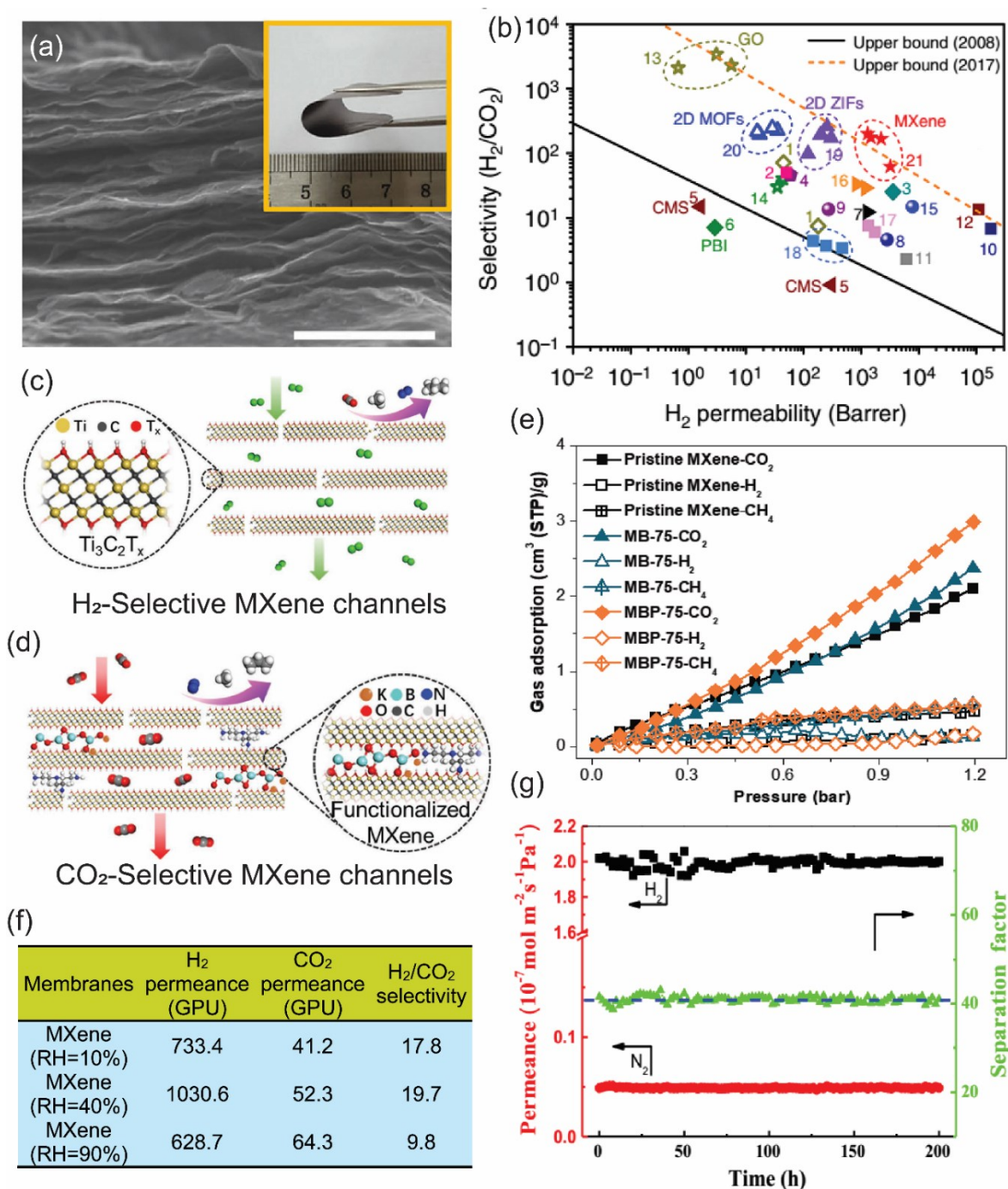


Figure 4. (a) Cross-sectional SEM image of a free-standing MXene membrane (scale bar is 1 μm)¹⁷; (b) Comparison of H_2/CO_2 separation performance of the MXene membranes with the reported membranes in the literature¹⁷; (c and d) The gas transport through the H_2 -selective and CO_2 -selective channels of the pristine MXene and MXenes functionalized with borate and PEI membranes¹³; (e) Comparison of the gas sorption of the pristine MXene and functionalized

MXenes with borate and PEI membranes ¹³; (f) Effect of humidity on the H₂/CO₂ separation properties of the MXene membrane ¹³; (g) Long term stability of the MXene membrane at 320°C ⁶⁹.

stacking and interlayer spacing of MXenes and allowed CO₂ to pass more quickly ¹³. The increase of the feed gas humidity to 90% leads to a decrease in the H₂/CO₂ selectivity from 19.7 to 9.8, which can be attributed to water intercalation between the MXene galleries, facilitating the transportation of CO₂ molecules [table (f) in Figure 4]. Similar behavior was observed in thiourea-crosslinked GO membranes with a ceramic support ⁷⁰, where the CO₂-philicity of the membranes caused a higher H₂/CO₂ selectivity than H₂/N₂. It seems that humidity boosts the effect of the surface modification of nanosheets on the CO₂ separation performance of the membranes. This is further supported by Shen et al.'s results ⁷¹ that their EFDA-functionalized GO membranes with a dry H₂/CO₂ gas feed showed a lower CO₂ flux. The enhanced H₂/CO₂ selectivity of the EFDA-GO membranes was explained by the strong adsorption of CO₂ on PEI molecules present in the EFDA-GO laminates, causing a delay in CO₂ transportation through the membrane. In another study, the high thermal stability of a MXene allowed the membrane to last up to 200 h of operation at 320°C without any sign of degradation or loss in the H₂/N₂ selectivity ~ 41 (Figure 4g) ⁶⁹.

Table 2. Gas separation properties of state-of-the-art membranes other than MXene-based membranes used for H₂/CO₂ separation.

