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Abstract

Two-dimensional (2D) material nanolaminate membranes (2DMMs) have garnered significant attention as next-generation separation membranes thanks to their superior molecular permeation properties and remarkable selectivity. The performance of 2DMMs is largely determined by nanochannel architecture and microenvironment, which are affected by the surface pattern and physicochemical properties of 2D nanosheets.

This review summarizes the nanochemistry strategies for engineering 2D materials and discusses the effect of nanosheet modification on the nanochannel architecture (interlayer space) and surface physicochemical properties (charge, affinity, and hydrophilicity) of the nanolaminate membrane. It also sheds light on the importance of the physical and chemical properties of the nanosheets in tailoring the performance of 2DMMs for selective sieving. We finally discuss the remaining challenges and

opportunities associated with the development of 2DMMs.

2D materials as separation membranes

Membrane separation is an energy-efficient and environmentally friendly method that has found widespread use in gas separation, ionic sieving, water purification, and seawater desalination [1,2]. **Membranes** (see Glossary) play a crucial role in the performance of separation techniques, and as such, there is an ongoing pursuit for better membranes with higher permeability, greater **rejection**, and improved stability.

Polymer membranes have dominated the separation membranes market due to their abundant species, easy processing, and scalability. However, the performance of conventional polymer membranes has hit an upper limit due to the trade-off between permeability and rejection [3]. Moreover, plasticization and fouling of polymer membranes can significantly degrade their performance and shorten their service life [4]. The search for new materials with high permeability and rejection as next-generation separation membranes has become a research hotspot.

Two-dimensional (2D) materials possess unique advantage in membrane separation due to their atomic thickness and large-lateral surfaces with abundant active sites and tunable charge density to construct channels with confined environments and have been proposed as membrane building blocks [5,6].

2D single-layer membranes consist of a single or a few-layer perforated nanosheets supported by a porous substrate (Figure 1A). The selectivity is achieved by the different permeation rates through the nanopores on the nanosheets, which are caused by size confinement, electrostatic interaction, and chemical or physical adsorption [9].

Conversely, 2D nanolaminate membranes are assembled by stacking 2D nanosheets, and the mass transport occurs in the confined interlayer **nanochannels** formed between

two adjacent nanosheets (Figure 1B) as well as in the intraplanar channels formed by intrinsic or perforated nanopores on nanosheets. High selectivity is typically achieved through sized exclusion, electrostatic repulsion, or adsorption inside the nanochannels [6]. By optimizing the interstitial nanostructure together with the physical and chemical properties of the nanosheet surface, nanolaminate membranes hold potential for breaking the permeability and selectivity tradeoff in traditional membranes.

Up to now, several important milestones have been achieved both in single-layer membranes and nanolaminate membranes. Different types of 2D materials with intrinsic nanoporosity such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs) and zeolite have been demonstrated [7,8]. These membrane building blocks have precise pore sizes ranging from subnanometer to tens of nanometers, offering promising prospects for fast ionic sieving and molecular separation [10-13]. Various perforation methods such as ion/electron beam irradiation, oxygen plasma etching, and ultraviolet-induced etching have been successfully used to create pores on nonporous nanosheets like porous graphene and MoS_2, resulting in single-layer membranes with ultrahigh permeability approaching the theoretical limit [14-16]. Despite the significant progress, single- and few-layer membranes still face two main challenges; namely (1) the synthesis of integrated large-scale nanosheets without defects/voids remains a challenge and (2) the poor mechanical strength resulting from their atomic thickness and high-density pore distribution on the nanosheets limits their practical applications. Comparatively, nanolaminate membranes significantly reduce the probability of pinholes and increase mechanical strength, making them more suitable for real separation processes and higher-pressure operations.

For nanolaminate membranes, the transport and sieving phenomena primarily occur in the interlayer nanochannels, which are regulated by their nanostructure and surface

physicochemical properties. Nanochemistry approaches have been proposed to engineer exfoliated nanosheets by attaching various groups, molecules, ions, or nanoparticles to their surfaces. These modifications are typically achieved through covalent or non-covalent strategies (*Boxes 1,* Figure I). Although nanolaminate membranes have been previously discussed in the literature [17,18], most of them are material-oriented reviews, focusing only on one typical membrane, such as GO, MoS_2 or MXene-based membranes. The present review aims to go beyond by exposing the recent developments in the engineering of the surface chemistry and the interlayer of 2D nanolaminates. This review will provide an original in-depth discussion on the two important research area associated with nanolaminate membranes: (1) the chemical modifications of exfoliated nanosheets and (2) the consequences on the nanostructure and microenvironment of membranes. By using selected examples from the literature, we will examine how surface engineering of the nanosheets can tailor the nanochannel architecture (**interlayer space**), the surface physicochemical properties (charge, affinity, and hydrophilicity), and the resulting separation properties. We finally provide an outlook on the remaining challenges and opportunities for 2D nanolaminate membranes towards realistic applications.

Box 1. Nanosheets modification strategies employed in nanolaminate membranes

Thanks to their large specific surface area, surface modification of the exfoliated 2D nanosheets via covalent or non-covalent strategies has proven to be an efficient strategy to tailor the local microenvironment of the nanolaminates (Figure I). Covalent ***functionalization*** *allows the stable attachment of molecules to the edges or the basal planes of exfoliated nanosheets. Due to the absence of dangling bonds on the basal*

planes of pristine 2D materials, covalent functionalization often necessitates the use of highly reactive reagents. This includes strong oxidants, reducing agents, nucleophiles, electrophiles, among others depending on the targeted reaction and the nature of the 2D material. 'Remarkably, functionalized nanosheets can be modified further by attaching more complex molecules using substitution, amidation, silanization and esterification reactions with the heteroatoms on their surfaces, such as -F, -OH, and -COOH groups [29,30]. Non-covalent functionalization of nanosheets has emerged as a promising approach to modify exfoliated nanosheets without inducing defects. This strategy takes advantage of attractive interactions, such as electrostatic and van der Waals forces or hydrogen bonding, rather than covalent bonding. The ions, molecules and polymers are commonly employed to attach to the 2D nanosheets surface. Non-covalent functionalization can also involve the use of nanospacers that physically interact with the surface of nanosheets. These spacers consist of 1D or 0D nanoobjects, which are typically mixed together with the 2D nanosheets before the nanolaminate assembly, and the resulting membranes can be viewed as composite structures.

In the context of engineering nanolaminate membranes, both functionalization strategies offer complementary advantages. For instance, compared to covalent functionalization, non-covalent functionalization is simpler to implement and more versatile in terms of available functionalization strategies and the types of molecules, ions, or nanospacers that can be used. Covalent functionalization of 2D materials typically involves the formation of defects that act as anchor sites, potentially altering the structure of the nanosheets over time. However, covalent bonding provides robustness and stability, preventing the leaching of intercalants during operation and thereby limiting contamination of the permeate solution.

Engineering of the interlayer space

The interlayer space between adjacent nanosheets is crucial for solvent transport and molecular sieving in nanolaminate membranes. As the diffusion of chemical species mainly occurs in the interlayer nanochannel, the functional groups grafted onto nanosheets act as pillars to increase the interlayer space. The role of the interlayer space in nanolaminate membranes can be perfectly illustrated by the example of graphene (Box 2). MoS_2, one of the most extensively studied TMDs, encounters similar challenges as graphene. In dry conditions, Wang *et al.* found that MoS_2 laminate membranes exhibit a d-space of around 0.62 nm, corresponding in a **capillary width** of less than 0.15 Å [61]. While the strong van der Waals forces can maintain this d-space in water, it renders the membrane impermeable to water molecules. The covalently functionalized MoS_2 membranes show an expanded interlayer space (Figure 2B) [62]. The meticulous selection of functional groups enables precise control of the interlayer spacing from 9.8 Å to 13.3 Å, tuned with ångström precision [63]. This modification provides high water permeability and highly efficient desalination performance [62-64]. Additional studies by Hoenig *et al.* have confirmed that this functionalization strategy effectively facilitates water transport pathways in MoS_2 nanolaminates [65].

