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Next-Generation Graphene-Based Membranes for Gas Separation and Water Purifications

Quan Xu and Wenwen Zhang

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Abstract

Advanced membrane systems are regarded as an important portion of controllable separation processes, such as gas separation and water purification. The ideal materials should have good permeability for selected particle sizes, high stiffness to withstand high pressures applied, large surface area and micro- or nanopore structures for excellent selectivity. Recently, graphene with oxygen-containing functional groups and graphene oxide (GO) nanosheets, obtained via chemical oxidation of graphite, achieved tremendous properties that include excellent mechanical strength, large relative surface area, unique honeycomb lattice two-dimensional structure as well as narrow pore distribution, offering platform to be used as advanced, ultrathin membrane for a wide variety of purification process with high efficiency. In this review chapter, the potential application of such advanced materials for gas separation and water purification process is discussed. The fabrication and modification process and innovation of such advanced two-dimensional functional structure for purification and separation process are introduced. This review chapter will offer opportunity to understand details involved in gas and/or water molecular transport through thin, laminar graphene oxide and derived structures, as well as up to now progress in the field.

Keywords: graphene, graphene oxide, membrane, purification, separation

1. Introduction

Separation, or separation technique, is regarded as an important process that converts a mixture of substances into distinct pure mixtures/fractions. In industry, separation is an important indispensable process for nature gas separation, hydrogen production, seawater desalination, etc. [1–3]. Traditional separation technologies, including distillation [4, 5],

adsorption [1], absorption [6, 7], etc., have been developed for decades. With the restriction of total energy resources on Earth and the continuous global population growth, the demand for high efficacy technologies to solve urgent environmental and energy problems urgently needs the formulation of advanced separation techniques. In comparison to traditional technologies, membrane separation technology has been developed and became a well-established separation technology over the past decennia, with the benefit of overall low energy usage, flexible arranged process conductions, safety, materials sustainability and being economical and environmental friendly [8, 9]. Membranes work as a selective separation wall which target substances that can pass through and block others [8, 10, 11]. Two important factors are used to evaluate the performance of membranes: flux and selectivity [12]. Flux is defined as the volumetric flow rate, and selectivity is the status of molecules being passed through. The traditional membranes generally made from polymers, zeolite and silicon have been successfully applied in industry [13]. A summary of membrane porous sizes *versus* application classification is exhibited in **Figure 1**.
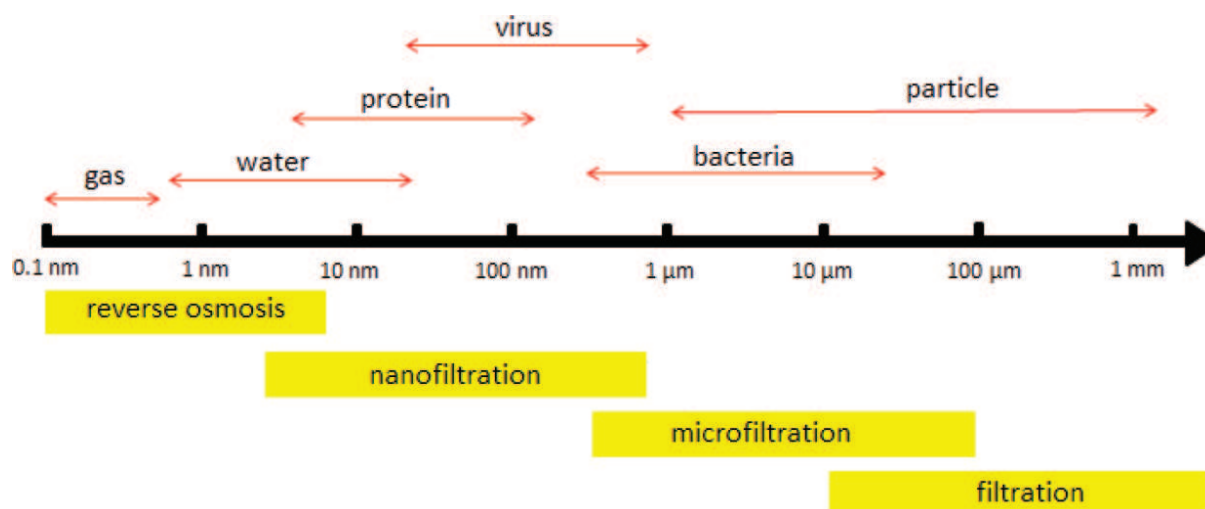

Figure 1. Summary of membrane classification according to their pore sizes.

Recently, carbon-based nanomaterials have attracted intensive attention from scientists, due to their abundant reserves, easy accessibility, remarkable mechanical properties, biocompatibility, as well as environmental friendly properties [14, 15]. Initially, carbon nanotubes (CNTs) were believed to be excellent candidates for membrane materials, due to their uniquely hollow structure with one open-end, and extremely high mechanical performance [16, 17]. However, the fabrication of vertically aligned CNT arrays with high density, large scale quantity and low defects is still challenging [18]. Thus, the generation of CNT-based separation membrane, for large-scale practical applications, remains a theoretical possibility. Another kind of carbon-based nanomaterials with great mechanical properties is carbon diamond. They contain amorphous sp^3-hybridized carbon atoms and are also considered as candidate materials for separation technology. Considered the large energy consumption and high cost, it is not economical and practical to use carbon diamonds for large-scale industrial applications [19].

Therefore, the development of more applicable and economically suited carbon-based nanomaterials for fabricating separation membranes is an urgent need.

The two-dimensional carbon, graphene, possessing a single-atom-thick sheet of sp^2-hybridized carbon atoms arrayed in a honeycomb pattern, opened a new door for researchers and scholars to fabricate the next generation of membranes with outstanding separation capacities [20, 21]. Graphene and its derivative, graphene oxide (GO), with very thin, stiff and large surface area and micro-/nanopore structure layers, are considered as the ideal candidates for membrane materials, due to their high durability, withstanding high applied working pressures and excellent selectivity [22–25]. Graphene is stripped out of graphite materials made of only carbon atoms, with a kind of two-dimensional crystal structures having just one-atom-thick sheet. The concept, graphene-based materials, as well as the preparation, has been explored for over a century. In the early middle of the nineteenth century, Brodie et al. [26] prepared GO and distinguished graphite as "lamellar" and "amorphous". In 1918, Haenni et al. [27] described in detail the properties of GO paper. Then Ruess et al. published the first transmission electron microscopy (TEM) images of a few layers of graphene (between 3 and 10 layers) imaged in 1948. Hummers [28] provided a redox method to prepare GO with outstanding properties. Tsotsis et al. [29] reported that graphene membranes can be used for gas mixture separation. In 2004, Andre Geim, a physicist from the University of Manchester, and his copartner Konstantin Novoselov, successfully isolated single-layer graphene from a sheet of graphite, providing evidence that two-dimensional materials can exist alone in nature, and they shared the 2010 Nobel Prize of Physics for this work [30]. Nowadays, graphene and derived materials have attracted worldwide attention, and the global market for graphene is reported to have reached $9 million in 2014 [22, 31, 32].

The first experimental use of graphene as membrane materials was performed by Bunch et al. [33], who demonstrated that graphene is impermeable to all standard gas atoms including helium. With high crystal quality of carbon atoms, the electron density of graphene aromatic rings can repel most atoms and molecules [34]. Scientists further suggest that nanoporous graphene (NPG), with monatomic layers, high mechanical strength and strong chemical stability, may have a great potential for nature-/biogas separation and seawater distillation [23, 24, 35, 36]. Moreover, its derived material, graphene oxide (GO), was identified as potential filtration/membrane, due to the controllable pore distribution, applicability under high-pressure conditions, simple preparation procedure and the possibility for easy large-scale production. Many attempts were conducted for gas mixture separation and water or liquid molecules purification [36, 37].