Membrane Material	Thickness (μm)	Temp. (°C)	H ₂ /CO ₂ Ratio	H ₂ Permeance (GPU)	H ₂ /CO ₂ Selectivity	Ref.
Modified MFI	2.000	500	50/50	627	105.0	72
ZIF-8	6.000	30	50/50	472	4.6	73
ZIF-7	2.000	220	50/50	136	13.6	74
COF300-ZIF8	97.200	25	N/A	110e+5	13.5	75
GO	0.002	20	50/50	360	2100.0	76
GO	0.009	20	50/50	344	3400.0	76

GO	0.018	20	50/50	311	2300.0	76
GO	0.003-0.010	130	N/A	~2200	~25.0	77
GO	0.003-0.010	140	N/A	~2500	40.0	77
GO/ND	0.008-0.012	25	N/A	1904	247.4	11
GO/POSS	0.008-0.012	25	N/A	2216	175.9	11
ZIF-8/GO	20.000	250	50/50	448	14.9	78
1T MoS ₂	0.5	25	50/50	619	7.6	79
2H MoS ₂	0.5	25	50/50	641	8.5	79
MoS ₂	0.017	35	N/A	27440	3.4	80
MoS ₂	0.035	35	N/A	7042	3.7	80
MoS ₂	0.060	35	N/A	2446	4.4	80
2D ZIFs	N.A.	25	50/50	~1202	172.0	81
2D ZIFs	N.A.	25	50/50	~1283	191.0	81
2D ZIFs	N.A.	25	50/50	~1364	261.0	81
2D MOFs	0.012	20	N/A	~8000	25.0	82
2D MOFs	0.040	20	50/50	~700	225.0	82
Zn ₂ (bim) ₃	N.A.	25	N/A	2598	166.0	37
Zr-MOF	0.03-1.0	25	N/A	182	3.7	39
Zr-MOF-Naph	0.03-1.0	25	N.A.	104	15.0	39
Zr-MOF-Anth	0.03-1.0	25	N/A	72	31.9	39
CuBDC-GO	N.A.	25	N/A	2867	95.1	83
Zn ₂ (bim) ₄ /GO	N.A.	25	N/A	418	106.0	43
Co ₂ (bim) ₄	N.A.	25	N/A	508	58.7	84

Membrane Material	Temp. (°C)	H ₂ /CO ₂ Ratio	H ₂ Permeance (GPU)	H ₂ /CO ₂ Selectivity	Ref.
MXene	25	50/50	3202	62.0	85
MXene	25	50/50	2226	167.0	85
MXene	25	50/50	1473	174.0	85
MXene	25	50/50	1302	200.0	85
Self-crosslinked MXene	25	90/10	17	16.0	86
Ni ²⁺ -MXene	25	50/50	249	615.0	87
MXene-Borate-PEI	25	50/50	350	28.0	13
MXene-Borate	25	50/50	322	19.0	13
ZIF-8/MXene	25	N.A.	178	77.0	88
Pd-MXene	25	50/50	538	242.0	89

Gas separation properties of MXene-based membranes used for H₂/CO₂ separation.

MXene membranes have shown higher permeabilities and similar selectivities compared to the existing 2D MOFs and zeolitic imidazolate frameworks (ZIFs) membranes (Table 2). Although GO membranes are more H₂ selective than MXenes, they have much lower H₂ permeabilities (Table 2). Membranes made from COFs have shown very high H₂ permeabilities but low H₂/CO₂ selectivities (Tables 2 and 3). Gas transport properties of MXene membranes can be adjusted through different modifications (Table 3).

5.2. Control Gas Transport Properties of MXenes Membranes

Similar to other 2D lamellar membranes, the gas permeation within the MXene membranes can take place in three different regions (Figures 1c and 1d): (i) in-plane slit-like pores formed from the non-structural defects between the adjacent MXene flakes; (ii) the plane-to-plane interlayer galleries which can be governed by coating methods and functional groups; and (iii) voids from the less ordered MXene layers that also were observed in GO and other 2D materials membranes^{90, 91}. The lateral size and functional groups of MXenes, the surface modification, the type of support, the MXene concentration in water, and the driving force during the materials deposition influence the packing density, layer orientation, and separation performance^{91, 92}. The membrane fabrication process, especially the rate of MXene deposition on the substrate, and the drying temperature are critical to preventing voids formation and advancing the membrane separation performance⁹¹. Furthermore, the strong repulsive forces between adjacent sheets disturb the ordered packing of layers during the self-assembly and deteriorate the gas selectivity (Figure 5a). The accurate control size of in-plane slit-like pores and interlayer spacing, and generating more

ordered nanolaminates are the main challenge to enhance permeability and selectivity^{13, 93, 94}. The use of external force during the membrane fabrication is a successful approach to overcoming the destructive repulsive forces and preparing highly ordered 2D membranes. The tailoring of the stacking structure by using external forces can be carried out by capillary force, compressive, centrifugal and shear force during the membrane fabrications (Figures 5b-f). Although the common membrane fabrications such as vacuum and pressure-assisted filtration, spin-coating, and spray coating are very effective, the control of the pore size and the uniformity of galleries are very difficult. Therefore, the fabrication method to obtain a membrane with uniform pores and interlayer structure need further investigation. In addition to tuning the casting methods, the interlayer spacing and layer stacking can be controlled by chemical modification and making the intra-molecular interactions (e.g. electrostatic interactions, hydrogen and covalent bonding) between the layers (Figure 5e).

5.2.1. Membrane processing parameters: casting, concentration, time and temperature

It was observed that applying rational external forces during the assembling of nanoflakes can change the in-plane and plane-to-plane structures. Several studies revealed that the gas permeation initiates from the gas diffusivity through the in-plane slit-like pores and then interlayer galleries^{67, 71, 95}. However, delicate control of channel size, and avoiding the formation of non-selective in-plane pores are very difficult. The most effective fabrication method is vacuum-spin coating where the vacuum-supplied capillary force along z-axis, and rotational force along the x, and y-axis can suppress the negative repulsion of in-plane and adjacent flakes (Figure 5f). Consequently, depending on the membrane fabrication methods, the packing and the alignment of layers differ in both in-plane and plane-to-plane directions. Atomic force microscopy (AFM) phase images also

show a smoother surface without visible defects for the membrane prepared via vacuum-spin coating ⁷¹.

Besides the type of a coating method, the MXene concentration in water, the rate of filtration, and the drying process can affect the structure and layer stacking. The porosity of MXene membranes decreased from 59% to 39% by increasing the MXene mass loading. This compaction resulted from more stacked MXene flakes and created more tortuosity and longer nanochannels which declined the permeation of molecules through the membrane⁹¹. In addition to the mass loading, the rate of deposition of MXene solution strongly affects the membrane flux. It was reported that faster vacuum filtration generates more random packing of 2D materials and significantly increased the flux ⁹². The unchanged d-spacing of the prepared MXene membranes from XRD data confirms the voids and non-packed structures in the membrane are the main reason for this noticeable difference in the membrane's permeation ⁹¹. The temperature of spin coating alters the interlocking and stacking of the 2D $\text{Zn}_2(\text{bim})_4$ MOFs nanoslits, leading to different structures. Coating at higher temperatures increased the packing density and interlocking of nanosheets, which made the nanochannels more size-selective ^{36, 37}.

