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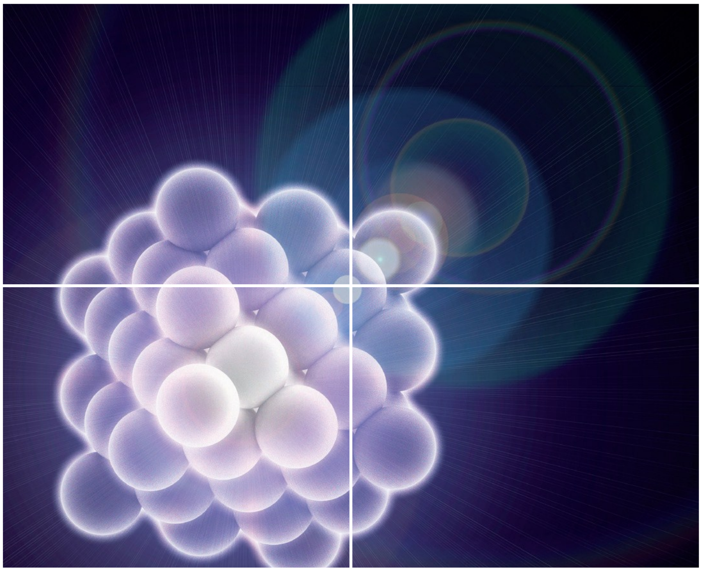

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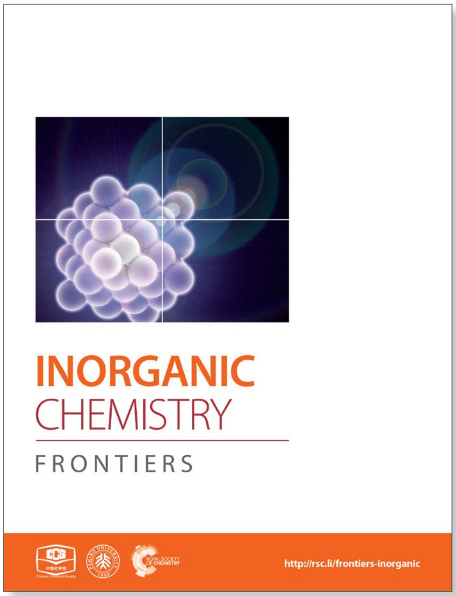
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Journal Name

RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Graphene and Graphene Oxide: Advanced Membranes for Gas Separation and Water Purification

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Advanced membrane system with excellent permanence is important for controllable separation processes such as gas separation and water purification. The ideal candidate materials should be very thin to provide high permanence, be stiffness enough to withhold work under high applied pressure, with large surface area and micro or nano pore structure for excellent selectivity. Graphene oxide(GO) nanosheet is graphene with oxygen-containing functional groups, obtained by treating graphite with strong oxidizers. Graphene-based materials, by virtue of their high mechanical strength, large surface area, single-atom-thick unique two-dimensional honeycomb lattice structure, and narrow pore distribution, provide exciting opportunities to assemble novel types of advanced, ultra-thin, high-efficient membrane devices. In this contribution, we discuss the progress made in the direction of using graphene oxide as, high-efficiency membranes for gas separation and water purification. The primary focus will be on introducing the fabrication processes, exceptional properties, and innovative membrane application of two-dimensional graphene oxide materials for controllable separation process. This state-of-the-art review will provide a platform to understand the intricate details of gas and water molecular transport through laminar graphene oxide membrane, as well as a summary of the latest process in the field.

Introduction

Separation is a critical industrial process that finds a broad range of application in nature gas purification, hydrogen production, and sea-water desalination.[1-2] The low efficacy of the prevailing technologies necessitates the formulation of advanced separating techniques to solve the urgent environmental and energy issues. In comparision to traditional distillation,[3] absorption,[4] adsorption[5-6] or sublimation,[7] membrane-based technology exhibited considerable promise. The key advantages of membrane-based strategies for small-to-medium scale gas separation and water filtration applications are (i) overall economics, (ii) safety, (iii) comparative environment friendly nature, and (iv) easy recycling.[8-9] Currently, membranes made from polymers, zeolite, silicon is being successfully applied in industry.[10] However, permeability and selectivity are two inherent trade-offs for conventional membrane materials that limit its usages.