In this chapter, the recent applications and research progresses of graphene and GO on separation membrane for gas separation and water purification are discussed. The chapter is divided into three sections. In the first section, the applications of graphene and GO on gas separation will be introduced. The second deals with water filtration. Finally, a summary and outlook of graphene-based separation membranes will be stated, including the recent challenges and the expected further developments in the future.

2. Graphene and GO for gaseous selectivity separation

Comparing with traditional membrane materials, graphene and GO membranes show remarkable properties, such as unique stiffness, hydrophobic characteristics and are easy scale up in various applications [38–41]. The monolayer graphene is known to resist to very small gaseous permeation, including He (helium) [33], as the electron-clouds on the graphene hexagonal rings could hamper the atoms and molecules to allow the transit of small molecules. Graphene is long being considered as an ideal gas barrier material. Although graphene prevents gas to pass through, nanoporous graphene (NPG), due to its high surface porosity, can efficiently allow gas flow to selectively pass through, thus becoming a potential membrane material candidate. The analysis of NPG as membrane materials starts with the simulation of this amazing material. In 2008, Sint et al. [42] designed functionalized nanopores in graphene monolayers and showed that they could provide highly selective passage of hydrated ions, using molecular dynamics (MD) simulations. In the same year, Jiang et al. [43] studied NPG and investigated the permeability and selectivity of NPG and demonstrated the remarkable potential of graphene as a membrane for the gas separation of H_2 and CH_4. Their results indicated that H_2 permeance could be up to 1 mol/$m^2s^1Pa^1$, with a selectivity of amazing 10^8 for H_2/CH_4, which was up to 10^7 improvement in the value obtained with silica membranes (**Figure 2**). Du et al. [44] designed a series of NPG for separating N_2 and H_2 and found that there were different mechanisms for H_2 and N_2 to
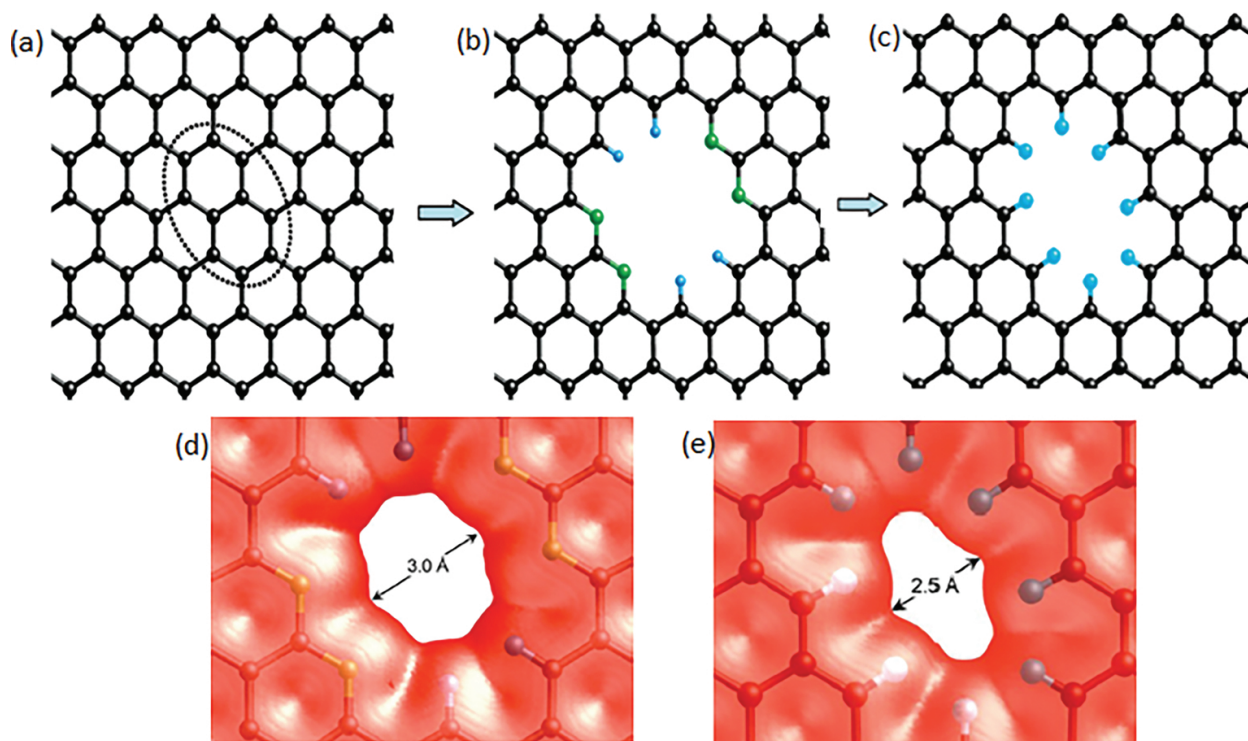

Figure 2. (a) Creating a nitrogen-doped pore within one graphene sheet; (b) graphene pores with mixed nitrogen (green) and hydrogen (blue) terminations and (c) only hydrogen-terminated pores. (d) Equivalent pore size from electron density calculations for nitrogen- and hydrogen-terminated pores; (e) pure hydrogen-terminated pores. Adapted with permission from [43].