5.2.2. Synthesis, modification of MXenes: flake size, functional groups and interlayer ions

The engineering of MXene synthesis to modify the flake size, surface functional groups, and interlayer galleries can promote gas selectivity of the resulting membranes ⁶⁰. The membrane is permeable to a

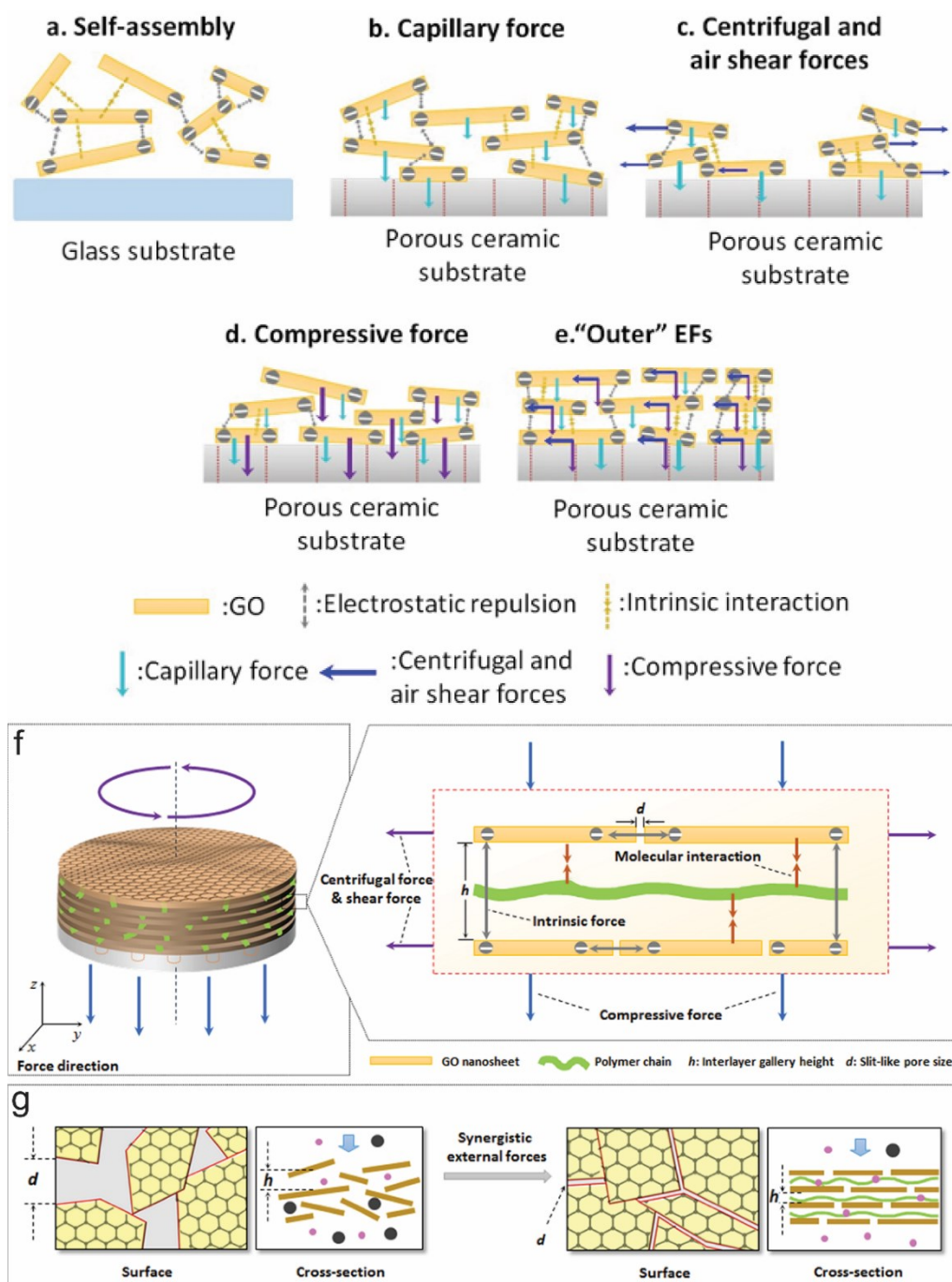


Figure 5. Schematics of 2D membranes fabricated by applying different forces. (a) Self-assembly without any external forces; (b) capillary force; (c) centrifugal force and air shear force; (d) compressive force; (e) inter force; and (f) external force driven assembly approach for fabricating 2D channels. It involves three-dimensional external forces along the x, y, and z axes. The enlarged schematic shows force analyses for a 2D channel unit and a polymer chain. Three main types of forces are included: intrinsic repulsive force, external forces (compressive force, centrifugal force and shear force) and inner force between the nanosheets and the polymer chain. (g) Hypothetical evolution of surface and cross-section of GO-assembled 2D channels from intrinsic force-induced disordered structure (left) to highly ordered laminar structures (right) driven by introduced synergistic external forces⁷¹.

gas molecule at the suitable transmembrane pressure to overcome the gas energy barrier of pores entry. The lower gas permeability of membranes prepared with larger flake sizes is explained by a higher energy barrier and longer gas diffusion path. Also, the higher selectivity and lower gas flux of thicker membranes are ascribed to the more tortuosity and fewer low-selective in-plane pores within the laminates ⁶⁶.

Via the intercalation of cations between the galleries, chemical reactions, and mixing MXenes with other inorganic fillers, the nanochannel of MXenes can be adjusted, thus enabling the control of separation performance of the membranes. The insertion of positively charged ions or small nanoparticles between MXene layers expands the channel's width and thus increases the membrane flux. The Fe(OH)₃ nanoparticles with a diameter of 4-5 nm were uniformly bound on the MXene surface via electrostatic interactions. After the removal of the nanofiller using an HCl solution, 2D nanochannels with d-spacing values of 2-5 nm were created ¹⁸. In another study, H₂/CO₂ selectivity was improved by intercalating MXene nanosheets with Ni²⁺ and coating the modified nanosheets on Al₂O₃ hollow fibers via vacuum-assisted filtration ⁹⁶. The prepared membranes demonstrated an excellent H₂/CO₂ selectivity of 615 and H₂ permeance of 8.35×10^{-8} mol·m⁻²·s⁻¹·Pa⁻¹ ⁹⁶. The enhanced hydrogen selectivity stems from strong interactions between MXene nanosheets and Ni²⁺, which tuned the interlayer spacing of the MXene. The membrane also showed stable gas separation performance during 200 h of operations ⁹⁶.

The interlayer spacing of the MXene galleries can be tailored using different synthesis methods. The presence of O, OH, and F functional groups expand the MXenes interlayer compared to the MAX phase. In addition to DMSO which was discussed earlier, the use of hydrazine, urea, thiophene, acetone, and formaldehyde for the intercalation of MXene layers increased the d-spacing of MXenes ⁹⁷. The interlayer spacing of MXene depends on the type of etchant used in the

synthesis of the MXene. For example, the c-lattice parameters for the MXene etched with HCl-LiF are 25% larger than the HF-etched MXene due to the presence of Li⁺ between the layers ³². Mixing a MXene with graphene increased the d-spacing value from 1.3 Å to 1.7 Å ⁹⁸. Apart from the physical mixing, the polymerization of organic molecules, such as pyrrole and layered double hydroxide, on MXene layers is another approach to tune d-spacing ⁹⁹. In gas separation membranes, the interaction of molecules with intercalants and accurate changes in the d-spacing of MXene layers are worth to be investigated.

