Two-Dimensional-Material Membranes: A New Family of High-Performance Separation Membranes

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1. Introduction

The discovery of graphene triggered a great deal of attention toward two-dimensional (2D) materials in condensed matter physics, materials science, and chemistry.[1–5] Owing to their unique atomic thickness and micrometer lateral dimensions, 2D materials have been explored increasingly as a fundamental platform to develop separation technologies.[6–14] Synthetic membranes are used widely in many separation processes, from industrial-scale processes such as removing salt from seawater and separating atmospheric gases, to smaller-scale processes in chemical synthesis and purification.[15] The membranes function by forming a barrier between the two phases, restricting the movement of some molecules while letting others through. In principle, membranes made from 2D materials can be as thin as a single atom to enable minimum transport resistance and maximum permeation flux. Nano- or sub-nanometer apertures derived from intrinsic porous structures, accurate perforation, or the controllable assembly of 2D materials allow for highly selective transport of liquids, gases, ions, and other species through membranes. In recent years, various 2D materials, including the graphene-family,[2–5] exfoliated dichalcogenides and layered oxides,[3] zeolites,[14] and metal–organic framework (MOF) nanosheets[13] have been demonstrated to be superb building blocks for high-performance membranes.

Based on their atomic structure, 2D materials are either porous or nonporous. They can therefore be fabricated as separation membranes with two basic forms: nanosheet and laminar membranes (Figure 1). In general, the former consists of a monolayer or a few layers of 2D material with intrinsically uniformly sized pores (for example, zeolite, MOFs) or drilled nanopores (graphene) for selective permeation. The latter is formed by assembling 2D material nanosheets (such as graphene oxide, GO) into laminates with interlayer galleries used to provide molecular passages. By tailoring the in- and out-of-plane nanostructures, these membranes derived from 2D materials exhibit extraordinary molecular separation properties in various membrane processes, such as ultrafiltration, nanofiltration, reverse osmosis, forward osmosis, pervaporation, and gas separation.

Does recent research indicate that 2D-material membranes are a temporary curiosity or a new family of high-performance separation membranes? In this Minireview, we aim to answer this question by analyzing recent progress in the design and fabrication of nanosheets and laminar 2D-material membranes. We focus on the summary and discussion of different approaches for the formation of 2D-material membranes and the role of the starting materials and transport channels, and we highlight the nanostructures and physicochemical properties that are essential for high-efficiency membrane separation. Fundamental and technical challenges for advancing 2D-material membranes for liquid and gas separations are also discussed.
Two-Dimensional-Material Nanosheet Membranes

Nanosheets of 2D materials with atomic thickness can be used as ultimate membranes for separation. Membrane pores are provided either by an intrinsic porous structure such as in zeolites and MOFs, or by drilled pores such as in graphene-like materials. The permeation flux and selectivity of nanosheet membranes are determined by the membrane thickness and pore structures. Important key points to produce high-performance nanosheet membranes include the high-quality fabrication of nanosheets and effective approaches for translating nanosheets into membranes. Reliable measurements of molecular permeation through 2D-material membranes that are a few nanometers thick remain an experimental challenge. This section focuses on 2D-material nanosheet membranes with regard to the issues mentioned above.

2.1. Zeolite Membranes

Zeolites are crystalline silica-based microporous materials with pore sizes that range from 0.25 to more than 1 nm. Two-dimensional zeolites, nanosheets with thickness comparable to the unit-cell-dimensions of the corresponding structure, offer exciting opportunities for the development of ultra-thin molecular sieve membranes. Fabrication of 2D zeolite membranes relies on: 1) an availability of suspensions that contain zeolite nanosheets with a uniform thickness and high aspect ratio, colloidal stability, and free of amorphous and non-exfoliated contaminants; and 2) the development of deposition techniques for the quantitative transfer of suspended zeolite nanosheets to porous substrates to form oriented thin membranes.

In recent years, the Tsapatsis group realized high-purity exfoliated MFI nanosheet (1.5-unit-cell thick, 300-nm lateral size) suspensions by developing a polymer-melt-compounding exfoliation technique combined with a density gradient centrifugation purification method (Figure 2a–c). The 2D MFI framework contains 10-member ring pores that run inside and through the layers; these are of extreme importance because they provide shape-selective diffusion inside the layers while reducing the characteristic diffusion length to ca. 1 nm. Filtration of suspensions through the porous supports is used to deposit oriented nanosheet multilayers with thickness of sub-100 nm. However, the filtered MFI nanosheet film contains non-selective gaps, and thus is unable to exhibit separation selectivity. These gaps were reduced by mild secondary solvothermal growth of the nanosheet film and the established orientation is preserved by using appropriate structure-directing agents such as tetrapropyl ammo-
mum cations. The thickness of the current state-of-the-art 2D zeolite membranes is \( \approx 100 \text{ nm} \) (Figure 2d,e),\(^{[14]} \) which is 10-times thinner than typical three-dimensional (3D) zeolite membranes, although it is much thicker than emerging nanosheet graphene-based membranes. The intergrown MFI nanosheets were preferentially \( \beta \)-oriented, as confirmed by X-ray diffraction, which indicates that the 5.5 \( \AA \) straight pore MFI channels were normal to the membrane surface. As a result, these 2D MFI membranes exhibited a high flux and selectivity for industrially important separations (for example, xylene and butane isomers). For instance,\(^{[20]} \) the \( p \)-xylene permeance was \( 1.3 \text{–} 3.6 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} \) and the separation factor was \( 185 \text{–} 1050 \), with an equimolar feed of \( p \)- and \( o \)-xylene at 150°C.