permeate through the NPG membrane. The hydrogen flux was linear in relation to the pore size of NPG, while nitrogen flux was not. This revealed that the mechanisms of hydrogen and nitrogen permeation through the porous graphene are different. Trinh et al. [45] calculated bonding energy between gas mixtures including molecules of CO_2 and H_2 and graphite by performing MD simulation, and then analyzed selectivity and self-diffusion of CO_2 and H_2 on graphite membrane layers at different temperatures. **Figure 3** shows a series of typical snapshots, at different temperatures, of mixtures of CO_2 and H_2 on graphite surfaces, and the number of particles, as shown by Trinh et al. [45]. These authors also reported that the binding energy of CO_2 on graphite surface was three times larger than that of H_2, and the separation of CO_2 over H_2 was five times larger at lower temperature, compared to the value obtained at higher temperature. Other mechanisms, such as the pore translocation-limited, surface adsorption and rearrangement reaction, have been in-depth explored and discussed in the literature [46–49].
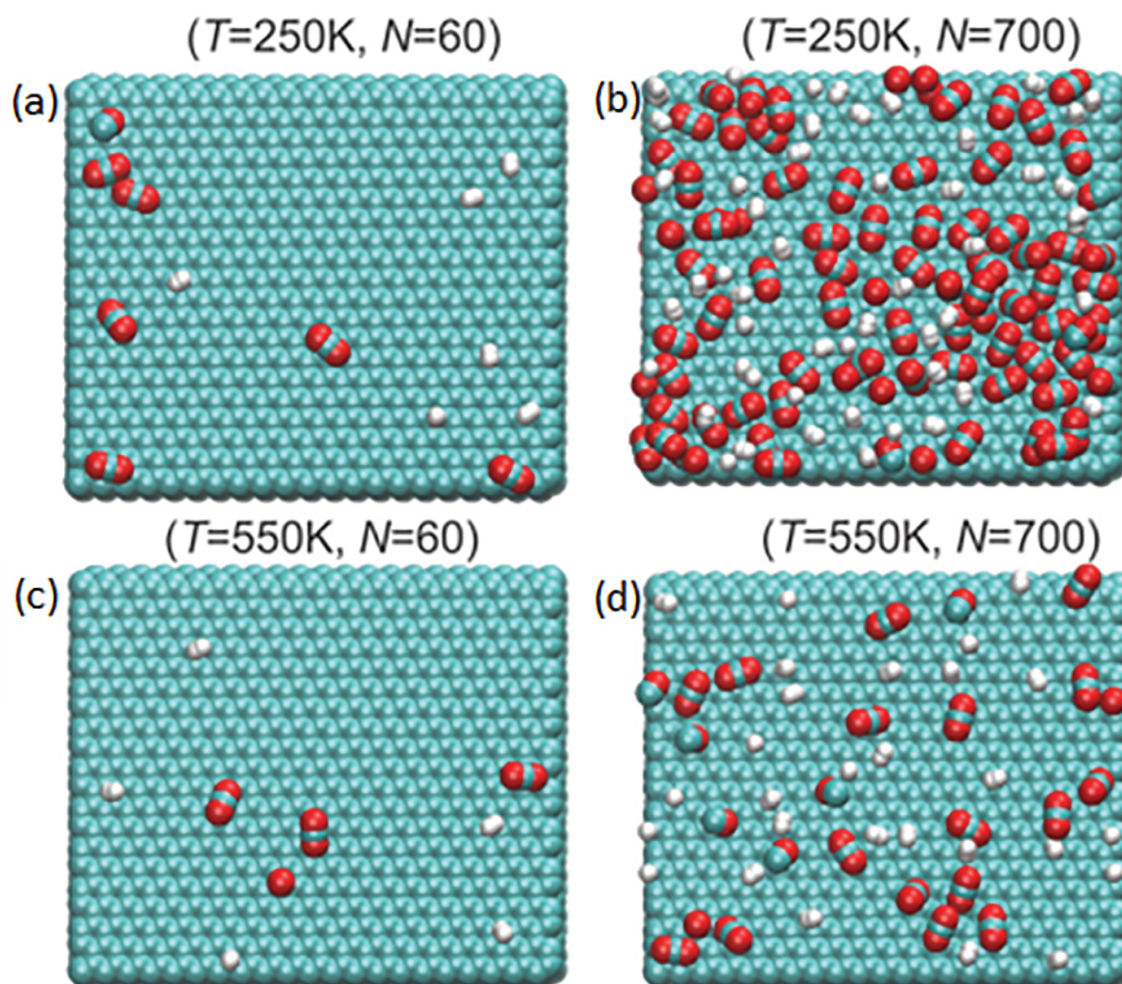

Figure 3. Typical snapshots of molecules absorbed on graphite surface at different temperatures (T) and total numbers of particles (N). The green, red and white represent C, O (oxygen) and H atoms, respectively [45].

Taking theoretical results into consideration, graphene and GO are promising materials to become the next-generation separation membranes. Scientists start to develop different strategies for synthesizing NPG. Most common methods include electron beam [50], ultraviolet-induced oxidative etching [51], electrochemical exfoliation [52] and creation of porous two-dimensional sheets by chemical synthesis [53] or 3D structures by sandwiching/tethering graphene with carbon nanotubes [54]. Fischbein and Drndić [50] introduced the use of e-beam irradiation to create nanopores on graphene sheets, allowing the porous size on the graphene to be controlled. Russo et al. prepared graphene nanopores with just a 3 Å radii, equivalent to 10 atoms removed, which is shown in **Figure 4** [55]. Ultraviolet light possesses energy to break certain chemical bonds and etching holes on graphene sheets. With this method, Bunch et al. [51] successfully prepared micrometer-sized graphene membranes with pores, which allowed smaller molecules to pass through but not larger molecules. Ambrosi and Pumera [52] tested different electrolytes in the method of electrochemically exfoliation, and suggested that graphene was a great candidate for electrochemical applications, such as biosensing and energy storage. O'Hern et al. [56] fabricated graphene composite membranes by transferring large area GO sheets onto polymer substrates. Strategies on how to precisely control the thickness and the chemical functionalization groups of graphene sheets [57] were also introduced. Recently, some novel methods are emerged to prepare graphene membranes. For example, Raghavan et al. [58] used plasma to prepare graphene membranes on the substrates including 6H-SiC etched by CF_4- and Cl_4-based plasmas and the results showed that the etching process could selectively etch silicon to produce carbon-rich surface layers on the silicon carbide substrate. When annealed, these carbon-rich layers formed graphene films with halogen- and oxygen-based defects. Reserbat-Plantey et al. [59] introduced an on-chip nanoelectromechanical system (NEMS) for preparing defect-controllable graphene which was believed to be the process allowing preparation of graphene at room temperature. Zhong et al. [60] reported that graphene sheets modified with the appropriate pore size of 4.06 Å could efficiently separate N_2 and CO_2 by molecular dynamic (MD) simulation and found that the graphene sheets behaved like a mesh that blocked CO_2 permeance but allowed N_2 to pass through. Besides that, Schrier [61] synthesized a porous graphene structure to separate He, Ne and CH_4, and observed that the porous graphene could separate He from alkanes and noble gases. Hauser and Schwerdtfeger [62] discovered that nanopores functionalized graphene membrane with nitrogen-doped porous had the ability to efficiently separate ^3He from ^4He. Zhang et al. [63] designed covalently cross-linked free-standing few-layered GO films using a layer-by-layer deposition technique, in combination with photochemical cross-links, and achieved a controllable and adjustable graphene membrane with good stability that lasted up to 9 days of use. In 2016, Lozada-Hidalgo et al. [64] used graphene membranes to filtrate hydrogen ion isotopes, like molecular sieves, and found that deuteron permeation through these membranes is much slower than proton permeation. This work implies that graphene has the potential to be used as nuclear waste treatment. With the developed technique, larger high quality and uniform graphene sheets can be transferred to various substrates. Graphene sheets, the ultimate membrane platform, will have wider usages in gas separation technology.
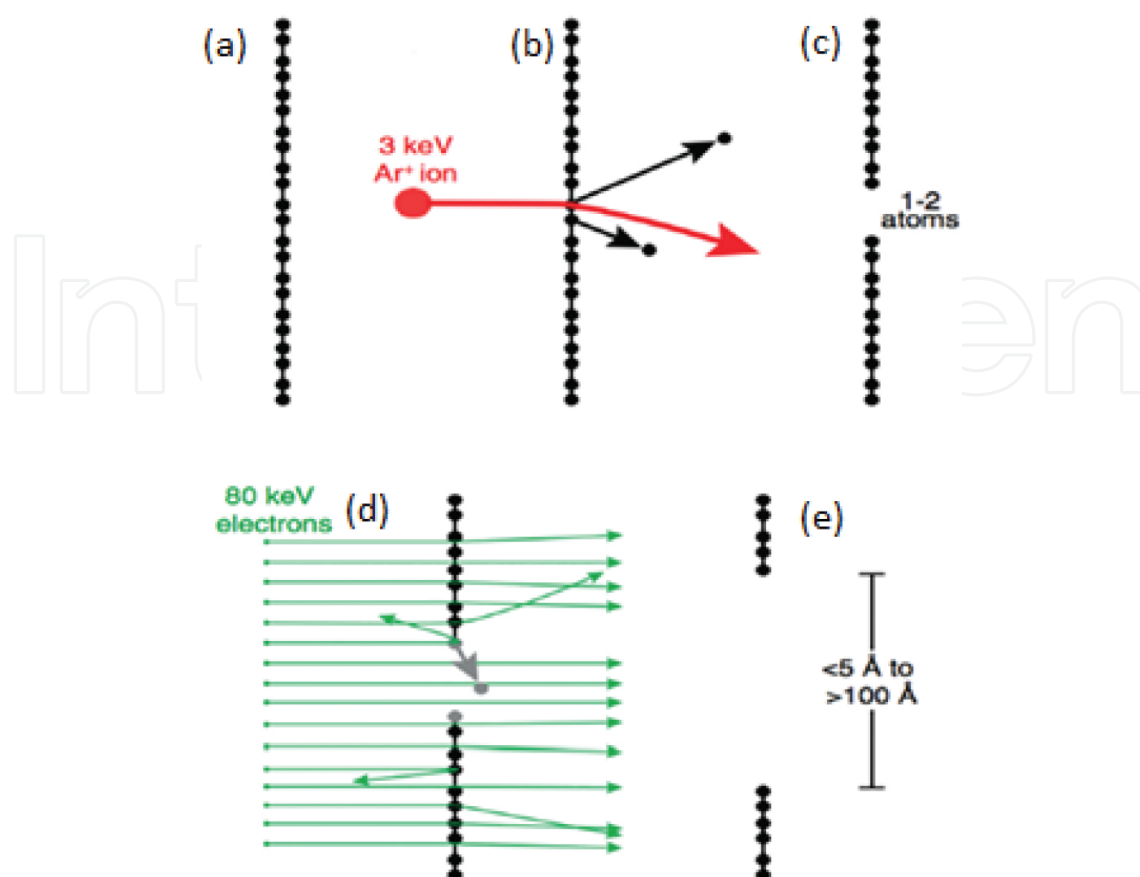
Figure 4. Preparation of graphene nanopores by e-beam. Starting with pristine, one-atom-thick graphene (a), a mona-tomic site is created by bombardment with 3 keV Ar (Argon)$^+$ ions, which remove a few carbon atoms in a single bombardment (b). After the single-bombardment, a small but stable defect-location is left in the layer surface (c). Then using a uniform e-beam enlargement of the defect-location is achieved by removing the edge atoms (d). Finally, the pore is opened until reaching the preferred size (e) [55].