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Recently, considerable interest has been aroused by carbon based nanomaterials because of their easy accessibility, excellent mechanical properties, biocompatibility, and environmental friendliness.[11-12] One-dimensional carbon nanomaterials (e.g. carbon nanotubes. CNTs) were initially believed to be promising candidate materials for membrane assembly due to their unique hollow structure with open ends and extremely strong mechanical properties. However, there is a technical barrier to assemble vertically aligned nanotubes arrays with high density on a large scale,[13] and the fabricate of CNT-based separation membranes remained theoretical probability. Another carbon-based nanomaterial with great mechanics properties known as carbon diamond composed of amorphous sp^3 hybridized carbon atoms, was also investigated for filtration applications. However, the large energy consumption due to the low utilization efficiency of carbon diamond materials based membranes devices inhibited their large scale industry application.[14] Thus, the development of a more applicable and economical carbon nanomaterials based separation membranes is an urgent need.

Graphene, a single-atom-thick sheet of sp^2 hybridized carbon atoms arrayed in a honeycomb pattern, has opened the door for assembling separation membranes with improved separation capability.[15] The concept and the preparation of graphene-based materials have been explored over 100 years. As early as in 1859, Brodie prepared graphitic oxide with strong oxidizing mixture.[16] In 1958, Hummers reported a redox method to prepare graphitic oxide.[17] Since its first isolation in 2004, graphene is drawing increasing attention in diverse branches of science and technology owing to its exceptional physicochemical properties including mono-atomic thickness, high mechanical strength, and significant chemical inertness.[18] With their ubiquitous properties, graphene displayed great potential for atomic permeation, water transportation, and gas separation.[19-21] For the mass production, user-controllable pore distribution, application under high-pressure condition, graphene's oxygen-containing analogue, graphene oxide (GO) is being considered for filtration/membrane fabrication and utilization. The possibility of facile and large scale production of GO and its unique properties has opened-up a new phase-space for the production of advanced membrane separation technology. GO-based membranes have been used in water treatment and liquid organic molecular separation.[22-23] It should be noted that the physicochemical status of oxygen-containing groups in GO sheets plays a significant role in determining their separation performance. This offers several straightforward strategies to control pore size in tiny channels of GO via tuning the types and forms of oxygen contained groups.

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In this mini-review paper, the application of graphene and GO under consideration for separation membranes applications is discussed. The discussion is divided into three parts. The first part describes the application of graphene and its derivatives utilization for gas separation, while the second part focuses on their unique applications for ion sieving, as well as their role in water purification with different mechanisms. Lastly, the final part of the review gives a summary and outlook of graphene-based separation membrane, the existing challenges and new directions in this emerging research field. This critical review offer a comprehensive discussion of graphene based membrane from the perspective of widely separation application, as well as the advanced progress in such membrane with improved separation performance.

Graphene and GO for gas and water molecules separation

Compared to polymer, zeolite, and silica membranes, layered graphene, and GO membranes display distinguished characteristics including excellent stiffness, large-scale production, and hydrophobic properties. Recent studies have demonstrated that graphene-based membranes exhibit significant potential for gas,[24-26] and water molecules separation.[27]

Graphene and GO for gaseous selectivity

A mono-layer of graphene is well known to resist the permeation of small gaseous molecules (e.g. He),[28] as the electron density of its hexagonal rings will repel the atoms and molecules trying to pass through them. Based on this, an atomic layer of pristine graphene can be considered as perfect gas barrier material. Although graphene is impermeable to gases, nano porous graphene (NPG), due to their high surface porosity can efficiently select gases. Hence, graphene with its mon-atomic thickness, can potentially surpass the permeability and selectivity limits of conventional membranes and is considered as the ideal membrane materials. Theoretical computational studies revealed NPG had higher selectivity and flow rates compared to traditional polymer and silica-based membranes. For example, Jiang *et al*[29] (Figure 1(a)) investigated the permeability and selectivity of nitrogen-doped porous single layer graphene and found that graphene layer exhibited high selectivity (up to 108) toward H_2/CH_4 gas flow after designing and adjusting subnanometer-sized pores. In addition, Schrier[30] simulated NPG for separating He, Ne and CH_4 with different functionalized porous and found the possibility of high helium selectivity using porous graphene membrane. Also, Hauser *et al*[31] pointed out NPG can efficiently select ^{3}He over ^{4}He with different functionalized graphene pores. Du *et al*[32] via a simulated separation process of H_2 and N_2 reported that the H_2 flow rate through NPG was linear related to the pore size of graphene while N_2 flow rate is independent. Trinh *et al*[33] with the help of calculated bonding energy between the molecule and graphene, analysed the selectivity and self-diffusion of CO_2 and H_2 on few-layer graphene (Figure 1 (b)) under different temperatures. It was suggested that the selectivity of CO_2 over H_2 is five times larger at lower temperatures compared to that at higher temperatures. The thickness of the graphene also was found to regulate the self-diffusion and flow rate of gases. The pore size, the nature of functional groups at the edges of pores, thickness, temperature, local defects and wrinkling (Figure 1(c))[34] are considered as the key factors affecting the selectivity of pristine graphene. Other mechanisms such as pore translocation-limited mechanism, surface adsorption mechanism and rearrangement reaction mechanism are also intensively evaluated and discussed in the literature.[35-38]