It was observed that the surface modification of nanosheets can change stacking structure and gas transportation regime from the permeation through the intrinsic defects of discrete flakes to 2D nanoslits formed between the interlocked adjacent sheets. For example, the GO-PEI interaction resulted in aligned GO nanochannels with a firm-ordered structure. Also, the intercalation of the polyethyleneimine (PEI) chain into the GO nanolayers enlarged the d-spacing and the actual interlayer distance, finely tuning the sieving ability and gas transportation through the GO assembled membranes. Also, the mechanical property and peeling-off force of the membranes were significantly improved by the intercalation of PEI molecules into the GO nanosheets ⁷¹. Crosslinking is an effective approach to enhance selectivity by narrowing the interlayer spacing and decreasing the repulsion force of the carboxylic functional groups on the 2D nanosheets ¹⁰⁰. The selectivity of GO membranes was enhanced by changing the reduction state and crosslinking the sheets. For example, the d-spacing of GO decreased to 3.6 Å after the removal of oxygen functional groups during the reduction process ¹⁰¹. The crosslinking of GO with thiourea also resulted in a smaller nanochannel, improving the H₂/CO₂ selectivity to 200 ⁷⁰.

5.3. Molecular Transport Mechanism of MXene-based Membranes

The mechanism of gas permeation through 2D inorganic membranes is not fully understood yet. The permeation is influenced by many factors such as membrane structural parameters and materials characteristics. The large aspect ratio of MXenes is responsible for different gas transport regimes such as molecular sieving, Knudsen diffusivity, surface diffusion, and capillary condensation. Fast gas permeation through the MXene membranes is the result of nanochannel with the d-spacing of 3.5 Å, and intrinsic pores formed during membrane fabrication. The Knudsen regime controls the diffusivity in pores of smaller or similar size than the mean free path of gas molecules ¹⁰². The flux of the membrane is calculated ¹⁰³:

$$J = \frac{\pi r^2 D_k n \Delta p}{RT \tau L} \quad (1)$$

where J is the membrane flux, r is the pore radius, n is the gas molar concentration, Δp is the transmembrane pressure, τ is the tortuosity of the channels, and L is the diffusion length. D_k is defined as $0.66r \sqrt{\frac{8RT}{\pi M_w}}$, where M_w is the gas molecular weight. The selectivity of the membranes is inversely proportional to the square root of the gas molecular weight ¹⁰⁴. In a study ¹⁰⁵, the gas transport mechanism through a $Ti_3C_2T_x$ membrane was assessed by the investigation of gas permeance vs. the inverse square root of the gas molecular weight (Figure 6a) and the gas kinetic diameter (Figure 6b). It is a common practice in the characterization of gas separation membranes to represent the flux versus the square root of the molecular weight ratio to check the influence of Knudsen diffusion in the molecular sieving mechanism of the membranes ^{103, 106}. The linear correlation of H_2 and N_2 permeance in contrast to the inverse square molecular weight and their constant diffusivity coefficients at different pressures indicate the domination of Knudsen diffusivity. The deviation of H_2S permeance from the model prediction (dashed line in Figure 6b) reveals that the labyrinthine hopping transport is the dominant mechanism ($D_{labyrinthine}$). Also, the

diffusivity of the condensable gases increases significantly with increased pressure, which can be related to the expansion of the interlayer spacing.

$$D_{\text{labyrinthine}} = \frac{P}{h \times S} \frac{L_{\text{av}}^2}{4} \frac{1}{d_{\text{int}}} \quad (2)$$

where P is the permeance, S is the sorption coefficient, l is the membrane thickness, h and d_{int} are the interlayer and slit thickness available for gas permeation, respectively, and L_{av} is the average lateral size of the MXene ¹⁰⁵.

