Two-Dimensional-Material Membranes: Manipulating the Transport Pathway for Molecular Separation

Long Cheng, Gongping Liu, Jing Zhao, and Wanqin Jin*

CONSPECUTUS: The discovery of graphene triggers a new era of two-dimensional (2D) materials, which exhibit great potential in condensed matter physics, chemistry, and materials science. Meanwhile, the booming of 2D materials brings new opportunities for the next generation of high-performance (high permeability, selectivity, and stability) separation membranes. Two-dimensional materials with atomic thinness can serve as new building blocks for fabricating ultrathin membranes possessing the ultimate permeation rate. The plane structure with micrometer lateral dimensions provides an excellent platform for the orderly alignment of the nanosheets. Moreover, the apertures of two-dimensional-material membranes (2DMMs), including the in-plane nanopores and interlayer channels, can contribute to the fast and selective transport of small molecules/ions related to molecular separation. Therefore, the emerging 2D materials with various nanostructures, including graphene oxide (GO), zeolite nanosheets, metal−organic framework (MOF) nanosheets, and transition-metal carbides/carbonitrides (MXene), can be assembled into high-performance membranes. Various assembly methods such as filtration, spin coating, and hot dropping have been employed to fabricate 2DMMs, while the processes for separating small molecules/ions tend to demand higher precision, especially in water desalination and gas separation. The nanostructures of 2DMMs and the physicochemical properties of transport pathway need to be finely tuned to meet the requirement. In addition, the stability of 2DMMs, which is critical to the large-scale implementation, must be taken into consideration as well.

In this Account, we discuss our recent progress in manipulating molecular transport pathways in 2DMMs by optimizing the assembly behavior of 2D nanosheets, tuning the microstructure of interlayer channels, and controlling the physicochemical properties of the membrane surface. Assembly methods, including vacuum suction assembly, polymer-induced assembly, and external force-driven assembly, have been proposed to construct ordered laminates for molecular transport. The size and chemical structure of interlayer channels were further tailored by strategies such as nanoparticle intercalation, cationic control, and chemical modification. Interestingly, the manipulation of surface properties of 2DMMs was proven to contribute to fast molecular transport through interlayer channels. Moreover, the issues concerning 2DMMs toward practical applications are discussed with an emphasis on the substrate effect, molecular bridge strategy, and preliminary progress in large-scale fabrication. Finally, we conclude this Account with an overview of the remaining challenges and the new opportunities that will be opened up for 2DMMs in molecular separation.

1. INTRODUCTION TO MEMBRANES FOR MOLECULAR SEPARATION

Membranes play an imperative role in systems such as batteries, barrier packages, and especially large-scale energy-efficient separation and purification systems. During the separation process, the membranes can restrict the movement of some components (molecules, ions, and small particles) while letting others penetrate by forming a selective barrier. Compared with
conventional separation technologies such as distillation and adsorption, membrane technology has advantages such as low energy consumption, simple operation, and environmental friendliness. High-performance (high permeability, selectivity, and stability) membrane materials are demanded for the practical application of membrane technology. Typically, polymeric membranes and ceramic membranes have been widely used in industrial separation processes. However, polymeric membranes usually exhibit a tradeoff between permeability and selectivity. Ceramic membranes face the issue of relatively high production cost. Since the successful fabrication of graphene by Geim and co-workers, graphene has demonstrated great potential in various fields such as condensed matter physics and materials science, triggering great attention for two-dimensional (2D) materials. With atomic thinness, 2D materials can be assembled into ultrathin membranes, thereby minimizing the transport resistance to maximize the permeation rate according to Poiseuille’s law. The intrinsic pores or subnanometer interlayer channels can provide a fast and selective transport pathway for small molecules/ions. The targeted molecules can directly diffuse across the in-plane nanopores to the permeate side, enhancing the permeation rate. The size-exclusion mechanism and the preferential adsorption at the membrane surface and inside the laminates jointly contribute to the high selectivity. Hence, the 2D-material family, including graphene and its derivatives (GO, reduced GO, etc.), zeolite nanosheets, metal–organic framework (MOF) nanosheets, and transition-metal carbides/carbonitrides (MXene), have become new building blocks for the next-generation membranes for molecular separation.

The ultrathin nanosheet with integrated structure is a prerequisite for fabricating high-performance 2D-material membranes (2DMMs). In general, top-down (exfoliation from the bulk layered crystals) and bottom-up (direct synthesis from the basic building units) methods are employed to synthesize ultrathin nanosheets. Afterward, the nanosheets can be assembled into a continuous separation layer via filtration, spin coating, hot dropping, and so on. The nanosheets are either porous or nonporous, and the as-fabricated membranes can be correspondingly categorized into two types: a porous nanosheet membrane and a laminar membrane (Figure 1). The nanosheet membrane is composed of monolayer or a few layers of 2D material with intrinsic or drilled in-plane nanopores, allowing for the selective permeation of molecules or ions. The latter (laminar membrane) is fabricated by assembling nanosheets into laminates with interlayer channels for molecular transport. The manipulation of the nanoarchitecture and the physico-chemical property of 2DMMs can enhance the selective molecular permeation property, contributing to extraordinary molecular separation performance in membrane processes such as nanofiltration, forward osmosis, pervaporation, and gas separation.

In this Account, we aim to describe the strategies for manipulating the transport pathway of 2DMMs for precise molecular separation. Two-dimensional nanosheets can be assembled into ordered laminates via vacuum suction, polymer induction, or an external-force-driven method. To further improve the permeation rate and separation efficiency, various strategies have been proposed to tune the aperture size and surface properties (such as hydrophilicity and charge density) of 2DMMs. From the aspect of practical applications, the stability and scalable fabrication of 2DMMs are discussed as well. Finally, future challenges and opportunities are prospored for 2DMMs research.