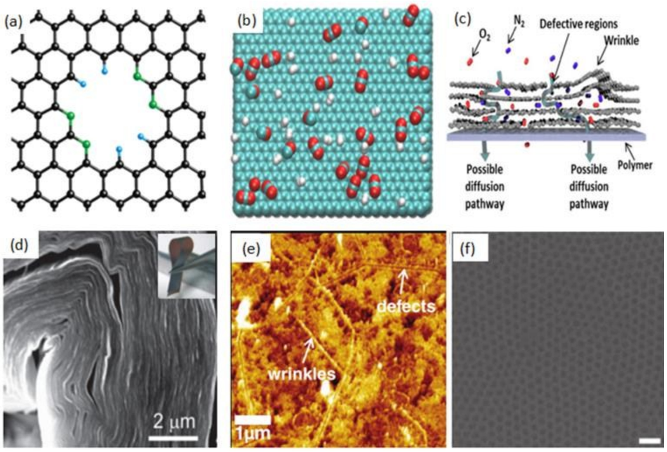

Figure 1 (a) Creation of a nitrogen-functionalized pore within a graphene sheet, Color code: C, black; N, green; H, cyan.[29] (b) Typical snapshot of the gas mixture of CO_2 and H_2 in equilibrium with a graphite surface. The temperature is T = 300 K and the number of particles is N = 700. The green, red, white are represented carbon, oxygen, and hydrogen atom, respectively.[33] (c) Schematic illustration of possible gas transport through few-layered, defective graphene membrane[34] (d) Large area GO can be bended over 90 degrees.[47] (e) Atomic force microscopy (AFM) images of a graphene/PTMSP membrane surface, wrinkles and defects are clearly seen in the surfaces.[34] (f) Manufacture graphene nanomesh,[40] the porous size on graphene sheet can be controlled.[52]

Since theoretical results illustrated the tremendous promise of graphene and GO as next generation membranes (Figure 2 (b)),[39] several strategies has been developed to synthesize NPG to achieve functional separation membrane. The most important methods include electron beam,[40-41] and ultraviolet-induced oxidative[42] etching of holes on graphene surfaces, creation of porous two-dimensional sheets from molecular building blocks,[43] and sandwiching/tethering graphene with carbon nanotubes to create 3D structures.[44] The progress in experimental processes allowed the successful transfer of large area GO sheets on different substrates under suitable conditions.[45] Further, the ability to precisely control the thickness and chemical functionalization of GO,[46] resulted in the development of facile approaches of fabricating GO-based membranes. Compared to graphite foils, the unique interlocking-tile arrangement of the nanoscale GO showed a higher fracture energy (350 kJm^{-3}) and high tensile strength(42 ±2GPa)[47]. Although GO has high tension strength and bending strength, it can still be folded over 90 degrees