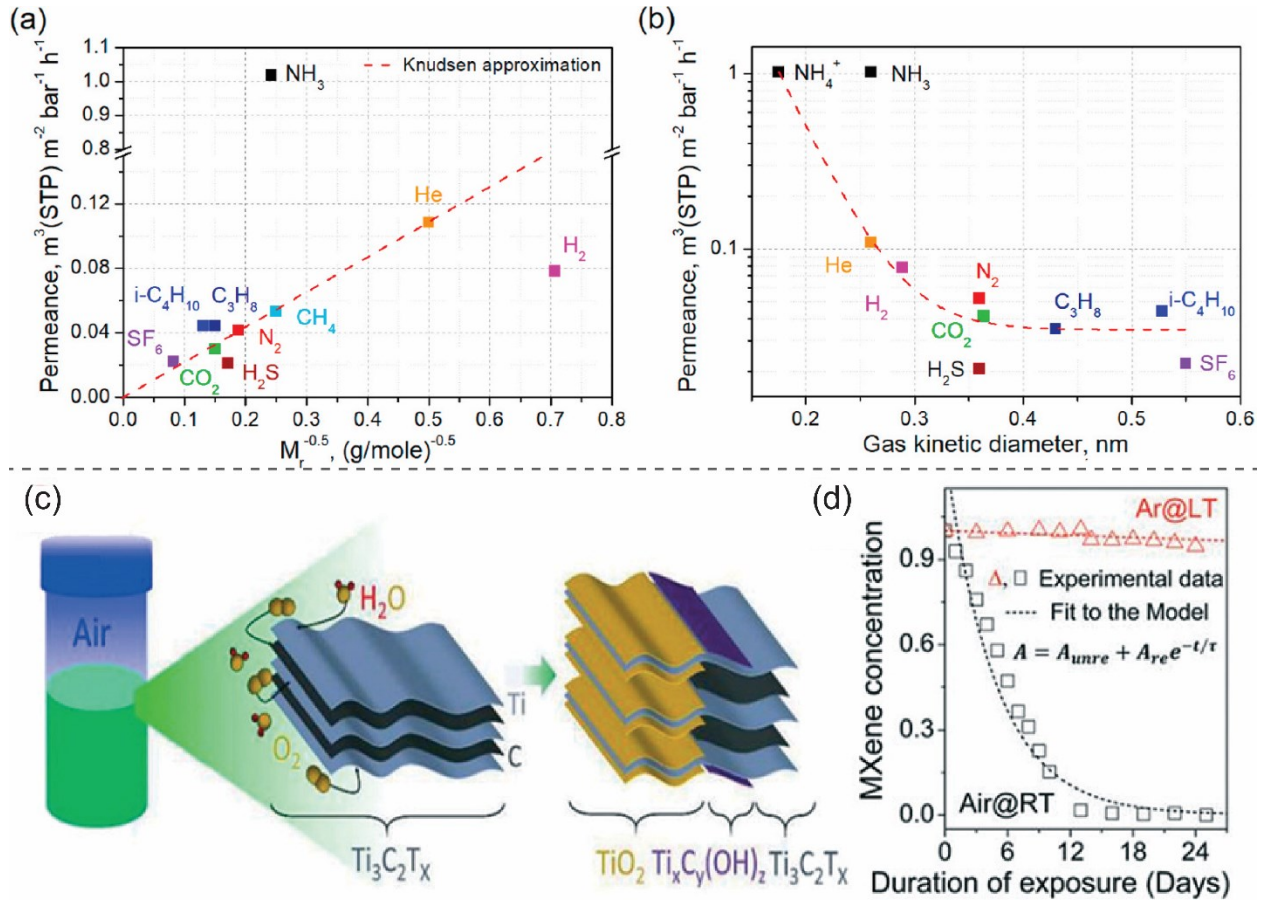


Figure 6. The dependence of gas permeance of Ti₃C₂T_x membranes vs. (a) gas molecular weight and (b) gas kinetic diameter ¹⁰⁵; (c) scheme showing the Ti₃C₂T_x degradation in an aqueous solution; and (d) Ti₃C₂T_x concentration in a water suspension vs. time ¹⁰⁷.

The main pathway for gas molecules through the laminated membranes are in-plane pores (pathway A in Figure 1c) and interlayer galleries (Pathway B in Figure 1c). The repulsion forces between MXene nanosheets, which are negatively charged, disrupt the orientation and stacking of

layers and caused larger d-spacing values. Therefore, for 2D materials, the control of interlayer spacing is critical to achieve excellent separation performance. The gas permeability is inversely proportional to the membrane thickness (h) and tortuosity (τ), and it is proportional to the membrane porosity (ϵ)¹⁰⁸

$$P = \left(\frac{1}{h}\right) \left[\left(\frac{\epsilon_A}{\tau_A}\right) D_A K_A + \left(\frac{\epsilon_B}{\tau_B}\right) D_B K_B \right] \quad (3)$$

where D_A and K_A are the diffusivity coefficient and adsorption equilibrium constant of a gas molecule passing through the in-plane pores (A), respectively, and D_B and K_B are those of a gas species permeating between the layers (B), respectively. Also, the tortuosity constant (τ) can be calculated from the aspect ratio. The diffusion length can be calculated by equation¹⁰⁸:

$$l = h + N \frac{Q}{2} \quad N = \frac{h}{Q+W} \quad (4)$$

where Q and W are the lateral size and width of the nanosheets, respectively.

The gas separation properties of the lamellar MXenes membranes can be mainly explained by the Knudsen diffusion and size sieving mechanisms. In general, the smaller gas species such as H_2 confront less hindrance to pass through the membranes. This indicates the significance of the size of nanochannels in the range of 3–4 Å, allowing the pores to separate H_2 from other molecules, via the size exclusion. Moreover, the gas permeation and selectivity are firmly affected by MXene characteristics such as the stacking density, lamellar size, defects, and functional groups¹⁰⁹.

5.4. Stability of MXene Membranes

Despite recent progress in commercial polymer membranes for gas separation applications, there are still many challenges under realistic conditions such as poor thermal-chemical stability, plasticization under condensable gases, and low H_2/CO_2 selectivity. There are only a few glassy (e.g. polybenzimidazole^{2, 110}) and rubbery polymers (e.g. Polaris™) available in the market with

long-term stability. The pilot-plant scale of the Polaris membrane exhibited 740h-stable CO₂/N₂ separation performance with a CO₂ purity of 68.2%¹¹¹. The stability of MXenes should be carefully considered in the MXene-based separation membranes. Although most of MXenes are synthesized in aqueous media, dissolved oxygen is the reason for the MXene degradation, which initiates from the edge of MXene sheets by the oxidation of Ti. The stability of MXenes strongly depends on the size of flakes; smaller flakes are more likely to degrade due to their longer edge length. It has been reported that a Ti₃C₂T_x solution completely degrades after two weeks of exposure to air (Figures 5c and 5d)⁴⁸. However, storing it at a low temperature and in a dark place can decrease the degradation rate¹¹². The hybridization of MXenes is also an effective strategy to protect the layers from oxidation by hindering the water intercalation between the galleries¹¹³. For example, the performance of Ti₃C₂T_x membranes under humidity and pressure was stabilized by the intercalation of MWCTs into the adjacent layers via the π - π stacking forces and van der Waals interactions. Mixing MXenes with polymers can be an effective strategy to prevent MXene degradation. Shamsabadi *et al.*¹¹⁴ observed no gas performance change of Pebax/MXene MMMs after storing the membranes in the ambient conditions for six months.

Functional groups, interactions, and interlayer spacing affect the tensile properties of MXenes¹¹⁵. The strong hydrogen bonds formed by –OH groups of MXenes cause much narrower d-spacing than the MXenes terminated by –O– and –F groups, leading to higher elastic modulus¹¹⁶. Strong interactions between Ti elements and MXene functional groups can compensate for the intrinsic fragility of the pristine MXene, thus improving the stiffness by up to 30% upon oxygen modification¹¹⁷. For example, it was shown that a folded MXene film in the shape of a cylinder with a thickness of 5.1 μm can support more than 4000 times its weight²⁰. The strong mechanical properties of MXenes have motivated researchers to utilize these nanomaterials in polymer matrices for different applications.

6. Role of MXenes in Enhancing the Performance of MMMs

The concept of MMMs fabricated by embedding MXene flakes into a polymer matrix is a promising approach to fabricate highly-selective gas membranes. Tuning the transport path through the polymer film, the size-sieving ability of the MXene galleries, and increasing the adsorption capacity due to the rich-functional groups on the MXene surface can improve the gas permeability and selectivity of the polymeric membranes. In contrast to the pure MXene membranes, the MXene in the MMMs and thin-film nanocomposite membranes acts as a filler and can alter the length and tortuosity of the gas passage length, or increase the gas solubility in the polymer matrix. According to the solution-diffusion mechanism, the gas permeability in the non-porous polymeric membranes is a function of gas diffusivity and solubility coefficients¹¹⁸: $P = D \times S$. The presence of MXene layers can alter the diffusivity of the gas. Also, the functional groups form strong bonds with the polymer chains (Figure 7a) and enhance the affinity toward condensable gases such as CO₂^{103, 114}. The interactions between amide groups and Ti₃C₂T_x, shown in Figure 7a, promote the dispersibility of the nanosheets into the polymer matrix. It has been observed that Ti₃C₂T_x can tune the morphology of the block copolymers and improve the separation performance, because of its excellent compatibility with polymer chains¹¹⁴.

