Lamellar Membranes

Asif Hafeez and Zakariya Zubair

Abstract This book chapter gives a comprehensive review of two-dimensional (2D) nanomaterials that provide tremendous potential for separation applications. By using 2D nanomaterials as a building block, various types of lamellar membranes are actively investigated. In lamellar membrane, the mass transport occurs through the inherent interplanar spacing of the nanomaterials and the nanochannels generated during the fabrication of lamellar membranes. However, the trade-off between permeability and selectivity in membranes is inevitable. Different strategies such as interlayer channel aperture, membrane nanopores, and appropriate functionalization can bridge this trade-off. Various routes for preparing lamellar membranes including 2D nanosheet synthesis strategies, assembling techniques, mechanisms involved in transportation, and regulation of nanochannels are discussed in detail.

Keywords Lamellar membrane · Porous nanosheets · Non-porous nanosheets · Transport mechanism

1 Introduction

Separation of the target component from a mixture plays a vital function in various fields such as water/air purification, medical, chemical engineering, etc. Membrane technology is advantageous over conventional separation techniques (sorption, distillation, filtration, etc.) due to its benign environmental impact, low-cost, ease of fabrication, and operational performance [1–3]. Separation through membrane-based processes has received increased attention with polymeric membranes being in the foreground in research as well as the separation industry.

Membranes act as a barrier that selectively separates entities based on their nature and properties. The membrane acts as a selective barrier, permitting a species smaller than the pores through it while selectively separating one or more species larger than

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the pores. These species could be molecules of inorganic or organic entities. The efficiency of a membrane is translated in terms of permeability and solute exclusion and is based on the physio-chemical properties as well as pore shape, size and tunability through precise control. The membrane efficiency features such as high selectivity and high permeability while exhibiting stability in a harsh environment are still a challenge, which provides an avenue for the advancement of membrane technology.

The cost-effective synthesis and fabrication of a membrane that demonstrates exceptional stable separation features under harsh process conditions is an ongoing challenge. The trans-membrane channels are either composed of voids from dense polymer films, nanovoids from semi-rigid polymeric structures, or permanent voids from crystalline frameworks [4]. Ideally, the trans-membrane channels should be small with a high degree of compactness to obtain high permeance along with chemical and mechanical stability to ensure long-term application. The pore size distribution throughout the membrane should be narrow to provide membranes with higher selectivity [5].

Till now, several materials have been synthesized and used for gas and water purification to improve their limitations. The progress in the advancement of membranes based on polymeric materials is considered a milestone in the history of membrane technology due to its cost-effectiveness, efficient performance efficiency, and easy and facile fabrication at small to large scale. However, the polymeric membranes are prone to swell in organic solvents and exhibit lower stability at high temperatures, and are bound by the trade-off effect, where highly permeable membranes are generally demonstrating selectivity on the lower side and on the other hand, a membrane with low permeability exhibits a high selectivity [6, 7].

Recently, two-dimensional (2D) nanosheets with single- or a few-atoms thickness have become the anticipated structural block for futuristic nano-channeled membranes. Based on the atomic structure, 2D nanomaterials are either non-porous or porous. They can thus be assembled as a selective barrier for separation applications in the form of nanosheets and lamellar membranes, as shown in Fig. 1. The nanosheet membranes consist of a monolayer or a few layered 2D nanomaterial with uniform inherent pores or engineered nanopores for selective permeation. The lamellar membranes are fabricated by assembling 2D nanosheets overlayed with interlayer spacing used to provide molecular transport [8]. After the successful exfoliation of graphene by Novoselov and Geim in 2004, 2D nanosheets have gained widespread attention. The exfoliation resulted in a hexagonal lattice consisting of carbon atoms on an atomic scale [9]. Due to their thickness and unique structural characteristics, 2D nanomaterials present an opportunity for the development of membranes that can theoretically withstand ultimate membrane performance properties [10]. The reduced thickness of the membrane results in superior performance. The ultimate desirable thickness of the membrane would be one-atom-thickness which is achievable by two-dimensional (2D) materials [11]. Furthermore, 2D nanosheets can be designed with specific channel dimensions coupled with aimed chemical functionalities, which enables an exceptional membrane that is capable of physical or chemical selectivities [12]. Up till now, in addition to graphene, other two-dimensional materials such as zeolites, metal–organic frameworks (MOFs), covalent organic
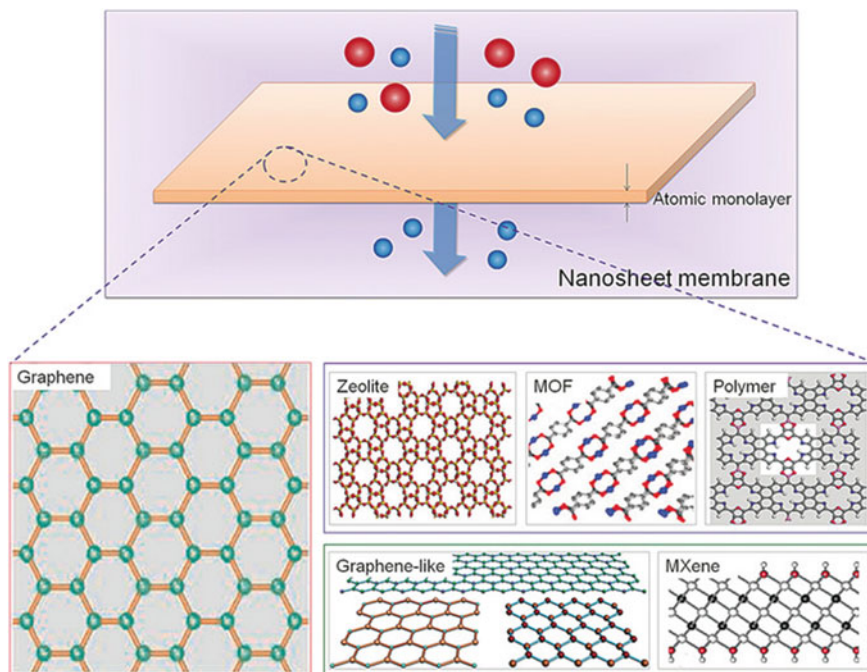
Fig. 1 Main Types of Two-Dimensional Materials and their Membranes. Reproduced with permission from [8]

frameworks (COFs), graphene oxides (GOs), hexagonal boron nitride, layered double hydroxides (LDHs), transition metal dichalcogenides (TMDs), MXenes and graphitic carbon nitrides (g-C_3N_4) have been employed for the fabrication of membranes [11, 13].
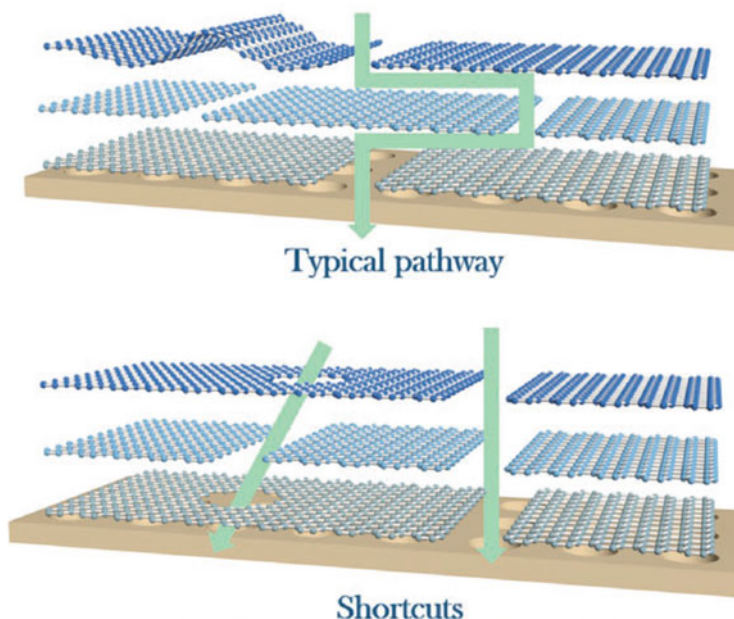
2 Lamellar Membranes

When 2D nanosheets are fabricated into membranes, ideally the single atomic thickness nanosheets with a high degree of porosity are mounted on top of the highly porous support [14]. The transmembrane short channels act as a transporting path for ultra-fast permeation. However, synthesizing such nanosheets with large intra-planar dimensions which are without any defects presents a challenge [15]. The lamellar membrane is another geometry that comprises prime quality 2D nanosheets as the main constituent and an impeccable membrane fabrication approach to fabricate a well-defined transmembrane pathway with abundant nanopores. These transmembrane channels provide a means of rapid transport to the penetrant. The mass

transport takes place in both the intraplanar either inherent or engineered channels, and the interplanar channels. The transmembrane channels that are based on nonporous nanosheets originate from the interplanar spacing. The interplanar spacing channels are usually tortuous. These channel results when nanosheets are stacked parallelly, and due to the interplanar attractive or repulsive interactions. These interplanar interactions create an interlayer void that is responsible for mass transport [16, 17]. Two-dimensional nanosheets that are inherently nonporous includes GO, h-BN, MXenes, etc. Intrinsically porous nanosheets stacked in the lamellar fashion have additional nanochannels, that are established on the inherent pores of the nanosheets. Intrinsically porous two-dimensional nanosheets are based on zeolites, MOFs, COFs, and graphitic carbon nitride (g-C_3N_4). Nanochannels based on post-perforation can either be intrinsically porous or nonporous nanosheets. These intraplanar perforations within the nanosheets are introduced physically by charged particle beam or chemically through oxidation, or plasma to obtain engineered 2D nanosheets with enhanced porosity [10].

The lamellar assembling of 2D nanosheets has been acknowledged as a next-generation membrane for applications as an effective selective barrier due to its capability of being environmentally friendly as well as conserving space and energy [18]. Ideally, a high-performance membrane should exhibit outstanding durability and nanochannels that are more compact than the target molecules to maximize its permeance and solute exclusion. To realize a well-ordered 2D nanosheet lamellar structure, homogeneity of nanosheets with controllable physical aspects (shape, size, and thickness), the interfacial affinity between the polymer and 2D nanosheets is simultaneously essential. The resulting lamellar architecture would be responsible for molecular transport through interplanar slit-like nanopores and nanochannels, as shown in Fig. 2.

The current advancement of the 2D-enabled membranes with either inherent or engineered nanopores shows a unique pattern that varies from the traditional membrane designs. Up until now, three major classes of 2D nanosheet-based membrane systems have emerged with the advancement of two-dimensional nanomaterials, as shown in Fig. 3. The class 1 membranes (see Fig. 3a) are lamellar that are composed of closely stacked intermeshed nanosheet layers, where the nanosheets do not possess in-plane intrinsic pores. The convoluted and tortuous transport pathways are formed between the nanoflakes, also termed nanochannels and nanopores, that allow size-specific permeation of molecules and passage to the interplanar spacing between adjacent nanosheets of the packed two-dimensional nanosheets. Furthermore, the practical membranes in this class will exhibit a distribution of pore sizes and defects, originating from exfoliation. This range of pore size distribution is directly linked with nanoflake size distribution and degree of compaction. These nanoscopic transporting channels are termed external nanoporosity, which is illustrated in the highlighted area of Fig. 3a. Traditionally, Class 1 membrane represents nanoparticles with no intrinsic porosity such as graphene oxide [20] and h-BN [21] nanosheets. The membranes fabricated from Class 1 have been reported to efficaciously remove solvated solutes from the feed at exceptional permeability, suggesting the external

Fig. 2 Possible pathways for mass transport through a 2D lamellar membrane (top) interplanar mass transport (bottom) intraplanar mass transport. Reproduced with permission from [19]

nanoporosity ranges from < 0.7 nm to 0.7–2.0 nm [22] depending upon nanosheets and nanosheet stacking technique.

The nanomaterials with intrinsic basal plane nanopores used for two-dimensional membranes are classified as Class 2 membranes. The in-plane nanoporosity of these membranes is extremely capable of excluding molecular sizes up to 0.01–0.05 nm [23, 24]. These intrinsic nanopores are embedded in the three-dimensional (3D) porous nano-architecture and are different from external nanopores as well as intrinsic crystallographic defects. Nanosheets procured or delaminated for Class
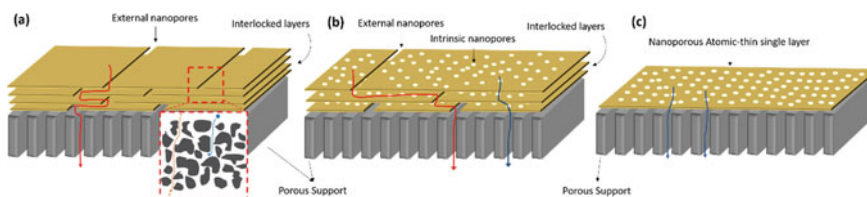
Fig. 3 Classes of 2D-nanosheet based membranes: **a** Class-1: membrane with intermeshed nanosheets, **b** Class-2: membrane with intermeshed nanosheets that have inherent nanopores, and, **c** Class-3: membrane with atomically thin layered nanosheet with inherent nanopores; red arrow indicates solvent transport through extrinsic nanopores and, blue arrow represent solvent transport through inherent nanopores

2 membranes originate from 3D microporous nanomaterials such as molybdenum disulfide (MoS$_2$) [25], zeolite [26], and, covalent- and metal–organic framework (COF and MOF) [24, 27]. Upon compaction of these intrinsic microporous nanomaterials into a lamellae formation, class 2 membranes exhibit synergistic enhanced size-specific permeation stemming from permeation promoting external nanopores and highly selective nanostructure-intrinsic nanopores, as shown in Fig. 3b. Recently, in-plane pore perforation in 2D nanomaterials is realized through elaborate oxidative etching and electron/ion bombardment employing microwave irradiation [28] and, plasma treatments [29]. Xu et al. (2018), used the oxygen plasma etching technique to introduce 0.6 nm in-plane pores, which enhanced the water permeation through reduced graphene oxide (r-GO) lamellar membrane.

The third class of 2D enabled membrane, see Fig. 3c, is an atomically thin 2D nanomaterial layer with induced or inherent in-plane nanopores. Class 3 membranes are an extension to the Class 2 membranes, yet they differ in thickness. Commonly class 2 membranes have a wider thickness ranging from tens of nanometres to micrometres due to nanosheet stacking. Nevertheless, class 3 membranes are distinguished as few-nanometre thick membranes assembled from 2D nanomaterials. Single- or few- atomic thick-layer membranes with inherent or engineered in-plane pores are representative of this class.