(Figure 1(d)), this stiff-yet- flexible property of GO give them a promising membranes. Moreover, various routes have been successfully reported to produce large area graphene[48-49] and GO[50] with an accurate evaluation of its mechanical property.[51] For example, Kim *et al*[34] successfully transferred large area of graphene and GO on a polymer substrate and measured the transport and selectivity of O_2/N_2 and CO_2/N_2 on graphene and its derivative-based membrane (Figure 1(e)). Selective gas diffusion can be achieved by controlling the gas flow channels and pores via different stacking processes. Heating the system, and application of pressure could also achieve better selectivity of the system. During the flux process, gases interact with both pores and interlayers. Thus, functional groups inserted at the pore edges or between layers can further enhance the selectivity of the system. Other effective methods are also reported to form structured pores on graphene membrane. Russo *et al*[41] successfully constructed NPG with pore radii as small as 3 Å with atomic precision using ion beam exposure. Bai *et al*[52] employed block copolymer lithography to prepare NPG with neck widths as low as 5 nm. Li *et al*[53] created GO with thickness approaching 1.8 nm, supported on porous anodic oxide (AAO). These membranes showed mixture separation selectivity (as high as 3400 and 900) for H_2/CO_2 and H_2/N_2 mixtures. Bai *et al*[52] made graphene nanomesh which could precisely control the pores size and pattern after a series processes (Figure 1 (f)).

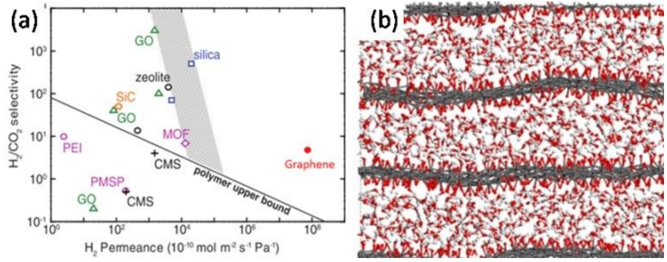

Figure 2 (a) Comparison of H_2/CO_2 separation performances of the porous graphene membranes (7.6-nm pore diameter, with 4.0% porosity) and other membranes: graphene oxide (GO)[34-53], poly(1-trimethylsilyl-1-propyne) (PMSP), polyetherimide (PEI), carbon molecular sieve (CMS) , zeolite, silica, metal-organic framework (MOF) , and SiC[54]. (b) Simulation result of CO_2 flow between GO layers.[39]

Traditional membranes such as silica, polymer, zeolite, follow the rule that selectivity is a product of diffusivity and solubility.[10] Numerical attempts have been developed to increasing those two parameters to obtain desired performance. However, this law is no longer valid for graphene and GO. For single layer graphene, the selectivity is closely affected by the porous size. The traditional concept of thickness is no longer linearly related to the diffusion speed and need to be regenerated. Although graphene is one of the strongest materials in the world, due to its unique 2D dimensional ultrathin structure, it has excellent flexibility, and high diffusion coefficient. For example, Celebi *et al*[54] deposited the pre-synthesized bi-layers graphene on a SiNx frame punctured with 49 pores each of 4 um in diameter, forming graphene with a calculated thickness of 1 nm. The H_2 separation permanence of the porous graphene membrane is much higher than membranes made of polymer, silicon or composite materials(Figure 2(a)). Defects and pore size are considered as two critical parameters which determine the selectivity. Pressures, and temperature which can control the effusion rate will also affect the permeation.[33]