Shamsabadi *et al.*¹¹⁴ highlighted the gas separation of Pebax/MXene MMMs for CO₂ capture. They reported an enhancement in the CO₂ permeability and CO₂/N₂ selectivity at a very low MXenes loading (0.1 wt.%). Moreover, the sub-nanometer thickness of MXenes sheets provided the opportunity to fabricate 100 nm thin-film membranes (Figure 7b) on polytetrafluoroethylene (PTFE) supports with exceptional CO₂ permeance ~1810 GPU and CO₂/N₂ selectivity of 42 (Figure 7c). Strong interactions between Pebax and the MXene were confirmed by FTIR, DSC and molecular dynamic (MD) simulations. Liu and co-workers¹¹⁹ reported a significant improvement for the Pebax MMMs at 0.15 wt.% MXene concentration. The

CO₂ permeance and the CO₂/N₂ selectivity were improved by 81% (21.6 GPU) and 73% (72.5), respectively, compared to the unloaded Pebax membrane. Similar behavior with improved CO₂ permeability and CO₂/N₂ selectivity was reported for Pebax/GO MMMs³⁵. An enhancement in the transport properties of the Pebax-Ti₃C₂T_x composite membranes was observed elsewhere¹²⁰. However, the agglomeration of fillers at high loadings creates nonselective voids between the nanosheets and the polymer chains and declines the permselectivity. A decrease in the gas solubility and diffusivity of Pebax/MXene composite membranes was observed at high MXene concentration, which was attributed to slight agglomeration in the permeable PEO domains¹¹⁴. Polyacrylonitrile (PAN) nanofiber filters were modified with Ti₃C₂T_x to enhance their adsorption capacity for the removal of particulate-matter particles with diameters $\leq 2.5 \mu\text{m}$. Interaction forces between the nanofibers and particles were analyzed quantitatively using force-distance curve-based AFM, which clearly showed three times stronger interactions after modification with Ti₃C₂T_x due to the strong interactions of the particles with the surface-terminating groups of the nanosheets. A high particle removal efficiency of $\sim 99.7\%$ with a low-pressure drop of $\sim 42 \text{ Pa}$ was observed for the modified filters¹²¹.

Physical mixing and in-site polymerization are two methods for the preparation of MMMs. To avoid non-selective defects in the membrane, the compatibility of the polymer solution with MXene is crucial. The *in-situ* polymerization generates uniform polymer films on the surface of MXene, although the number of monomers is limited due to the insufficient polymerization energy. The rich termination groups on the surface of MXenes facilitated the polymerization of pyrrole and 3,4-Ethylenedioxythiophene (EDOT) monomers (Figure 7d), followed by vacuum filtration of the solutions on porous supports^{99, 122}.

Shi *et al.*¹²³ compared the impact of a MXene and GO on the thermal resistance, mechanical properties, and separation performance of Pebax membranes. The better dispersion and stronger interaction of the MXene than GO with the polymer chains led to higher mechanical properties. This also enabled the preparation of Pebax MMMs with a maximum of 20 wt.% MXene fillers without any decline in the membrane transport properties, while the maximum affordable GO concentration was only 5wt.%. This benefit of Pebax-MXene membranes is not significant in the separation in the dry state. However, higher MXene contents showed a remarkable advantage under a humidified gas feed, where the water intercalated in the nanochannels facilitating CO₂ transportation.

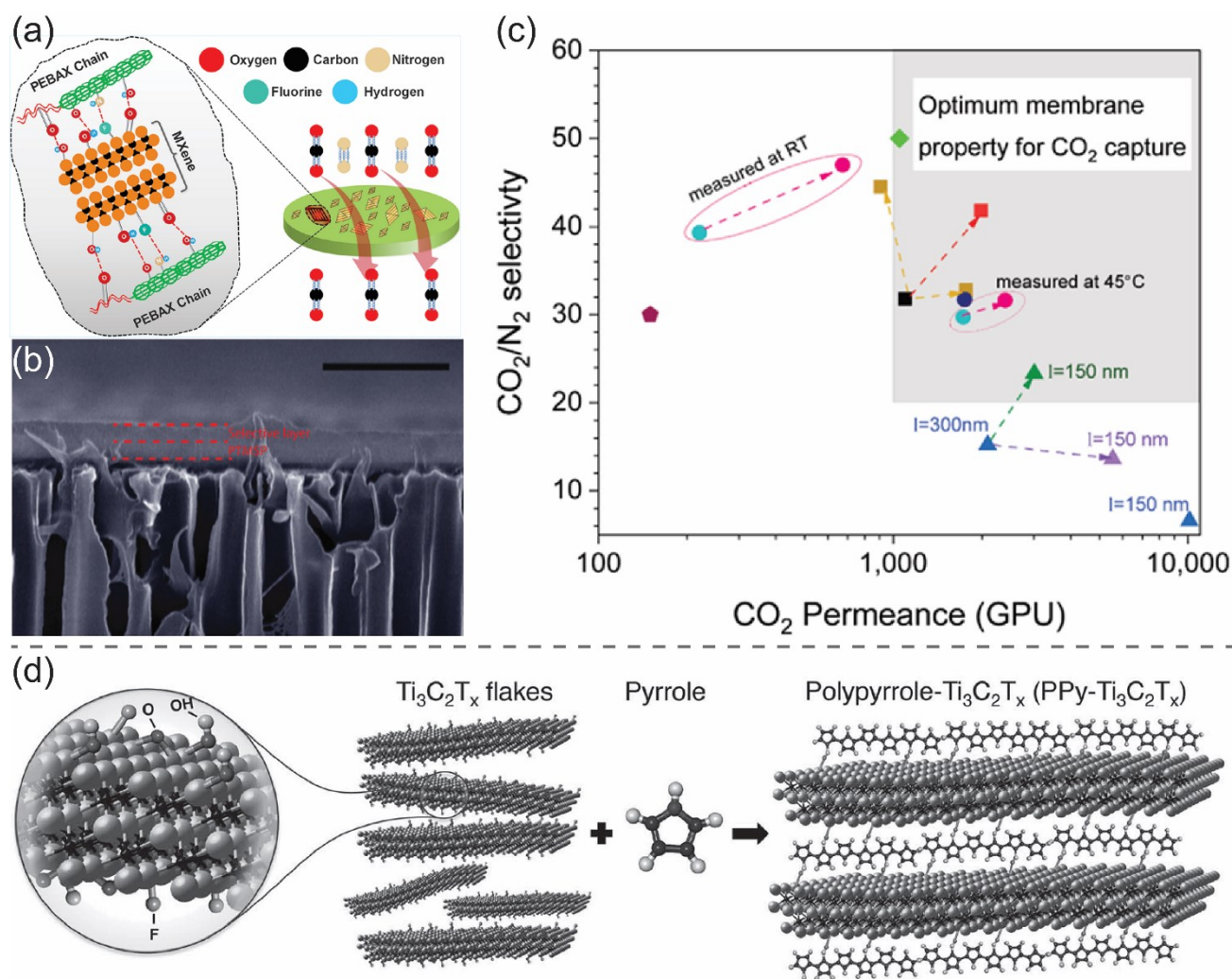


Figure 7. (a) Schematic illustration of hydrogen bonds formed in Pebax/MXene MMMs; (b) cross-sectional SEM image of thin-film Pebax composite at 0.1 wt.% MXene (the scale bar is 500 nm); (c) comparison of the performance of Pebax-MXene thin-film composite membranes with other reported polymer composites in the literature ¹¹⁴; and (d) pyrrole polymerization on the surface of MXene ⁹⁹.