Compared to graphene, GO membrane materials have a higher fracture energy (350 kJ m^{-3}) and tensile strength (42 ± 2 GPa) [65]. GO can be bent over 90° and form a simple curve (**Figure 5a**) [65]. This stiff-yet-flexible property makes GO an ideal candidate as membrane material. Various routes have been reported for preparing graphene and its oxide derivative with good mechanical properties for different applications. Pierleoni et al. [66] used soluble graphene derivatives to fabricate gas separation membrane coatings on the surface of polymers and found that the use of 2D materials as surface coatings, instead of bulk additives, overcame common issues related to dispersion of graphene into a polymer matrix, and gave a remarkable advantage in preserving the mechanical properties of the bulk polymer. Kim et al. [67] successfully loaded a large area of graphene and GO on the polymer substrate and then measured the transport and selectivity of O_2-N_2 and CO_2-N_2. They considered that the defects and the wrinkles on the graphene and GO surfaces (**Figure 5b**) conferred the selectivity and the controllability to the membranes. Bai et al. [68] invented a new graphene nanostructure named graphene nanomesh (**Figure 5c**). They used block copolymer lithography to prepare NPG with neck widths as low as 5 nm and such materials exhibited great membrane performance. Yang et al. [69] noticed that the wrinkles on the graphene could lead to buckling behavior,

which would significantly influence graphene membrane performance. Li et al. [70] reported ultrathin GO membranes with thickness approaching 1.8 nm, loaded on porous anodic aluminum oxide (AAO). The selectivity of the membranes could reach as high as 3400 and 900 for H_2/CO_2 and H_2/N_2, respectively. With successful fabrications of gas flow channels and pore sizes, one can optimize the performances of graphene and GO membranes. Other parameters, including temperature and pressure of the system, can affect the effusing rate, selectivity and flux of graphene and GO membranes. Functional groups inserted at the edge of the pores or between the interlayers can also significantly enhance the selectivity and flux of the graphene-based membranes.
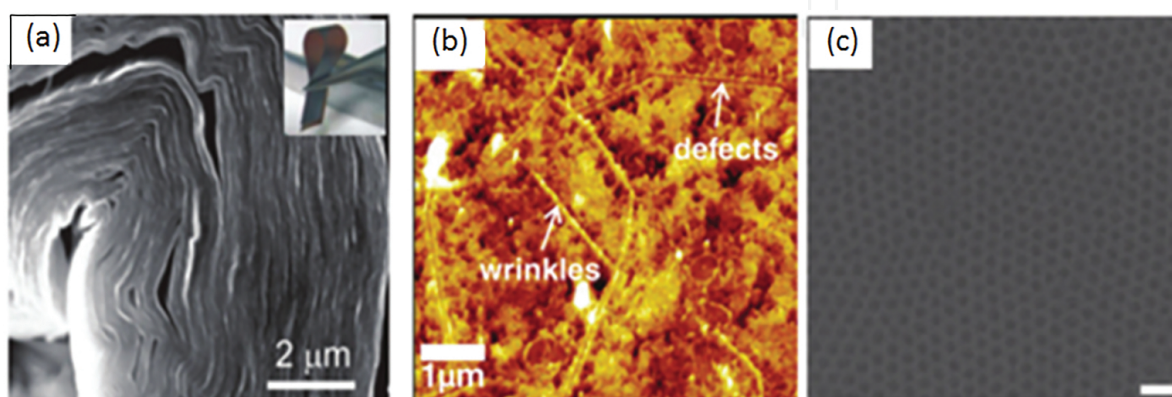

Figure 5. (a) GO materials can be folded over 90° [65]. (b) Atomic force microscopy (AFM) image of graphene membrane surface showing the defects and the wrinkles [67]. (c) Scanning electron microscope (SEM) image of graphene nanomesh [68].
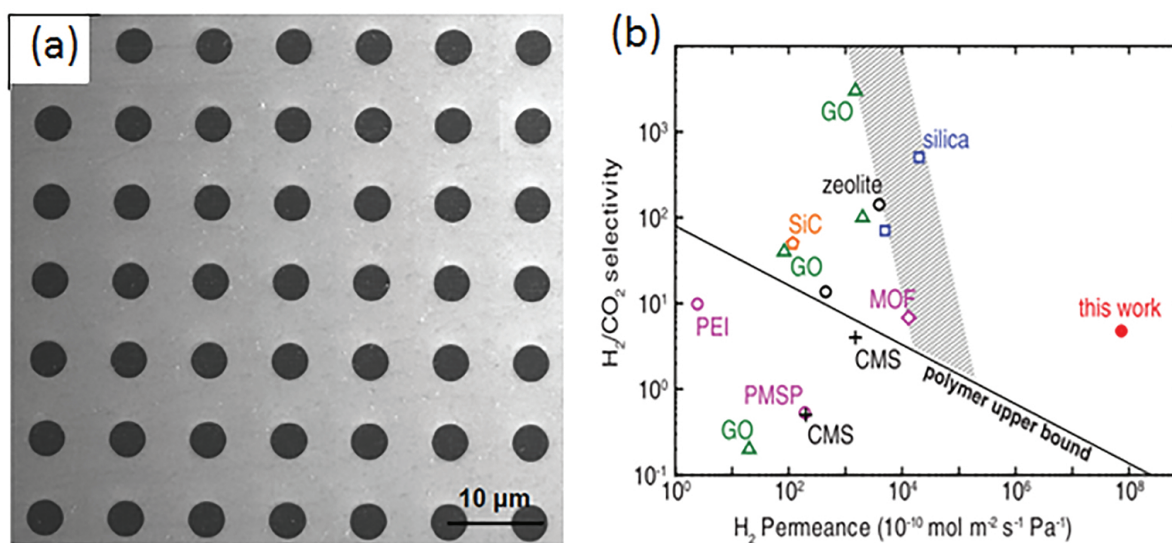

Figure 6. (a) The SEM image of the SiN$_x$ membrane with 49 pores showed. (b) Comparison of hydrogen-carbon dioxide gas mixture separation performances between the graphene membranes and other membranes: GO, poly (1-trimethyl-silyl-1-propyne) (PMSP), polyetherimide (PEI), carbon molecular sieve (CMS), zeolite, silica, metal-organic framework (MOF) and SiC [71].

Traditional membranes, including silica-, polymer- and zeolite-based, follow the well-known law that selectivity is determined by the product of diffusivity and solubility [13]. However, this rule is no longer valid for graphene- and GO-based membranes. For atom-thick graphene, the selectivity is determined by the pore size of GO. The thickness of graphene or GO is also no longer linearly related to the diffusion rates. Although the mechanism is still under intensive study, NPG has shown fluxes of gas in far excess, compared to that of traditional membranes. For example, Celebi et al. [71] fabricated highly efficient mass transfer porous bilayer NPG onto a SiN$_x$ frame punctured with matrix pores with 4 μm in diameter (**Figure 6a**), which physically perforated double-layer graphene. The results (**Figure 6b**) showed that the permeation of the NPG membranes is much higher than that of other traditional membranes, including polymer, silicon and composite materials.

3. Graphene and GO for water purification

Oceans contain about 97% of the world's water. Nowadays the cost of reverse osmosis (RO) decreased to 1.8 KWh/m^3, which is only 1/3 of the cost as was in 1990 [9]. Thermal desalination, such as multiple-effect distillation and multistage flash, needs much more energy to be used, compared to RO. Thus, the development of desalination can only become a sustainable option for water supply if a dramatically new technology is developed.

Graphene, with its extraordinary properties and environmentally friendly nature, has attracted the scientists' interest due to its potential applications in wastewater treatment and water desalination. As a single layer of graphene is impermeable to gases and liquids, NPG is considered as a potential membrane material for molecular sieving or water filtration. Advantages of NPG over RO membranes include negligible thickness and high mechanical strength, indicating faster water flux, with low pressure requirements. The first simulation work on water flux across graphene membrane was conducted by Suk et al. [72]. As shown in **Figure 7**, these authors compared the water flux performances of NPG and CNTs. Results indicated that NPG had higher water flux which did not significantly vary with the thickness of NPG. Then, Cohen-Tanugi and Grossman [73] showed that nanometer-scale pores in single-layer freestanding graphene could effectively filter NaCl salt from water through MD simulation results. They demonstrated that NPG membrane had the ability to prevent salt passage, critically depending on the pore diameter and chemical functional groups bonded to the edges of graphene pores. Nair et al. [74] indicated anomalous water permeation to low friction between the water monolayer and pristine graphene regions. Based on that assumption, a capillary-driven flow mechanism was established for graphene-based membranes. Boukhvalov et al. [75] analyzed the hybrid systems consisting of water and GO and believed formation of hexagonal ice bilayer in between the flakes, as well as melting transition of ice at the edges of flakes, were crucial to understand the water permeation across GO. Ma et al. [76] discovered the fast diffusion of water nanodroplets on graphene and opened a prospect for achieving fast and controllable motion of adsorbates across graphene and GO surface materials.
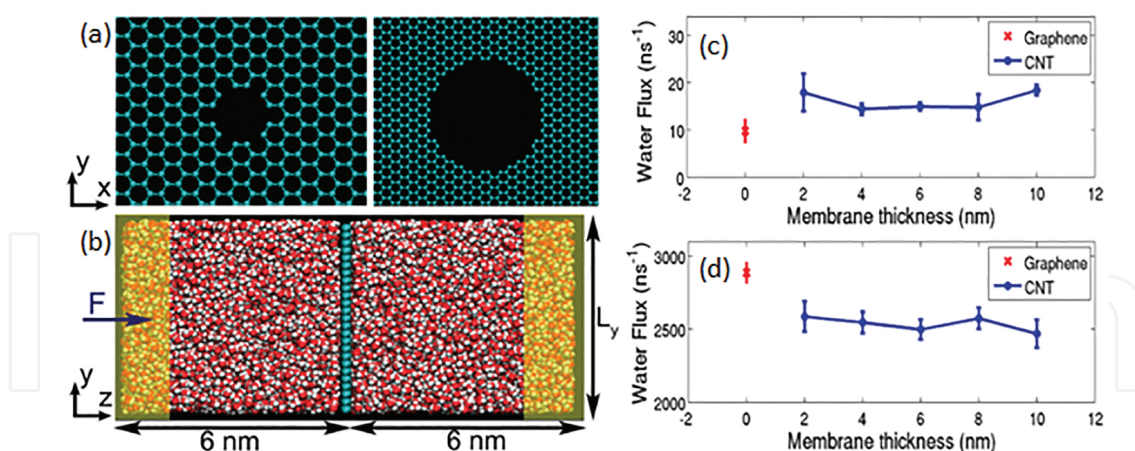
Figure 7. (a) Graphene membrane with nanopore diameter: D_{avg} = 0.75 nm (left) and D_{avg} = 2.75 nm (right). (b) Simulation setup. Cyan color represents carbon atoms; red and white colors represent oxygen and hydrogen atoms of a water molecule, respectively. Two water reservoirs are attached to each side of the porous graphene membrane. Ly=Lx=4 nm when the pore diameter is 0.75 nm, and Ly = Lx = 6 nm when the pore diameter is 2.75 nm. In the shaded region (Δz =1 nm), external forces are applied on water molecules to create a pressure drop across the membrane. (c) Water flux through a (10, 0) CNT with a diameter of 0.78 nm and through a graphene nanopore with a diameter of 0.75 nm. In both cases, a single-file water structure is observed. (d) Water flux through a (20, 20) CNT with a diameter of 2.71 nm and through a graphene nanopore with a diameter of 2.75 nm. A single-file water structure is not observed in this case [72].

In order to improve water permeability, small sheet size, high density of interedge spaces and wide nanochannels are required in graphene and GO membrane fabrication. Wei et al. [77] enhanced water flow in graphene membranes into the unique porous microstructures. These authors pointed out that the side-pinning effects caused by H-bonds between water molecules and oxidized regions could help fast water transportation in graphene channels, and that this, along the porous microstructure, were the principal factors responsible for the enhanced water flow. Other studies also indicated that intercalation of different-sized cross-linkers can tune the interlayer channel size [78]. Furthermore, Wei et al. [79] investigated interlayer flow and demonstrated that the breakdown of flow enhancement could be derived from GO chemical functionalization as well as relaxation of nanoconfinement. Also, both simulation and experiment were performed to evaluate the characteristics of membrane structure and operation parameter affect water flux in graphene and GO-based membranes. Cohen-Tanugi and Grossman [73] found out that the water flux through monolayer graphene had a linear relationship with the pore area by computational methods. They also proposed that hydrophilic pores could increase water permeation, due to H-bonding between water molecules and pore edges. Hu and Mi [80] fabricated a series of novel GO membranes with different numbers of layers and tested their water purification performance. These authors observed that there was no evident correlation between water flux and the number of layers of graphene. Sheath and Majumder [81] prepared graphene membranes by evaporation-induced capillary-force self-assembly and found out that membranes had higher space rejection properties, while simultaneously enhancing water flux, compared to analogous materials produced by the traditional vacuum filtration technique. Han et al. [82] synthesized ultrathin graphene nanofiltration membranes (uGNMs) on

nanoporous microstructure substrates, using chemically converted graphene. The uGNMs showed high retention (>99%) for organic dyes and moderate retention (≈20–60%) for ion salts. The physical sieving and electrostatic interaction were considered as two important factors dominating the rejection process (**Figure 8**).
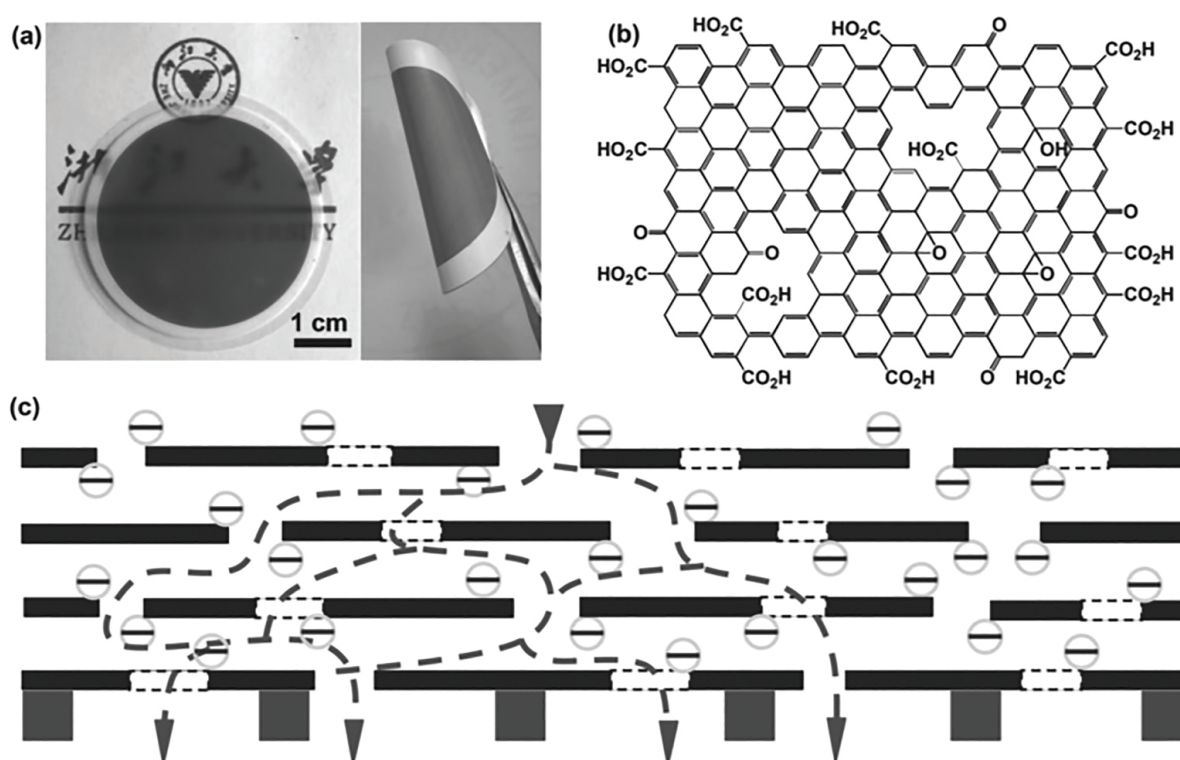

Figure 8. (a) Digital photo of an uGNM coated on an AAO disk (left) and a twisted uGNM coated on a PVDF membrane (right). (b) Schematic representation of a brGO: graphene sheet with a certain amount of holes; most of the oxidized groups are located on the edges and the periphery of the holes. Note that the real graphene sheets extend further than depicted. (c) Schematic view of possible permeation route: water molecules go through the nanochannels of the uGNMs and holes of the graphene sheets and finally reach the pores of supporting membranes. The blank squares present the holes on the graphene sheets (black line). The edges of the brGO and the periphery of the holes are negatively charged [82].

In order to further optimize the performances of NPG or GO for water treatment, the mechanism involved needs to be intensively studied. There are two main primary factors concerning the selectivity of the materials used in this process: size exclusion and interactions with functional groups, including chemical and electrostatic ones. Using classical molecular dynamics, Cohen-Tanugi and Grossman [73] concluded that nanopores in single-layer freestanding graphene could effectively filter NaCl salt from water. Small pores, low pressure and hydrophobic pores refuse salts more efficiently, due to direct size exclusion, while the larger effective volume of ions and the lack of H-bonding can lead to a higher energy barrier to ions passage. Prince et al. [83] devised an ultrawetting graphene-based membrane by incorporating amine and carboxyl functionalities onto graphene and then covalently attaching it to a polymer matrix to fabricate a water filtration membrane. They concluded that the graphene increased the water permeability of the membrane by 126% compared with stable

membrane selectivity. Hu and Mi [84] prepared a kind of water separation membrane using GO nanosheets and this membrane displayed remarkable rejection of monovalent and divalent salts and moderate or high rejection of organic dyes. Yin et al. [85] prepared a thin-film nanocomposite (TFN) membrane containing GO sheets to enhance polyamide (PA) membranes for water purification application. These GO sheets were well dispersed in the polyamide (PA) layer and their incorporation improved membrane performances. Authors suggested that interlayer spacing of GO may serve as water channels and hence contribute to the water permeability enhancement. Independently, Han et al. [82] obtained similar results, showing that the observed rejection organic dyes could be assigned to size, electrostatic interaction, and the rejection of ions is based on Donnan's exclusion (or Donnan effect, a name for the behavior of charged particles near a semipermeable membrane that sometimes fail to distribute evenly across the two sides of the membrane). Additionally, Huang et al. [20] investigated different factors including salt concentration, pH and pressure effects on the separation performance of GO membrane toward small molecules and demonstrated how these factors affect such process. Sun et al. [86] confirmed the selection ion penetration and water purification properties of GO membranes. They reported that sodium salts could quickly pass through GO membranes, while heavy-metal salts moved slower (**Figure 9**). Copper salts were absolutely unable to permeate through, as well as organic contaminants. Their follow-up work [87] revealed, by theoretical calculations, that the coordinative interactions play an important role on the selectivity of the transmembrane transport of alkali and alkaline earth cations. Joshi et al. [88] designed an experiment (**Figure 10a**) to measure the permeation properties of micrometer-thick GO laminates. The normalized permeation rates as per 1 M feed solution (**Figure 10b**) show that ultrafast permeation is only possible for ions smaller than a specific size. Size exclusion affected the selectivity as well as capillary forces could induce the anomalous fast transportation. Their follow-up work [89] indicated that graphene had a large possibility to be used as membranes for desalination and confirmed that 100% salt rejection could be achieved for commonly used ions by utilizing single-layer nonporous graphene. Liu et al. [90] studied the pressure-driven water transport inside the nanochannels of graphene membranes. They found that an ultrafast water flux was observed inside the channels, which increased linearly with the driving pressure, but decreased as the interaction strength between the water molecules and the bilayer increased.
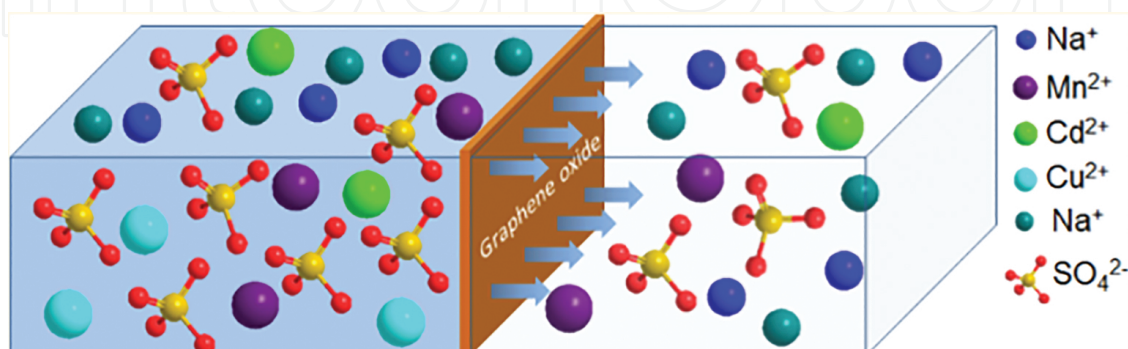

Figure 9. Schematic diagram of the penetration processes of different ions through GO membranes [86].
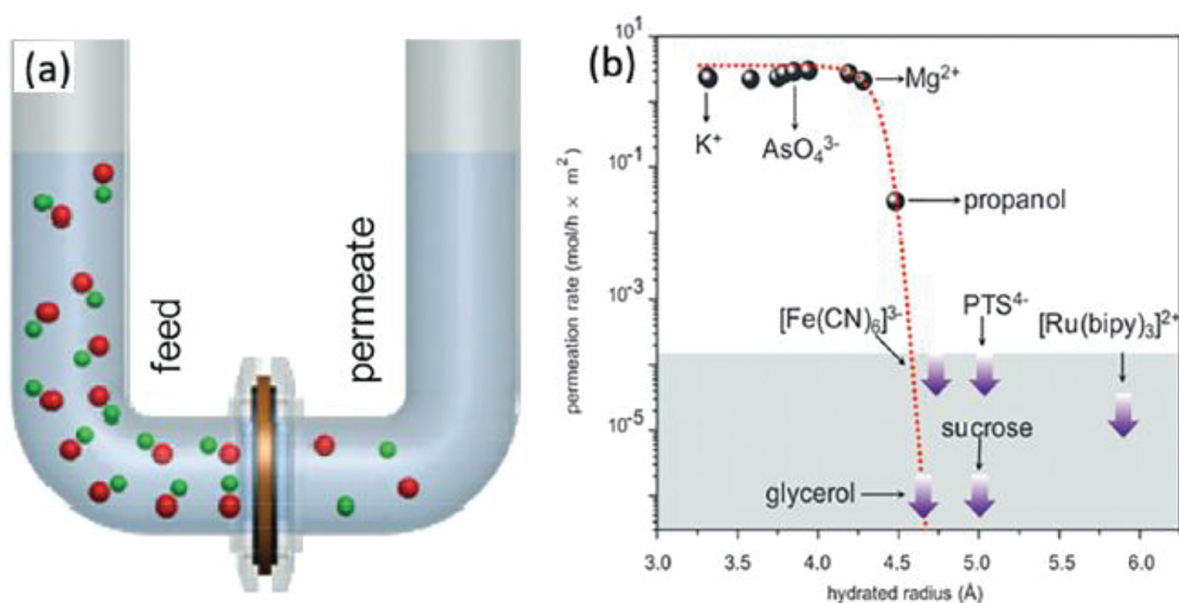
Figure 10. (a) Experimental setup. A U-shaped tube is partitioned by GO membrane into two compartments that are referred to as feed and permeate. (b) Sieving through atomic-scale mesh. The small species permeate with approximately the same speed, whereas large metal ions and organic molecules exhibit no detectable permeation [88].

Apart from water dissipation and purification, graphene and GO can also be used on other water treatment applications, such as recovery of acids from iron-based electrolytes. Sun et al. [91] reported that nano-GO (**Figure 11**) membranes could completely block Fe^{3+} when the ion concentration reached a certain extent (0.01 mol L^{-1}), whereas the H^+ permeated through unimpeded. This implies that the use of GO membranes can be applied to the recovery of acids from an $FeCl_3$ solution. On the other hand, Huang et al. [21] prepared a GO membrane supported on a ceramic hollow fiber for separating dimethyl carbonate–water mixtures through a pervaporation process. They considered that the separation process followed a sorption-diffusion mechanism. Tang et al. [92] also utilized a pressurized ultrafiltration for dehydration of ethanol using GO membranes. However, the results obtained from binary-component feed tests were lower than the ideal water/ethanol selectivity, found by calculation. This may be attributed to the effects of intermolecular H-bonding between water molecules and the functional groups of GO nanosheets that may enlarge the interlayer spacing and allow more ethanol transport through the GO membrane. Recently, Lin et al. [93] devised a way to fast produce graphene in a CVD process and then grow it on Ni, Cu and a Cu-Ni alloy with proper composition. This work provided a possibility to produce large-scale graphene single crystals, which paved the route towards reaching practical applications of graphene, such as in wafer-scale electronic and optoelectronic devices. Wu et al. [94] used a similar approach to fast grow inch-sized single-crystalline graphene by letting a single nucleus interact with a monolayer at a fast rate. They synthesized a roughly 1.5-inch-large graphene one-atom-layer in 2.5 h and suggested that this method may prove effective for the synthesis of wafer-scale single-crystalline monolayers of other two-dimensional materials.
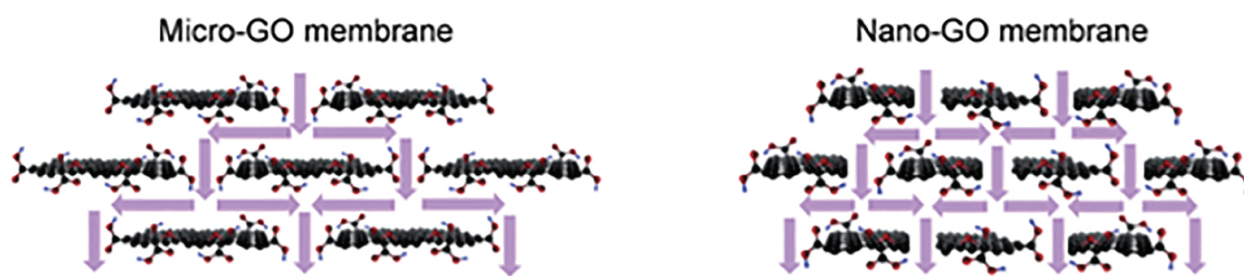
Figure 11. Schematic diagrams of the structure of nanocapillary networks in nano- and micro-GO membranes. It can speculated that when the lateral dimensions of the GO sheets used to form the membranes were reduced from micrometer (left) to nanometer (right), the amount of nanocapillaries formed within the membranes should significantly increase, resulting in the enhancement of ion penetrations through GO membranes [91].

In summary, graphene and GO membranes are believed to be the next-generation separation materials for applications in water purification due to their significant intrinsic mechanical strength [95], high chemical stability [57], high antibacterial activity [96] and exquisite antifouling properties [65], as mentioned above. The narrow pore size and nanochannels of GO membranes can be tuned by induction and modification of surface functional groups. For water separation and purification, an ideal pore size distribution should be achieved as this is beneficial to precisely sieving ions through the size exclusion mechanism.

4. Conclusions and perspective

Graphene and its oxide derivative, having two-dimensional one-atomic-layer, ultrafast permeation, remarkable mechanical properties and outstanding energy-efficiency, are promising candidates for the next-generation separation membranes for precise and selective gas separation (**Figure 12**). Although graphene and GO have been reported as being extraordinary in both selectivity and flux when separating multiple gas mixtures and water purifications, there are still several challenges that need to be solved in order to achieve industrial applications. Firstly, the pores on the surface of graphene and GO sheets can be blocked by defects, impurities, polymer, molecular residues and grain boundaries. They will affect the performance of the membranes, namely the flux rate [97]. Therefore, the mixture should be carefully purified before entering into the graphene membrane systems. The operating conditions, such as pressure, temperature and flux rate, will affect membrane selectivity. These factors must be considered before using graphene- and GO-based membrane materials. Secondly, the selectivity for H_2/H_2S, CO_2/CH_4 or mixtures of three or more gases on gas separation applications of graphene and GO membranes still needs to be fully characterized. A reasonably analysis of the parameters that influence the process of graphene and GO is needed for predicting the mechanism of membrane selectivity. Those information are of great interest for industries, such as nature and shale gas companies. Although graphene is considered as the world's strongest material with Young's modulus up to 1 TPa, local defects, cracks and wrinkling of graphene and GO will affect the excellent property of graphene sheets [98]. The local bond breaking and bond rotation at the crack tip

of the graphene could lead to dramatic losses of mechanical properties of corresponding products, which may cause the membranes to be less robust and more fragile, and even generate unexpected large pores during constant usage. To solve this issue, a good solution might be to use a reliable porous substrate as support structure for graphene membranes. The connection and adhesion properties between membranes and support structures thus need to be fully revealed. Then, for the membrane itself, pore size is the most critical parameter in controlling the performance of graphene-based membranes; graphene and GO can enhance the selectivity of separating mixtures by adjusting its layer-to-layer distance and/or inserting functional groups on the surfaces and interlayer-faces of graphene sheet. The last challenge is the overall cost for the industry demands. Large-scale graphene and GO membrane fabrication techniques need to be developed, and related standard quality control tests need to be created to meet the industry requirements. Although the high production cost of GO so far impeded the development of large-scale applications, the coming advances on technology will certainly decrease the manufacturing prices of graphene and GO, and more methods will be developed to generate defect-free, larger area graphene, with controllable pore structure/size and interlayer distance. It is believed that this promising field will attract increasing interest from both academia and industry in the future.

Water purification is also a promising topic worth exploring, in order to achieve the fundamental understanding that might lead to the specialized industrial application of graphene- and GO-based membranes. The first challenge is the precise design of user-controlled GO membranes, including the pattern of oxidized regions, interlayer space, pore size, modification of pore chemistry and the number of graphene layers. Further developments on the parameters that determine the small molecule permeation and separation performance are also necessary. Meanwhile, the effect of the interlayer space and surface defect of graphene and GO on fluid flux is being carefully studied. With those information, the mechanism affecting the selectivity of NPG and GO may be solved. The contradiction between flux and selectivity is considered to determine the optimal membrane fabrication parameters. Modification of the surface of GO membranes with different atoms and functional groups, to adjust water affinity, can achieve higher flux, without sacrificing selectivity of the membrane system. The second topic that needs to be considered is the state of GO in aqueous conditions. The swelling needs to be regulated in order to achieve the ideal selectivity. For industrial processes, the operating pressure is an important factor to both separation system and membrane materials. Operation in a large range of pressures will be highly beneficial. Finally, the last issue is the cost. For some special industrial applications, such as producing high purity acid from high-concentration $FeCl_3$ solutions, pretreatment or posttreatment will increase energy consumption and total investment. Researchers are also suggested to minimize the gap between theoretical and experimental results on water/ion transport mechanisms across GO nanosheets in water and to solve impurity issue on the graphene- and GO-based membranes, including adsorption of metals and organic dyes [99], ionic clogging inside the capillaries, as well as coordination occupation on the surface of oxidized regions. These effects still need investigation and optimization. The key to successfully fabricate adequate membrane systems is to balance the antimicrobial efficiency and mechanical strength of the freestanding membranes.
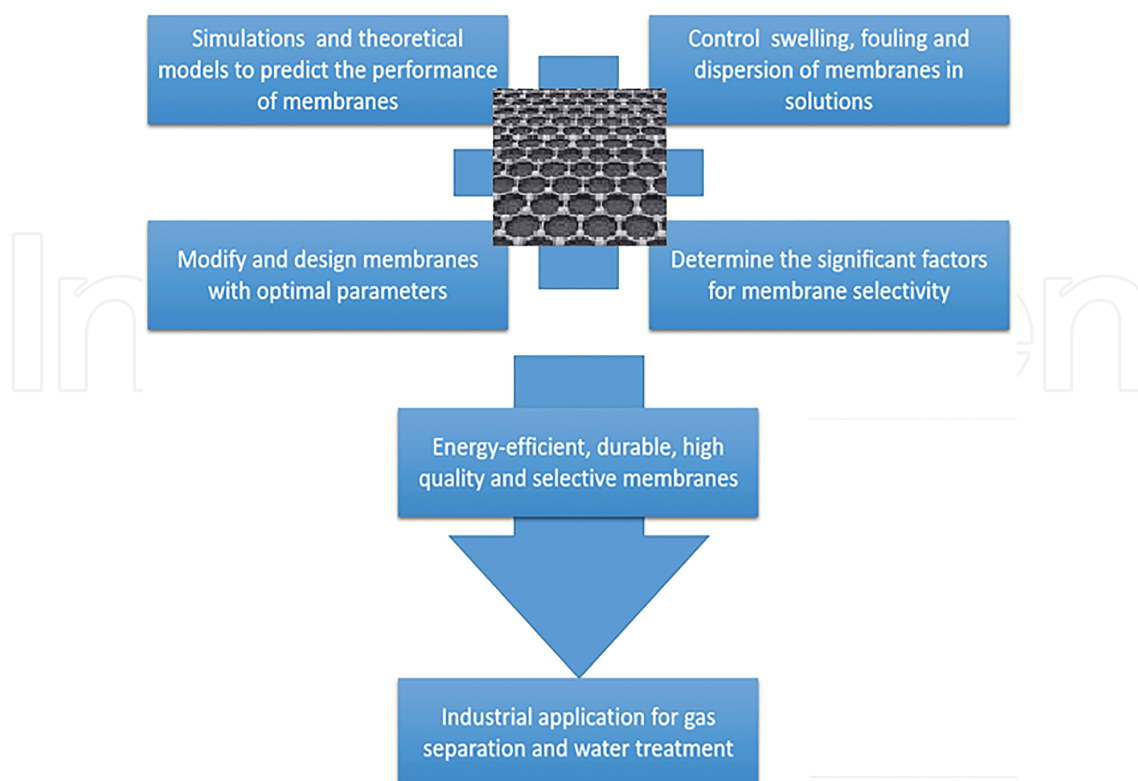
Figure 12. The outlook of the research on graphene and GO membranes.

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