2. OVERVIEW OF TWO-DIMENSIONAL-MATERIAL MEMBRANES AND CHALLENGES

The diversity of 2D materials provides great opportunities for the development of 2DMMs. On one hand, the nanosheet membranes can be derived from zeolite nanosheets, MOFs, or porous graphene. By rationally designing the aperture size and porosity of in-plane nanopores, the permeation rate and selectivity of the membranes can be simultaneously enhanced. On the other hand, nonporous nanosheets including graphene oxide (GO) and MXene can be assembled into a laminar membrane with ordered structure. The tuning of the interlayer channels dominates the molecular transport through the laminates. In terms of the separation performance, the porous nanosheet membrane could exhibit a higher permeation rate than laminar membranes due to the ultimate membrane thinness. However, the porous nanosheet membrane would bring about a greater challenge in the membrane sealing and durability during practical applications. In addition, the laminar membrane is relatively more convenient to fabricate, which is favored over the large-scale fabrication of membranes. Many efforts have been devoted to designing the nanostructures of membranes and improving the separation performance. Nevertheless, great challenges still lie in the manipulation of transport channels for precise molecular separation such as the rejection of ions from water. In addition, the stability and the scale-up fabrication of 2DMMs should be seriously taken into account to promote practical applications.
2.1. Porous Nanosheet Membranes

Zeolites are crystalline silica-based materials with pore sizes ranging from 0.25 to more than 1 nm, which are close to the size of small molecules and thus can realize efficient separation based on molecular sieving. Tsapatsis and co-workers successfully synthesized ∼3.4-nm-thick MFI (an aluminosilicate zeolite belonging to the pentasil family of zeolites) nanosheets via a top-down method and applied the MFI nanosheet membrane supported on the α-Al₂O₃ substrate to the separation of xylene isomers (Figure 2a–c). The nanopores along the direction of membrane thickness can greatly shorten the transport pathway and enhance the molecular sieving property. The permeation system was operated in Wicke–Kallenbach mode (Supporting Information Note 1). They also proposed the bottom-up synthesis of high-quality MFI nanosheets via a nanocrystal-seeded growth method. Depositing the nanosheets with large lateral sizes can efficiently cover the support during the seed-coating process and lower the density of grain boundaries, which can decrease the nonselective pathway and further enhance the separation performance. As was shown in Table 1, the p-xylene/o-xylene separation selectivity of MFI membranes fabricated with high-quality nanosheets was enhanced ∼30 times, demonstrating the crucial effect of high-quality nanosheets on the fabrication of high-performance 2DMMs. Recently, Agrawal et al. reported the condensation of RUB-15 zeolite nanosheets to prepare H₂-selective zeolite membranes without the traditional hydrothermal treatment, which is beneficial to promoting the reproducibility and scalable synthesis of zeolite membranes.

Figure 2. Porous nanosheet membranes for molecular separation. (a) Structure of MFI nanosheets. (b) AFM image of the MFI nanosheet and the corresponding height profile. Scale bar: 100 nm. (c) Cross-sectional SEM images of MFI membranes. (d) Grid-like structure of the Zn₂(bim)₄ nanosheet. (e) TEM image of Zn₂(bim)₄ nanosheets, with the Tyndall effect of a colloidal suspension. (f) Cross-sectional SEM image of an ultrathin Zn₂(bim)₄ nanosheet layer on an α-Al₂O₃ substrate. (a and b) Reproduced with permission from ref 10. Copyright 2011 American Association for the Advancement of Science. (c) Reproduced with permission from ref 14. Copyright 2014 John Wiley & Sons. (d–f) Reproduced with permission from ref 9. Copyright 2014 American Association for the Advancement of Science.

Table 1. Gas Separation Performance of the Representative Nanosheet Membranes and Laminar Membranes

<table>
<thead>
<tr>
<th>membrane type</th>
<th>no.</th>
<th>membrane structure</th>
<th>fabrication method</th>
<th>feed condition</th>
<th>permeance</th>
<th>selectivity</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanosheet membrane</td>
<td>1</td>
<td>MFI/α-alumina</td>
<td>vacuum filtration and secondary growth</td>
<td>p-xylene/o-xylene/He (0.5:0.5:99, 150 ºC)</td>
<td>3 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹</td>
<td>64</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>MFI/porous silica</td>
<td>vacuum filtration and gel-free growth</td>
<td>p-xylene/o-xylene/He (0.5:0.5:99, 150 ºC)</td>
<td>5.6 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹</td>
<td>2000</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>RUB-15 /AAO</td>
<td>vacuum filtration</td>
<td>H₂/CO₂ (250 ºC)</td>
<td>219 GPU</td>
<td>90</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Zn₂(bim)₄/α-Al₂O₃</td>
<td>hot-drop coating</td>
<td>H₂/CO₂</td>
<td>2700 GPU</td>
<td>291</td>
<td>9</td>
</tr>
<tr>
<td>laminar membrane</td>
<td>1</td>
<td>GO/AAO</td>
<td>vacuum filtration</td>
<td>H₂/CO₂</td>
<td>10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹</td>
<td>3400</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>GO/PES</td>
<td>spinning coating</td>
<td>CO₂/N₂</td>
<td>120 GPU</td>
<td>55</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>GO/PES borate cross-linking</td>
<td>thermal reduction</td>
<td>H₂/CO₂ (140 ºC)</td>
<td>1000 GPU</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>GO/PES hollow fiber</td>
<td>bovine cross-linking</td>
<td>CO₂/CH₄</td>
<td>665 GPU</td>
<td>79</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CO₂/N₂</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CO₂/N₂ (15:85, 80 ºC)</td>
<td>1020 GPU</td>
<td>680</td>
<td>30</td>
</tr>
</tbody>
</table>

Operated for a feed of mixed gas (50:50 v%/v%) and at room temperature unless otherwise indicated. ¹1 GPU = 10⁻⁶ cm³ (STP)/(cm² s cmHg). AAO: anodic aluminum oxide. PES: polyether sulfone.