7. Other 2D Materials for Membrane Separation

There are many 2D materials with various features and properties for different applications. This section briefly describes existing 2D nanosheets and their advantages and disadvantages in the fabrication of thin-film inorganic membranes.

7.1. 2D Zeolite Membranes

The first research on the zeolite membranes showed the potential of these membranes due to their thermal stability, robustness, preferred orientation, and hydrophilicity/hydrophobicity properties ¹²⁴. The MFI-based membranes demonstrated high performance in separating ammonia/nitrogen and hydrocarbons/hydrogen ¹²⁵. MFI-based zeolite membranes have also been studied extensively for the separation of para/ortho-xylene isomers, with a selectivity of > 3000 at 150°C ¹²⁶. The intergrowth of 1D MEL-type zeolite within 2D-MDI allowed for tuning the planar structure and the direction/orientation of the channels led to improvement in the selectivity of para/ortho-xylene isomers ¹²⁷.

Moderate selectivity, high cost, low flux, and poor processibility are the main obstacles to the extensive use of zeolites in the membrane industry ¹²⁸. Moreover, zeolites have been found to be hardly exfoliated into nanosheets at enough quantity and appropriate quality for membrane application ¹²⁹. The fabrication of thin 2D zeolite membranes requires a controlled deposition process on costly rigid supports ^{126, 130}. For example, the preparation of an exfoliated MFI nanosheet with a thickness of 3 nm is possible. However, the fragmentation during the exfoliation process limits the in-plane dimension below 1 μm . Some progress to address this issue has recently been reported ¹³¹. In this study, the direct synthesis of MFI nanosheets by using zeolite flake as

the seeds advanced the uniformity of the MFI membranes and allowed for better control over the thickness of their membranes.

In summary, extensive progress has been made in the synthesis and modification of zeolite membranes. However, the random orientation of the layers, non-uniform thickness, and difficulty in the fabrication of thin-film membranes have limited the use of zeolites for high-selective gas separation membranes.

7.2. 2D MOF Membranes

Metal-organic frameworks (MOFs) are promising for use in molecular-sieving membranes due to their adjustable pore size and functionality for the desired separation. Both top-down and bottom-up methods have been employed for the preparation of thin-film MOF membranes. In the top-down method, the exfoliation of MOFs in suitable organic solvents and careful delamination to prevent structural collapse, and assembling of defect-free exfoliated nanosheets on porous support limit the fabrication of high-selective MOF membranes. To fabricate a highly selective MOF membrane using a top-down method, the monolayer $\text{Zn}_2(\text{bim})_4$ crystals were obtained by ball milling and sonication, and they were coated on alumina supports by the hot drop coating method^{36, 37}. In similar work, Zhao *et al.* used the structural flexibility of 2D NAMS-1 for the preparation of ultra-thin membranes by the hot-casting method on AAO support¹³². Although an excellent molecular sieving property resulted in an H_2/CO_2 selectivity of 290 and H_2 permeance of 2700 GPU, this method should be examined for other MOFs with different ligands and functionalities. The bottom-up methods are suitable for growing MOFs on porous solvents to construct defect-free ultra-thin membranes without having the concerns of poor adhesion and the compatibility of the MOFs with the sublayer. The development of a simple reaction for direct synthesis of 2D MOF nanosheets with high efficiency and yield has been a struggle. Nian *et al.*⁴² designed a facile

bottom-up method to develop 2D Co-MOF nanosheets with the assistance of NH_4OH as a modulator (ammonia-assisted strategy). A similar approach was employed to make a 2D-ZIF membrane on porous alumina hollow fiber with the help of ZnO self-conversion and ammonia as a modulator⁸⁴. Zhang *et al.* developed H_2/CO_2 membranes by deposition of 2D-Co-MOF nanosheets on a tubular porous ceramic support via ligand vapor phase transformation approach⁴¹, which could be very challenging by the conventional casting methods (e.g. vacuum filtration, spin coating, etc.). The 2D MOF membrane with a thickness of 57 nm exhibited a very high H_2/CO_2 selectivity of about 59. In another study, 2D Zn-MOF membranes with the H_2/CO_2 selectivity of 106 were developed using ZnO particles as seeds to grow the MOF nanolaminates⁴³. Ghalei *et al.*³⁹ prepared different MOFs membranes on alumina supports using the *in-situ* solvothermal method. It was observed that using bulky ligands improves the sieving ability and H_2 selectivity against other gases. Density functional theory (DFT) calculations also confirmed that the diffusivity of CO_2 , N_2 , and CH_4 molecules through the pores decreased in MOFs with bulkier organic ligands, while the H_2 permeation was not affected. In conclusion, MOFs membranes are well-studied due to the facile tuning of the pore size, versatile structures, and abundant functional groups. However, the delamination of 2D MOFs and the high flexibility of the membranes are two weaknesses that have hindered their use as self-standing membranes, despite many advantages that they can offer.

7.3. Graphene Oxide Membranes

While graphene is impermeable to small gases such as H_2 and He due to the π -electron clouds density of aromatic rings¹³³, GO with hydroxyl, epoxy, and carboxyl functional groups is extensively investigated in the gas separation membrane field. The GO membranes have been prepared via the membrane fabrication methods previously described. The channels between the adjacent GO sheets and the gas interactions with oxygen-containing functional groups control the

mass permeation. The external force during the membrane preparation induces the alignment of nanosheets and tunes the spacing between the adjacent GO sheets ⁷¹. Generally, controlling the spacing between the GO layers is an effective approach for designing high-performance separation membranes. The introduction of cations and other inorganic fillers (e.g. MOFs) into the interlayer region has been employed to control the d-spacing of GO membranes ¹³⁴. The physical mixing of UiO66 with GO and the interactions between the functional groups resulted in a higher H₂ permeability and H₂/N₂ and H₂/CO₂ selectivities ¹³⁵. In addition, the intergrowth of zeolite on the GO layers lowered the d-spacing and caused an improvement in the separation performance of the GO membranes ¹³⁶. Moreover, the covalently bonded organic molecules on the GO layers increased the stability and narrowed the interlayer spacing ⁷⁰. There have been studies on GO-based membranes to investigate the effects of GO properties (lateral size, oxidization, defects, etc.), different supports, functionalization, and their composites with inorganic and polymer matrices on the gas separation performance of the membranes. However, more efforts should be allocated to scale up the membrane separation process, enhance the stability of the membranes against humidity, and reduce the pinholes and defects during the coating process.

