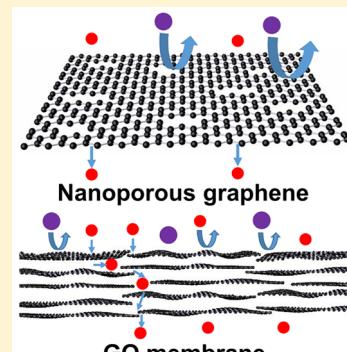


Graphene-Based Membranes for Molecular Separation

Liang Huang, Miao Zhang, Chun Li, and Gaoquan Shi*

Country Collaborative Innovation Center for Nanomaterial Science and Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

ABSTRACT: In comparison with traditional chemical separation processes, membrane separation is much simpler and more efficient. An ideal membrane for molecular separation should be as thin as possible to maximize its solvent flux, be mechanically robust to prevent it from fracture, and have well-defined pore sizes to guarantee its selectivity. Graphene is an excellent platform for developing size-selective membranes because of its atomic thickness, high mechanical strength, and chemical inertness. In this Perspective, we review the recent advancements on the fabrication of nanoporous graphene membranes and graphene oxide membranes (GOMs) for molecular separation. The methods of fabricating these membranes are summarized, and the mechanisms of molecular separation based on these two types of graphene membranes are compared. The challenges of synthesizing and transferring large-area nanoporous graphene membranes and engineering the performances of GOMs are discussed.



Membrane separation technology plays an important role in water treatment, food processing, and the chemical and pharmaceutical industries.^{1–3} So far, the majority of separation membranes are based on polymeric materials, such as cellulose, polyamide and polysulfone.^{1,4} However, polymeric membranes often show poor tolerance to high temperatures, oxidants, strong acidic/alkaline reagents, or organic solvents.^{1,2,4} Therefore, separation membranes with better thermal and chemical stability are highly desirable. Recently, graphene has been confirmed to be an excellent platform for developing size-selective molecular separation membranes because of its atomic thickness, high mechanical strength, and chemical inertness.^{5–9} Graphene composes of a single layer of carbon atoms arranged in a sp^2 -bonded aromatic structure.¹⁰ The delocalized electron clouds of π -orbitals occupy the voids of aromatic rings in a graphene sheet, thereby effectively preventing the permeation of even the smallest molecule, helium.^{11,12} Therefore, graphene was tested to be an impermeable material in its pristine state.¹² Nevertheless, protons were reported to be able to penetrate through monolayer graphene.¹³ The impermeability of graphene for molecules makes it is applicable as a barrier layer for gases and liquids,¹⁴ or to protect metallic surfaces against corrosion.¹⁵ For molecular separation, a graphene-based membrane has to be functionalized with nanopores or nanochannels through chemical or physical approaches. The typical graphene-based materials for this purpose are nanoporous graphene and graphene oxide (GO) membranes (GOMs, Figure 1).¹⁶

Nanoporous Graphene Membranes with Well-Defined Pores Are Highly Efficient for Molecular Separation Because of Their Atomic Thicknesses. Molecular dynamics (MD) simulations have predicted that monolayer graphene with subnanometer pores could act as a highly selective and permeable separation membrane with much higher efficiencies than those of state-of-the-art polymeric filtration membranes.^{7,17–20} The selective

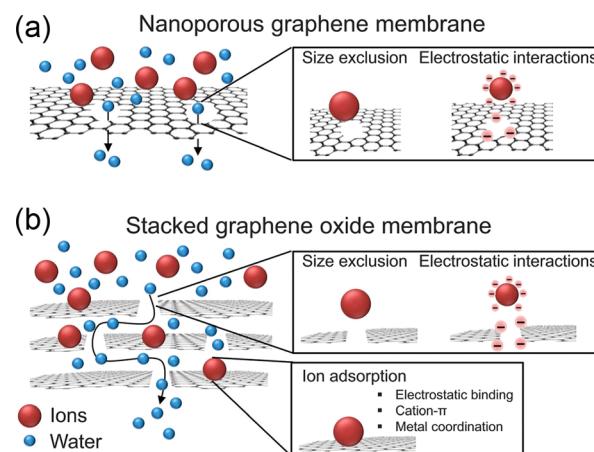


Figure 1. Schematic diagram of the two types of graphene-based membranes. (a) Nanoporous graphene membrane consists of a single layer of graphene with nanopores of defined sizes. Selectivity is achieved by size exclusion or electrostatic repulsion between charged species and the pores. (b) GOM composed of stacked GO sheets. In a GOM, the transport passages are the interlayer spaces between the sheets, the wrinkles and holes within GO sheets. Reprinted with permission from ref 16. Copyright 2015, RSC Publishing.