2.1. Porous Nanosheet Membranes

Zeolites are crystalline silica-based materials with pore sizes ranging from 0.25 to more than 1 nm, which are close to the size of small molecules and thus can realize efficient separation based on molecular sieving. Tsapatsis and co-workers successfully synthesized ∼3.4-nm-thick MFI (an aluminosilicate zeolite belonging to the pentasil family of zeolites) nanosheets via a top-down method and applied the MFI nanosheet membrane supported on the α-alumina substrate to the separation of xylene isomers (Figure 2a–c). The nanopores along the direction of membrane thickness can greatly shorten the transport pathway and enhance the molecular sieving property. The permeation system was operated in Wicke–Kallenbach mode (Supporting Information Note 1). They also proposed the bottom-up synthesis of high-quality MFI nanosheets via a nanocrystal-seeded growth method. Depositing the nanosheets with large lateral sizes can efficiently cover the support during the seed-coating process and lower the density of grain boundaries, which can decrease the nonselective pathway and further enhance the separation performance. As was shown in Table 1, the p-xylene/o-xylene separation selectivity of MFI membranes fabricated with high-quality nanosheets was enhanced ∼30 times, demonstrating the crucial effect of high-quality nanosheets on the fabrication of high-performance 2DMMs. Recently, Agrawal et al. reported the condensation of RUB-15 zeolite nanosheets to prepare H₂-selective zeolite membranes without the traditional hydrothermal treatment, which is beneficial to promoting the reproducibility and scalable synthesis of zeolite membranes.
As a new class of porous crystalline materials, MOFs are composed of metal clusters and organic ligands. The physicochemical properties of MOFs can be finely tuned by selecting the appropriate building blocks or by postsynthetic modification, thus leading to tailored pore sizes and transport properties for molecular separation. Yang and co-workers successfully synthesized Zn₂(bim)₄ (bim = benzimidazole) MOF nanosheets and assembled them into ultrathin MOF membranes (Figure 2d−f). By investigating the structure−performance relationship of the MOF membranes, they showed that the disordered nanosheets could lead to high-performance gas separation membranes while the ordered laminates blocked the permeation pathway for gas molecules. The as-prepared Zn₂(bim)₄ membrane exhibited extremely high separation performance with an H₂ permeance of 2700 GPU (gas permeation unit, 1 GPU = 10⁻⁶ cm³ (STP)/(cm² s cmHg)) and H₂/CO₂ selectivity of up to 291. The gas separation performance of the nanosheet membranes is summarized in Table 1. It is worth mentioning that the stacking mode of porous nanosheets, namely, the configuration of vertical neighboring nanosheets, will influence the molecular transport (Supporting Information Note 2). However, on the basis of an assembly method such as filtration or hot-drop coating, it remains quite challenging to realize the alignment of nanopores within subnanometer precision.

A porous graphene membrane holds the potential to achieve superior separation performance because of its ultimate thinness. The impermeability and chemical inertness of graphene motivated the studies on perforating graphene nanosheets to prepare porous graphene membranes. The molecular dynamics simulation by Grossman and co-workers demonstrated the great potential of nanoporous graphene for water desalination. Moreover, perforation technologies such as ultraviolet-induced oxidative etching, focused ion beam etching, and oxygen plasma etching have been used to fabricate porous graphene membranes. Despite recent progress, porous graphene membranes still face several challenges: (i) the intrinsic defects produced during the CVD process and the extrinsic defects generated from the transfer of graphene to the support would affect the separation performance; (ii) the current technology cannot realize the precise perforation and the fabrication of high-density nanopores on the large-area membrane for industrial application; (iii) the ultimate thinness and the perforation process would cause poor mechanical stability, restricting the practical implementation. By contrast, the laminar membrane fabricated by assembling multilayer nanosheets demonstrates greater potential in the large-scale fabrication and practical application, which will be further discussed later.

2.2. Laminar Membranes

In addition to the in-plane intrinsic pores, 2D nanosheets can be facilely assembled into laminar membranes with interlayer channels for selective molecular transport. GO is the mostly studied building block for laminar membranes because there are abundant oxygen-containing functional groups distributed on the surface and edges of the nanosheets, which enable GO dispersibility in water for easy processing and provide active sites for chemical modification. Nevertheless, based on the numerous studies on GO-based membranes, a large variability in the separation performance of membranes was observed as a result of the differences in membrane synthesis conditions and
the measurements of transport properties. Vecitis et al. proposed the standardization of raw GO powders, membrane fabrication methods, and performance testing experiments to promote the development of reliable high-performance GO membranes.

Geim’s group first reported the unimpeded water permeation in GO membranes while being completely impermeable to liquids, vapors, and gases (the transmembrane differential pressure during the permeation test was less than 100 mbar; Figure 3a,b). On the basis of the theoretical calculation, they found that the nearly frictionless surface of the nanoxidized region of GO nanosheets facilitates the ultrafast flow of water molecules. They further found that the size sieving effect of the 2D GO channels enabled the fast permeation of ions with a small hydrated radius while rejecting species with radii larger than 0.45 nm in water (the membrane was tested under an osmotic pressure of ~25 bar for a 1 M sucrose solution). The molecular dynamics simulations revealed that ultrafast ion permeation was attributed to a capillary-like high pressure acting on ions inside graphene capillaries. In 2014, we first prepared laminar GO membranes on scalable ceramic hollow fiber substrates, which exhibited the selective transport of water molecules from a dimethyl carbonate/water solution (Figure 3c,d).