Graphene and GO as membranes for water purification

Water flux and rejection of the dissolved impurities are two main aspects governing the productivity and separation performance of graphene and GO-based membranes in water purification processes. When pore diameter is larger than 0.8 nm, graphene membrane shows higher water flux than CNT membrane due to higher velocity in the centre region.[55] An interesting study indicated that graphene nanopores are able to block salt ions with 2−3 orders of magnitude greater water permeability than commercial reverse osmosis membranes.[56] However, helium-impermeable GO membrane allows the unimpeded water permeation.[57] Since unusual molecular behaviour occurs at nanometer length scales, various mechanisms of water permeation through the layer-by-layer and porous microstructure of the GO membrane are proposed by molecular dynamic(MD) simulation. Nair *et al*[57] attributed the anomalous water permeation to low friction between water monolayer and pristine graphene regions and proposed a capillary-driven flow mechanism. Based on the work of Nair *et al*, Danil *et al*[58] suggested interlayer spaces determine formation of hexagonal ice bilayer between flakes in pristine regions and melting transition of ice at the edges and are responsible for perfect water permeation and the water flux. Since monolayer graphene sheet is hydrophobic with water contact angle of 95-100 [59], Wei *et al*[60] investigated the wetting properties of GO and found that patterns of the oxidized region and the morphological corrugation of the sheet critically influences the spreading of water droplets (Figure 3(a)). Huang *et al*[61] recently developed advanced filter membrane with superior separation performance, by constructing nano strand-channelled GO ultrafiltration membranes with a narrow pore size distribution (3–5 nm). The enhanced viscous water flow through the channels was attributed to the intricate porous structure and significantly reduced channel length in the device. Wei and co-authors also attributed the enhanced water flow in graphenic membranes to the unique porous microstructures and pointed that the side-pinning effect caused by H-bonds between water molecules and oxidized regions could inhibit fast water transport in graphene channels, and enhanced water flow was prominently attributed to porous microstructures.[62] Therefore in order to improve water permeability, small size of sheets, high density of inter-edge spaces, and wide nanochannels are suggested in GO membrane fabrication.[62] The interlayer channel size can be tuned by intercalating different-sized cross-linkers.[63] Furthermore, Xu *et al*[64] quantified the nature of interlayer flow and concluded that the chemical functionalization and relaxation of nano-confinement in GO can cause the breakdown of flow enhancement. On the other hand, the effect of membrane structure and operation conditions on water flux in graphene and GO-based membranes have been explored both via simulation and experiments. By using computational methods, David *et al*[65] proposed that water flux through monolayer graphene has a linear relationship with pore area. Moreover, it was understood that, hydrophilic pores increased water permeation due to H-bond between water molecules and pore edge, and quantitatively, the hydrophilic edges on the pores contributes more to high water flux compared to pore area and sizes on graphenic membranes. As for traditional polymeric membranes, flux is inversely proportional to the thickness. However, the same argument seems invalid for GO membrane. Meng Hu *et al*[66] synthesized GO membranes with different numbers of layers and tested water separation performance and found no obvious correlation between water flux and the number of layers. Yi Han *et al*[67] via an investigation on base-refluxing induced reduced GO concluded that water flux increased linearly with pressure under 7 bar and decreased exponentially with GO loading. The above two studies showed contradictory conclusions on the relationship between GO thickness and water flux, and reiterated that there is a need to comprehensively investigate this aspect.

Rejection of ions and organic dye molecules by graphene and GO membranes is also intensively studied. The selectivity in this process is primarily attributed to size exclusion and interactions (including chemical and electrostatic ones) with functional groups. Grossman et al.[65] proposed the high performance of monolayer graphene to filter out NaCl from water via their computational investigation. Small pores, low pressure, and hydrophobic pores reject salts more efficiently due to direct size exclusion, while the larger effective volume of ions and the lack of H-bond, can lead to higher energy barrier to ionic passage. Hu *et al*[66] reported that GO membranes display significant rejection of monovalent and divalent salts and moderate or high rejection of organic dyes. Similar results are also observed in Han *et al*[67] work. The high rejection for organic dyes is ascribed to size exclusion and electrostatic interaction and the rejection of ions to Donnan's exclusion. Huang *et al*[68] investigated the effects of salt concentration, pH, and pressure on the controlled separation of small molecules through GO membranes. All these factors modulated the separation performance due to their role in changing the interlayer spacing. Specially, low pH (<6) and high pressure could result in low water flux and high rejection for organic dyes. Xu *et al*[69] demonstrated GO's selective permeation of different metal salts and reported the fast permeation of sodium salts, slow permeation of heavy-metal salts and no permeation of copper ions and organic impurities (Figure 3(b)). The simulation of the trans-membrane transport of alkali and alkaline earth cations indicated that the coordinative interactions are responsible for selectivity.[70] Joshi *et al*[71] tested the permeation characteristics of micrometer-thick GO laminates the permeation ability (Figure 3(d)). It was observed that ultrafast permeation is possible only for ions smaller than a specific size. In this work, the permeation rate was first quantified by the slope of the concentration curve(Figure 3(e)). The permeation selectivity was attributed to size exclusion and the anomalous fast transportation is due to a capillary force.

Graphene and GO can be used as other kinds of water treatment membranes as well. Sun *et al*[72] used micron-sized and nano-sized GO (Figure 3(c)) as cation exchange membranes for acid recovery from $FeCl_3$ solution. Nano-GO membrane exhibited enhanced penetration of both H^+ and Fe^{3+}. While H^+ transporting through the nano-GO membrane was two orders of magnitude greater, no Fe^{3+} transportation occurred at very low concentrations (e.g.0.01 mol L^{-1}). Huang *et al*[73] employed GO membrane to separate dimethyl carbonate/water mixture through a pervaporation process. The separation process was believed to follow a sorption-diffusion mechanism. Tang *et al*[74] also pervaporation process for dehydration of ethanol using GO thin films. The selectivity obtained from the binary-component test was much lower than the ideal value calculated from single-component feed analysis. This can be attributed to the increased ethanol flux through the thin films caused by the enlarged interlayer space due to the H-bonding between water molecules and the functional groups on GO surface.