passage of ions through nanoporous graphene is determined by pore sizes and the electrostatic interaction between the ions and the pores.^{7,8} Accordingly, ion rejection can be tuned by functionalization of the nanopores (Figure 2a and b). Hydrophilic pores provide higher water flux but lower salt rejection than that of hydrophobic pores (Figure 2c).⁷ Theoretically, the nanoporous graphene can reject salt ions

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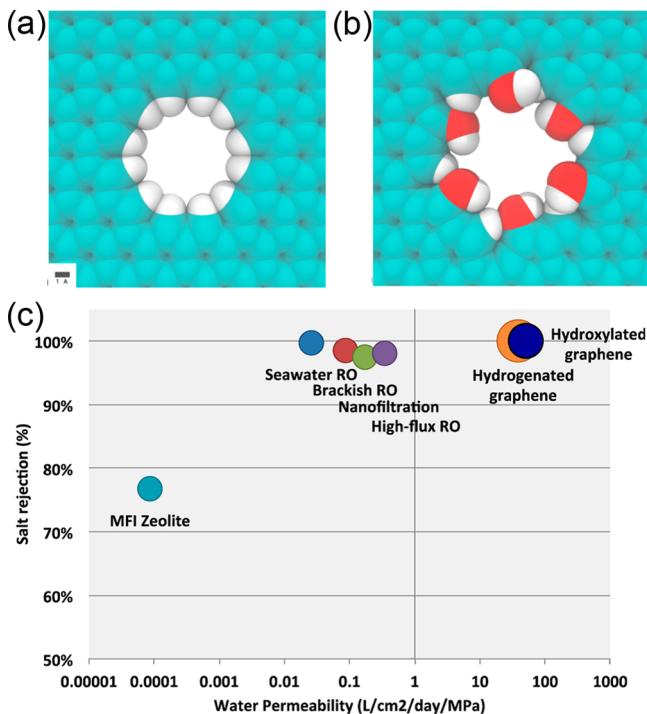


Figure 2. Functionalization of the pores in graphene with hydrogen atoms (a) or hydroxyl groups (b). (c) Performance chart for functionalized nanoporous graphene versus existing technologies. Reprinted with permission from ref 7.

with a water flux 2–3 orders of magnitude higher than those of commercially available reverse osmosis (RO) membranes (Figure 2c).

In MD simulations, nanopores with a high number density and predefined sizes can be ideally introduced into a monolayer graphene membrane. Unfortunately, precisely controlling pore sizes and achieving high pore density on a large-area graphene are technically challenging. Nevertheless, extensive efforts have been devoted to reaching this aim.^{5,6,21–24} The advantages and limitations of different perforation methods were summarized in Table 1. Focused electron beam irradiation of single layer graphene can create nanopores with controlled sizes (Figure 3a).²¹ However, this approach is inefficient and not scalable for fabricating large-area porous graphene with high pore density.

Bunch et al. created pores in graphene by ultraviolet-induced oxidative etching and demonstrated the selective gas transport through nanoporous graphene.⁵ This method is scalable but the pore size distribution is too wide to perform precise molecular sieving, and the number density of pores is also insufficiently high for practical application. O’Hern et al. used ion bombardment to introduce isolated and reactive defects on