7.4. 2D COF Membranes

Covalent organic frameworks (COFs) are porous crystalline polymers with highly ordered and coplanar backbone structures, which can be easily exfoliated into single layers ^{137, 138}. Therefore, they were vastly investigated in membrane and storage applications; however, there are few reports on using COFs membranes for gas separation because their large pore size (>1 nm) is larger than all gas kinetic diameters leading to no molecular sieving. The post-modification of COFs with different functional groups (e.g. hydroxyl, epoxy, and acetyl) ¹³⁷, and bilayer composites were introduced as effective approaches to reduce the aperture size to about 3–5 Å. Fan *et al.* reported H₂-selective COFs membranes by successfully growing azine-based ACOF-1 and imine-based

COF-LZU1 layers by the solvothermal method ⁹⁴. The fabrication of bilayer COFs membranes requires a pore engineering technique to obtain high-selective membranes. The COF-COF membranes exhibited much higher H₂/CO₂, H₂/CH₄ and H₂/N₂ selectivities than the individual COF membranes. The concept of COF and cellulose nanofibers (CNFs) composites was later introduced by Yang *et al.* to tune the pore size of 2D COFs membranes for different applications ¹³⁹.

7.5. Transition Metal Dichalcogenides Membranes

2D Transition metal dichalcogenides (TMDs) are nonporous layered materials with the formula of X-M-X, where M is a transition metal (IV, V or VI) placed between two chalcogen atomic layers (mostly S and Se) ¹⁴⁰. The weak van der Waals interactions between the layers facilitate the intercalation of organic molecules and delamination of TMDs into monolayers, making them desirable for separation and storage ¹⁴¹. MoS₂ and WS₂ membranes have been extensively studied for gas separation. For example, the full exfoliation of MoS₂ was accomplished by butyl lithium, followed by coating on alumina supports to evaluate the H₂/CO₂ separation efficacy of the membranes. Although the 17 nm thick membrane demonstrated a very high H₂ permeance (27440 GPU), the H₂/CO₂ selectivity was 3.4, lower than the Knudsen selectivity of H₂/CO₂ ~4.7 ¹⁴². In another work ¹⁴³, a 500 nm membrane was prepared from a 1T-MoS₂ solution on an alumina support. The H₂/CO₂ selectivity of 8 was explained by the higher chemical/physical properties of the 1T-MoS₂ phase than the typical 2H-MoS₂, however, the synthesis of 1T phase was challenging ¹⁴⁴. The filtration of CO₂-philic [BMIM][BF₄] ionic liquid through the assembled MoS₂ film membranes resulted in CO₂ selective membranes with an acceptable CO₂/N₂ selectivity ¹⁴⁵. Although there have been several studies on the TMDs-based membranes, the weak interactions between layers during the membrane fabrication led to poor mechanical integrity and improper layers assembly, which caused poor separation properties.

8. Conclusion and Outlook

The ideal material for gas and liquid separation should exhibit simultaneously high permeability and selectivity to ensure satisfactory energy efficiency and productivity. The discovery of the 2D nanomaterials, MXenes, which have good thermal and chemical stability, has motivated researchers to use them for the fabrication of gas and liquid separation membranes. This review put into perspective the attractive gas-separation properties of MXene-based membranes. Both pure MXene and polymers embedded with MXene flakes were considered in this review. The unique structure and the surface functional groups of MXenes have a substantial effect on the membrane separation performance. Tuning of the interlayer spacing and the packing density of nanoslits through the surface modification of MXene flakes enhance the gas diffusivity and solubility coefficients.

The research on MXene-based membranes for gas separation shows the high potential of the membranes. So far, the research has been limited to laboratory-scale studies. The membranes' performance under realistic conditions such as high feed pressure deviates from that measured under laboratory ideal conditions. Although 2D materials have high mechanical properties (e.g. tensile strength > 50 MPa and Young's modulus of 3.8 GPa for 2 μ m MXene membrane¹⁷), it is still not certain if the membranes can withstand a realistic harsh pressure such as the pressure of a natural gas sweetening process (ca. 65 bar)¹⁴⁶. Moreover, the separation properties of most 2D membranes reported in the literature have been recorded under zero transmembrane pressure in Wicke-Kallenbach gas permeation cells. The gas selectivity of uncoated support needs to be determined beforehand to check if the backflow of carrier gas takes place. At best, the selectivity of the support is Knudsen selectivity, and any larger values ascertain the backflow and pseudo-separation properties. An unreal selectivity can be avoided by conducting the gas permeation testing of 2D laminar membranes at a minimum feed pressure.

Thus, studies on the commercialization of these membranes need to be conducted. First, industrial-scale production of MXenes should be addressed. The harsh chemical etching method for MXene synthesis not only could damage the flakes and reduce the lateral size, but also it would limit scaling up the production. The recently developed 2D transition metal borides (MBenes) are worth mentioning due to their high stability and milder etching reaction, which makes them more valuable over MXenes in terms of sustainability for gas separation membranes ¹⁴⁷. Second, the long-term stability of MXenes is another obstacle in using these materials for practical applications. Luckily, many efforts have been devoted to stabilize the MXene structure against oxidation and ultraviolet (UV) light by modifying MXene's surface, mixing MXenes with polymers, preparing MXene/inorganic materials composites, and optimizing synthesis methods and sonication ¹⁴⁸. Third, the interactions of MXenes with gas molecules, the interactions of composite membranes with other 2D materials, and the effects of termination functional groups and the MXene flake size on the gas separation performance are still not well understood. Fourth, most MXene-based membranes, or generally laminated films, are still prepared with filtration and spin coating methods, which are hard to scale up. Electrophoretic deposition is an effective strategy to scale up the 2D membrane production. The assembly of negatively charged MXene nanosheets on the anode facilitates the control of the membrane thickness by changing the electrophoresis deposition time ¹⁴⁹. Fifth, the fabrication of MXene-based membranes on a large scale with an acceptable homogenous structure and reproducibility is probably the bottleneck for the commercialization, as the pressure difference is not uniform over the porous support. Sixth, computational/theoretical methods such as molecular dynamics (MD) simulations and DFT should be applied more to understand the governing mechanisms of gas transport, especially the dominant transport regimes for each gas at the different sizes of nanochannels and functional groups.

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