Box 2. Water diffusion in graphene and graphene oxide nanolaminates

In hydrophobic graphene and carbon nanotubes, water molecules can diffuse by slipping at the liquid/solid interface. The ***slip length****, which is defined as the extrapolated distance relative to the wall where the tangential velocity component vanishes, can reach several hundred nanometers inside carbon nanotubes and tens of nanometers in graphene capillaries [54,55]. This large slip length in graphene and*

carbon nanotubes is of quantum origin, as recently identified [56]. Multilayer graphene membranes possess laminate structures with turbo-stacked nanosheets creating an interlayer space of ~0.34 nm. However, this size is insufficient to allow for the transport of small molecules (Figure 2A). Graphene oxide (GO), the oxidized counterpart of graphene, is one of the most studied 2D materials due to its ease of preparation and high stability in solution when exfoliated. GO nanolaminates, with an interlayer distance of 0.8 nm created by the oxygenated groups acting as pillars, are suitable for small molecule transport, such as H_2 [57]. In graphene oxide, the functional groups allow chemical species to diffuse by increasing the interlayer distance, while the pristine conjugated and hydrophobic regions of graphene allow a fast diffusion of water molecules. The oxygen-containing groups of GO however turn graphene nanosheets hydrophilic, leading to a larger friction force between water molecules and the capillary walls and a reduced rate of water diffusion [58]. By contrast, hydrophobic surfaces minimize friction during water diffusion, leading to faster flow. The slip length of water in graphene oxide decreases to 1-2 nm due to the presence of functional groups on the nanosheets and the subsequent modification of the surface properties. This behavior has been confirmed experimentally and investigated by several theoretical studies, which have highlighted the unique properties of graphene oxide nanosheets as membrane building blocks [59,60].

In MXene nanolaminate membranes, the presence of terminated -F and -OH groups results in extremely small capillary widths. This unique characteristic contributes to high hydrogen (H_2) permeation rates compared to other common gas molecules like CO_2, N_2, and CH_4 [66]. To increase the interlayer space of MXene nanolaminate membranes for solvent transport, silane coupling agents have successfully been

employed to react with surface -OH groups. By utilizing silane-functionalized MXene, the interlayer space is effectively increased, thereby enabling enhanced solvent permeability through the membranes [67].

Functional groups play a crucial role in opening up the interlayer space of nanosheets. However, when hydrophilic groups, such as oxygenated groups, are grafted onto the nanosheet surface, a potential issue arises when operating the membranes in aqueous solutions. This is due to the propensity of these hydrophilic groups to cause swelling, which can lead to an undesired increase in interlayer spacing. Additionally, as penetrants diffuse within the tortuous transmembrane pathway, they can reduce the interactions between the nanosheets, ultimately resulting in the delamination of the membrane structure. These factors combined can contribute to an increased interlayer space, ultimately leading to poorer sieving performance in the membranes. In this context, an effective strategy for tackling the challenges linked to swelling and uncontrolled fluctuations in the interlayer spacing of nanolaminate membranes is to incorporate bridging molecules capable of crosslinking adjacent nanosheets. These bridging molecules react with the existing functional groups on the nanosheet surface, effectively fixing the interlayer space and limiting undesired swelling. By introducing crosslinking agents, the nanosheet structure is reinforced, enhancing the stability and preventing excessive expansion of the interlayer space. Hung *et al.* employed diamines with different sizes to crosslink GO nanosheets and tune the interlayer space, while demonstrating a limited swelling in water (Figure 2C) [68]. The crosslinked GO membranes show highly efficient and long-time stable ethanol dehydration performance under pervaporation. A similar strategy has been widely applied to GO laminate membranes for the different separation applications, such as ionic sieving [69], water purification and desalination [70] and organic solvent nanofiltration [71]. In

addition to diamine, other compounds such as organic acids (dicarboxylic acids) [72] and inorganic acids (boric acid) [73] have been successfully used for crosslinking GO (graphene oxide) nanosheets to address interlayer spacing issues. Thiourea, urea, diols and dopamine with available -NH_2 and -OH groups in the end are also employed to react with the oxidation groups on GO nanosheets to stabilize the nanochannels in nanolaminate membrane [74].

Non-covalent strategies allow for easy and reversible modifications, making it particularly attractive for fine-tuning the behavior of nanosheets in nanochannels. Intercalated ions within the nanochannels serve a dual role: enhancing the stability and mechanical strength of membranes through strong electrostatic attractions and mitigating swelling effects. Chen *et al.* firstly use different cations (K^+, Na^+, Ca^{2+}, Li^+ and Mg^{2+}) to decorate the GO nanolaminate membrane, showcasing the ability to finely tune the interlayer spacing with remarkable precision, ranging from 11.4 Å to 13.6 Å in aqueous solutions [31]. The strong cation–π interactions between hydrated cations and the aromatic rings from GO nanosheets and electrostatic attraction are responsible for the contracted interlayer space, which can efficiently and selectively exclude other ions that have larger hydrated volumes, demonstrating great promise for precise ion and molecular sieving in aqueous solutions. The ion modification strategy has also proven successful in negatively charged MXene membranes. Multivalent ions and poly-cations have been tested for controlling the swelling of MXene membranes, [75] [38] [33]. By introducing Al^{3+} or Ca^{2+} ions into the interlayer spaces, the swelling of MXene membranes can be effectively limited and regulated [38] [33]. Similar to GO nanolaminates, the controlled swelling ensures a fixed interlayer spacing, which in turn contributes to highly efficient desalination performance in both forward and reverse

osmosis processes.

Nanoparticles and polymers, characterized by their larger size compared to ions and molecules, have been investigated as spacers. The utilization of SiO_2 nanoparticles to decorate GO nanosheets, for instance, results in the formation of an hourglass-shaped nanochannel structure that is analogous to the conformation of water transport proteins in GO nanolaminate membranes [52]. The resulting heterostructure design provides a wider interlayer space, enabling enhanced solvent filtration permeability without compromising rejection efficiency thanks to the presence of numerous narrow slits within the membrane. The intercalation of stimuli-responsive polymers could allow the preparation of membranes with dynamic behavior. Proof of concept was demonstrated by Andreeva *et al.*, who reported the fabrication of a pH responsive membrane by strategically intercalated polyamine macromolecules (PA) into GO nanolaminates [50]. The use of pH-responsive polymers introduces the capability to induce morphological changes within the nanochannels, leading to varied interlayer spacing in the complex membrane structure (Figure 2D). This responsive feature enables dynamic control over water transport, providing an environment-responsive functionality to the membrane.

Beyond separation properties, the interlayer spaces of nanochannels induce a confinement phenomenon at the nanometer level, which has profound consequences on the transport of molecules such as water. Both numerical simulation and experimental investigations have revealed that, under nanoconfined conditions between 2D nanosheets, water molecules exhibit remarkable structuring, forming orderly layers – typically one or several adjacent to the surface – while maintaining a disordered, bulk-like internal region. Calero *et al.* have determined the correlation between the structure of the water layer and the interlayer spacing in graphene slabs, revealing that optimal

slit-pore sizes at T = 275 K are approximately $6.5 \leq \omega/\text{Å} \leq 7.0$ for a single layer, $9.0 < \omega/\text{Å} < 10.0$ for two layers, and $12.5 < \omega/\text{Å} < 14.0$ for three layers (Figure 3A) [98]. The water layer exhibits a higher density than that of bulk water [99], with water dipole orientations also undergoing notable alterations (Figure 3B) [100]. These orientation distributions are intimately tied to the strength of the confinement. Generally, the water dipoles in the interface layer preferentially orient parallel to the interior surface of the nanoconfinement, leading to a reconfiguration of hydrogen bonding networks. As the system reaches subnanometer confinement – wherein only a single layer of water is formed – the average hydrogen bond number sharply decreases (Figure 3C) [101]. Monolayer water confined within nanochannels manifests 'ice-like' structures, exhibiting multiple shapes and patterns that are markedly influenced by the substrate material, such as square formations in graphene, rhombic in h-BN, and diamond shapes with isogonal tiling structures in MoS_2 [102,103]. Moreover, through adjustments of temperature and van der Waals pressure, monolayer water demonstrates various phase behaviors within the 2D slits, encompassing hexagonal, pentagonal, square, flat-rhombic, hexatic, superionic, and liquid phases (Figure 3D) [104].

The translational dynamics of water undergo notable alterations under nanoconfinement. Leoni *et al.* observed a substantial increase in water diffusion within sub-nanometer graphene slit pores, with rates surpassing those in bulk phases. Intriguingly, the longitudinal diffusion coefficient of water in graphene nanochannels is dependent on the slit size, reaching its maximum when the graphene plate separation distance measures 8 Å [101]. The hydrodynamics of water are also modified within nanoconfined spaces. While the slip length remains independent of the confinement size of the graphene slab [105], the viscosity of water is profoundly influenced by the layered structure of the confined water, especially when the capillary size is reduced to

less than 2 nm [106]. Notably, the shear viscosity of water is not only significantly augmented in subnanometer capillaries but also exhibits pronounced oscillations, emanating from commensurability between the channel size and the spatial requirement to accommodate a single layer of water molecules. Consequently, the synergistic effect of the ordered structure of nanoconfined water, the atomic smoothness, and electron distribution of the surface, coupled with the "frictionless" slip, translate to ultrafast water transport within graphene nanochannels.

When introducing oxygen-containing groups to the graphene basal planes, the capability to induce a layered structure under confinement is retained. The average distances between layers in GO laminates favor the creation of water layers distinct from those observed in graphene channels: 8.0 Å for a single layer, 9.3 Å for two layers and 11.7 Å for three layers of confined water, respectively [107]. The behavior also differs from the case on functionalization MoS_2 capillaries, for which the water structure is rapidly lost upon functionalization [62]. Within these confined layers, water density is typically larger than bulk [108]. However, the regular pattern of water molecules is disrupted by the presence of epoxide and hydroxide groups, translating to an increase in long-range disorder, especially evident within single-layer confined water [93]. Yet, a preference for the orientation of water dipoles remains, with a tendency towards a distribution parallel to the restricted direction [109]. Simultaneously, the number of hydrogen bonds witnesses a notable reduction, particularly as confined water transitions from a two-layer to a single-layer configuration and is independent of the functional group arrangement on the graphene surface [107]. Contrasting with confinement between graphene slabs, the oxygen-containing group in GO nanosheets limits the flow of confined water, resulting in a reduced diffusion coefficient compared to bulk water. Furthermore, the axial shear

viscosities of water are heightened within 2D GO nanochannels, wherein the viscosity exhibits a declining pattern concomitant with increasing confinement [110].

Precise control over the interlayer spacing in nanolaminate membranes significantly influences the transport properties of solvent molecules and enhances separation performance by restricting ion and contaminant diffusion. Beyond the adjusting the architecture of these membranes, regulating the microenvironment also provides an efficient strategy for fine-tuning separation performance. This requires meticulous engineering of the membrane's composition, surface chemistry, and overall structure to achieve desired functionalities. In the following sections, we will discuss how modifications to the nanosheets adjust the physiochemical properties of the nanochannels in nanolaminates.

Controlling the electrostatic interactions within the nanochannels

Chemically exfoliated nanosheets, including positively charged layered double hydroxide (LDH), as well as negatively charged materials such as GO, TMDs, and MXene are the most studied 2D materials for nanolaminate membranes. The presence of charge excess carried by the nanosheets combined with the confined spaces within the interlayer gives rise to ion transport behavior governed by surface charge interactions [76,77]. When assembled into a nanolaminate membrane, negatively charged nanosheets facilitate faster transport of cations while blocking anions. Consequently, many 2D nanolaminate membranes can serve as cation/anion sieving membranes [78]. By modifying the nanosheets, it becomes possible to achieve reinforced charge distribution or reversed charge, leading to novel, tunable and efficient ion sieving performance in nanolaminate membranes. To neutralize the negative charge

of graphene oxide (GO), Zhang *et al.* employed 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide (EDC) to react with the carboxylic groups and subsequently graft branched polyethylenimine (PEI) through covalent coupling, resulting in GO nanosheets enriched with positive charges (p-GO) [79]. The p-GO membranes exhibited inhibited proton transport behavior compared to the pristine GO membrane. p-n heterojunctions consisting in n-GO and p-GO were found to generate an internal electric field, leading to salt-ion-blockade transport behavior [80]. By synergistically applying an external electric field, a depletion area is formed in the transition zone, resulting in significantly lower ionic concentration compared to the bulk phase. Deionized water could be extracted from the depletion zone, achieving a high rejection rate of 97.0% for NaCl and a water flux of 1529 L m^{-1} h^{-1} bar^{-1}. Yang *et al.* employed 3-aminopropyl triethoxysilane (APTES) to functionalize MXene nanosheets *via* a silane coupling reaction, successfully synthesizing aminated MXene (AM-MXene) with a net positive charge [81]. Notably, the membranes formed by stacking AM-MXene nanosheets exhibited an anion-selective nanofluidic behavior, preferentially transporting Cl^- over Na^+. When utilized in osmotic power harvesting applications, this optimized membrane demonstrated a peak power density of 10.98 W/m^2 under a natural salinity gradient, significantly outperforming the commercial benchmark of 5 W/m^2.

Noncovalent approaches involving the combination of polymers can be utilized to tune the surface charge of nanosheets. For instance, positively charged MXene nanosheets (p-MXene) were synthesized by adsorbing the positively charged polymer polydiallyl dimethyl ammonium (PDDA) onto the surface through electrostatic attraction [82]. The resulting p-MXene membrane exhibited excellent anion selectivity. Combining the p-MXene membrane with a pristine MXene membrane possessing cation selectivity, led to the creation of a heterogeneous MXene membrane with

asymmetric ionic diode behavior, thereby offering promising prospects as a high-performance osmotic power generator. Rather than reversing the surface charge, the same charged polymer can be used to enrich the surface charge of nanosheets through hydrogen bonding and van der Waals attraction. Zhang *et al.* employed negatively charged Kevlar nanofiber to modify the MXene nanosheets [49]. Assembling into a composite membrane led to an enhanced charge density in the nanochannels, resulting in increased cation selectivity. Consequently, this composite membrane exhibited superior osmotic power density when mixing river water and sea water.

Controlling the chemical interactions within the nanochannels

The interplay between contaminants and nanosheets plays a pivotal role in influencing the adsorption and diffusion of penetrants within the nanochannel. By incorporating various functional groups and molecules onto the basal plane of the nanosheets, the affinity of the nanochannel can be tailored, thereby tuning the separation properties. To illustrate this strategy, the following section will focus on controlling interactions inside nanochannels for gas separation and ion sieving.

Oxygen-containing groups present on the GO nanosheets not only create unobstructed nanochannels but also exhibit a stronger affinity for polar molecules such as CO_2 compared to N_2. This strong adhesion between CO_2 and the oxygenated groups leads to preferential adsorption, thereby enhancing the CO_2 separation performance of GO membranes. To further enhance the oxygen content of GO nanosheets, Wang *et al.* employed poly(ethylene glycol) diamines (PEGDA) to covalently modify GO nanosheets by reacting with epoxy groups [83]. This modification enables the construction of CO_2-philic nanodomains enriched with abundant oxygen-containing groups. Simultaneously, the unreacted GO surfaces exhibit weak adhesion to CO_2,

facilitating low-friction diffusion, leading to excellent CO_2 separation performance. The strategy has been extended to other nanolaminate membranes, such as MXene. Zhang *et al.* intercalated PEGDA within the MXene interlayers to form heterogeneous nanochannels composed of both CO_2-affinitive and non-CO_2-affinitive nanodomains [84]. This rational architecture led to enhanced CO_2 separation efficiency (Figure 4A). In addition to oxygen groups, amino groups have also been employed to modify nanosheets and increase the affinity of the nanochannel. Zhou *et al.* grafted piperazine, an effective CO_2-philic agent, onto GO nanosheets [85]. The grafted amine-brushes within the GO nanochannels facilitated the transport of CO_2 molecules, resulting in improved CO_2/N_2 selectivity and CO_2 **permeance.**

Specific molecules like borates, ionic liquids or amino and carboxyl groups can create a favorable environment for CO_2 within the nanochannel [86-88]. The presence of ILs, which are characterized by nearly zero vapor pressure and high thermal and chemical stability, in the nanochannels induces strong interactions with CO_2, bringing priority CO_2 transfer and inhibited N_2 permeance for the composite membrane, leading to improved CO_2 selectivity comparing with pristine nanolaminate membrane [89].

Controlling the affinity of nanochannels has additional advantages, particularly in enhancing ion sieving capabilities. Zhang *et al.* incorporated 1-butylsulfonate-3-methylimidazolium, an ionic molecule, into the GO membrane (i-GO) [90]. This charged molecule not only establishes appropriate physical confinement through its ionic imidazole group but also fosters a favorable chemical environment for 2D ionic transport channels via its ionic sulfonic group. The presence of the ionic sulfonic groups in the i-GO membrane creates a hydrophilic environment, which boosts water affinity. This, in turn, ensures a high partition coefficient for K^+, culminating in a significantly enhanced transport rate for monovalent ions. Lu *et al.* employed poly(sodium 4-styrene

sulfonate) (PSS) to intercalate into the 2D MXene nanolaminate membrane to achieve selective Li^+ transport [91]. The modified membrane efficiently filters out Li^+ from mixtures containing Na^+, K^+, and Mg^{2+}. This high Li^+ selectivity originates from precise interlayer spacing and the weak interaction between Li^+ and the sulfonate terminal ($-SO_3^-$) (Figure 4B).

Tuning the hydrophilicity of nanochannel

The wettability of 2D nanolaminate membranes is determined by the surface properties of the nanosheets, which can easily be manipulated by tuning the surface chemistry of the nanosheets. Intercalated molecules residing within the nanochannels create hydrophilic or hydrophobic transport pathways. A hydrophobic nanochannel exhibits weak friction with water molecules due to their weak interaction, resulting in high water transport speeds. Conversely, a hydrophobic nanochannel restricts the entry of water molecules, whereas a hydrophilic nanochannel promotes water entry but hinders water transport due to strong adhesion interactions.

Graphene nanochannels with hydrophobic surfaces have demonstrated an exceptionally high water permeation rate due to their low hydraulic resistance [92]. However, when graphene oxide (GO) nanochannels undergo oxidation, the presence of grafted oxygen groups on the nanosheets' surface significantly reduces the diffusion rate of water molecules by strongly absorbing them and impeding their movement [93]. Unlike graphene nanochannels, which can be considered "frictionless" pathways for water transport, GO nanochannels exhibit a distinct parabolic velocity profile that indicates increased friction with water. The higher hydraulic resistance of GO membranes suppresses water shuttle and hampers efficient water permeation. To

leverage the potential of graphene nanochannels for ultra-fast water permeation, the concept of angstrom-channel graphene membranes (ACGMs) has been proposed by intercalating chitosan into thermally reduced graphene oxide (GO) sheets [94]. The hydrophobic ACGMs exhibited high flux for both water and organic solvents in pervaporation processes. Interestingly, when the feed solution consists of an ethanol and water mixture, the membranes prioritized water permeation over ethanol during pervaporation operations. Rather than reducing GO, Prabhakaran *et al.* enhanced its hydrophobicity by grafting imidazolium-based ionic liquids (ILs) onto its epoxide sites through a ring-opening reaction [43]. The longer alkyl chains attached to the imidazolium rings made the GO more hydrophobic. The adjustment optimizes water transport dynamics at the GO/IL interface, resulting in increased water flux. In addition to graphene and its derivatives, MoS_2 membranes with different grafted groups also exhibit varying surface wettability [62]. Hydrophobic groups, such as -CH_3 membranes lead to increased slip lengths when grafted on MoS_2 compared to the hydrophilic pristine MoS_2 nanosheets, resulting in higher water flux for membranes. Evidence of the reduced friction between the water molecule and the surface of the methyl functionalized MoS_2 nanosheets was provided by mapping the velocity of the confined water molecules between two MoS_2 slabs using molecular dynamic simulations (Figure 5A). Water molecules were found to exhibit higher velocities on the methyl group, which was attributed to the screening of the electrostatic interactions between MoS_2 and the water molecules. This high-water flux makes hydrophobic membranes particularly advantageous for water permeation applications, similar in nature to the phenomena observed for hydrophobic systems such as carbon nanotubes and graphene. MXene laminated membranes possess hydrophilic nanochannels. Yet, by introducing poly(ionic liquid)s with readily exchangeable counter anions, their wettability can be

tuned (Figure 5B) [46]. Through straightforward anion exchange, the interlayer galleries transition from hydrophilic to more hydrophobic, doubling the water permeance.

In contrast to the high transport efficiency of hydrophobic nanochannels, hydrophilic nanochannels present advantages in antifouling and exhibit enhanced water-selective properties for membranes. Li *et al.* developed a zwitterionic polymer-brush-modified graphene oxide membrane featuring trimethylamine-N-oxide (TMAO) head groups [95]. This design created a strong surface hydration layer for the membrane. The hydrophilic surface and the disinfection effect provided by the quaternary ammonium groups both contribute to the T-GO membrane's impressive anti adhesion and contact inactivation abilities. Huang *et al.* were the first to discover that vermiculite laminates can be tuned from superhydrophilic to hydrophobic simply by intercalating hydrated cations into the membrane [96]. Lithium-intercalated vermiculite laminate (LiV-laminate) exhibits a zero contact angle under wet conditions. The super-hydrophilic surface of LiV-laminate originates from the anomalous hydrated structure of Li at the vermiculite surface. These super-hydrophilic membranes demonstrated excellent oil-water separation performance attributed to their outstanding antifouling property. Dai *et al.* introduced sodium polystyrene sulfonate (PSSNa) to create high-density hydrophilic microregions in the GO membrane [97]. These high-density ionized sulfonate groups within the polymer chains facilitate water sorption, enabling high-efficiency water-selective permeation. Simultaneously, the intercalation of polymer chains restricts swelling in the composite membrane due to robust π-π interactions. The synergy between enhanced hydrophilicity and strict size confinement allows the PSSNa/GO membrane to exhibit superior separation performance in butanol pervaporation dehydration.

Conclusions and outlook

In the past decade, the field of membranes based on 2D materials has experienced remarkable growth, driven by the implementation of diverse chemical strategies to engineer the surface properties of these materials. This has paved the way for the creation of tailored 2D nanolaminate membranes with exceptional characteristics and functionalities. By precisely modifying the nanosheets, researchers have been able to assemble them into customizable nanochannels with controllable structures and favorable microenvironments. As a result, these chemically engineered nanolaminates have exhibited outstanding permeance and sieving performance across a wide range of applications, encompassing water desalination, nanofiltration, osmotic power harvesting, gas separation, and organic solvent dehydration. Despite the significant progress achieved in the fabrication of 2D material membranes, there still exist several challenges that demand attention to propel their further development (see Outstanding Questions):

(1) Advancing the functionalization strategies for 2D Nanosheets: Over the years, numerous functionalization strategies have been successfully adapted for the modification of 2D nanosheets. However, the achievement of a controllable degree of functionalization remains to be explored. The existence of different functionalization contents, coupled with uneven size distributions and varying layer numbers of 2D nanosheets, poses a significant challenge for 2D material membranes. Addressing this challenge holds importance as it can unlock the full potential of 2D nanosheets for various applications. Achieving uniformity in the degree of functionalization and controlling the distribution of functional groups across the nanosheet surface are crucial factors in enhancing the repeatability of 2D material membranes. Such advancements

will not only ensure reliable and consistent performance but also enable the reproducibility of experimental results across the different research groups.

(*2) Understanding the role of decorated molecules or groups:* The assembly of modified nanosheets into membranes offers remarkable opportunities to achieve tunable architectures and regulated microenvironments. However, a comprehensive understanding of how the surface chemistry of the nanochannels affects the transport of targeted penetrants is still lacking. It is imperative that future research efforts are dedicated to addressing this knowledge gap. Gaining insights into the intricate interactions between the surface functional groups and the transport of penetrants within the nanochannels holds significant implications for the optimization of 2D material membranes. This could be addressed by the development of theoretical models that can elucidate the underlying mechanisms governing the influence of functional groups on penetrant transport.

(3) *Generating a synergistic relationship between the nanostructure and the surface physicochemical properties:* Considerable progress has been made in understanding the impact of nanostructure and surface physicochemical properties on the performance of separation membranes. Existing studies have primarily focused on two aspects: the tunability of channel size to achieve physical separation confinement and the regulation of surface physicochemical properties to prioritize the transport of penetrants. However, a comprehensive approach that combines both aspects, encompassing the synergistic regulation of interlayer space and controlled surface physicochemical properties through modification, is essential to fully exploit the potential of physical and chemical separation mechanisms for the development of highly efficient separation membranes.

Acknowledgments

D.V. and W.W. acknowledge funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement no. 804320). W.W. acknowledge Ph.D. scholarship from the China Scholarship Council (CSC). D.V. and C.S. acknowledge funding from the French National Agency (ANR, programme 2D-MEMBA, ANR-21-CE09-0034-01). C.S. acknowledges funding from the French National Agency (ANR, JCJC programme, MONOMEANR-20-CE08-0009).

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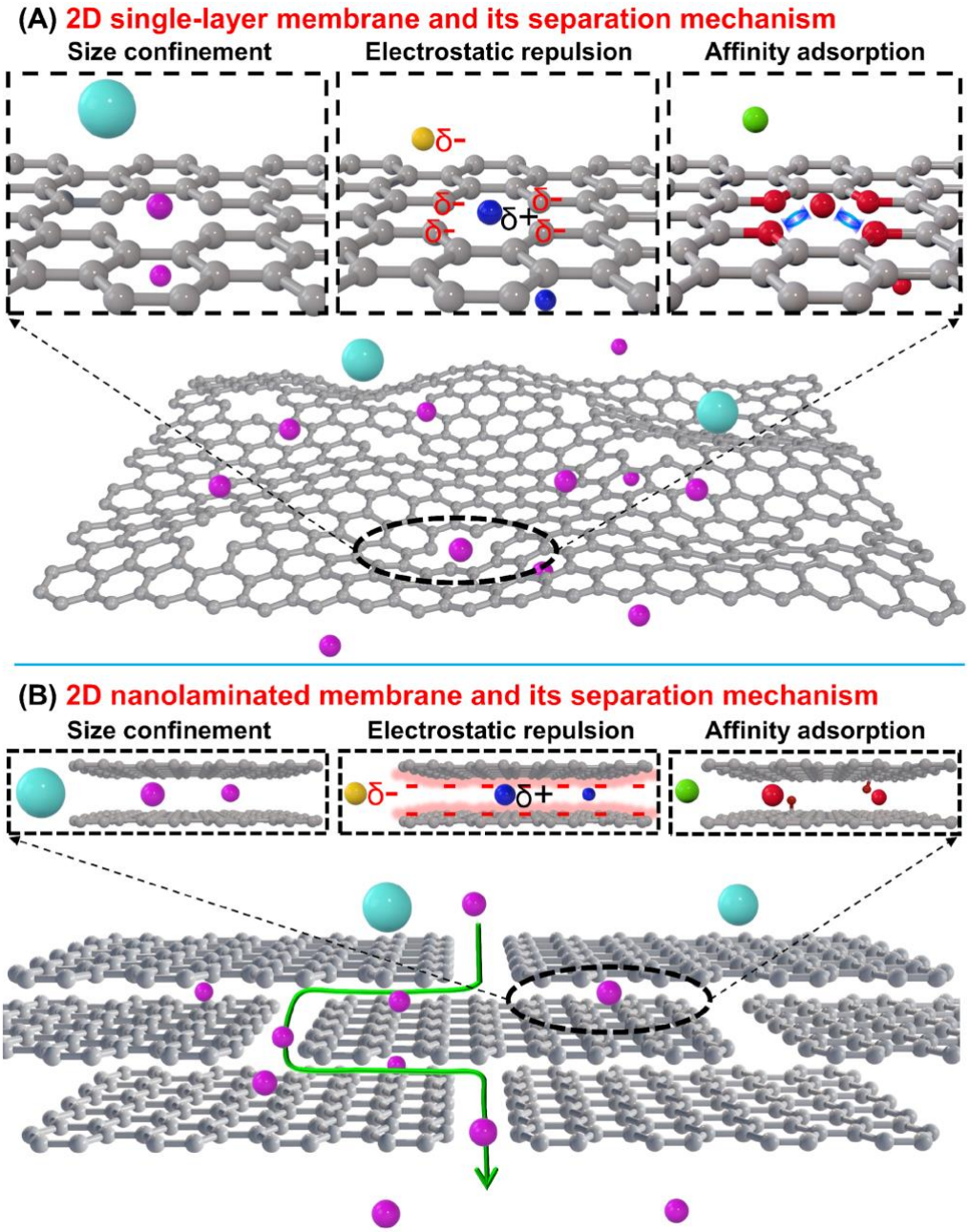


826

827 **Figure 1.** Schematic diagram of two types of selective channels constructed by 2D
828 materials and their separation mechanism. (**A**) 2D single-layer membranes. The
829 selectivity originates from the size confinement, electrostatic interaction and chemical
830 or physical adsorption of nanopores for the penetrants. (**B**) 2D nanolaminate
831 membranes. The selectivity comes from the sized exclusion, electrostatic repulsion and
832 prior adsorption of nanochannels for the penetrants.

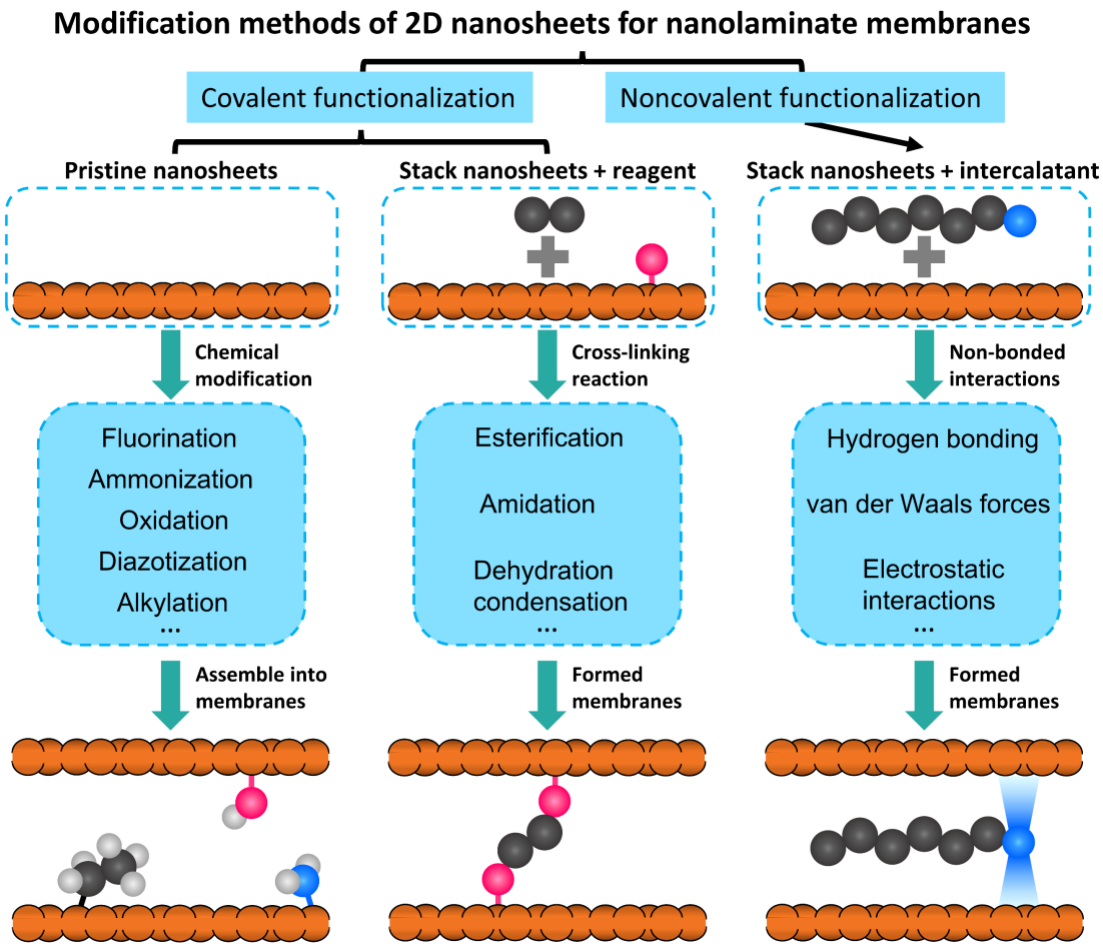


Figure I. The nanosheets modification strategies employed in 2D nanolaminate membranes.

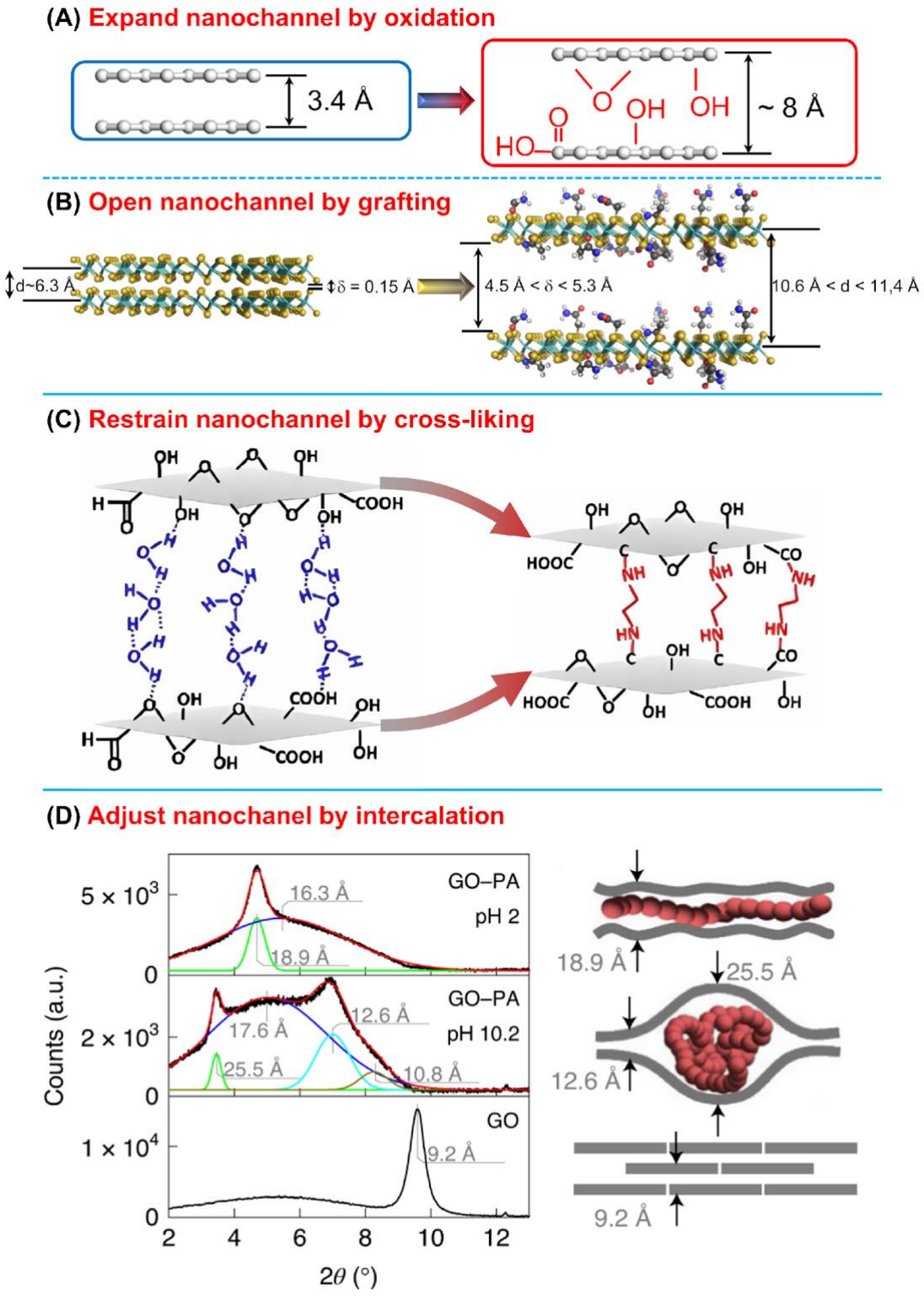


Figure 2. The interlayer space changes of 2D nanolaminated membranes aroused by covalent or non-covalent modification. (**A**) Schematic illustration of d-spacings of

graphene and GO nanochannel. (**B**) Schematics of restacked pristine MoS_2 and functionalized MoS_2 nanosheets with the interlayer spacing d and the capillary width δ. (**C**) Structural diagram and d-spacing of wet GO and diamine monomer cross-linked GO membrane. (**D**) X-ray reflection spectra for the GO–PA membranes prepared at different PH solutions with extracted interlayer distances (left) and schematic illustrations for the membranes' structure (right). Images adapted, with permission, from [31,50,62,66,68,93].

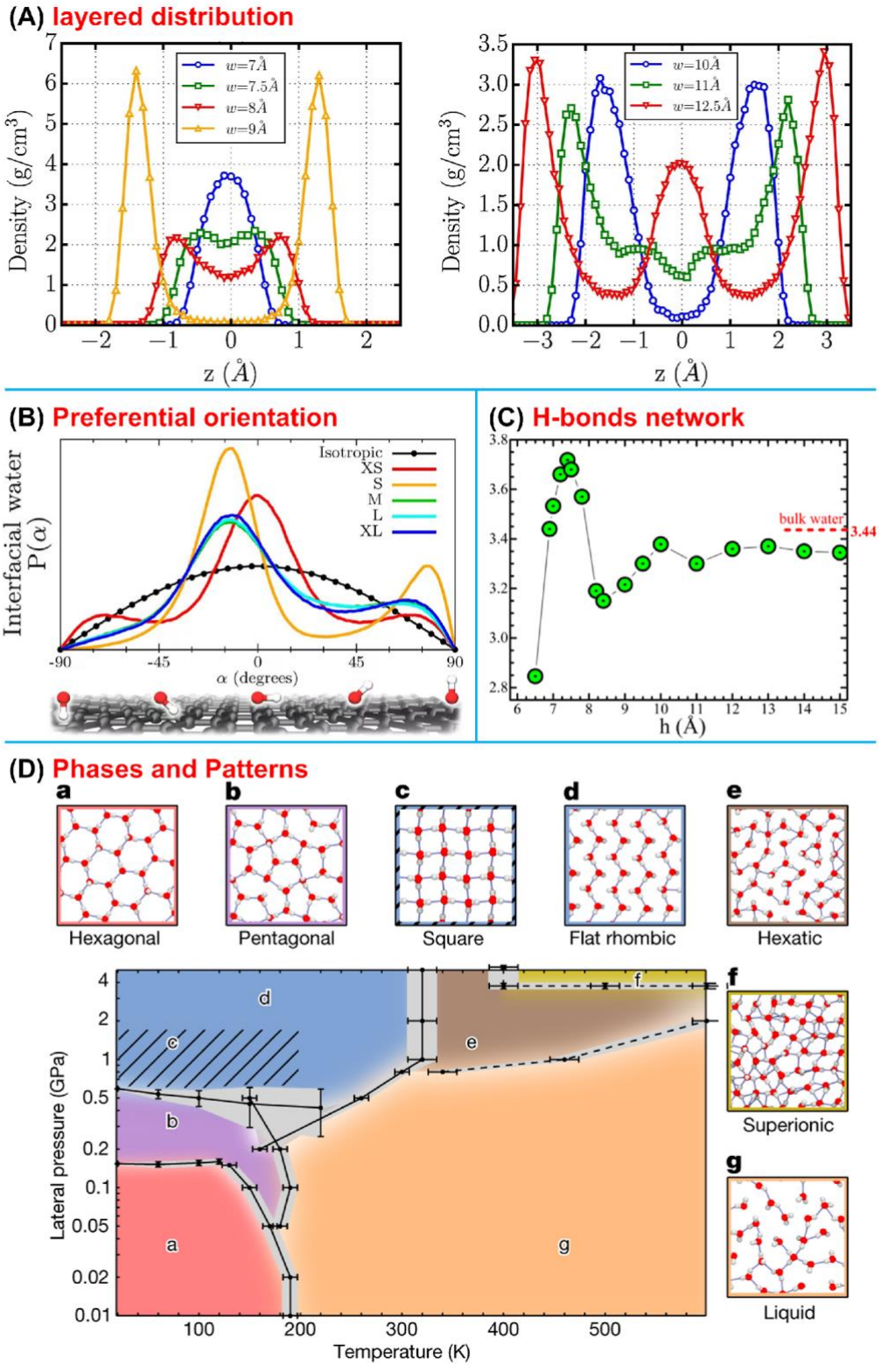
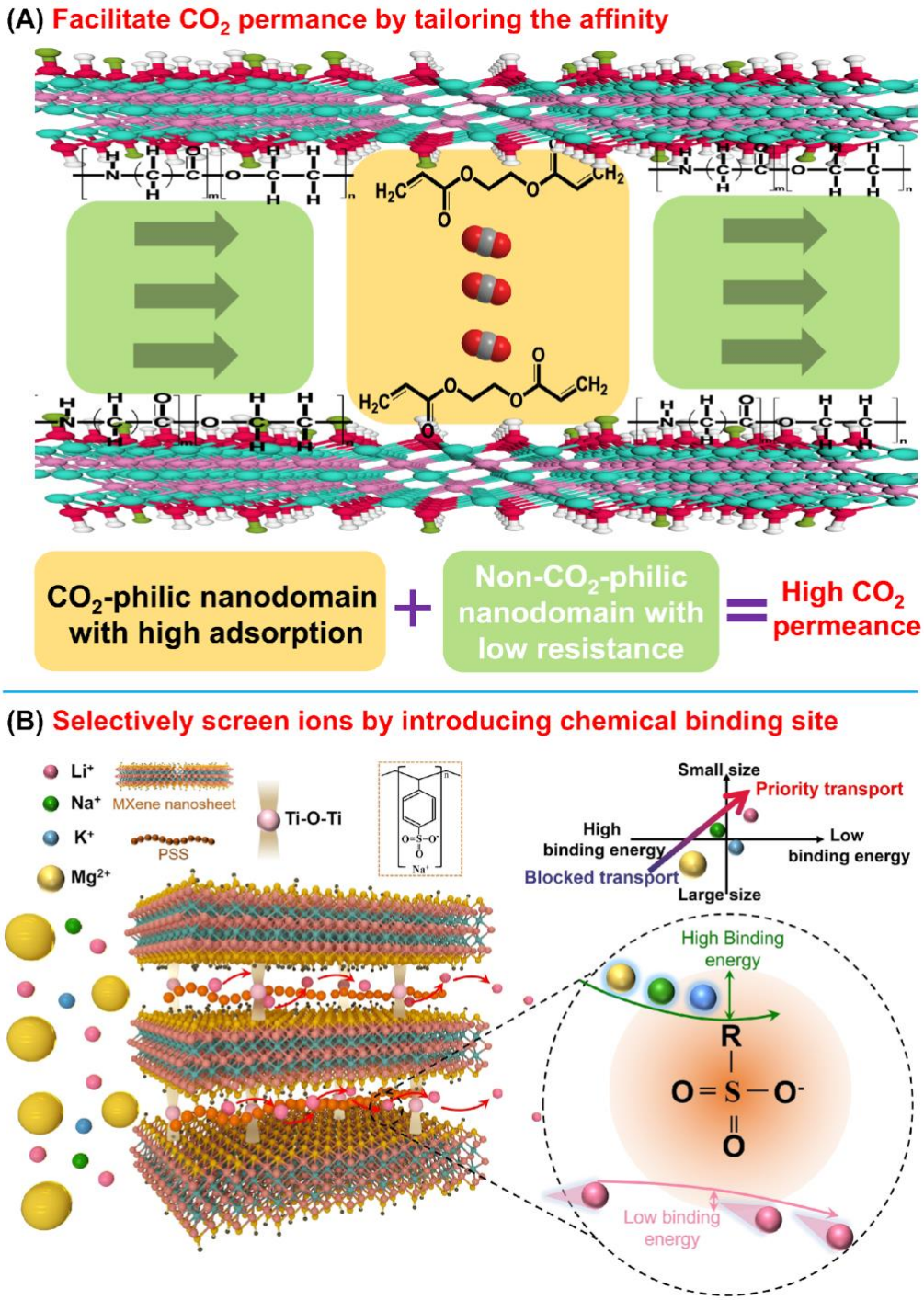


Figure 3. The structure of nanoconfined water under 2D nanochannel. (**A**) Water density distribution at different graphene-plate distances (ω). (**B**) Orientation distribution of of interfacial layer water under confinement. (**C**) Evolution of the

average number of hydrogen bonds per molecule as a function of nanochannel height h in the confined subvolume. (**D**) Phase diagram of monolayer nanoconfined water. Images adapted, with permission, from [98,100,101,104,106].



859

860 **Figure 4.** The nanochannel affinity adjustment of 2D nanolaminated membrane based
861 on the chemical modification. (**A**) Representation of gas molecules transport in the
862 MXene stacking membranes channels containing both CO_2-philic and non-CO_2-philic
863 nanodomains. (**B**) Schematic diagram of the rapid transport subnanochannels for Li^+ in
864 MXene/PSS composite membranes. Images adapted, with permission, from

[84,85,89,91].

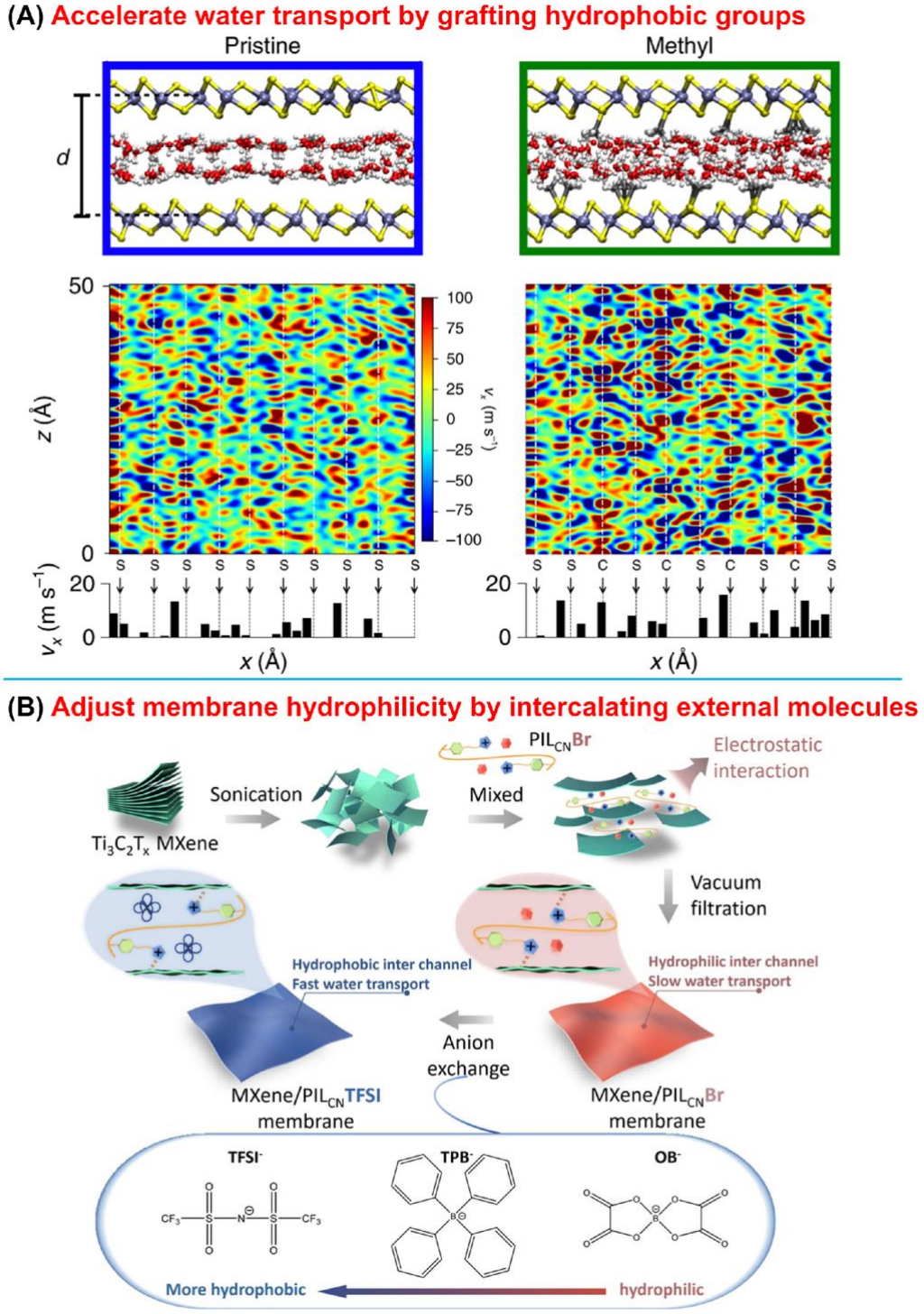


Figure 5. The surface wettability control of 2D nanolaminate membranes based on the chemical modification. (**A**) Averaged speed distribution of the first layer of water molecules in the pristine (left) and methyl functionalized (right) MoS_2 nanochannel and

its projection along the channel direction (Vx). (**B**) Schematic illustrating the preparation of MXene/PIL membranes with tailorable hydrophilicity. Images adapted, with permission, from [46,62,93,96].

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Highlights

Membranes are key for many important technological domains including energy storage, energy conversion, water treatment and separation of chemicals.

Exfoliated two-dimensional (2D) materials, when used as membrane building blocks, lead to remarkable separation capabilities for gas separation, micropollutant removal, desalination and organic solvents.

The sieving behavior of nanolaminate membranes is controlled by the properties of the nanochannels formed between the nanosheets, which result from the subtle balance between attractive van der Waals forces and repulsive forces resulting from hydration and electrostatic repulsion.

Strategies have been proposed to tailor the surface characteristics and physiochemical properties of the 2D nanosheets, thereby enabling the creation of tailored transport pathways with intriguing nanofluidic behavior.

Glossary

2D materials: A family of materials characterized by an atomic thickness, exhibiting a sheet-like morphology. By extension, the definition of 2D materials has broadened to encompass materials with negligible thickness in comparison to their lateral dimensions (height and width).

Nanochannel: The confined space within the nanometer range between the nanosheets in the nanolaminates.

Interlayer space: The interatomic distance between two successive nanosheets in the nanolaminate. The value is obtained from the position of the (002) peak in the X-ray diffraction pattern or high resolution electron microscopy

Capillary width: The space accessible in the nanochannel. The capillary width is calculated by subtracting the thickness of the nanosheets to the interlayer space

Membranes: A semi-permeable material employed to separate two regions and facilitate the selective diffusion of chemical species.

Functionalization:

The process of surface modification of (nano)materials with molecules or functional groups involves functionalization, which can be either covalent or non-covalent. Covalent functionalization induces the formation of a chemical bond, while non-covalent methods rely on physical forces such as van der Waals or electrostatic interactions.

Rejection: The separation capability of a membrane refers to its ability to isolate a specific chemical species from others. This property is commonly quantified as a percentage, with 100% rejection indicating complete prevention of the substance from crossing the membrane.

Permeance: A quantitative metric assessing the flow through a porous material.

Slip length: A parameter used to characterize the interaction of a fluid with a solid surface. A high slip length indicates minimal interactions between fluid molecules and the solid surface.