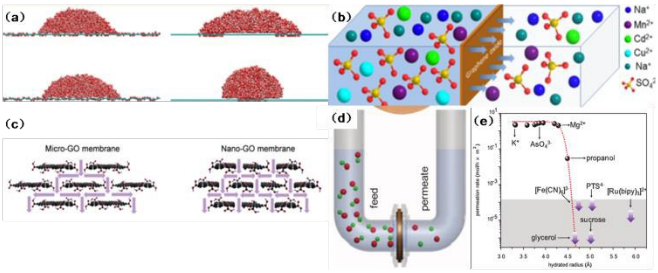

Figure 3 (a) (left)Simulation snapshots of a water droplet on wrinkled graphene with different corrugation amplitude (right)Simulation snapshots of a droplet on GO patterned with separated oxidized regions (upper) and a single oxidized region covered by the droplet(down)[60] (b) Schematic diagram of the penetration processes of different ions through GO membranes.[69] (c) Schematic diagrams of the structure of capillary networks in nano- and micro-GO membranes.[72] (d) Schematic of the experimental setup. A U-shaped tube 2.5 cm in diameter is divided by the GO membrane into two compartments referred to as feed and permeate. Each is filled to a typical level of~20 cm. Magnetic stirring is used so as to ensure no concentration gradients.[71] (e) Sieving through the atomic-scale mesh. The shown permeation rates are normalized per 1 M feed solution and measured by using 5-mm-thick membranes.[71]

Due to excellent intrinsic mechanical strength,[75] high chemical stability,[76] high antibacterial activity,[77] and exquisite antifouling properties,[47] GO membranes demonstrated significant promise for application in water purification in various studies. By adjusting the pore size and nanochannels via induction and modification of surface oxygen contained groups, GO membrane can be oriented towards a narrow pore size distribution, which is advantageous for precise sieving based on size exclusion mechanism.

Conclusions and outlook

In summary, two-dimensional monolayer graphene and its functionalized analogue GO based membranes with their ultrafast permanence, outstanding mechanical properties as well as exceptional energy-efficiency is increasingly emerging to the fore as promising candidates for precise and selective gas separation and water purification processes (Figure 4).

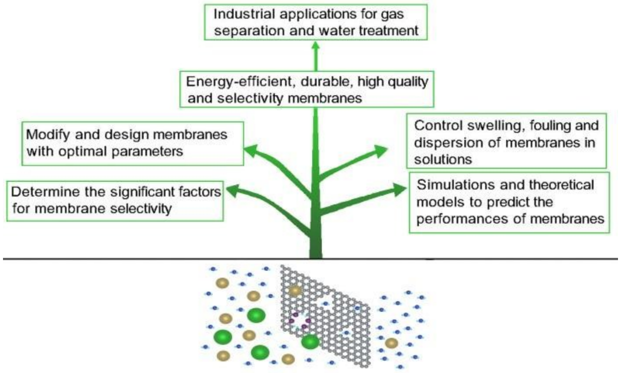

Figure 4 The outlook of the researches on graphene and GO membranes

Although graphene and GO demonstrate excellent selectivity and superior performance against multiple gas mixtures, several challenges still exist in its path to industrial application. Firstly, the grain boundary, defects, impurities, polymer, or molecular residues can block the pores on graphene or GO sheets. This will result in the dramatic reduction of the flow rate. Hence, the mixture needs to be carefully purified before entering graphene membranes systems. The humidity is also reported to affect the selectivity. In addition, for graphene or GO-based gas separation membranes, the selectivity of H_2/H_2S, CO_2/CH_4 or selectivity of three or more mixture gas is still not well characterized. Thus a comprehensive analysis of parameters that influence the process is necessary before predicting the mechanism of selectivity. These studies are expected to attract great deal of interest from the industry, especially for nature gas and shale gas industry, due to the importance of the separation process in their sustainability. Secondly, the possibility of finding a large number of inherent defects in the products hurt the chance for graphene and GO's large scale industrial application. Although single layer of graphene has a Young's modulus up to 1 TPa, local bond breaking and bond rotation at the crack tip of the graphene[50] could lead to dramatic loss of mechanical properties in products. This can render the membranes less robust and fragile, even create unexpected large pores during use, and the resultant failure of separation system. Since pore size is the most important parameter that control the performance of graphenic membrane systems, GO can selectively separate gas mixtures by its modulating its layer to layer distance and chemical groups on the surfaces and layer interfaces as well. The third challenge is the cost. Previously, the high cost of production of GO was retarding its large scale applications. However, the advent of newer technologies have decreased the cost of graphene and GO and more and more methods are being developed to fabricate defect-free, larger area, graphene with controllable pore structure/size and interlayer distance. The authors envisage that this particular field to attract increased academia and industry interest in the coming years.