Besides possessing a prominent water/ion transport ability, the GO laminar membrane exhibited huge potential in gas separation. In 2013, Park and co-workers fabricated several-layer (3–10 nm) GO membranes via spin-coating, resulting in tunable gas transport behavior for H2 and CO2 molecules. By the manipulation of face-to-face and edge-to-edge interactions of nanosheets during the assembly process, the as-prepared membranes can form highly interlocked structures, realizing the selective permeation of CO2 molecules. Meanwhile, Yu’s group employed a filtration method to prepare ultrathin (1.8–18 nm) GO membranes that showed extraordinarily high permeation selectivity toward H2 over CO2 (N2) molecules, which was attributed to selective structural defects on GO nanosheets.

Apparently, the assembly method plays a significant role in determining the membrane microstructures and thus the molecular transport behavior. In addition, the size of interlayer channels of laminar GO membranes can be tuned by cross-linking, contributing to the enhanced molecular sieving property. In some cases, the cross-linkers can serve as carriers for facilitating the transport of targeted molecules, further improving the separation performance.

2.3. Critical Challenges

On the basis of the early research on 2DMMs, the critical progress can be summarized as the synthesis of high-quality nanosheets with integrated structure and the construction of in-plane or interlayer channels for molecular separation. Compared with traditional membranes, 2DMMs exhibited outstanding separation performance mainly because of the ultrathin property and ordered transport pathways. For the nanosheet membranes, the challenges lie in the difficulties of synthesizing nanosheets with integrated structure and improving the yield and reproducibility of nanosheets, which can push the fabrication of large-area membranes for practical application. For the laminar membranes, although some strategies such as cross-linking have been proposed to tune the interlayer channels, the separation efficiency remains to be improved for applications in more demanding systems such as water desalination and olefin/paraffin separation. Compared with the nanosheet membranes, the laminar membranes possess several advantages: (i) the membrane fabrication process such as simple filtration and blade coating is more convenient than that of nanosheet membranes (secondary growth, uniform perforation, etc.); (ii) the membrane structure of assembled laminates is more durable and can bear a higher operation pressure; and (iii) the size of interlayer channels is more controllable than the pore size of nanosheet membranes via physical or chemical approaches.

3. MANIPULATING THE TRANSPORT PATHWAY IN A TWO-DIMENSIONAL-MATERIAL MEMBRANE

To realize the fast and selective transport pathways in 2DMMs, we proposed three main strategies for designing the nanostructures and tuning the physicochemical properties of laminar membranes to enhance the molecular separation performance. Particular attention should be paid to the stability of 2DMMs for real-world applications. In this regard, we introduced new tools such as molecular bridges to strengthen the stability of GO membranes in an aqueous system, which can be extended to other kinds of 2D materials.

3.1. Creating Laminar Structures

The selection of a nanosheet assembly strategy can determine the membrane nanostructures and transport behavior. For instance, during the self-assembly of GO nanosheets, intrinsic repulsive forces between the carboxyl groups of neighboring nanosheets would lead to random plane–plane stacking and oversized interlayer channels. Moreover, during the air–water interfacial assembly, even low ionic strength would cause the aggregation of GO nanosheets. The oversized interlayer spacing or defects generated from aggregation could greatly decrease the molecular sieving property of 2D channels and thus the membrane separation performance. Therefore, driving forces such as external forces (pressure difference, shear force, centrifugal force, etc.) or additional molecular interactions are demanded to simulate the ordered stacking of nanosheets. We have proposed polymer induction and external-force-driven (vacuum suction force, molecular interaction, etc.) methods to create well-defined interlayer channels, providing an excellent molecular sieving property.

With the vacuum suction assembly approach, we successfully fabricated laminar GO membranes on a ceramic hollow fiber substrate. A digital photograph showed the uniform coverage of GO nanosheets on the curved surface of the ceramic hollow
From the cross-sectional view, the GO layer exhibited typical laminar structure with a thickness of ∼1.5 μm, indicating the ordered stacking of GO nanosheets on the support. The as-fabricated GO membranes exhibited selective water permeation with a separation factor of 740 and a total permeation flux of 1702 g m⁻² h⁻¹ during pervaporation separation of dimethyl carbonate/water mixtures (at 25 °C, a pressure difference of ∼1 bar and a 2.6% feedwater content). The extraordinary separation performance is attributed to the preferential water sorption ability and fast water diffusivity through the GO laminates. This work demonstrated the feasibility of employing a driving force to simulate nanosheet assembly.

The vacuum suction method and polymer-induced assembly have proven the validity of mechanical external force and molecular interactions for the assembly of nanosheets into ordered laminates. To further regulate the interlayer channels and avoid the formation of defects, we reported an external force-driven assembly approach that combines the effect of the mechanical external force and molecular interaction on the nanosheet assembly (Figure 5d). Specifically, the outer external forces, composed of a compressive force, a centrifugal force, and a shear force, were applied outside the laminates, and the inner external force, namely, the molecular interaction between GO and intercalated molecules, was applied inside the laminates. The self-assembled GO membrane induced by...
intrinsic forces exhibited a poorly stacked structure with visible defects (Figure 5e). Figure 5f,g showed that the individual effect of outer or inner external forces would lead to a relatively random stacking of GO nanosheets in different orientations. In contrast, under the synergistic effect of outer and inner external forces, GO nanosheets were assembled in almost the same direction to form a highly ordered laminar structure with subnanometer channels (Figure 5h,i). The introduced polymer with positively charged amine groups could form an electrostatic interaction and covalent bonds with GO nanosheets, which was confirmed by the molecular simulation and XPS characterization.31 As a result, tiny defects were efficiently eliminated to form ordered laminates, contributing to the high H₂/CO₂ selectivity of 29. The as-prepared GO membranes with excellent an molecular-sieving property exhibited a 2 to 3 orders of magnitude higher H₂ permeability and a 3-fold enhancement in H₂/CO₂ selectivity compared to commercial gas separation membranes (Figure 5j,k). In all, the assembly strategies of GO nanosheets laid the foundation for the further precise manipulation of 2DMMs applied for the separation of even more challenging species such as water and ions.