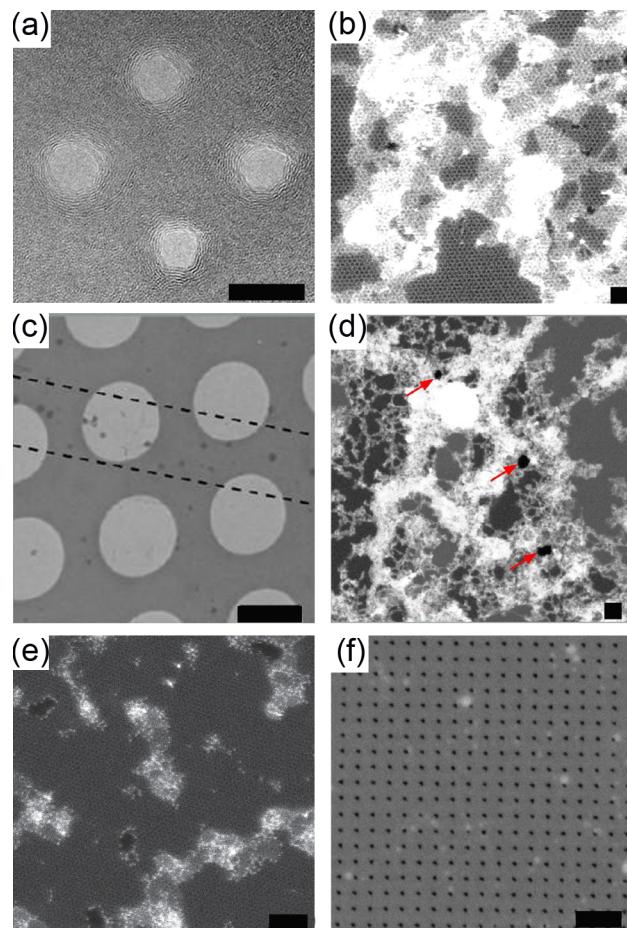


Figure 3. (a) Four adjoining nanopores made by electron beam ablation; the scale bar is 10 nm. Reprinted with permission from ref 21. Copyright 2008, American Institute of Physics. (b) Nanopores created by ion bombardment and subsequent chemical oxidative etching; the scale bar is 1 nm. Reprinted with permission from ref 6. (c) High concentration of defects exists in CVD graphene (the region between the dashed lines); the scale bar is 1 μ m. (d) Magnified view of defective area in CVD graphene (pores can be seen in the graphene lattice, as indicated by red arrows); the scale bar is 10 nm. Panels c and d reprinted with permission from ref 30. (e, f) Nanopores generated by oxygen plasma etching (e) and focused ion beam (f); the scale bars are 2 and 100 nm. Panel e reprinted with permission from ref 22. Copyright 2015, Macmillan Publishers Limited. Panel f reprinted with permission from ref 24. Copyright 2014, AAAS.

single layer graphene and further enlarged these defects to nanopores by controlled chemical oxidative etching.⁶ The resulting porous graphene possesses high-density nanopores with a size distribution less than 0.2 nm (Figure 3b). The pore

Table 1. Advantages and Limitations of Different Perforation Methods

method	pore size (nm)	advantage	limitation	reference
focused electron beam ablation	~3.5	tunable and well-defined pore size	limited to small area	21
ultraviolet-induced oxidative etching	<10	can treat large-area samples	low pore density, wide size distribution	5
ion bombardment and chemical oxidative etching	<1	can treat large-area samples, tunable pore size	moderate pore density	6
oxygen plasma etching	~1	can treat large-area samples, tunable pore size	moderate pore density	22
focused ion beam irradiation	5–100	tunable and well-defined pore size	limited to small area, pores too large for salt rejection	24

size can be tuned by controlling the etching time. The nanopores formed at short etching time can prevent the passing of anions because of the electrostatic repulsion from the negatively charged functional groups at the pore edges. At a longer etching time, the steric size exclusion effect dominated the permeability of the membrane, allowing salts to pass through, whereas larger organic molecules were blocked. This work presents the first step toward the production of large-area nanoporous graphene membranes with well-defined pore size distribution. However, in this case, the performances of nanoporous graphene membranes were severely limited by the quality of raw graphene monolayers.

This work presents the first step toward the production of large-area nanoporous graphene membranes with well-defined pore size distribution.

Fabrication of Large-Area Single-Crystal Monolayer Graphene Is Expensive, And Defect-Free Transfer of This Graphene Is a Challenge. The most commonly used technique to fabricate large-area monolayer graphene is chemical vapor deposition (CVD).^{25–28} Recently, wafer-scale single-crystal monolayer graphene has been successfully grown on single-crystal Ge surface.²⁷ However, this graphene membrane is too expensive and still too small to be practically used for molecular separation. Relatively cheap large-area graphene monolayers can be grown on copper foils; however, they typically have polycrystalline structures consisting of many single-crystal grains separated by defective boundaries.^{25,26,28} Although the single-crystal domains are impermeable, the defects and holes (ranging from 1 to 15 nm) in grain boundaries allow the transport of ions and even big organic dye molecules (Figure 3c and d).^{29,30} Surwade et al. successfully avoided accessing the grain boundaries by suspending a monolayer graphene with grain size of 50 μm over a 5 μm pore and then created