As for water purification; although considerable progress has been achieved in fundamental understanding and specialized industry applications of graphene and GO based membranes, there are still several promising topics that are worth exploring. For example, the precise design of user controlled GO membranes including the pattern of oxidized regions, the interlayer space, the pore size, modification of pore chemistry, and the number of graphene layers is still not entirely successful. The lessons learned about the parameters that determine the small molecular permeation and separation performance can be transplanted to fabricate solid-state ionic devices or microfluidic devices. Likewise, detailed investigations of the effect of the interlayer space or surface defect on water flux, and whether size exclusion or interaction contributes more to the selectivity also are essential. A compromise between water flux and selectivity may be made to determine the optimal membrane fabrication parameters. In order to achieve higher water flux without sacrificing selectivity, modifying the membrane with different atoms and functional groups to adjust water affinity could be employed. In addition, the swelling of GO in aqueous solutions need to be regulated to achieve expected selectivity. Moreover, for industrial processes, the operating pressure is an important factor which needs to be considered. Operating without applying a differential pressure will be highly beneficial. Furthermore, if high purity of the product (e.g. to produce high purity of the acid from high concentration $FeCl_3$ solution) is required, pre-treatment or post-treatment will be needed, which increases energy consumption and total cost. Therefore, additional efforts are needed for minimizing the difference between theoretical and experimental results on water/ion transport mechanisms across GO nanosheets in water. There is also a need to consider and solve the contamination issue for graphene or GO based membranes. The effects of adsorption of metals and organic dyes, ionic clogging inside the capillaries, and coordination occupation on the surface of oxidized region needs further investigation and optimization. To further improve the outstanding antifouling capability of GO based membranes, it is crucial to tune the balance between the fouling rejection and flux decline. Improving the antimicrobial efficiency and mechanical strength of the freestanding membranes can be the key to the successful balancing act.

Compared to GO, graphene is simpler to design, more toxic to microbacteria,[78] more resistant to swelling in water, ionic clogging inside the capillaries and coordination occupation on the surface of oxidized region. Thus, it is more competitive compared to GO. For large scale productivity, and industrial use, novel reduction methods need to be developed. A suitable substrate is imperative to avoid dispersion in the liquid phase and to ensure water transportation. Experiments illustrated that the water flux is approximately linear to the applied pressure, and so graphene membrane cannot be used without energy input. Study also showed that even at low pressure (<100 bar), graphene still allows ultra-high water flux,[79] indicating it is a promising membrane for water desalination. David *et al*[80] examined the mechanical strength of nanoporous graphene as a reverse osmosis membrane and GO showed robustness to be suitable for reverse membranes. To further improve the productivity, it is crucial to achieving high pore density without compromising the mechanical strength.

Currently, MD simulation is used to explore the mechanism of molecular permeation, and various theories have been put forward. Experimental studies analysing the effect of pressure, pH, pore chemistry, pore area, and number of layers on water flux and the permeation selectivity of various ions and molecules. However, discrepancies exist between theory and experiment. To solve this problem, dedicated MD simulation focusing on the permeation of different ions and molecules through graphene and GO membranes should be performed to correct the existing theoretical models and bring them close with experimental results. On the other hand, further simulation and experimental studies are needed to determine whether size exclusion or interaction contributes more to the permeation selectivity of ions and molecules. This could provide insights to design next-generation membrane technology and evaluate their application potential in various fields.

Acknowledgements

We thank Science Foundation of China University of Petroleum Beijing (No. 2462014YJRC011) for the support.

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