3.2. Tuning Interlayer Channels

As we know, GO nanosheets are highly dispersible in water due to the hydrophilicity derived from the oxygen-containing groups on the nanosheets. On one hand, the good dispersibility contributes to the easy processing of GO nanosheets in aqueous solution for membrane fabrication. On the other hand, however, GO nanosheets become negatively charged upon hydration, and the electrostatic repulsive force will lead to the disintegration of GO laminates.41 Therefore, chemical cross-linking or reduction of GO nanosheets was employed to stabilize the membrane structure.41,42 Nevertheless, the narrowed interlayer spacing sacrificed water permeance.43 To address this issue, we synthesized Fe₃O₄@GO nanosheets as the building blocks for...
fabricating 2DMMs,45 in which Fe₃O₄ nanoparticles with an average diameter of 200 nm were uniformly distributed on the GO nanosheets via \textit{in situ} growth, enlarging the interlayer space to enhance the water permeance without affecting the ordered stacking of GO nanosheets (Figure 6a−c). During the \textit{in situ} growth of nanoparticles, the GO nanosheets were partially reduced, with the C/O ratio increasing from 1.9 to 3.1, thereby enhancing the GO membrane stability in water. In another work,36 we investigated the effect of the extent of GO reduction on the membrane stability. The result showed that the GO membrane with the highest extent of reduction possessed the lowest \textit{d}-spacing expansion when changing from the dry to the wet state, namely, the highest water stability. The as-fabricated Fe₃O₄@GO membranes exhibited a high water permeance of 296.03 L m⁻² h⁻¹ bar⁻¹ while maintaining a high dye rejection of 98.14%. The \textit{in-situ}-synthesized Fe₃O₄@GO building blocks endowed the membranes with 1 to 2 orders of magnitude higher water permeance compared to that of the counterparts and excellent rejection for various organics and ions.

The challenge of GO membranes for water desalination is mainly the fact that the empty interlayer space of hydrated GO laminates was \textasciitilde 9.0 Å,35 which is larger than the diameters of hydrated ions of common salts and thus insufficient for the rejection of these ions. Wang and co-workers proposed the coassembly of GO nanosheets and the polymer, followed by reduction and carbonization, contributing to the tunable subnanometer pores in ultrathin graphene membranes.46 The as-fabricated intercalated graphene membranes exhibited ultrafast water evaporation in the desalination process and extraordinary pervaporation dehydration performance for ethanol/water mixtures.47 Seo et al. fabricated CVD graphene membranes for water desalination via a membrane distillation process.48 The synthesized graphene membranes possessed a high density of nanochannels distributed across the graphene grains, realizing high water vapor flux, excellent salt rejection, and sustained antifouling capability. Nair and co-worker reported a physical confinement method to tune the interlayer spacing of GO membranes from 9.8 to 6.4 Å by controlling the relative humidity.49 Although efficient ion rejection was obtained, such a physical confinement method is rather complicated and difficult to realize on a large scale. Vecitis et al. employed easy-to-implement photoreduction to control the oxygen content and thus the interlayer spacing of GO nanosheets, demonstrating the predominant effect of the nanochannel height on water transport.50 Nevertheless, the achieved interlayer spacing did not hold in hydrated environments with swelling.
In 2017, we discovered that cations can precisely manipulate the interlayer spacing of GO laminates (Figure 6d−f).35 The GO membrane was simply immersed in a salt solution such as KCl for several minutes, leading to a fixed interlayer space. Theoretical calculation revealed that the interactions between the hydrated cations and aromatic rings of GO (cation−π interactions) and between the hydrated cations and the oxidized groups from GO nanosheets determined the fixing of the interlayer space. We demonstrated various cations including K+, Na+, Ca2+, Li+, and Mg2+ to control the interlayer space of GO membranes with Ångström precision. The GO membranes treated with KCl solution showed the narrowest interlayer space of 11.4 ± 0.1 Å because of the smallest hydrated diameter of K+. With the distortion of the hydrated structure of K+ inside the GO nanosheets, the K+-controlled membranes can reject K+ itself as well. As a result, the GO membranes controlled by K+ realized efficient ion rejection (the reduction in the ion permeation rate) of more than 99% relative to the pristine GO membrane. Other cations such as Fe2+, Co2+, Cu2+, Cd2+, Cr3+, and Pb2+ were theoretically proven to form a stronger cation−π interaction with graphene, demonstrating a wider range of interlayer spaces of GO membranes with potential applications in water desalination, ion separation, gas separation, and energy storage.

Besides cationic control of the interlayer spacing of GO laminates, other strategies including intercalation and chemical modification were proposed to tune the apertures and physicochemical properties of the interlayer channels of other 2D nanosheets. MXene possesses a formula of $\text{M}_{n+1}\text{X}_n\text{T}_x$, where M is an early transition metal, X is carbon and/or nitrogen, and n ranges from 1 to 3.33 The synthesis of MXene in an aqueous medium endows the nanosheets with terminal functional groups (Tₓ) including −Hₓ, −O, and −F groups, which is beneficial for chemical modification. Wang et al. introduced Fe(OH)₃ nanoparticles as spacers to expand the interlayer channels of the MXene laminar membrane and then removed the nano-
particles with an acid solution to create nanochannels for molecular transport.\textsuperscript{11} The resulting MXene membranes with effective pore sizes of 2–5 nm showed excellent water permeance (\(\sim 1000 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}\)) and a favorable rejection rate for molecules with sizes larger than 2.5 nm. Similarly, the nanostrand-channeled GO membrane with an effective pore size of 3–5 nm had a comparable water permeance of \(575 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}\), demonstrating the advantage of ultrafast water transport in the nanomaterial-intercalated 2DMMs.\textsuperscript{31} They further reported MXene membranes with highly ordered nanochannels with an interlayer height of \(\sim 0.35 \text{ nm}\), serving as excellent molecular sieves with a \(\text{H}_2\) permeability of \(\sim 2200\) Barrer and a \(\text{H}_2/\text{CO}_2\) selectivity of \(\sim 160\).\textsuperscript{32} For comparison, the GO membrane with a similar interlayer height of \(\sim 0.4 \text{ nm}\) had a \(\text{H}_2\) permeability of 1200 Barrer and a \(\text{H}_2/\text{CO}_2\) selectivity of 29.\textsuperscript{31} The differences in both of the membrane physical structure (minor defects) and chemical structure (\(\text{CO}_2\)-philic groups) could affect the gas separation performance of MXene membranes and GO membranes even with similar interlayer heights.

Besides the size sieving effect of interlayer channels, the molecular transport through 2DMMs is also influenced by the preferential adsorption properties of nanochannels. In this regard, we proposed a chemical modification of MXene interlayer channels to enhance the adsorption toward targeted molecules (Figure 6g–i).\textsuperscript{33} The pristine nanochannels of ultrathin (\(\sim 20 \text{ nm}\)) MXene membranes exhibited ultrafast molecular sieving performance for \(\text{H}_2/\text{CO}_2\) separation. To realize the chemical tuning of transport nanochannels, the borate and poly(ethyleneimine) (PEI) molecules were introduced into interlayer channels, delicately regulating the interlayer space and \(\text{CO}_2\) affinity of MXene nanosheets. On one hand, the \(\text{H}_2\) diffusivity of the modified MXene membrane was decreased due to the shrinkage of transport channels (from 0.52 to 0.34 nm) caused by the cross-linking, while the diffusion of \(\text{CO}_2\) was promoted by the \(\text{CO}_2\) carrier effect of the introduced borate molecules. On the other hand, the \(\text{CO}_2\)-philic PEI and borate agents further enhanced the \(\text{CO}_2\) solubility in the MXene membrane to boost the \(\text{CO}_2\) permeation. As a result, the MXene nanochannels were transformed from \(\text{H}_2\)-selective to \(\text{CO}_2\)-selective. Studies on the manipulation of 2D nanochannels with tunable interlayer spaces and the stacking behavior of nanosheets are beneficial to using 2DMMs for precise molecular separation and nanofluidics applications.

\subsection*{3.3. Controlling the Surface Properties}

Generally, the selective transport through membranes for pervaporation and gas separation can be described by a solution-diffusion model.\textsuperscript{34} On the basis of the solution-diffusion theory, permeants dissolve in the membrane and then diffuse through the membrane down a concentration gradient. A separation is achieved between different permeants because of the difference in the number of molecules dissolved in the membrane and the rate at which the molecules diffuse through the membrane. One of the critical factors, the dissolved amount, is dominated by the adsorption property of the membrane material. For the construction of 2DMMs, tuning the surface properties such as the hydrophilicity can intensity the water adsorption ability, which is favorable to the sufficient utilization of fast transport channels and enhances the water permeation rate. Bearing this in mind, we proposed a bioinspired surface hydrophilization strategy to construct ultrafast water channels of GO membranes (Figure 7a).\textsuperscript{32} The GO membranes were prepared by the vacuum suction method, followed by the deposition of an ultrathin (<10 nm) water-capturing polymer layer (chitosan, CS) on the membrane surface. The quartz crystal microbalance (QCM) technique was employed to prove the much stronger water-sorption ability of CS over GO. Moreover, the water contact angle of the CS@GO membrane was lower than that of the pristine GO membrane, indicating that the membrane became more hydrophilic. The enhanced water sorption ability from the polymeric layer and ultrafast water transport in the GO laminates contributed to the highly selective water permeation with an outstanding water flux of >10 000 g m\(^{-2}\) h\(^{-1}\) (the pressure difference is \(\sim 1\) bar), exceeding the performance upper bound of state-of-the-art membranes for butanol dehydration (Figure 7b).

On the basis of the surface hydrophilization strategy, we verified that controlling the surface properties of 2D nanochannels would facilitate the full utilization of interlayer channels and further enhance the molecular-transport efficiency. Aimed at realizing the controllable ion transport, we proposed a strategy of manipulating the surface charge property of GO membranes (Figure 7c).\textsuperscript{35} Various polyelectrolytes were deposited on the surface of GO laminates to create membranes with positive/negative charge and different charge densities. On the basis of the Gouy–Chapman equation and membrane zeta potential, the surface charge densities of membranes can be calculated to be +1.8 and \(-2.32\) mC m\(^{-2}\) for the most positively charged membrane (GO-PDDA) and the most negatively charged membrane (GO-PSS), respectively. The positively charged membrane can prevent the transport of high-valence cations (cations) owing to its high interaction energy barrier while blocking the permeation of electrostatically attracted low-valence counterions (anions) based on balancing the overall solution charge (Figure 7d) and vice versa. Meanwhile, the interlayer channels of GO laminates provided a fast water transport pathway. With the rational design of membrane surface charge and interlayer transport channels, the as-fabricated surface-charged GO membranes showed a prominent
rejection of salts and ultrahigh water permeance, fairly exceeding the performance limit of state-of-the-art Nanofiltration membranes (Figure 7e). The above results in controlling surface hydrophilization and charge demonstrated that the molecular/ionic transport behavior of GO membranes can be manipulated by controlling the surface properties of membranes, which provides new strategies for the design and construction of 2D nanochannels.

4. STABILITY AND LARGE-SCALE FABRICATION

Owing to the synthesis of high-quality nanosheets and the fine-tuning of the transport pathway, the 2DMMs have exhibited unprecedentedly high separation performance in fields such as nanofiltration, solvent dehydration, and gas separation. Further efforts could be devoted to the implementation of 2DMMs for practical separation, mainly involving two critical issues: (1) membrane stability during long-term operation and (2) the fabrication of large-area and defect-free membranes.

One of the great challenges is the structural stability of 2DMMs in water.54 Taking GO membranes, for example, the hydrophilicity of GO nanosheets with oxidized groups will lead to the intercalation of water molecules into interlayer channels, breaking the originally ordered structure and decreasing the separation performance (Figure 8).55 Hence, it is imperative to prevent the swelling of GO membranes to enhance the stability.

Besides the intrinsic stability of the GO laminate, the interfacial adhesion between the GO layer and the substrate is another critical issue for long-term operational stability. First, we proposed to optimize the properties of substrates to enhance the stability of the GO membrane (Figure 9a,b).37 An inorganic ceramic tube, polyacrylonitrile, or polycarbonate was chosen as the substrate for fabricating GO membranes. On one hand, the surface morphological and chemical structures of the substrates were proven to play an important role in the assembly of nanosheets and determine the interfacial adhesion. On the other hand, the bulk pore structure of the substrates directly affected the whole transport resistance of GO membranes. We found that the ceramic substrate with a rigid structure could provide sufficient mechanical strength to GO layer. In addition, the inorganic substrates with chemical inertness, such as the ceramics and carbon nanomaterials, can endure the harsh cleaning with hypochlorite solutions and annealing cycles, endowing industrial applications with great potential.56 The polycarbonate substrate, although possessing straight-through pores for high water permeance, showed poor interfacial adhesion with the GO layer due to its inert surface. In contrast, the polyacrylonitrile substrate with abundant oxidized functional groups after hydrolysis treatment exhibited a remarkably enhanced interfacial adhesion of the GO membrane. Meanwhile, its flat surface with a highly porous sublayer allowed the
formation of a thin, defect-free GO layer and low transport resistance, which is beneficial for achieving fast, selective molecular transport properties. Hence, the requirement for the substrate of GO membranes is a flat surface with oxidized functional groups, straight-through pores, chemical inertness, and sufficient mechanical strength. This work demonstrated the fundamental principles of the substrate effect on the interfacial and transport properties of GO membranes, guiding the design of highly durable GO membranes for water purification.

The swelling of GO membranes in aqueous solution will enlarge the interlayer channels and decrease the sieving property, thereby leading to the disintegration of GO laminates and affecting the long-term operation. Therefore, in addition to the interfacial adhesion between the GO layer and the substrate, the interaction force between the neighboring nanosheets should be enhanced as well. We proposed to build molecular bridges to enhance both the interactions between GO nanosheets and the interactions between the GO layer and substrate\(^6\) (Figure 9c). The interlaminar short-chain molecular bridge was formed by the condensation and nucleophilic addition reaction between polydopamine and GO nanosheets, ensuring the robust assembly of GO laminates and resisting the tendency toward swelling (Figure 9d). Meanwhile, modified chitosan was introduced as the interfacial transition layer to connect the GO layer and substrate by physicochemical interactions, forming the interfacial long-chain molecular bridge. Compared with the chemical reduction of GO nanosheets that can also be employed to stabilize GO membranes, the molecular bridge strategy exhibited a much lower expansion of interlayer spacing (changing from the dry state to the wet state). The rational design of the molecular bridges endowed GO membranes with outstanding durability that could survive harsh conditions (cross-flow and pressure of up to 10 bar), demonstrating their superior stability compared with that of other 2DMMs for water-based separations (Figure 9e). Moreover, this general strategy can be easily applied to other kinds of laminar membranes, promoting the development of reliable 2DMMs for practical application.

Another challenge of 2DMMs toward practical application lies in the membrane-scalable fabrication. In most work, the separation performance of laboratory-scale membrane samples was tested, but tiny defects in large-area membranes will greatly affect the performance. Hence, the strategies for fabricating 2DMMs with a larger membrane area should be proposed, and their separation performance should be further investigated. We proposed to deposit GO membranes on ceramic hollow fibers (Figure 3c), which possess a high packing density and are beneficial to increasing the membrane area in a limited space. Moreover, we scaled up the GO membrane on the inner surface of ceramic tubes with a length of up to 40 cm, further improving the mechanical strength and providing better protection for the GO layer (Figure 10a–c). The ceramic-supported GO membranes exhibited extraordinary structural stability under high pressure and the cross-flow process of water purification, which is considered to be a notable step toward realizing scalable GO-based membranes.

Apart from employing the inorganic hollow fibers and tubes, we demonstrated the scalability of GO membranes on a polymeric substrate with a diameter of 15 cm (Figure 10d). The effective membrane area reaches 176.7 cm\(^2\), which is 10–60 times larger than the reported GO-based membranes. Besides the membrane fabrication method of pressurized filtration, the blade coating has been employed to fabricate GO membranes with a membrane area on the m\(^2\) scale. Majumder et al. employed the conventional gravure printing machine and doctor blade to fabricate shear-aligned GO membranes on Nylon substrates with an area of 182 cm\(^2\).\(^57\) Moreover, Bae and co-workers proposed to fabricate ion/polymer-cross-linked GO membranes with a membrane area of up to 1333 cm\(^2\) via a blade-coating method,\(^58\) which in principle can be used to fabricate our proposed surface-charged GO membranes. In future work, more attention should be paid to further scaling up the fabrication of 2DMMs while preserving the superior separation performance. By improving the membrane stability and realizing the large-scale fabrication, 2DMMs are believed to be practically applied.
5. CONCLUSIONS AND OUTLOOK

The field of two-dimensional material membranes is rapidly growing, and many critical issues have been overcome during the past 10 years. High-quality monolayers and few-layered nanosheets with different material compositions (graphene and its derivatives, MXene, zeolite, MOFs, etc.) have been synthesized and act as building blocks for the fabrication of high-performance separation membranes. Owing to their 2D properties, the nanosheets are solution-processable and can be easily fabricated into ultrathin membranes down to 10 nm thickness. By manipulating the architecture (interlayer spacing and pore size) and chemical structure of the molecular transport pathway, 2DMMs exhibited state-of-the-art separation performance in a wide range of applications including organic solvent dehydration, nanofiltration, and gas separation. Moreover, many approaches have been developed to fabricate large-area 2DMMs and improve the performance stability under application conditions, pushing them closer to practical applications. These extraordinary achievements established 2DMMs as a new family of advanced membranes, which can tackle a number of separation challenges unattainable by conventional membrane materials. With regard to the future development of 2DMMs, we encourage the community to pay more attention to the following topics:

(i) Nanochannel regularity for challenging separations. Because of the uneven distribution of functional groups or intercalators in 2DMMs, the interlayer nanochannels are not sufficiently uniform for many challenging separations in which the molecular sizes are very similar. For instance, 2DMMs have not yet demonstrated attractive performance for olefin/paraffin, O₂/N₂, and xylene separations. To overcome these issues, we suggest that the community develop novel 2D materials that have uniform functional groups and well-defined pore apertures. New strategies to regulate the nanochannels to sub-angstrom-scale precision are also highly demanded.

(ii) Nanochannel characterization and transport mechanism. At present, it remains challenging to accurately characterize the subnanometer transport channels in 2DMMs. Advanced characterization techniques with atomic-scale resolution, such as positron annihilation lifetime spectra and in situ high-resolution transmission electron microscopy, are required to reveal the structures of the nanochannels of 2DMMs and probe the real-time molecular/ionic transport behaviors in nanochannels, which can be combined with membrane separation performance to further elucidate the structure–performance relationship. In addition, there is a lack of theoretical models for the description of mass-transfer behavior through 2DMMs. Theoretical calculations can be employed to study the transport mechanism in 2DMMs (such as the confined mass-transfer mechanism), and theoretical models need to be established to predict the influence of membrane structure (aperture size, functional groups, charge property, etc.) on the transport properties, providing guidance for the rational structural design and performance optimization of 2DMMs.

(iii) Large-scale fabrication. This includes the preparation methods of 2D materials and membranes and the design of modules for ultrathin membranes. More green and safe synthesis methods for 2D materials need to be developed, and the yield of high-quality nanosheets needs to be enhanced to satisfy production demands. In addition, new methods for fabricating defect-free, large-scale 2DMMs should be investigated. In this regard, the synthesis of large nanosheets (μm-to-mm scale) with atomic thickness would be very helpful. Since the thickness of 2DMMs is 1 to 2 orders of magnitude lower than that of traditional membranes, it is necessary to design specially made membrane modules to maintain the structural integrity and thus the separation performance of 2DMMs.

(iv) Performance evaluation under practical conditions. Currently, the separation performance of 2DMMs was mostly evaluated under relatively ideal or less harsh conditions, such as in high-purity gas, an ideal binary gas mixture, or a high-purity liquid with few contaminants. However, the real application conditions are much harsher, such as high temperature, high pressure, and steam-complicated contamination. An investigation of the separation performance under these practical conditions would raise new challenges for 2DMMs and definitely bring them a step closer to industrial applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/accountsmr.0c00092.

Testing condition of the Wicke-Kallenbach mode; discussion of the stacking mode of porous nanosheets; discussion of the importance of the ultrathin property and ordered transport pathways for 2DMMs; characterization of the interlayer spacing of GO laminates; and discussion of the universality of the polymer-induced assembly method (PDF)

AUTHOR INFORMATION

Corresponding Author

Wanqin Jin — State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, P. R. China; orcid.org/0000-0001-8103-4883; Email: wqjin@njtech.edu.cn

Authors

Long Cheng — State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, P. R. China
Gongping Liu — State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, P. R. China; orcid.org/0000-0002-3859-1278
Jing Zhao — State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, P. R. China; orcid.org/0000-0002-1423-0291

Complete contact information is available at: https://pubs.acs.org/10.1021/accountsmr.0c00092
Notes
The authors declare no competing financial interest.

Biographies
Long Cheng received his B.S. in chemical engineering from Nanjing Tech University in 2017. He is currently a Ph.D. candidate under the supervision of Prof. Wanqin Jin at Nanjing Tech University. His research focuses on the design and fabrication of two-dimensional-material membranes for gas separation.

Gongqing Liu received his Ph.D. under the supervision of Prof. Wanqin Jin at Nanjing University of Technology in 2013 and then joined Nanjing Tech University as an assistant professor. From 2015 to 2017, he worked as a postdoctoral fellow in Professor William J. Koros group at Georgia Institute of Technology. He is currently a professor in the College of Chemical Engineering at Nanjing Tech University. His research focuses on ultrathin polymeric membranes and 2D-material membranes for molecular separation.

Wanqin Jin received his Ph.D. from Nanjing University of Technology in 1999. He was a research associate at the Institute of Materials Research & Engineering of Singapore (2001), an Alexander von Humboldt Research Fellow (2001–2013), and a visiting professor at Arizona State University (2007) and Hiroshima University (2011, JSPS invitation fellowship). He is currently a professor in the College of Chemical Engineering at Nanjing Tech University. His research focuses on membrane technology for sustainable energy and environmental issues.

ACKNOWLEDGMENTS
The authors acknowledge support received from the National Natural Science Foundation of China (22038006, 91934303, and 21921006), the Innovative Research Team Program by the Ministry of Education of China (IRT_17R54), and the Topnotch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP).

REFERENCES