2.1   Synthesis of Two-Dimensional Nanosheets

A high-performance 2D nanosheet-based lamellar membrane requires superior quality 2D nanosheets with a precise membrane fabrication technique for the assembly and incorporation of nanochannels, that would provide a transportation pathway. Therefore, attention is required to the physical and chemical aspects of the nanosheets. The physical requirements of a nanosheet are its size, shape, and longitudinal and transverse dimensions. The chemical aspects that assist the transportation of entities either from nanopores or nanochannels are their defects and surface functionalities. These parameters dictate the selection criteria for fabrication techniques. The synthesis approach for 2D nanosheets can be generally divided into top-down and bottom-up routes, as shown in Fig. 4. The top-down technique signifies the disintegration of materials from the bulk into few-layered delaminated nanosheets, although the bottom-up route indicates the straightforward synthesis of 2D nanosheets from the corresponding starting materials. For a high-performance lamellar membrane fabricated, the nanosheets should be atomically thin to minimize the tortuosity of the mass transport. The longitudinal dimensions of the nanosheets should be wide to decrease the number of less selective intraplanar gaps. The nanosheets have intercalated moieties which facilitate scrupulous transport of penetrants in separation applications.
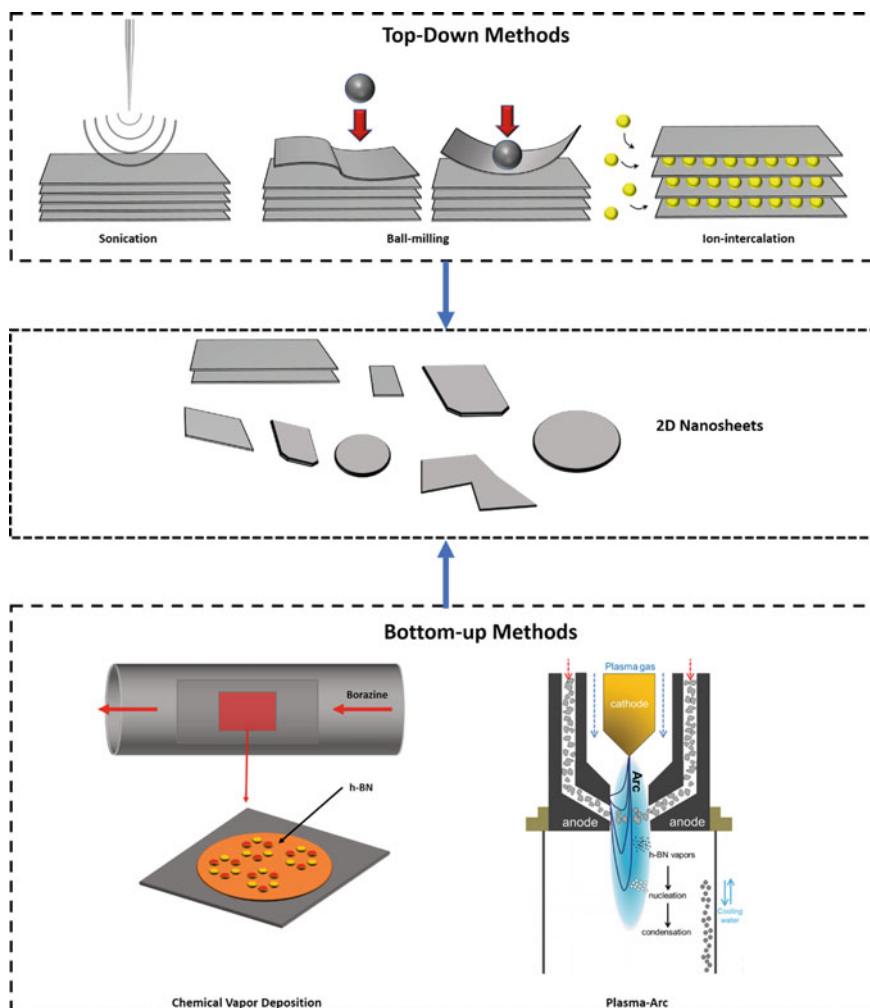
Fig. 4 Schematic illustration of 2D nanosheet synthesis techniques

2.1.1 Top-Down Route

2D nanosheets are assembled by stacking monolayers epitaxially. The layered structure of nanosheets is linked with strong covalent bonds within a lattice, while the weak interlayer interactions (vdW forces, H-bonding, and, π-π interactions) exist amongst the layers. As a result of the weak interlayer interactions, few-layered 2D nanosheets can be obtained from the bulk through the application of external force. The top-down methods are divided into solid-phase and liquid-phase exfoliation.

The disintegration of 2D nanosheets can be realized by solid-phase exfoliation using mechanical force. Single to few-layered nanosheets through microcleavage

of the bulk layered crystals by peeling exfoliation technique. Exfoliation of bulk layered crystals is through adhesive tapes, in a study by Novoselov et al. (2004), they reported successful seclusion of graphene monolayers [9]. However, different studies by Pacile et al. (2008), Meyer et. al (2009), and Gorbachev et al. (2011) adopted mechanical exfoliation of h-BN by providing enough peeling force from adhesive tape to break the weak vdW forces, the process yielded very thin sheets of layered h-BNs, while the primary B-N covalent bond was intact. However, due to the stacking characteristic of h-BN, peeling exfoliation is not efficient [30].

In comparison to peeling a more efficient solid-phase exfoliation technique to disintegrate 2D bulk nanosheets through mechanical force is accomplished through ball-milling. The main principle behind the nanosheet disintegration from the bulk is the shear forces being delivered by the high-speed rotating balls, as shown in Fig. 4. The principal forces involved in the exfoliation of 2D bulk nanosheets through ball milling are shear forces and vertical impact. The disintegration of bulk layered crystals occurs majorly due to the shear forces generated by the rotating balls within the ball mill, which results in nanosheets of larger lateral dimensions. The other force involved in the exfoliation of 2D nanosheets is the force that originated due to the vertical impact and collision of the balls, this results in severe crystallographic defects with smaller lateral dimensions [31]. The vantage of ball-milling operation over other techniques is its scalability, convenience, and process optimization through milling parameters such as ball type and size, milling rpm, and ball/bulk nanosheet ratios [32]. This technique is a powerful process that introduces crystalline lattice defects and is even capable of destructing the crystalline lattice structure of the 2D nanosheets. Due to this introduction of lattice defects, the atoms around the defect sites are highly active and vulnerable to bonding, which provides an opportunity to introduce new functionalities to the exfoliated nanosheets [33].

Nowadays, the more widely adopted approach to disintegrate the 2D nanosheet from the bulk is by employing liquid-phase exfoliating techniques. These techniques are based on the dispersion of nanosheets in a liquid medium followed by the application of mechanical forces or introduction of an entity that disrupts the interplanar interactions and then applying the mechanical force to exfoliate the few-layered nanosheets. The mechanical force to the bulk nanosheets is delivered by ultrasonication technique. The colloidally stable exfoliated 2D nanosheet that is comprised of small and few-numbered stacked layers requires further separation by sequential centrifugation to yield the exfoliated nanosheets. The liquid-phase ultrasonication-based exfoliation of nanosheets is favored due to its process optimization through sonication intensity, amplitude, and period. A strategic solvent selection is also crucial for effective exfoliation, Exfoliation by sonication is effortless when the difference in surface energy of the solvent and nanosheets is marginal, hence the smaller mixing enthalpy. Therefore, the surface energy of the solvent plays a vital role in optimizing the sonication conditions. However, the surface energy is primarily dependent upon the temperature, which alters with the sonication intensity and duration. The surface energy of the solvent can be further enhanced by using a co-solvent or using a solute.

   The liquid-phase exfoliation of 2D nanosheets which is assisted through interca-lating ions or molecules into the layers is another route of liquid-phase top-down exfoliating nanosheets from the bulk, as illustrated in Fig. 4. The basic principle behind this technique is to attach ions of the small ionic radius into the interplanar spacing of the layered nanosheets. The ion attachment results is a significant increase in the interplanar spacing, thus weakening the vdW interactions amongst the consec-utive layers in the layered bulk crystals. The intercalation of external moieties func-tions either by weakening the layer-to-layer interactions or by enhancing the surface polarity which improves the solvent dispersion. The ion-intercalated 2D nanosheets can be readily exfoliated into single/few-layered nanosheets under gentle sonication conditions. As a typical example various cationic entities such as Li^+, K^+, Zn^{2+}, Na^+, etc., are intercalated in the interlayers of the bulk crystals through forced hydra-tion. In most cases, the ion-intercalated 2D nanosheets interact with the solvent and generate hydrogen gas upon reaction, which can also assist in expanding the layers in close vicinity during the sonication process and therefore results in promoting the exfoliation efficiency [34]. Molybdenum disulfide (MoS_2) and, transition metal dichalcogenides (TMDs) are usually exfoliated by this technique. This intercala-tion exfoliation technique enables a highly stable dispersion of 2D nanosheets in a different solvent. However, the prerequisite of this technique requires a longer time and smaller nanosheet dimensions for proper diffusion of ions within the interlayers [34]. Further purification by removal of large and thick flakes by centrifugation enhances the yield of single- or few-layered nanosheets.

2.1.2   Bottom-Up Route

The top-down synthesis route is limited to the presence of layered nanomaterial as the predecessor, whereas the bottom-up technique is related to almost all 2D nanomate-rials. This technique involves the build-up of materials from scratch (atom-by-atom or cluster-by-cluster), generating a uniform nanosheet size, contour, and, distribution. Bottom-up synthesis techniques are mainly comprised of wet-chemical synthesis and chemical vapor deposition (CVD) growth. These processes are equipped to precisely control the synthesis process to maintain the nanoparticle size by inhibiting the reac-tion process. Furthermore, these techniques surpass in regulating the quantity and quality of the nanosheets with homogenous size distribution and morphology.

   The wet-chemical synthesis is employed for the synthesis of the typical porous 2D-nanosheets that are made from nodes and linkers like zeolites, MOFs, and COFs. The synthesis process selectively inhibits the growth of the material unidirection-ally [35]. Hydrothermal, interfacial synthesis, and solvothermal techniques are the most popular strategies. These techniques involving the synthesis of 2D-nanosheets in aqueous and solvents are often carried out under high temperatures and pres-sures [34]. The lateral and transverse dimensions as well as the size and degree of crystallinity of the 2D nanosheets can be precisely controlled through meticu-lously changing the synthesis parameters and by utilizing surfactants and structure-directing agents. The interfacial synthesis applies to thin-film membranes (TFN) as

well as nanosheets. In this method, the low thickness is insured through the reacting monomers in a confined interface. The interfaces include liquid–liquid, liquid–gas, or liquid–solid. The structural integrity of the produced 2D nanosheets and TFN membranes is regulated by the diffusivity of the monomers towards the interface [36].

CVD is a proficient and effective technique to synthesize high-quality 2D nanoparticles and few-layered films of atomic thickness on a solid substrate. In CVD, the precursors gas or vapor are reacted or disintegrated on the substrate at high temperature in a vacuum chamber, as depicted in Fig. 4. In this technique, 2D nanosheets augment the substrate in the absence or presence of a catalyst. CVD have been employed for the epitaxial growth of various 2D-nanosheets, such as transition-metal dichalcogenide (TMD) [37], metal carbides [38], graphene [39], borophenes [40], silicene [41] and, h-BN nanosheets [41, 42]. The CVD method allows the production of highly crystalline 2D-nanosheets with desirable longitudinal and lateral dimensions, for being potentially utilized as membrane precursors.

2.2 Preparation of Nano-Channeled Lamellar Membrane

2D nanosheets with atomic thickness can be employed as a means of separation in membranes. The presence of pores is provided either by 2D nanosheets that have an inherent porous structure such as in zeolites and MOFs or by drilling pores such as in nanosheets like graphene. The performance of membrane-based nanosheets in terms of permeance and selectivity is directly related to the thickness and porosity of the 2D nanosheets. These performance characteristics are predominantly defined by the selection of high-quality synthesis routes and an effective approach for transforming these 2D nanosheets into a membrane. This section focuses on the preparation of 2D nano-channeled membranes.

2.2.1 Development of Single-Layered Membranes

The single-layered film with an atomic thickness anchoring nanopores is regarded as an ultimate membrane. However, realizing such membranes presents an immense challenge due to their crack-free transformation into large-area nanosheets with the ability to control their pore generation. Graphene is deemed an ideal candidate for a single-layered membrane while factoring in the requirements of a 2D nanomaterial which have the potential of scalability while exhibiting robust mechanical properties. However, membrane fabrication defects like cracks, tears, or wrinkles are usually evolved during transferring graphene onto a porous substrate, which results in poor membrane separation performance [17]. To rectify the membrane fabrication defects two different approaches are adopted. Firstly, a common solution is to coat graphene with a reinforcing polymer i.e., polymethylmethacrylate (PMMA) to improve its mechanical durability [43]. However, the polymeric coating incapable of

permeating must be removed in the post-processing of the single-layered membrane, which inevitably introduces cracks. The second approach to remedy these fabrication defects is to use a porous substrate material instead of a nonporous polymeric material. The porous substrate material should have a preferential affinity towards graphene which assists in a more effective large-area transfer [44]. Although considerable advancements have been made in single-layer 2D nanosheet membranes, the scalability of these membranes is difficult due to the introduction of membrane fabrication defects. These difficulties can be partially relieved by increasing the number of layer stacking by compromising the membrane permeance. Furthermore, eliminating the transfer process is another aspect of single-layer 2D nanosheet membrane fabrication. This is realized by bottom-up direct and *in-situ* development of continuous single-layer porous nanosheet membranes on a porous substrate.

2.2.2   Development of Lamellar Membranes

Two-dimensional nanosheets which manifest stable nanosheet suspension in a solvent being deemed as solution-processable can be easily transformed into a lamellar structure. The prerequisite for two-dimensional nanosheet transformation to the lamellar membrane is its ability to be solution processable. Furthermore, 2D nanosheets should exhibit excellent solvent dispersibility to materialize the nanosheet suspension in different solvents. This means nanosheet dispersion is readily processable into a lamellar structure through traditional casting or coating techniques [17]. Lamellar membrane fabrication with 2D nanosheets in-plane to the support has precedence in terms of reducing hydrodynamic resistance through deposition thickness and generation of adequate through-plane channels. Ideally, the lamellar membrane should hold being aligned parallelly and with intermeshed layers. Various techniques like filtration, coating, and layer-by-layer (LBL) deposition have been used to fabricate 2D nanosheet lamellar membranes, as shown in Fig. 5.

Filtration

The positive and negative force applied to filter through substrate via pressure and vacuum is one of the most frequent and effective deposition techniques, as shown in Fig. 5a. This vertical downward push, provided by positive/negative force drives the nanosheet suspension into an interlocked layered structure on the substrate [27]. Class 1 (Fig. 3a) and Class 2 (Fig. 3b) nanosheet membranes are most fabricated using this technique. The deposition can be easily modulated from nanometre to micrometre scale by varying the deposition concentration. This technique offers the liberty to intercalate other dispersible nanoparticles or ions during the deposition to regulate the nanochannel structure [45]. Chen et al. (2019), developed h-BN based lamellar membrane through vacuum filtering of amine-functionalized nanosheets. The thickness through deposition is adjustable through varying concentrations of
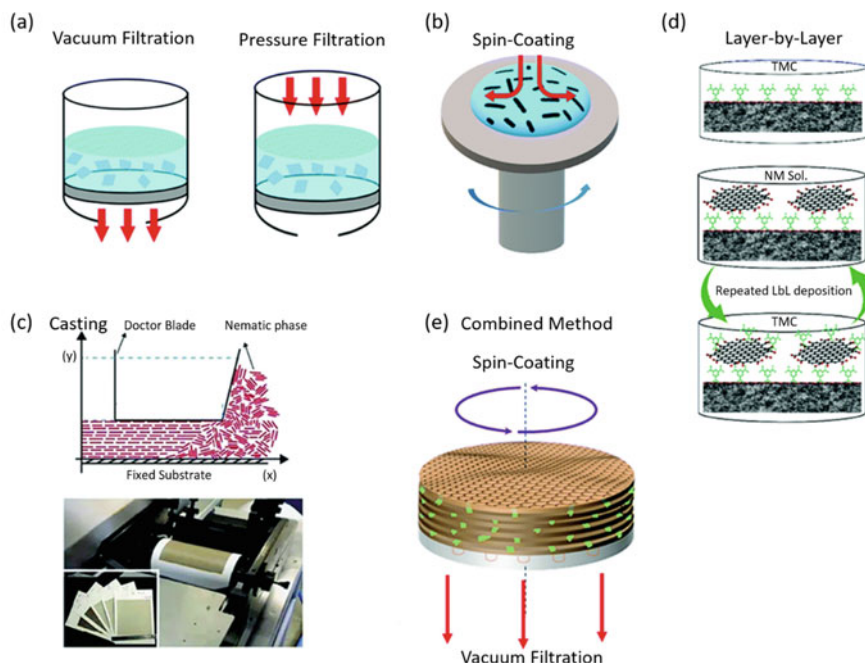
Fig. 5 Schematic illustration of lamellar membrane fabrication methods: **a** Vacuum/Pressure filtration, **b** Spin-coating, **c** Casting, **d** layer-by-layer deposition and **e** combination of spin-coating and vacuum filtration [17]

amine-functionalized h-BN suspension. The fabricated lamellar membranes demonstrated excellent water and organic solvent permeability while excluding various cationic as well as anionic dyes [46]. Recently, Lin et al. (2020), crosslinked activated h-BN and GO to assemble an a-BN/GO hybrid membrane that demonstrates remarkable exclusion efficiency as well as resilience in liquid separation. The compact lamellar structured hybrid membrane was fabricated through pressurized filtration. The a-BNGO membrane exhibited 99.98% methylene blue rejection with water permeance of 4.15 L m^{-2} h^{-1} bar^{-1} [47].

Coating

There are different coating techniques used to assemble 2D nanosheets into lamellar membranes. The most common technique employed for this fabrication method involves spray-coating, casting, spin-coating, and dip-coating. Uniform assembly and nanosheet distribution of the coating depends upon the nanosheet-solvent interaction (surface tension of the solution) and, interfacial properties of the nanosheet suspension (rate of evaporation) and substrate (smooth surface). The spray-coating method involves spraying a dilute yet volatile nanosheet-solvent suspension onto

the support. The evaporation of the solvent leaves a self-assembled pseudo-lamellar structure on the support. The thickness of the coating can be maneuvered by changing the suspension viscosity and spray pressure. Casting is also categorized as under-coating and has been vastly applied for polymeric membrane fabrication. The casting method is easily controllable and scalable. This technique has also been reported to fabricate 2D-nanosheet laminar membranes, as shown in Fig. 5c. The shearing forces generated by the transverse movement of the doctor-blade assists the nanosheet alignment in the cross-direction. In the spin-coating method (Fig. 5b), the nanosheet-solvent suspension is poured onto the center of the support and is evenly distributed through centrifugal force. This technique enables a thin, evenly distributed, and highly interlocked nanosheet lamellar membrane. Lastly, dip-coating involves dipping the support membrane into the nanosheet suspension and drawing it out while allowing the solvent to evaporate and form a self-assembled lamellar structure. This technique is majorly employed for Class 1 2D-enabled membranes. An et al. (2019), transformed the hydrophobic surface of polyvinylidene fluoride (PVDF) into a superhydrophobic surface by incorporating functionalized boron nitride nanosheets in the dope solution. The composite functionalized h-BN and PVDF membrane were fabricated through the solution casting method and phase-inversion technique. The composite membrane shows excellent performance for oil separation from an oil–water mixture [48].

Layer-By-Layer (LbL) Assembly

This is the method of alternatively depositing materials of different characteristics on the substrate surface, Fig. 5d. This technique primarily depends upon the interaction between the alternating and adjacent layers. The interaction between the adjacent layers could be electrostatic, vdW forces, H-bonding, or even covalent bonding. Layer-by-Layer (LbL) lamellar membrane fabrication technique presents precedence over other fabrication methods in precisely controlling the deposited thickness of the selective layer by changing the cycles of deposition. However, this technique requires 2D nanosheet compatibility in various polar solvents as well as the adjacent layer material. Abdikheibari et al. (2019), established a modified LbL technique for the assembly of highly permeable, highly selective yet fouling resistant thin-film membrane being decorated with few-layered amine functionalized h-BN nanosheets for the separation of hydrophilic natural organic matters. In their fabrication process, h-BN was covalently bonded to the adjacent layer of the membrane [49].

Combined Method

At present, lamellar membrane preparation solely depends on a single method. The combined tuning of nanosheet alignment in the vertical and horizontal directions is difficult. The filtration through pressure and vacuum can align the nanosheets vertically, while the casting and coating technology has the capability of aligning

nanosheets horizontally. A merger of processes, as shown in Fig. 5e, where filtration is combined with spin casting could allow tuning of stacking both vertically as well as horizontally. This technique employs a combination of filtration and spin-coating technique that was reported to fabricate GO lamellar membranes which resulted in a well-detailed 2D-nanosheet lamellar membrane with tailored intraplanar and interplanar nanochannels [50].

The scalability of the membrane preparation technique is essential in the implementation of practical applications. The techniques involving casting and coating that are easily scalable and can be adopted at an industrial level production of thin lamellar flat sheet membranes. Moreover, the deposition and attaching of the 2D nanosheets to the flat sheet and hollow fibers through the pressure-filtration technique could assist in scale-up. It is worth mentioning that all the processes are fundamentally dependent upon the uniform suspension of these 2D nanosheets in a solvent. However, the necessary modifications to enhance the dispersion of 2D nanosheets in a lamellar membrane fabrication technique appropriate solvent is the most important prerequisite.

3   Mechanism of Transportation

In the membrane exclusion process, penetrants pass through the membrane based on their size and the membranes serve as a selective barrier. Membranes achieve this selective transport through various mechanisms, which are dependent upon the pore size, see Fig. 6. Furthermore, the smallest pore size scale ranges from 0.3–0.6 nm, corresponding to dense membranes having no specific pores such as reverse-osmosis membranes for water desalination and various gas separation membranes utilizing the solution-diffusion mechanism [51]. The selectivity and exclusion of the solute result from solubility as well as diffusivity differences in the membrane material. The solubility of the solute is dependent upon its molecular structure, the porosity of the membrane, and the chemical affinity, whereas the solute's ability to diffuse in the membrane material is controlled by the rearrangement of the polymeric chains which are activated thermally that favors size-based diffusion of smaller molecules. When the pores are wider than the molecular size but smaller than the gas mean free path, the transmembrane transport is governed by Knudsen diffusion [5].