nanometer-sized pores on grain region by oxygen plasma etching (Figure 3e).²² The resulting membrane showed a nearly 100% salt rejection and a water flux up to $10^6 \text{ g m}^{-2} \text{ s}^{-1}$ at 40 °C, whereas the effective filtration area is very small ($19.6 \mu\text{m}^2$). The defects in grain boundaries can also be covered by coating one more graphene layer.^{24,31} Transferring two layers of monolayer graphene consecutively onto a porous substrate, the leakage of gases through grain boundaries was tactfully prevented.²⁴ Successively, well-defined nanopores on double-layer graphene have been generated with a focused ion beam (Figure 3f). These porous graphene membranes showed much higher permeability of gas and liquid than those of conventional polymeric membranes because of their atomic thicknesses.

Although membranes with multilayer graphene do not have the negative effects of grain boundaries, the successful transferring of CVD graphene membrane from Cu foil to the target porous substrate is extremely difficult. Wrinkles and cracks are easily induced, especially for large-area membranes.^{25,28,32,33} These wrinkles and cracks greatly degrade the performance of the resulting nanoporous graphene membrane. CVD graphene membranes can be transferred to target substrates via either dry or wet approaches.³³ The dry transfer method has been tested to be able to transfer a 30 in. graphene membrane onto a flexible substrate, but it induced many cracks, folds, and wrinkles into the membrane.²⁵ The wet transfer method is difficult to scale up because floating a graphene sheet at air–water interface may cause rippling, warping, and rolling of the membrane during transfer.²⁸ Therefore, a new method has to be developed to realize the defect-free transfer of large-area CVD graphene onto porous substrate.

GOMs Are Possibly Good Compromise Replacements of Large-Area Nanoporous Graphene Membranes. GO can be regarded as the oxidized form of graphene, having a high density of oxygen-containing functional groups and few vacancy defects distributed in the carbon lattice (Figure 4).³⁴ It can be cheaply produced in a large scale by oxidation and exfoliation of graphite.^{35,36} GO sheets are dispersible in water caused by the

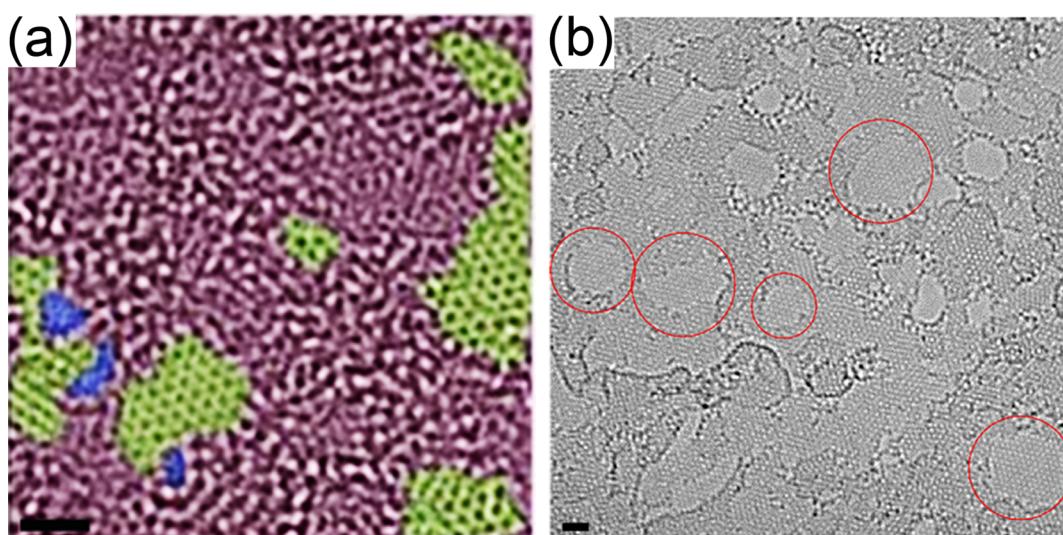


Figure 4. (a) TEM image of single-layer suspended GO sheet; holes, graphitic areas, and oxidized regions are marked in blue, yellow, and red, respectively. Reprinted with permission from ref 46. Copyright 2010, Wiley-VCH. (b) Atomically resolved TEM image of a GO sheet; patches of pristine graphene are circled, and the most area of this sheet is the oxidized domains. The scale bars are 1 nm. Reprinted with permission from ref 47. Copyright 2010, Elsevier Ltd.

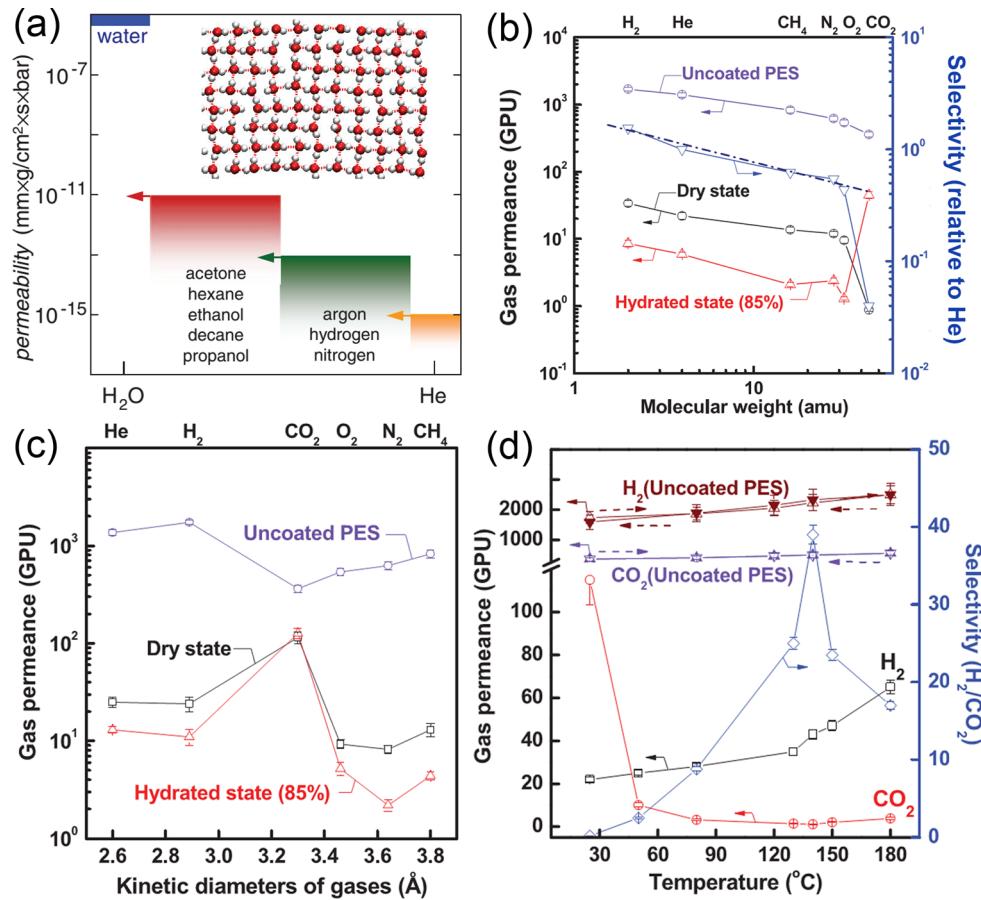


Figure 5. (a) Permeability of GOMs with respect to water and various small molecules (arrows indicate the upper limits set by the experiments). Reprinted with permission from ref 43. Copyright 2012, AAAS. (b) Gas permeances of GOMs as a function of molecular weight (method one; dashed line represents the ideal Knudsen selectivity) under dry and humidified conditions. (c) Gas permeances of GOMs as a function of kinetic diameter (method two) under dry and humidified conditions. (d) H₂ and CO₂ permeability of thermally treated GOMs (method two) as a function of temperature. Panels b, c, and d reprinted with permission from ref 51. Copyright 2013, AAAS.

electrostatic repulsion of their ionized functional groups,^{37,38} Compared with nanoporous graphene membranes, fabricating membranes from GO dispersions is much cheaper and more scalable. Vacuum filtration,³⁹ layer-by-layer deposition,^{40,41} and drop-casting³⁸ have been used to prepare layered GOMs with arbitrary thicknesses. The two-dimensional (2D) nanochannels between adjacent GO layers can be used as 2D passages for molecules smaller than the thicknesses of the channels while blocking the larger species. As the first attempt, Li et al. found that the nanochannels within chemically reduced GO (rGO) membranes could be tuned by hydrothermal treatment to allow the transport of water and small nanoparticles.⁴²

Geim et al. reported the unimpeded evaporation of water through submicrometer-thick GOMs, whereas these membranes were completely impermeable to liquids, vapors, and gases including helium (Figure 5a).⁴³ They explained this phenomenon as follows. A GO sheet composes of two types of regions: oxidized and pristine graphitic regions. The oxidized regions act as spacers to keep adjacent GO sheets apart and help water molecules to intercalate between GO sheets. The pristine graphitic regions in GO sheets formed a network of capillaries that allow nearly frictionless flow of a water monolayer, similar to the case of water transport through carbon nanotubes.⁴⁴ However, GO is known as an insulator.⁴⁵ Thus, the pristine graphitic regions are unlikely to form a

continuous network across a GO sheet. On the other hand, ultrahigh-resolution transmission electron microscopy (TEM) studies indicated that an as-synthesized GO sheet consisted of three types of regions: holes, pristine graphitic, and oxidized regions with areal percentages of approximately 2%, 16%, and 82%, respectively.^{46,47} The oxidized regions form a continuous network across a GO sheet with pristine graphitic regions as isolated islands (Figure 4). The isolated pristine graphitic regions were also confirmed by Raman spectroscopic studies.⁴⁸ Recently, Wei et al. explored water transport in GO membrane using atomistic simulations by considering water transport through the interlayer spaces, wrinkles, and pores within GO sheets.^{49,50} They concluded that the fast water transport through pristine graphene channels could be prohibited by a prominent side-pinning effect from capillaries formed within oxidized regions and attributed the efficient water vapor permeation to the porous microstructures of GOM.

It should be noted here that the GOMs prepared by Geim et al. were relatively thick (about 1 μ m).⁴³ Recently, Li et al. fabricated ultrathin GOMs with thickness as thin as 1.8 nm via a facile filtration process.⁹ These membranes showed much higher permeability to gases than those of thick GOMs.^{9,43} More interestingly, their separation selectivity for H₂/CO₂ or H₂/N₂ mixture was tested to be extraordinary high.⁹ The gas permeance of a GOM did not show obvious change after annealing in H₂ or under vacuum at 220 °C; thus, they

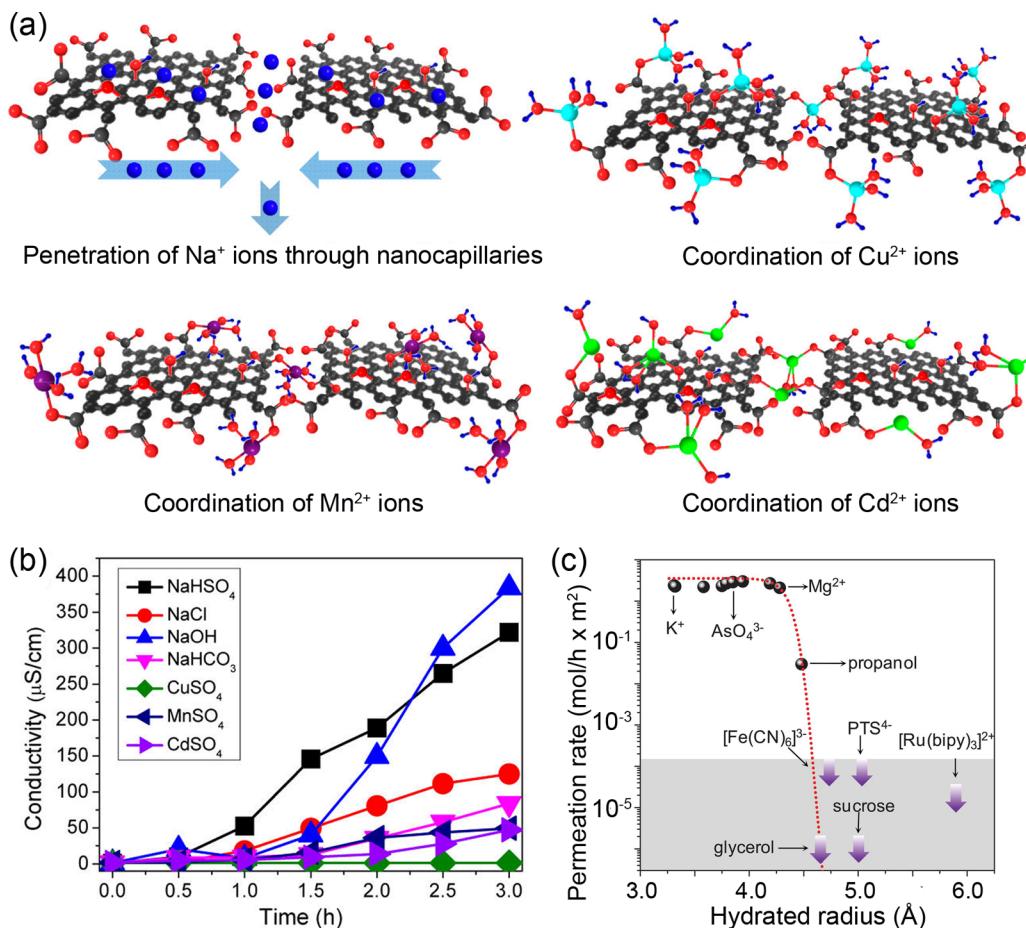


Figure 6. (a) Interaction of GO sheets with different ions. (b) Penetration processes of different ionic compounds through GOMs. Panels a and b reprinted with permission from ref 53. (c) Permeation rates of different species through GOMs. Reprinted with permission from ref 55. Copyright 2014, AAAS.

concluded that the interlayer spacings between GO sheets were not the main transport pathways and attributed the permeation of gases to the structural defects within GO sheets.

The gas permeability tests described in the last paragraph were conducted without applying a transmembrane pressure (TMP). Kim et al. found that the application of a TMP could enhance the permeability of GOMs to gases, because a TMP is able to overcome the energy barriers of molecules entering and diffusing within nanochannels.⁵¹ Gases could permeate through even thick GOMs at elevated TMPs.⁵¹ Furthermore, they used two methods to prepare very thin GOMs (3 to 10 nm) on microporous polymeric membranes (poly(ether sulfone), PES): (1) Contacting the surface of a supporting membrane to the air/liquid interface of a GO solution and then spin-coating to form a relatively heterogeneous GO coating. (2) Direct spin-casting a GO solution on the surface of a supporting membrane to generate a more compact and uniform GOM. Both of the GOMs showed high gas permeances at a TMP of 1 bar (Figure 5b and c). The thin GOMs prepared by method 1 showed typical gas permeation behavior following Knudsen transport of gases in nanoporous membranes (Figure 5b). Gas permeation occurred through nanopores created by the edges of noninterlocked GO sheets. However, the thin GOMs prepared by method 2 were less permeable but more selective than those prepared by method 1, indicating they behaved more like molecular sieving membranes (Figure 5c). In this case, gases diffused selectively

between the GO interlayers. These results imply that the molecular separation performance of a GOM also depends on the stacking mode of GO sheets. In general, all gas permeances decreased as the humidity in the feed increased (Figure 5b and c) because condensed water molecules in the pores or between GO layers hindered the transport of noncondensable small gas molecules. In addition, more permeable and selective GOMs can be prepared by creating pores on the basal plane via thermal reduction. Above 130 °C, H₂ permeance increased distinctly and CO₂ permeance increased slightly, resulting a high H₂/CO₂ selectivity (Figure 5d).

The permeability of GOMs to ions and molecules has been studied in aqueous media. Huang et al. first observed the surface-charge-governed ion transport through nanochannels between GO sheets under a bias voltage.⁵² Later, Zhu et al. demonstrated the selective ion penetration and water purification properties of GOMs using a homemade diffusion cell.⁵³ Sodium salts permeated through GOMs quickly, whereas heavy-metal salts infiltrated much more slowly (Figure 6a and b). More interestingly, copper salts and organic dye molecules were entirely blocked. They believed that the nanochannels between GO sheets are responsible for the permeation of metal ions, whereas the coordination interaction between heavy-metal ions and GOMs restricted the diffusion of these ions (Figure 6a). In another paper, they extended the selectivity of GOMs to alkali and alkaline earth cations.⁵⁴ In this case, the metal ions do not have d or f electrons, and the typical coordination

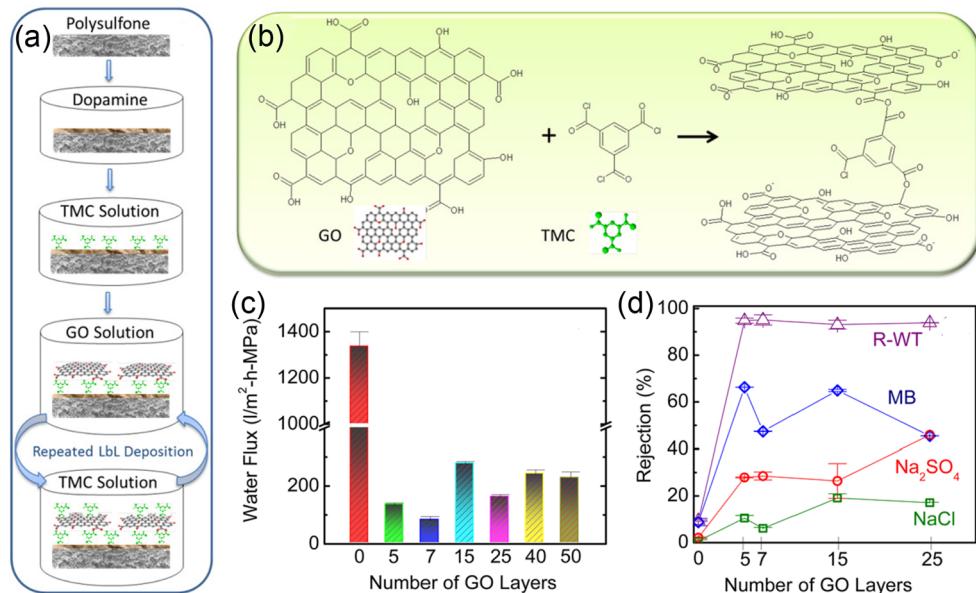


Figure 7. (a) Schematic illustration of a step-by-step procedure to synthesize the GOM. (b) Mechanism of reactions between GO and TMC. (c) Water flux with different numbers of GO layers. (d) Rejection of salts and organic dyes with different numbers of GO layers. Reprinted with permission from ref 41.

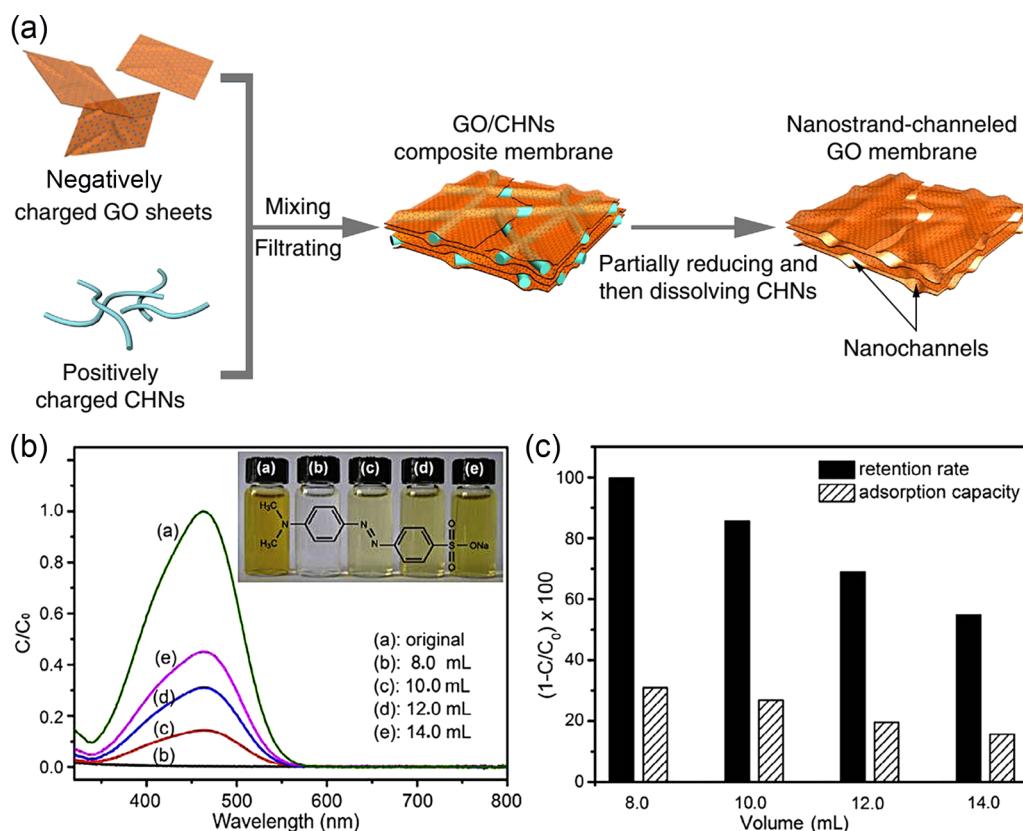


Figure 8. (a) Illustration of the fabrication process of an NSC-GO membrane. Reprinted with permission from ref 61. