1 Introduction

In this chapter, the state-of-the-art development of membranes is briefly highlighted. Two-dimensional (2D) membranes and their separation mechanisms and fabrication processes are introduced to emphasize the high potential of 2D membranes for permeation separation. Finally, some applications of 2D membranes are briefly discussed.

1.1 Membrane Development at a Glance

Separation processes are important for industrial development and also in our daily life. They have been implemented for various purposes (Figure 1.1) such as the treatment of environmental pollutants (including particulate matter $(PM)_{2.5}$ rejection, wastewater treatment, and oil removal from seawater), drinking water production (including residential water softening and water purification and desalination of seawater), food production (ethanol dehydration for liquor purification and production of milk and drinks), drug delivery in biomedicine, gas separation, chemical separation in petrochemical and chemical industries, as well as military and defense. Most separation processes involve distillation based on heating, which accounts for 10–15% of the world's energy consumption [1, 2].

Membrane-based separation technologies have attracted increasing attention in recent decades because of their low energy consumption, easy operation, and environmental friendliness. However, conventional membranes, such as organic membranes, typically suffer from a trade-off between selectivity and permeability, as expressed through the Robeson plot [3]. Thus, novel membranes that surpass the Robeson upper limit must be developed.

1.2 Two-Dimensional Membranes

With the emergence of novel 2D materials, such as graphene, a new era of membrane development has begun. The discovery of monocrystalline graphitic films by Geim's group in 2004 has drawn widespread attention to 2D materials for membrane separation [4]. In addition to the earliest studied graphene, other novel 2D materials such as

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Figure 1.1 Separation processes in our society.

zeolites, metal–organic frameworks (MOFs), covalent organic frameworks (COFs), graphene oxide (GO), layered double hydroxides (LDHs), transition metal dichalcogenides (TMDs), MXenes, and g-C_3N_4 have also been used as nano-building blocks to prepare 2D membranes. Since the precise control of interlayer channel/pore size and reduction of mass transfer resistance became feasible, ultrathin 2D nanosheet membranes achieve high permeability and high selectivity, surpassing the Robeson upper limit, thus making these novel 2D membranes promising candidates for permeation separation.

1.3 Separation Mechanisms of 2D Membranes

In membrane separation, ions, atoms, or molecules selectively pass through a membrane, which serves as the separation medium. 2D membranes can be assembled using two types of nanosheets. One membrane type is the porous 2D nanosheets, such as zeolite [5, 6], MOF [7–9], COF [10, 11], and g-C_3N_4 [12, 13]. In 2D membranes assembled with porous nanosheets, the interlayer nanochannels/sub-nanochannels are utilized for mass transportation, and the pores in each nanosheet contribute to the permeation flux. More importantly, the mass transportation path length can be drastically reduced because of the presence of nanopores/sub-nanopores in the nanosheets. The small molecules to be separated diffuse only a shorter way through the pores in the nanosheets, thus avoiding a tedious, long, zigzag pathway as the large molecules that cannot pass the pore in the nanosheets (Figure 1.2a). The other type is the nonporous 2D nanosheets, such as GO [14–16], MXene [17, 18], and TMDs [19, 20]. In the 2D membranes constructed by using the nonporous nanosheets, the permeate flux goes only through the interlayer spacing between the nanosheets (Figure 1.2b).

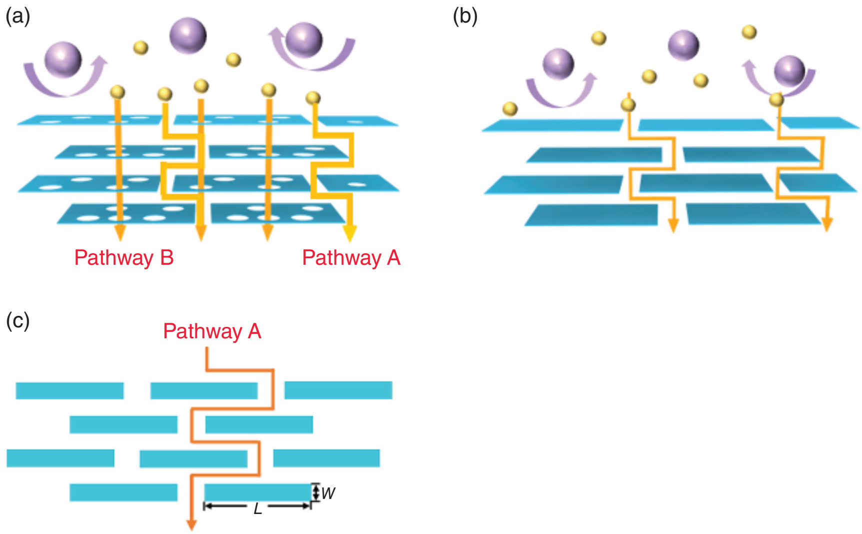

Figure 1.2 Transport models of 2D membranes. (a) Porous nanosheets, (b) nonporous nanosheets, and (c) inter-sheet pathway A.

In general, there are two types of pathways for mass transportation through 2D membranes: inter-sheet pathway A (which refers to the interlayer spacing between the nanosheets) and intra-sheet pathway B (which refers to the in-plane pore-based transport). For gas separation, the membrane permeability P can be calculated using the following equation [21]:

$$P = \left(\frac{1}{h}\right)\left[\left(\frac{\varepsilon_A}{\tau_A}\right) D_A K_A + \left(\frac{\varepsilon_B}{\tau_B}\right) D_B K_B\right] \tag{1.1}$$

where h is the membrane thickness; ε and τ are the porosity and tortuosity for the pores of A and B pathways, respectively; D and K are the gas diffusivity and adsorption equilibrium constant in the A and B pathways, respectively. The tortuosity (τ) of 2D membranes can be approximately calculated as the ratio of the lateral size to the thickness of a nanosheet, while porosity (ε) is related to the interlayer d-spacing, thickness, and porosity of the nanosheets.

For inter-sheet pathway A, the diffusion length can be estimated using the Nielsen transport model [22]:

$$l = h + N\frac{L}{2} \tag{1.2}$$

$$N = \frac{h}{d + W} \tag{1.3}$$

where l is the diffusion length, h is the membrane thickness, L and W are the lateral dimensions and thickness of the platelet, respectively, and d is the effective distance between the platelets (Figure 1.2c).

1.4 Fabrication Methods for 2D Membranes

Pressure-assisted filtration, as the most widely used method to fabricate 2D membranes, has distinct advantages over other methods, such as simple operation and low cost. The nanosheets are filtered on a porous substrate from a nanosheet suspension with or without vacuum support (Figure 1.3) [23]. Notably, the membrane thickness can be adjusted by the nanosheet concentration in the dispersion and the duration of deposition. However, for the large-scale and reproducible fabrication of membrane layers with appropriate thickness, pressure-assisted filtration is not the optimal approach. As the membrane becomes thicker, cracks and wrinkles can generate on its surface, resulting in low separation performance. Further, as the filter cake thickens, the filtration resistance increases, which increases the preparation time for membranes with larger thickness [24].

Moreover, main coating methods for fabricating 2D lamellar membranes are spin coating, spray coating, and drop casting [25]. In drop casting, 2D membranes are obtained by depositing nanosheet suspensions in a dropwise manner onto a porous support. However, in spin coating, the nanosheet suspension is dropped on a spin coater, which promotes solvent evaporation if heated, to prepare the membrane layer during rotation. In spray coating, the nanosheet solution is dispersed into small drops and sprayed onto the (heated) substrate surface, which also facilitates solvent evaporation. Although drop casting and spray coating have many advantages such as simple processing, wide-scale applicability, and high speed, these methods have some problems that need to be solved. For example, it is difficult to prepare homogeneous membranes on a large scale using drop and spray coating.

Layer-by-layer (LbL) assembly is the process of depositing multilayers having interactions such as electrostatic attraction, hydrogen bonding, and even covalent bond formation. In the LbL process, the membrane thickness can be precisely controlled by the number of deposition cycles. In addition, different materials can be deposited in each cycle to improve membrane performance. The LbL assembly method is simple but not efficient for practical application because it

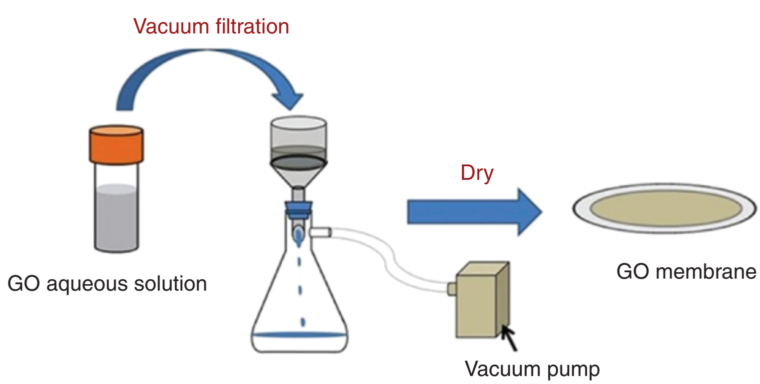

Figure 1.3 Fabrication of GO membranes via vacuum filtration. Source: Yang et al. [23]. Reproduced with permission of Elsevier.

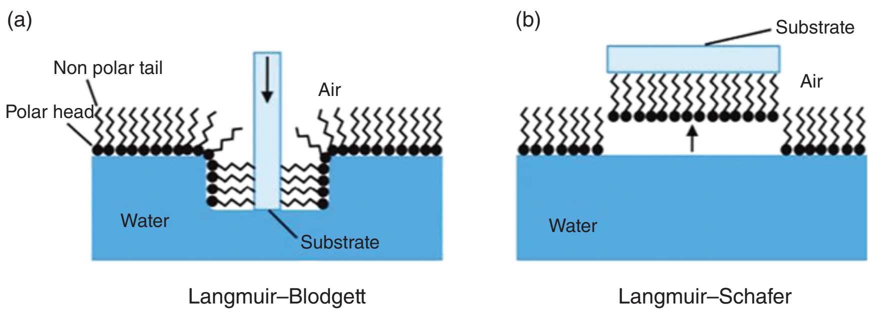

Figure 1.4 Comparison between (a) Langmuir–Blodgett (LB) and (b) Langmuir–Schaefer (LS) films. Source: Puzzovio et al. [26]. Reproduced with permission of American Scientific Publishers.

is time-consuming. The Langmuir–Schaefer (LS) and Langmuir–Blodgett (LB) methods are two types of the LbL assembly method and have been used to prepare 2D membranes. A nanosheet layer is formed on the liquid surface and then transferred to the surface of a solid porous substrate. The difference between the LB and LS methods is the way of transferring the nanosheet layer (Figure 1.4). In the LB method, nanosheet deposition is achieved by vertically lifting a planar substrate, but tubular geometries are also possible. In the LS method, a substrate is contacted face-to-face with a nanosheet layer at the interface [26]. High-quality monolayer

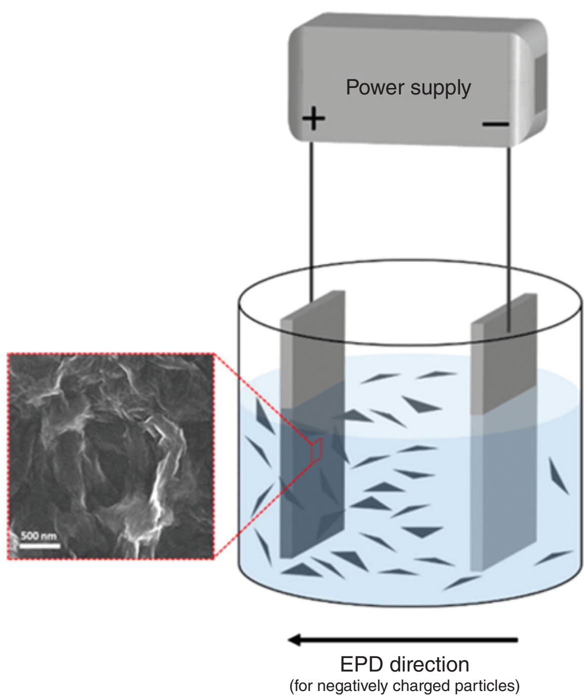

Figure 1.5 Schematic illustration of electrophoretic deposition (EPD). Source: Diba et al. [27]. Reproduced with permission of Elsevier.

membranes can be obtained by these methods. However, these methods require special experimental equipment and, thus, incur high operation cost.

In recent years, electrophoretic deposition (EPD) is widely used as a fabrication method, although it is effective only for the assembly of electrically charged 2D materials. In EPD, electrically charged nanosheets move toward the electrode with opposite charge in the presence of an electric field, and the deposited nanosheets directly form a thin membrane layer on the substrate (Figure 1.5) [27]. A stable dispersion of charged nanosheets is crucial for electrostatic deposition with a concentration of approximately $0.1\,g\,l^{-1}$ and a Zeta potential of <-30 mV or $>+30$ mV. As the thickness of the deposited membrane increases, EPD becomes difficult because the nanosheets are nonconductors and membrane thickness is limited, which is favorable for the fabrication of thin membranes [28]. Also, the substrate material used as an electrode should be electrically conductive, but sputtering thin layers of metal or carbon can easily provide the necessary conductivity. EPD is a technique with enormous commercial potential because it is suitable for the preparation of large-area 2D membranes. The applicability of EPD at the membrane scale will be discussed in detail in Chapter 10.

1.5 Applications of 2D Membranes

2D membranes can be used for gas separation, ion rejection, dehydration of organic solvents, and nanofiltration. For various types of separation, 2D membranes with different properties are required, such as membranes with appropriate pore size for sieving (normally depending on the interlayer spacing of 2D membranes), stability for long-term separation, mechanical strength, and anti-swelling ability in liquids. A detailed introduction to 2D membranes with various separation applications is provided in Chapter 2.

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