To improve the membrane throughput, Tsapatsis pointed out that the thickness of 2D zeolite membrane can be reduced to 10 nm if sufficiently compact layers can be deposited.\(^{[14]} \) This enables them to be competitive nanosheet membranes. Future efforts could focus on increasing the aspect ratio and its uniformity in the zeolite nanosheet. However, broad implementation of 2D zeolite membranes is restricted by the limited number of recognized 2D zeolite forms. Furthermore, the current synthesis is costly and produces a low yield of high-quality 2D zeolite nanosheets. Alternatively, incorporating 2D zeolite nanosheets into a polymer matrix to form mixed matrix nanostructures would be a good compromise with regard to the engineering aspect.\(^{[21]} \) Sufficient utilization of zeolite molecular sieving properties is also strongly dependent on whether the zeolite nanosheets are fully exfoliated with a thin and intact structure.

2.2. MOF Membranes

As a new family of nanoporous molecular sieves, MOFs with an abundant porous structure and functional surface groups have been demonstrated to be an excellent candidate for use as molecular sieve membranes with superior performance.\(^{[22]} \) Layered crystalline structures have been found in a large number of MOFs\(^{[23]} \) which highlights the great potential of MOF-based 2D membranes.\(^{[13]} \) Despite challenges in pursuing MOF nanosheets with preserved morphological and structural integrity, two successful cases were achieved recently based on the top-down\(^{[24]} \) and bottom-up\(^{[25]} \) synthesis of MOF nanosheets. In the top-down strategy, the Yang group\(^{[24]} \) treated a layered MOF precursor, \( \text{Zn}_2(\text{bim})_4 \) (bim = benzimidazole), using low-energy wet ball milling followed by ultrasonication in methanol/propanol mixtures. This exfoliation approach created 1-nm-thick \( \text{Zn}_2(\text{bim})_4 \) monolayers with \( \approx 600 \text{ nm} \) lateral size and high crystallinity (Figure 3a,b). The bottom-up case\(^{[25]} \) was accomplished by diffusion-mediated modulation of the MOF growth kinetics. Dispersible copper 1,4-benzenedicarboxylate (CuBDC) MOF nanosheets were formed in the contact zone (solvent spacer layer) of a linker solution (benzene 1,4-dicarboxylic acid) and a metal solution (Cu\(^{2+} \) ions). CuBDC
lamellae of 5–25 nm thickness and 0.5-4 µm lateral dimension were produced by this three-layer approach.

Similar to the 2D zeolites, two general approaches exist for making 2D MOFs as separation membranes: 1) deposition of MOF nanosheets on the porous substrate surface to form a pure 2D MOF membrane, and 2) incorporation of MOF nanosheets into polymers to make a 2D MOF-based composite membrane for making 2D MOFs as separation membranes: 1) deposition of MOF nanosheets, the assembled 2D Zn$_2$(bim)$_4$ membranes were only several nanometers thick (Figure 3c,d). The porous ceramic substrate is used to provide substantial mechanical strength that enables the actual permeation measurement of such thin membranes (gas mixture feed up to 150°C), but no pressure drop was applied across the membranes to prevent distortion of the MSN layers. The Zn$_2$(bim)$_4$ unit has an estimated aperture size of ≈ 0.21 nm and pores in the nanosheets are constructed with four flat bim molecules, which offers an exciting opportunity for sieving gases rapidly. The effective pore size should be slightly larger because of the structural flexibility of the nanosheets. The 2D Zn$_2$(bim)$_4$ membranes exhibited superb separation for H$_2$ (0.29 nm) over CO$_2$ (0.33 nm): H$_2$ permeance of up to several thousand GPUs (1 GPU = 1 × 10$^{-6}$ cm$^2$·cm$^{-3}$·s$^{-1}$·cmHg$^{-1}$ at STP) with a H$_2$/CO$_2$ selectivity higher than 200. It is interesting to find that the suppression of the ordered lamellar stacking of MOF nanosheets could achieve a simultaneous increase in permeance and selectivity. It was explained that the lamellar ordering of the nanosheets would block the permeation pathway for H$_2$ but have only a small effect on CO$_2$ leakage. In another study, Gascon and co-workers incorporated CuBDC nanosheets into polyimide (Matrimid 5218) matrices to fabricate CuBDC/polyimide nanocomposite membranes. This led to a remarkable improvement in CO$_2$/CH$_4$ separation performance, together with an unusual but desired increase in the selectivity with feed pressure. An improved efficiency of the molecular discrimination and elimination of unselective permeation pathways by the MOF nanosheets were regarded as the main contributions. These two breakthroughs opened the door to the rational design and fabrication of 2D membranes based on MOF nanosheets, which led to a highly improved separation performance compared with the 3D MOF membranes.

**2.3. Nanoporous Graphene Membranes**

Graphene, the monolayer of graphite, is a well-known 2D material however, its perfect single-layer is impermeable to molecules, including the smallest gas, helium. This is because the π-orbitals of graphene form a dense, delocalized cloud that blocks the gap within its aromatic rings. No gap exists in electron density around the aromatic rings through which molecules may pass. This barrier property, and the carbon atomic thickness, preeminent mechanical strength, and chemical inertness of graphene, motivated intense studies in drilling holes in graphene nanosheets for developing nanoporous graphene membranes.

Nanoporous graphene with a high density and uniform subnanometer pores is predicted to allow ultrafast high permeance and high selectivity because the atomic thinness provides little resistance to flow, yet blocks the passage of species that are larger than the pores. Calculations by the Grossman group highlighted the potential of nanoporous single-layered graphene for water desalination. Their results indicate that the nanopores created in graphene nanosheets exhibited full salt rejection and water passage (23.1 Å$^2$ hydrogenated pore and 16.3 Å$^2$ hydroxylated pore) and the water permeability was as high as 39–66 L·cm$^{-2}$·day$^{-1}$·MPa$^{-1}$. The water permeability was 2 to 3 orders of magnitude greater than that of conventional reverse osmosis membranes with a similar salt rejection of 99%. Arulu and co-workers found that a graphene with a pore larger than 0.8 nm would allow faster water transport through the membrane compared with thin carbon nanotube (CNT) membranes. The feasibility of using nanoporous graphene nanosheets for ion and gas separation has also been demonstrated by molecular dynamics simulation studies.

Continuous experimental efforts have been devoted to explore the potential of nanoporous graphene membranes using various perforation techniques, including focused electron beam ablation, focused ion beam irradiation, ultraviolet-induced oxidative etching, ion bombardment and chemical oxidative etching, and oxygen plasma etching. Well-defined pore sizes can be created by focused electron beam irradiation of the graphene monolayer, but this approach is limited to a small membrane area, and the pore size ranging from 3.5 to 100 nm is unsuitable for effective molecular sieving separation. The oxidative etching route effectively improved the scalability and reduced the pore size to the sub-nanometer scale. However, from a practical engineering standpoint, the pore density is still insufficient and the pore size distribution requires improvement. It remains technically challenging to perform precise, large-area, high-density perforation in graphene nanosheets. Nevertheless, recent experimental advances have demonstrated that single-layer nanoporous graphene can be used as nanofiltration and desalination membranes. Surwade et al. generated tunable nanometer-sized pores (0.5–1 nm) in a graphene monolayer using an oxygen plasma-etching process (Figure 4a,b). The resulting membranes exhibited nearly 100% rejection for dissolved monovalent ions (K$^+$, Na$^+$, Li$^+$, Cl$^-$) with water fluxes of up to 10$^6$ gm$^{-2}$·s$^{-1}$.

Nanoporous graphene membranes must also confront the challenge of intrinsic defects from the growth processes (for example, defects with diameter of 1–15 nm during chemical vapor deposition of graphene on copper) and extrinsic defects from graphene transfer (≈100–200 nm in diameter). To address this critical problem, the Karnik group recently developed a multiscale leakage-sealing process that exploits the nonpolar nature and impermeability of pristine graphene to block defects selectively (Figure 4c–e). A centimeter-scale defect-sealed monolayer graphene nanosheet membrane was produced. Subsequently, they introduced pores in the membrane by high-energy gallium-ion bombardment to nucleate...
isolated defects followed by etching of the defects into subnanometer pores. The pore size ranged from 0.162 to 0.5 nm, with a pore density of $10^{12}$–$10^{13}$ cm$^{-2}$. The membrane rejected multivalent ions and small molecules, and exhibited a water flux that was consistent with prior molecular dynamics simulations.

Recently, findings from the Geim group appear to refute the well-demonstrated atomic impermeability of single-layer graphene. They reported that graphene and boron nitride (hBN) are excellent conductors of protons across their 2D structure, so protons can pass through graphene or hBN nanosheets. They explain this observation by the different electron densities of electron clouds that can be pierced by incident protons in the 2D materials. Proton transport is a thermally activated process, with energy barriers $E$ of $0.8$ and $0.3$ eV for monolayers of graphene and hBN, respectively. This unexpected finding may make nanosheet membranes promising candidates for use in hydrogen-based technologies (such as fuel cells). Recently, they also showed that monolayers of graphene and hBN can be used to separate hydrogen ion isotopes. Graphene and hBN monolayers were exfoliated mechanically and suspended over micro-sized holes etched in silicon wafers. As shown in Figure 5, a proton-conducting polymer, Nafion, and Pd electrodes were used as coatings to facilitate the permeation measurements. Based on two complementary approaches, electrical measurements and gas-flow detection by mass spectrometry, they demonstrated that deuterons (D) permeated through as-prepared nanosheet membranes much slower than protons (H), which results in a H/D separation factor of $10$ at room temperature. The highly selective permeation of isotopes is attributed to the different activation barriers posed by 2D materials that result from a difference of $60$ meV between zero-point energies of incident protons and deuterons. Furthermore, the scalability was shown by using CVD-grown graphene nanosheets to build centimeter-sized membranes, which effectively pumped out hydrogen from a mixture of deuterium and hydrogen. The energy cost of this approach was estimated at 0.3 kWh per kilogram of feed water, which is much lower than the cost of existing enrichment processes (for example, cryogenic distillation). Their results may give rise to new research directions for nanosheet membranes.

**2.4. Other Nanosheet Membranes**

In addition to graphene, the potential of other 2D nanosheet membrane materials with an assumed imperviousness to atoms is being investigated, although most studies remain at a molecular simulation stage. Heirianian et al. achieved water desalination with a single-layer molybdenum disulfide (MoS$_2$). The optimized pores lead to a 70% greater flux than that of graphene nanopores. This behavior was attributed to the unique structures and chemistry of Mo-only pores. The potential advantage of fabricating high-quality monolayers with large area makes MoS$_2$ a promising candidate for developing new kinds of 2D-nanosheet membranes. Recently, porphyrin-based 2D polymers, with uniform micro-pores and close to atom-thin thicknesses, were explored for gas separation by designing expanded porphyrins computationally with different pore sizes. The ideal selectivity that was evaluated from passing-through barriers was of the order of $10^5$–$10^6$ GPU for CO$_2$, separation, and a permeance of $10^{12}$–$10^{13}$ for CO$_2$. This was determined based on classical molecular dynamics simulations. This result indicated that 2D polymers may offer a bottom-up platform for 2D nanosheet membranes.

Broadly speaking, self-assembled monolayers (SAMs), namely monomolecular films formed by the spatially controlled organization of molecules on solid surfaces, could be...
considered as a special kind of 2D nanosheet membrane. Persistent interests in SAMs lay in their providing a straightforward approach to coat and functionalize solid surfaces with molecule-thick nanolayers. A typical example of SAM membranes are the so-called layer-by-layer (LBL) membranes, with well-defined molecular composition and thicknesses from ten to several hundreds of nanometers. The introduction of graphene stimulated the pursuit of carbon nanomembranes (CNMs), which are derived from various aromatic self-assembled monolayers, combining the atomic thickness and excellent toughness of graphene with the chemical functionality of SAMs. In general, CNMs are fabricated by generating a functional molecular monolayer on a solid surface and then crosslinking this layer to form a molecularly thin membrane that is able to be released from the surface. Recently, Schrettl et al. developed an approach for making 2D CNMs with extended lateral dimensions based on the self-assembly and subsequent carbonization of the n-hexane amphiphile at the air/water interface. They demonstrated that CNMs are mechanically stable and can be functionalized, which is similar to reduced GO, with a molecularly defined thickness of 1.9 nm and lateral dimensions on the order of centimeters. It is presumed that these dimensions are limited by dimensions of the self-assembly (Langmuir) trough. Fabricating approaches and the mechanical, optical, and electrical properties of these functional CNMs have been studied widely, which is instructive for designing 2D-material membranes.

3. Two-Dimensional-Material Laminar Membranes

Although extraordinary separation properties have been predicted and achieved in nanosheet membranes, the challenge of fabricating large-area and integrated nanosheets with uniform nanopores remains. Laminar membranes assembled from 2D materials provide a more practical approach for using 2D materials for separation. Two-dimensional interlayer channels between nanosheets could yield fast and selective transport of small molecules. To date, various 2D materials have been fabricated as laminar membranes, including GO, transition metal dichalcogenides and carbides, and layered double hydroxides (LDHs). Laminar structures have also been introduced into existing membrane materials to form hybrid membranes. Issues related to laminar membranes are discussed in this section.

3.1. Graphene Oxide Membranes

As one of the most important derivatives of graphene, GO is an essential 2D building block for separation membranes. Similar to graphene, GO nanosheets are also single-atom thick with lateral dimensions as high as tens of micrometers. Moreover, they contain plenty of oxygen-containing groups, such as hydroxyl, carboxyl, carbonyl, and epoxy groups, on the edges and basal planes of the GO...
fibers). The membrane thickness can be controlled readily by arbitrary configuration (for example, flat, tubular, and hollow forward route to fabricate GO membranes on substrates with casting,[54] spin-coating,[55,56] LBL deposition [57] and other deposition.[12] A detailed summary and discussion of fabrica-

channel, with the prerequisite of no defects during the stacked GO nanosheets are adequate to create a sieving thickness precisely at molecular level. Ideally, as few as two nanosheets. The LBL strategy is able to tailor the GO layer process and potential in-plane ordered arrangement of GO nanosheets. Besides making GO dispersible in water, also provide convenient sites for enhancing specific interactions (for example, hydrogen bonds, electrostatic) with transport components (water, CO2, and ions).

With the advantages of a high aspect ratio structure and water-dispersible property, GO nanosheets can be assembled readily into laminar membranes by filtration.[40–53] Drop-casting,[54] spin-coating,[55,56] LBL deposition[57] and other methods. Vacuum filtration is the most common and straightforward route to fabricate GO membranes on substrates with arbitrary configuration (for example, flat, tubular, and hollow fibers). The membrane thickness can be controlled readily by the amount of GO in the introduced suspension.[53] Drop-casting is usually used to fabricate free-standing GO mem-

branes, which shows a drawback in the composite system because of the insufficient interfacial adhesion between the GO layer and the substrate. The inherently weak adhesion can be improved by surface modification of the substrate.[58] The advantages of spin-coating came from the rapid assembly process and potential in-plane ordered arrangement of GO nanosheets. The LBL strategy is able to fabricate GO membranes as they are applied in organic solvent nano-

structures in the intergalleries becomes a fundamental issue to achieve high-performance GO laminar membranes. It also generates common interest in communities for studying molecular transport through 2D channels. Mi summarized several methods to obtain tunable interlayer galleries and their different applications for separation (Figure 6).[12]

The face-to-face interactions, oxygen-containing functional groups, and corrugation of GO nanosheets generate interlayer galleries in GO laminar membranes,.[12] According to studies by Geim and co-workers,[50] the typical empty interlayer spacing of GO laminar membrane was estimated at ≈0.5 nm. When the GO membrane was immersed in an aqueous solution, the empty spacing could be increased to more than ≈0.9 nm because of the hydration of oxygen-containing groups on the GO nanosheets. The resulting 2D interlayer channels exhibited a sharp cut-off for species with radii larger than 0.45 nm. Solvation phenomena in ethanol were also used to tune the interlayer spacing of GO laminar membranes as they are applied in organic solvent nano-

filtration.[59] In contrast, intergalleries can be narrowed by the reduction of oxygen-containing groups on GO nanosheets, by either thermal or chemical routes. Su et al.[61] showed that hydroiodic- or ascorbic-acid-reduced GO laminates could

![Figure 6](image)

**Figure 6.** Schematic of tuning of interlayer galleries of laminar membranes. a) Separation capability of GO membrane is tunable by adjusting the nanochannel size. b) Several methods to synthesize GO membranes have been reported or envisioned; GO nanosheets can be packed physically by vacuum filtration (options 1 to 3), or they can be stabilized by covalent bonds, electrostatic forces, or both (options 4–6) during layer-by-layer assembly. Reproduced with permission. Copyright 2014 the American Association for the Advancement of Science.

of water through free-standing 0.1–10 μm-thick GO laminar membranes. Water molecules permeate through the 2D interlayer channels formed between GO nanosheets and follow a tortuous path primarily over the hydrophobic nonoxidized surface rather than the hydrophilic oxidized GO region. They claimed that the nearly frictionless surface of the non-oxidized GO nanosheets facilitates the ultra-fast flow of water molecules. Subsequent to this pioneering work, many studies have demonstrated that the intergalleries between GO nanosheets play a vital role in the fast and selective transport of water, ions, and gases. This also accounts for the significant potential of GO nanosheets in water and gas separation membranes. Therefore, precise tuning of the nanostructures in the intergalleries becomes a fundamental issue to achieve high-performance GO laminar membranes. It also generates common interest in communities for studying molecular transport through 2D channels. Mi summarized several methods to obtain tunable interlayer galleries and their different applications for separation (Figure 6).[12] The face-to-face interactions, oxygen-containing functional groups, and corrugation of GO nanosheets generate interlayer galleries in GO laminar membranes,.[12] According to studies by Geim and co-workers,[50] the typical empty interlayer spacing of GO laminar membrane was estimated at ≈0.5 nm. When the GO membrane was immersed in an aqueous solution, the empty spacing could be increased to more than ≈0.9 nm because of the hydration of oxygen-containing groups on the GO nanosheets. The resulting 2D interlayer channels exhibited a sharp cut-off for species with radii larger than 0.45 nm. Solvation phenomena in ethanol were also used to tune the interlayer spacing of GO laminar membranes as they are applied in organic solvent nano-

filtration.[59] In contrast, intergalleries can be narrowed by the reduction of oxygen-containing groups on GO nanosheets, by either thermal or chemical routes. Su et al.[61] showed that hydroiodic- or ascorbic-acid-reduced GO laminates could
exhibit excellent barrier properties, highly impermeable to all gases and liquids because of the significantly decreased interlayer spacing. One challenge in the reduction treatment on GO membranes is how to maintain the structural integrity of GO nanosheets and the entire laminate.

Intercalation chemistry is thought to be a controllable approach for modulating the intergalleries of GO laminar membranes. Various nanomaterials and molecules have been intercalated into GO nanosheets to form hybrid structures. When intercalating nanomaterials, one should consider their compatibility with GO. Carbon-based materials such as carbon dots,[62] single-walled carbon nanotubes (SWCNTs),[63] and multi-walled carbon nanotubes[64] are preferred in the literature. Owing to the expanded interlayer space between neighboring GO nanosheets, the intercalated GO laminar membranes exhibited 1–2-fold water flux improvements at the same rejection rate.[62–64] By using a similar intercalation route, nanomaterial was also used as a sacrificial template to create more 2D interlayer channels in the GO ultrafiltration membranes, which lead to a 10-fold enhancement in water flux while maintaining the same rejection rate.[53] In general, molecular intercalation involves a crosslinking reaction between intercalated molecules (for example, diamine,[65] 1,3,5-benzenetricarbonyl trichloride [57]) and GO nanosheets. Thus, the interlayer spacing was finely tuned and the stability of the GO laminar structure could be improved. It has been demonstrated that the intergallery size is closely related to the dimensions of the intercalated molecules or nanomaterials, which enables intercalation as a flexible approach to control the nanostructures of 2D materials laminar membranes.

Regardless of the above achievements in GO membranes with well-tuned interlayer spacing and high water flux, the rejection rates of state-of-the-art GO membranes are rarely better than those of commercial nanofiltration (NF) membranes.[64] GO membranes must still confront the challenge of regulating subnanometer-sized intergalleries that are necessary for precise sieving of monovalent ions (water desalination) and small gases (gas separation). Very recently, we proposed the rational design of external forces to manipulate the nano-architecture of GO-assembled 2D channels precisely with an empty interlayer height of ≈0.4 nm for fast transport and selective sieving of gases.[66] As shown in Figure 7, the designed external forces are applied both outside and inside the GO laminate. They overcome the intrinsic repulsive electrostatic interactions between GO layers collaboratively, with the aim to eliminate non-selective stacking defects and stimulate a highly ordered assembly of GO nanosheets. This approach enabled the development of highly permeable 2D GO membranes with remarkable molecular-sieving properties, and offered a 2- to 3-orders of magnitude higher H2 permeability and 3-fold enhancement in H2/CO2 selectivity compared to commercial membranes. This work contributed a notable step to push 2D-material membranes toward implementation for precise molecular separation. The extension of this approach to water desalination membranes is underway.

GO laminates possess unparalleled rapid water-transport channels; however, the majority of GO membranes fail to achieve the theoretically predicted results in real separation processes. With the premise of well-controlled 2D intergalleries between GO nanosheets, the full utilization of these rapid GO laminate transport channels is an emerging challenge. For instance, the separation process of GO membranes for solvent dehydration is governed by a preferential sorption–diffusivity mechanism.[64] Water molecules are first adsorbed into the membrane surface and are then transported through the GO intergalleries across the membrane. Our recent study[49] found that the water sorption process can be regarded as the control step. This means that fast 2D channels are most likely not utilized fully during the separation if the surface adsorption is insufficient. Therefore, we designed a bio-inspired membrane that coupled an ultrathin surface water-capturing polymeric layer (<10 nm) with GO laminates.[67] As shown in Figure 8, the hydrophilic polymer (chitosan) acts as a surface layer to capture a large number of water molecules preferentially from feed mixtures, and results in an increase in driving force across the GO laminates. Two-dimensional water channels within the interlayers of GO nanosheets could be used fully to achieve fast and selective water permeation through the integrated membrane. The prepared membrane exhibited highly selective water permeation with an excellent water flux of over 10000 g m⁻² h⁻¹, which exceeds the performance of state-of-the-art membranes for butanol dehydration.[68]

Although it has received less attention, the critical role of in-plane structural defects and/or slit-like pores that participate in the separation should not be ignored, particularly for the ultra-thin membranes with only a few interlayer galleries. Li et al.[53] used a facile filtration process to fabricate GO membranes as thin as 1.8 nm, showing surprisingly high selectivity for H2/CO2 (3400) and H2/N2 (900) mixtures. The ultra-thin GO layer requires extra care to prevent potential damage when conducting gas permeation experiments. The authors attached heat-resistant Kapton tape with a hole on the GO membranes to expose the desired membrane area for gas permeation. No pressure drop was applied across the membranes to prevent the thin supports from breaking or deforming. These GO membranes, after reduction, showed a three-orders of magnitude lower water flux; however, the gas permeance remained almost unchanged. They proposed that the main transport pathway and permeation of gas molecules was attributed to selective structural defects rather than interlayer spacing. Other groups who have studied GO laminar membranes also attributed shortcuts provided by defects in GO nanosheets to a higher water flux than the calculated value based on Poiseuille’s law.[51,52] Inspired by the phenomena, in-plane mesoporous GO sheets were prepared by re-oxidation and subsequent assembly into laminar membranes.[69] The introduced in-plane pores increased the effective path, and shortened the mass transport path significantly, which resulted in a 2- to 3-times higher water permeance than that of the pristine GO membrane, while preserving the rejection for small molecules. Nevertheless, similar to the situation in nanoporous graphene membranes, the precise generation and introduction of selective defects in GO laminar membranes still requires much effort.

In addition to the transport channels either from plane-to-plane intergalleries or in-plane defects/pores, the functional
groups on GO nanosheets could influence the molecular transport at least in two manners: 1) oxygen-containing groups on the basal plane and edge of GO could form hydrogen bonding with water or gases to achieve preferential adsorptions in the GO membrane. For instance, a much higher water sorption ability than organic compounds (methanol, butanol, and dimethyl carbonate) was found in quartz crystal microbalance measurements.[49,67] Adsorption tests indicated that the gas adsorption of GO powders and resultant membranes followed the order of \( \text{CO}_2 > \text{CH}_4 > \text{N}_2 > \text{H}_2 \).\] These strong interactions between permeate species and GO may promote or prohibit the diffusion through GO membranes, which was found to be dependent on the GO laminar nanostructures.[53] 2) Negatively charged groups on GO nanosheets could afford electrostatic interactions with the charged molecules or ions in nanofiltration and salt rejection.[52] According to the exclusion theory, the potential at the interphase of solution and membrane tends to exclude co-ions, and counter ions are rejected to maintain the solution electro-neutrality on each side of the membrane. Zhu and co-workers[54,71] carried out systematic studies on selective ion transport through GO laminar membranes in which diverse interactions were formed between different ions and GO nanosheets.

The exciting nanostructures and transport properties of GO laminar membranes led them to great success in the high-efficiency purification of liquids and gases by pressure filtration, pervaporation, and gas separation. A detailed summary of separation performance can be found elsewhere.[6] Nowadays, engineering of GO membranes has received increasing attention. The feasibility of large-scale fabrication and operational stability is particularly significant currently.[9] We developed a type of hollow fiber GO membrane using the facile filtration method.[49] Hollow fibers are an industrially preferred membrane form because of its advantages in high-packing density, cost-effectiveness, and self-supporting structure. GO nanosheets can be stacked easily on the curved surface of hollow fibers despite their high curvature and elongated shape. The hollow fiber GO membrane exhibited selective water permeation and showed great potential in solvent dehydration applications.[29–32] The viability of GO hollow fiber membranes in wastewater treatment and organic solvent nanofiltration has been demonstrated recently.[73–74] Furthermore, the instability of the interlayer nanochannels formed by stacking GO sheets represents a major challenge when using GO laminar membranes for water purification. The crosslinking of GO nanosheets using chemical groups could offer stable, covalently bound GO laminates with well-defined interlayer spacing.[28,32] These can be produced by mixing GO sheets and linking agents and

Figure 7. External force-manipulated subnanometer 2D channels for ultra-fast gas sieving:[66] (a) External force-driven assembly (EFDA) approach for fabricating 2D channels, which involves 3D external forces in \( x, y, \) and \( z \) axes. Enlarged schematic shows force analysis for one 2D channel unit consisting of GO nanosheets and polymer chains. Three main forces are included: intrinsic force, outer external forces (compressive force, centrifugal force and shear force), which are applied outside the 2D channel unit, and inner external force (GO-polymer molecular interactions), which are applied inside the 2D channel unit. b) 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 forces. c) Cross-sectional SEM and TEM images of EFDA-GO membrane. Reproduced with permission. Copyright 2016 American Chemical Society.
filtering the suspension on a support layer, or by using the LBL assembly approach.

3.2. Transition Metal Dichalcogenide and Carbide Membranes

After the discovery of the first 2D material, graphene, 2D atomic crystals such as transition metal dichalcogenides and carbides have received increased attention in recent years because of their unique physics and chemistry. However, only a few studies have reported the use of these types of 2D materials for membrane separation. This may be related to the low aspect ratio of the exfoliated nanosheets that make it difficult to form robust and defect-free membranes. Recently, monolayers of molybdenum disulfide (MoS$_2$), tungsten disulfide (WS$_2$), and MXene that had been exfoliated chemically with a micrometer lateral size, were fabricated as laminar membranes by a filtration method (Figure 9). The different surface chemistries of these 2D atomic crystals provide these membranes with several new features compared to graphene-based membranes.

Peng and co-workers reported a laminar MoS$_2$ membrane with almost the same thickness ($\approx$ 1.8 μm) and channel size ($\approx$ 3 nm) as that of the GO membrane, which exhibits a 3- to 5-times higher water flux for the filtration of Evans blue (EB) molecules. They attributed this flux improvement to the exposure of the sulfur atoms in the MoS$_2$ monolayer sheets that provide a higher hydrophilicity and more passage channels for water molecules. Recently, they reported thinner WS$_2$ laminar membranes ($\approx$ 0.5 μm; Figure 9a, b) with a two times higher water flux (450 Lm$^{-2}$h$^{-1}$bar$^{-1}$) than that of MoS$_2$ membranes with a similar EB rejection (89%). The water flux was improved by duplicated nanochannels using ultra-thin nanostrands as templates without loss of rejection efficiency. They found that 0.3–0.4 MPa transmembrane pressure-induced nano-cracks could generate new fluidic nanochannels that result from increased porosity and decreased transport path, and led to a much higher water flux in the channelled WS$_2$ membrane. It is worth noting that both

![Figure 8. High-efficiency water-transport channels using the synergistic effect of a hydrophilic polymer and GO laminates](image-url)

![Figure 9. Several kinds of 2D laminar membranes. a, b) WS$_2$ membrane: a) AFM image of WS$_2$ nanosheets, and b) cross-sectional SEM image of 500-nm-thick WS$_2$ membrane. c, d) MoS$_2$ membrane: c) AFM image of single-layered MoS$_2$ nanosheet, and d) cross-sectional SEM image of 35-nm-thick MoS$_2$ membrane on anodic aluminum oxide support. e, f) MXene membrane; e) photograph and f) cross-sectional SEM image of Ti$_3$C$_2$T$_x$ membrane. g, h) LDH membrane: g) top and h) cross-sectional image of NiAl LDH membrane. Reproduced with permissions. Copyright 2014–2015 American Chemical Society. Copyright 2014–2015 RSC.](image-url)
the MoS₂ and WS₂ laminar membranes exhibited at least a 1-week stability for water filtration,[60,73] which is rarely reported for GO membranes. The absence of oxygen-containing groups may contribute to the structural stability of laminates when immersed in water. The possibility of using 2D dichalcogenide membranes for gas separation was also explored by Jin and co-workers.[76] Ultrathin (17–60-nm-thick) laminate-stacked MoS₂ membranes were developed for H₂ separation (Figure 9c,d). Although high gas permeance resulted, the Knudsen diffusion selectivity suggested the existence of excessively large gas channels in the MoS₂ membranes.

In 2011, the Gogotsi group reported a family of 2D early transition metal carbides termed MXenes, which were produced by etching out A layers from the layered Mₜₙ₋₁AXₙ phases.[79] MXenes have shown promising application in electrochemical energy storage owing to ion interactions between the atomically thin layers.[80] For instance, a wide range of cations with varying sizes and charges (Na⁺, K⁺, NH₄⁺, Mg²⁺, and Al³⁺) can be intercalated into the Ti₃C₂Tx interlayer, which results in structural expansion or contraction. Moreover, Ti₃C₂Tx is an efficient adsorbent for cationic dyes and heavy metal ions. Until recently, this Ti₃C₂Tx MXene 2D material was used in ion separation membranes based on charge- and size-selective permeation (Figure 9e,f).[77] Similar to GO laminar membranes, the hydrophilic nature of Ti₃C₂Tx, with water within the intergalleries promoted water flow. The MXene membrane rejected cations with hydration radii larger than the interlayer spacing (~0.6 nm). Moreover, cations with a larger charge showed an order of magnitude slower permeation compared with single-charged cations.

### 3.3. Layered Double Hydroxides Membranes

Layered double hydroxides (LDHs) are typically layered compounds that consist of regularly arranged, positively charged brucite-like 2D layers and charge-compensating anions located in interlayer galleries.[81] They have the general formula [Mₙ⁺ₓMₚ⁺ₓ(OH)₂]ₙ[A⁻ₓ⁻/n] · zH₂O (M²⁺, M³⁺, A⁻⁻, and H₂O represent di- and tri-valent metal ions, n-valent anions, and the interlayer water, respectively). By varying the metal ions and charge-compensating anions, the gallery height can be tuned from nano- to subnanometer scale. More importantly, in contrast to the typical exfoliation-assembly procedure for most 2D membranes, the formation of 2D sheets, self-assembly into crystallites and their deposition on a substrate can be completed in one step under hydrothermal conditions.[82] This smart membrane formation process offers an exciting opportunity for cost-effective fabrication of 2D-material membranes.

The Caro group have started to explore the potential of LDHs in 2D-material membranes.[78,85] In contrast to the top-down synthesis route, an in situ growth method was used to prepare well-intergrown NiAl-CO₃ LDH membranes on porous alumina substrates (Figure 9g,h).[79] A 2D intergallery height of 0.31 nm was formed in this kind of carbonate-intercalated laminar membrane, which fulfills the requirement of size-discrimination-based gas separation (that is, molecular sieving separation). As expected, the prepared LDH membranes exhibited remarkable molecular sieve properties (for example, selectivity for H₂/CH₄ mixtures of ~80), which makes them attractive in H₂ purification. They further demonstrated that CO₂ dissolved in the precursor solution could be used to control the preferred orientation and thickness of the LDH layers.[83] Trace CO₂ induced ab-oriented membranes, whereas saturated CO₂ produced random-oriented membranes. In principle, the ab-oriented LDH membrane was expected to yield a higher gas performance because its interlayer gallery was arranged perpendicular to the substrate, which minimizes the mass transfer resistance. However, the high aspect ratio of LDH crystallites and the insufficient supply of CO₂ may have caused the formation of non-selective defects within the LDH layer. This led to the formation of an ab-oriented membrane with lower H₂ selectivity compared with the compact random-oriented one. In addition, the in situ growth method was also applicable for fabricating ZnAl-NO₃ LDH membranes. In this case, the intergallery height of 0.41 nm was larger than that of the NiAl-CO₃ LDH membrane, because of the intercalation of different anions. The rich intercalation chemistry places LDH membranes with a widespread application in molecular separation.

### 3.4. Hybrid Membranes

The versatile physicochemical properties of 2D materials can extend the spectrum of laminar membranes significantly from pure to hybrid nanostructures formed by 2D laminates combined with another polymeric or inorganic membrane material. Most hybrid laminar membranes are mixed matrix membranes (MMMs) that are fabricated mainly by incorporating nanosheets into a polymer matrix.[86] The main advantage of the mixed-matrix strategy is the facile combination of the excellent processability of polymer and the unique characteristics of the 2D materials. Moreover, compared with the commonly used aqueous environment for pure laminar membranes, the polymer matrix with various functional groups could provide 2D materials with a more flexible assembly environment. This would offer a variety of opportunities for constructing delicate 2D laminate-based nanostructures. The well-established polymeric membrane technology could be applied readily for 2D material MMMs, which represent the most realistic approach for pushing 2D-material membranes into practical implementation.[9]

Like the pure laminar membranes, 2D material MMMs have been well-studied for water and gas separation and ion/proton exchange.[10,11] The hydrophilicity of GO nanosheets is used to enhance the water permeation properties of polymeric membranes through the effective mixed-matrix strategy. Biological fouling can also be reduced by the introduction of GO into existing membranes for water treatment by blending GO into the polymer matrix or membrane surface functionalization of GO. Graphene nanomaterials possess intrinsic antimicrobial properties,[87] which induces inactivation of bacterial cells upon direct contact by physical and oxidative damage to cell membranes. Furthermore, the high
specific surface area of graphene makes it an ideal scaffold material for anchoring different types of antimicrobial compounds, with silver being the most extensively studied material thus far. Additional details can be found in a recent review paper.[9]

We reported GO/polyether block amide (PEBA) MMMs for selective CO$_2$ separation.[85] Induced by the hydrogen bonding between GO and PEBA, GO nanosheets were assembled into several-layered GO laminates with molecular-sieving interlayer spacing and straight diffusion pathways (Figure 10a). Besides the improved selective diffusion, the preferential CO$_2$ adsorption of GO nanosheets enhanced the adsorption selectivity. Fast and selective gas transport channels existed in the uniformly dispersed GO laminates, which provides the GO MMMs with excellent preferential CO$_2$ permeation performance ($P_{CO_2}$: 100 Barrer [1 Barrer = 10$^{-10}$ cm$^3$ (STP) cm cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$]), $\alpha$(CO$_2$/N$_2$): 91) and extraordinary operational stability (over 6000 min). Further studies demonstrated that the gas permeation properties could be finely manipulated by controlling the lateral size and oxidation degree of GO nanosheets.

With the aid of a polymeric matrix, several 2D materials that face challenges of forming pure laminar membranes could start as MMMs. For instance, graphitic carbon nitride (g-C$_3$N$_4$, CNs), an emerging graphene-analogue material that possesses regularly distributed triangular nanopores (estimated as 0.31 nm) throughout the entire laminar structure, was incorporated into a sodium alginate matrix to determine its effect in membrane separation (Figure 10b).[86] The horizontally aligned laminar structure of CNs embedded in MMMs could afford ordered channels for water transport, whereas the nanoporous structure of CNs could provide a molecular sieving effect. Thus, the water flux and ethanol/water separation factor improved significantly by increasing the CN loading by 3 wt%. In addition, a reduced GO-modified CNs was used as a 2D filler to enhance the substrate properties of porous polyethersulfone for thin composite forward osmosis membranes.[86]

In addition to MMMs, 2D materials were used recently as a platform to advance the fabrication techniques of existing membranes. Current studies focused mainly on the hybrids of GO and MOF. Hu et al.[87] proposed 2D GO nanosheets for MOF nanocrystal growth, and obtained MOF GO hybrid nanosheets as the seeding layer to synthesize ultrathin MOF molecular sieving membranes (Figure 10c). The 2D seeding layer acted as a barrier between two different synthesis solutions, which self-limited crystal growth and eliminated defects during the contra-diffusion process. The resulting ultrathin ZIF-8/GO membranes ($\approx$ 100 nm thickness) showed excellent molecular sieving gas separation properties, with a high selectivity of 7.0 for CO$_2$/N$_2$, and 405 for H$_2$/C$_3$H$_8$. Huang et al.[88] used the intrinsic barrier property of graphene monolayers to seal the MOF crystal gaps to improve the MOF membrane gas selectivity. Bicontinuous ZIF-8@GO membranes were fabricated by LBL deposition of GO on the semicontinuous ZIF-8 layer. By patching the non-selective crystal gaps with a GO layer, gases permeated through the ZIF-8 micropores (0.34 nm), which resulted in an improved hydrogen selectivity for H$_2$/CO$_2$, H$_2$/N$_2$, H$_2$/CH$_4$, and H$_2$/C$_3$H$_8$ mixtures. Caro and co-workers[90] demonstrated the concept of “partial conversion of LDH laminates” for designing and fabricating high-performance MOF gas separation membranes.

4. Summary and Outlook

The rapid growth in interest and the large number of achievements in recent years suggests that 2D-material membranes are becoming a family of high-performance separation membranes. The unique atomic thickness of 2D materials stimulates the continuous pursuit of ultrathin and selective membranes for separation, regardless of fundamental and engineering studies. Recent breakthroughs in exfoliation and perforation of monolayers promoted the throughput and accuracy of nanosheet membranes for molecular separation. Although they were initiated from GO, and GO still...
remains a focus, laminar membranes have been explored in several other graphene-family 2D atomic crystals and layered oxides. Their fabrication approaches have been well-established and the precise manipulation of intergallery dimensions for efficient separation is of great importance. Two-dimensional-material membranes with well-defined transport channels and ultrathin thickness have demonstrated extraordinary performance for water and gas separations.

Current challenges that restrict the wide implementation of 2D-material membranes include the limited available techniques for exfoliating the high aspect ratio and intact nanoporous monolayers from bulk crystals, and drilling uniform, high-density, large-area, subnanosized pores in graphene nanosheets, together with how to scale such atomically thick membranes into applicable separation devices. Applying these ultra-thin membranes in practical separation remains a technical challenge in this emerging field. Moreover, the performance of state-of-the-art laminar membranes is far from the theoretical predicted values. This may be the result of an ambiguous understanding of structure–property relationships for the complicated nanochannels. To address these challenges, future directions may focus on exploring emerging 2D-material membrane platforms by including new kinds of 2D materials that have already shown success in other related fields. Theoretical models should be updated to describe the particularly confined transport behavior through 2D-material membranes accurately, accompanied by the in-depth characterization of transport passages. Significant effort should be applied to develop robust membranes with stable performance under realistic operating conditions. More research is also required to address specific requirements concerning various exciting, yet challenging, applications such as desalination and fuel cells.

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Two-Dimensional-Material Membranes: A New Family of High-Performance Separation Membranes

Separation goes small: Two-dimensional materials of atomic thickness have emerged as high-performance separation membranes. The latest advances in the design and fabrication of 2D-material membranes are reviewed, along with a discussion about the challenges for future applications.