The pathway for mass transportation across a 2D lamellar membrane depends upon the in-plane porosity, as shown in Fig. 7c. For a lamellar membrane fabricated from intrinsically porous nanosheets, the pathway for transportation includes the pathway through nanochannels i.e., the interplanar spacing of neighboring nanosheets and nanopores i.e., intraplanar porous structure. In addition, the lamellar membranes fabricated from the 2D nanosheets that do not have inherent or perforated nanopores present a pathway through the interplanar spacing between the consecutive nanosheets. The permeance through the membranes is dependent upon lamellar membrane porosity and tortuosity. In particular, the porosity is associated with nanosheet interplanar spacing, the thickness of the nanosheets, and the pore
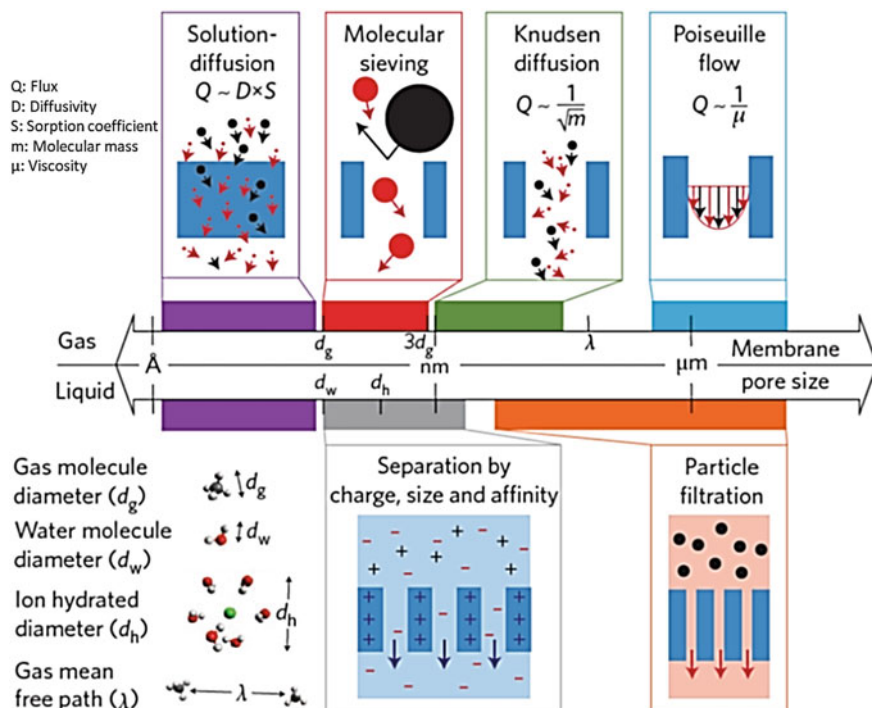
Fig. 6 Membrane transport mechanisms based on the membrane pore size. Reproduced with permission from [5]

size of the intrinsic or perforated nanosheets, while the tortuosity is a ratio of lateral dimensions to the thickness of the 2D nanosheets. In the interplanar pathway, as shown in Fig. 7c, the length of diffusion can be estimated by the Nielsen transport model [52].

$$l = h + N^L/_{2'}$$

$$N = \frac{h}{d + W'}$$

where l is diffusion length, h is the lamellar membrane thickness, L and W are the lateral length and thickness of the nanosheet, and d is the basal spacing of the nanosheets. In this section, the transportation mechanism of lamellar membranes fabricated through 2D porous and nonporous nanosheets is discussed.
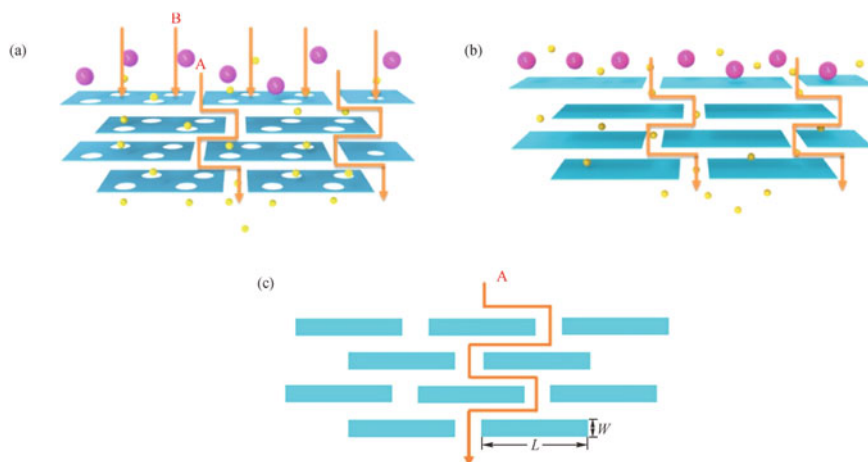
Fig. 7 Molecular transport model for **a** Intrinsically/post-perforated porous 2D nanosheet lamellar membrane, **b** Nonporous 2D nanosheet lamellar membrane, and, **c** Interplanar pathway. Reproduced with permission from [11]

3.1 Porous Nanosheet-Based Lamellar Membranes

The specific molecular exclusion of inherently porous nanosheets-based membranes is dependent on the size of intraplanar pores, as shown in Fig. 7. Due to the size of the nanopores, intrinsically porous nanosheets-based lamellar membranes will permeate and exclude ions or molecules based on size, see Fig. 7a. According to the nanopores and nanochannel size, the molecular diffusion across the membrane is derived by surface, molecular, and Knudsen diffusion and viscous flow [53]. The lamellar membrane fabricated through stacking intrinsically porous nanosheets exhibits a regular nano-porous structure coupled with an ultrathin thickness which presents an ideal separation membrane morphology, exhibiting limited hydrodynamic resistance to the mass transfer and promoting very high flux and maintaining high solute exclusion resulting from precise pore sieving.

3.2 Non-Porous Nanosheet-Based Lamellar Membranes

Two-dimensional nanosheets without intrinsically in-plane nanopores stacked to form a lamellar membrane resulting in the formation of interplanar nanochannels that provide a mean for the transportation of ions or molecules, as shown in Fig. 7b. The interplanar spacing between the 2D nanosheets between the consecutive nanosheets provide a pathway of transportation for small entities whilst restricting the flow of entities that are larger than the nanochannels. For 2D lamellar membranes that are based on non-intrinsic pores, the development and modulation of the interplanar

spacing is a fundamental design characteristic for membrane performance in terms of permeance and solute exclusion.

3.3 Transportation Through Interlayer Channels

Two-dimensional nanosheets when stacked by the lamellar membrane fabrication techniques result in the creation of interlayer nanochannels. The interlayer spacing in 2D- nanosheets based membranes is dictated by the pathways amongst the nanosheets. These channel size and the chemical functionalities present on the nanosheets dictates the separation efficiency of these membranes [12]. As shown in Fig. 8a, the larger ions and molecules that are hydrated are stopped through a lamellar membrane assembled using GO nanosheets while permitting smaller ions and molecules to transport through these channels. The separation mechanism of these hydrated ions and molecules can be explained with the help of size exclusion theory [54]. Thin layered nanosheet films fabricated by chemically exfoliating WS_2 nanosheets have been reported to separate 3 nm small particles. Furthermore, the permeance of the lamellar membrane could be enhanced through pressure-assisted cracks and utilizing templates, which generate more fluidic channel networks, as shown in Fig. 8b [55].

The development mechanism of nanochannels can be associated with interplanar interactions that include non-covalent and covalent interactions. The nanochannels can be modulated by changing these interactions. These non-covalent interactions
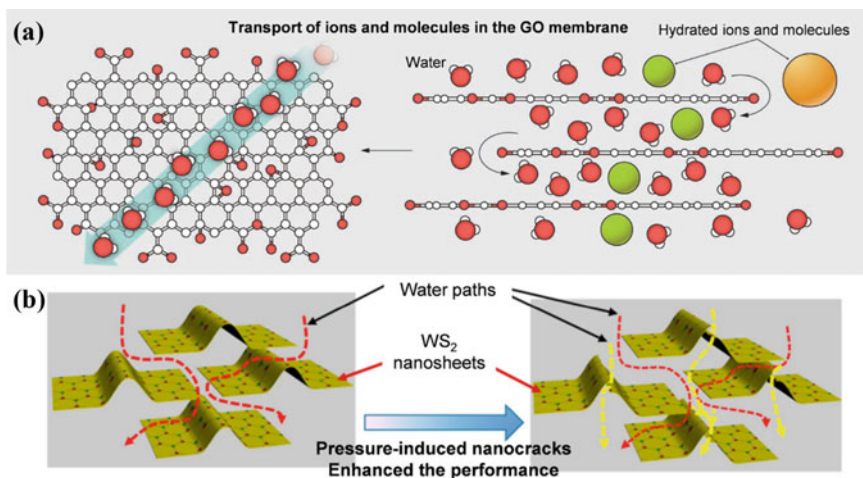
Fig. 8 a Water and small-sized ions and molecules are being permeated through stacked GO nanosheet superfast membrane, while inhibiting the larger molecules, **b** Illustration of ultrafast molecule separation through layered WS_2 nanosheet membranes and its enhanced permeance due to the introduction of pressure-induced nano cracks. Reprinted with permission from [56]
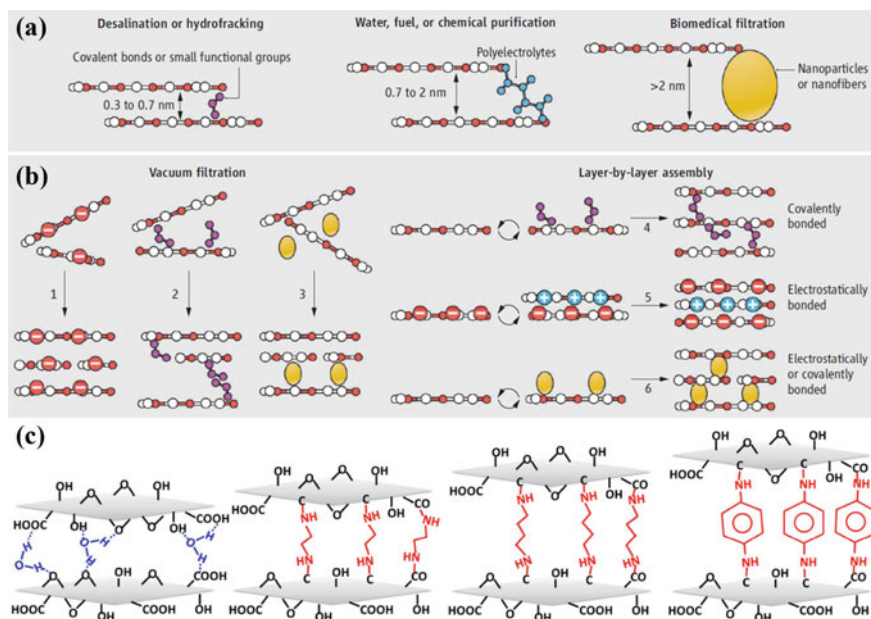
Fig. 9 **a** The membrane performance of the GO membrane is tunable through modulating inter-planar spacing, **b** Different approaches for the fabrication of GO nanosheet-based membrane; (options 1–3) GO nanosheets stacked through vacuum filtration, (options 4–6) nanosheets being stabilized through covalent, electrostatic or combination of covalent and electrostatic bonding

being responsible for the formation of interlayer channels are further segregated into physical interactions and internal and external forces. The internal forces refer to the secondary bonding at play in adjacent monolayers, and these forces include hydrogen bonding, hydrophobic effects, vdW, and π-π interactions. The internal forces play a vital role in holding the multilayers together.

3.4 Transportation Through Membrane Nanopores

The driving force behind the transport of entities through a nanoporous 2D-nanomaterial-based lamellar membrane is mainly dictated by the pore dimensions. As discussed in Sect. 3.0, membrane nanopores allow entities with a smaller diameter than the pore size and block the larger hydrated ions and/or molecules. The dimension of nanoporous 2D nanosheet pores can be modulated during the synthesis. In a typical top-down synthesis, pores are created from a nonporous atomically thin material, and from bottom-up synthesis, the nanoporous structure can be created through intrinsically porous materials such as 2D-MOF, 2D-COF, and 2D-polymers [5].

In a top-down synthesis, a homogenous distribution of sub-nanometer pores can be achieved through the utilization of ion irradiation or chemical/plasma etching. The chemical processes influence the stability of the pores, and the functional groups present in the vicinity of the pores. The size and the density of the nanopores are dictated by the interplay between the nucleation of the defects and their growth. Thermal oxidation, oxygen, and hydrogen plasma are capable of producing uniform nanopores with tunable size and density [57]. Furthermore, nanopore generation through ion irradiation is realized where the defect nucleation is controllable. The nanopore optimization in terms of size and density is achieved by changing the type of ions, their angle, and energy. In addition, a high density of sub-nanometer pores is also achievable by electron-induced sputtering or chemical etching.

In the bottom-up synthesis techniques, intrinsically porous materials are the building blocks for a well-detailed porous structure and a high density of atomically precise pore size [58]. Cheng et. al., fabricated a two-dimensional MOF nanosheet lamellar membrane through the spin coating method. The membrane exhibited a precise pore size of 0.52 nm, which allows the permeation of smaller gas molecules (CO_2, kinetic diameter of 0.330 nm), while the membrane presents resistance to larger gas molecules (CH_4, kinetic diameter of 0.376 nm) [59].

4 Nanochannel Architecture and Its Regulation

A nanochannel is the building block of 2D nanomaterial-based membranes, which connects the membrane fabrication and its separation process. The separation performance of the membrane is determined by the architecture and microenvironment of the nanochannels. The performance of the membrane can be fine-tuned through the optimization of nanochannel architecture and its surrounding environment.

4.1 Surface Functionalization

The selectivity and permeability tradeoff of membranes has always been a challenging problem. The selectivity and permeability of 2D nanomaterial-based membranes are not completely dependent on the interlayer channels and nanopores in the 2D nanomaterials, which utilize the interplanar electrostatic interactions and size exclusion mechanisms. Meanwhile, advancements in the development of 2D nanosheet-based lamellar membranes have been achieved by adopting versatile approaches for the modification of interplanar channels or nanopores. Modulated pore size, adjustable inter and/or intraplanar electrostatic interactions, and improved solid–liquid and solid–gas interfacial properties have been made possible with the surface functionalization of the 2D nanosheet-based lamellar membranes. The gap between the selectivity and permeability tradeoff can be bridged to some extent through the 2D nanosheet surface functionalization.

Inspired by the applications of 2D nanosheets-based lamellar membranes in ions or molecules separation various theoretical studies simulated the transport performance of 2D nanomaterial materials through molecular dynamics simulations [60, 61]. Konatham et al., studied the transport of water and ions through the nanopores of porous graphene nanosheets by MD simulation [62]. The simulation results suggested that the nanopores are tunable with the introduction of various charged surface functionalities. The diameter of graphene nanopores with charge groups OH^-, COO^-, and NH^{3+} were 0.75, 1, and, 1.1 nm, respectively. It was found that the OH^- functionalized nanopores with a narrow diameter of 0.75 nm were highly stable in excluding Cl- ions even at a moderate ionic strength of the solution. Experimentally, Hafeez et al., functionalized h-BN nanosheets with different molecular weight polyethylene glycol and fabricated lamellar membrane through filtration on a substrate membrane [63]. The study revealed interplanar modulation through soft spacer molecules.

4.2   Nonporous 2D Nanomaterials

A lamellar membrane fabricated through stacking nonporous 2D nanomaterials is primarily separated by the interplanar spacing which provides a means of transport. The formation mechanism of nanochannels is closely associated with non-covalent and/or covalent interlayer interactions. These non-covalent and covalent interactions can be adjusted to regulate the nanochannels. The non-covalent interactions are further categorized into intrinsic interactions (hydrogen bonding, hydrophobic effects, van der Waals and π-π interactions), and the forces that are applied during the nanochannel formation or operation that are referred to as extrinsic interactions (centrifugal force, pressure, etc.).

In 2D nanomaterial-based lamellar membranes, the interplanar interactions such as van der Waals, π-π interactions, hydrogen bonding, etc., are referred to as internal forces which hold the adjacent layers. The intensity of these internal forces can be regulated through various pre or post-thermal or chemical treatments, which alter the aperture of the interplanar nanochannels. The homogenous distribution of functional groups on the nanosheets will result in uniform interplanar interactions which would bring a well-ordered structure. Uniform distribution of functional groups on the nanosheets enables a regular lamellar structure, MXenes are decorated with homogenous abundant surface-terminating groups as compared to GO which has randomly distributed oxygen groups. The regular free spacings generated by interplanar secondary forces could perform as an effective nanochannel that separates based on the size exclusion mechanism [64]. The oxygenated groups on GO prevent interplanar restacking through π-π interactions. The π-π interactions in GO can be enhanced through thermal annealing or chemical reduction, which would allow interplanar restacking. Furthermore, these post-treatments would produce robust and narrow apertured nanochannels [12].

During 2D nanosheet deposition, external forces such as positive or negative pressure, shear forces, etc., can be modulated to orient the nanochannels, which

provides effective control over the fabrication process. Two-dimensional h-BN and GO nanosheets are typical examples of lamellar membranes prepared by pressure, vacuum filtration, or evaporation which results in ordered, partially ordered, and random ordered nanochannels respectively [13, 63, 65]. The evaporation and drop-coating methods predominantly rely on the slow evaporation of the solvents to form a lamellar structure, which results in a lamellar structure with nanochannels that are less ordered [66]. The nanochannel orientation can be further improved through the application of shear force which creates an interlocked nanochannel structure. Furthermore, the combination of pressure exertion in the vertical direction and shear forces in the horizontal direction produces a highly ordered nanochannel structure [50]. Besides the type of force, the magnitude of forces provides a higher tunability of the nanosheet stacking mode.

For 2D nanosheets that can be covalently bonded, chemical intercalation through crosslinking is the most common route to enhance the interplanar forces and improve the mechanical stability of the membranes. The intercalating agents encompass charged entities, small molecules, or macromolecules. GO is the most explored 2D nanosheet for chemical intercalation considering the abundant functional groups. Diamines are versatile intercalating agents of GO, which is performed through nucleophilic substitution reaction between epoxy and amine. The aperture of nanochannel can easily be regulated by changing the chain length of diamines [67, 68]. The lamellar membrane application varies from gas separation, water purification, and organic solvent filtration. Covalent crosslinking requires the presence of anchoring functional groups on the nanosheets, and strong covalent interactions can ensure structural integrity to avoid swelling in liquid filtration. These intercalated molecules not only serve as a means to fine-tune the interplanar spacing but can also introduce a chemical microenvironment in the nanochannel that is penetrant-philic, which facilitates targeted molecule transportation.

4.3   Intrinsically Porous 2D Nanosheets

The nanochannels for the mean of transportation in intrinsically porous 2D nanosheets are the nanosheet interplanar spacing and the intrinsic porosity of the nanosheets. This intrinsic porosity presents an opportunity for building a selective transport pathway. This versatility is provided by 2D nanosheets of zeolite, metal-covalent organic framework (MOF), and covalent-organic framework (COF). The majority of 2D zeolite nanosheets have a narrow pore size distribution of 0.2–1 nm, which is close to the molecular sizes of most of the gases. However, depending upon the organic linkers of MOFs, they have a wide pore size distribution ranging from 0.3 to 10 nm, which makes them a suitable candidate for gas and liquid separations. Furthermore, COFs have a pore size distribution ranging from 0.8 to 5 nm. Due to the high degree of crystallinity, intrinsically porous 2D-nanosheets are brittle, which makes its single-layer membrane processing challenging and as a result, structural defects are introduced [36]. The nanochannel modulation based on the penetrant

molecular size is mainly focused on the pre-design of nods and linkers of the starting intrinsically porous 2D nanosheets [66]. The aperture of the nanochannel and the chemical functionality present can be easily manipulated.

4.4 Perforated 2D Nanosheets

Pore generation on a nanoscale in 2D nanosheets is another important nanochannel regulation strategy. The prerequisite for pore generation in 2D nanosheets through peroration is that the nanosheet exhibits inherent superior mechanical strength. The various approaches used for perforation include physical techniques with focused electron beam irradiation, focused ion beam irradiation, and ion bombardment and chemical techniques involving chemical oxidative etching, plasma, and ultraviolet (UV) light etching. The perforation of nanosheets using focused electron beam irradiation uses a high-energy electron beam to etch carbon atoms and induce structural rearrangement, forming nanopores in the range of 5 to 100 nm on the graphene. The degree of perforation from the micron to the nanoscale can be optimized by controlling voltage, exposure time, and beam dosage. The chemical perforation techniques involve the introduction of sp^3 hybridized sites or vacancy defects. In these techniques, carbonyl or hydroxyl functional groups are introduced through oxidative processes forming nanochannels with nanoscale precision [69]. The nanopore generation through perforation is capable of high precision over pore size and density.

5 Conclusion

The emergence of various 2D nanomaterial-based lamellar membranes offers a unique opportunity for developing ultra-thin nanochannel membranes which cater to many fields, ranging from daily life to medical science. In terms of transportation routes, 2D nanomaterials present two ways for the separation of solid–liquid or solid–gas interaction. Meanwhile, to unravel the selectivity-permeability tradeoff, interlayer functionalization has been considered one of the most viable options which improves the microenvironment for the penetrant molecules. The vast diversity of synthesis routes, nanosheet functionalizing, and nanochannel modulation enables the application of 2D nanomaterials in application-specific membranes.

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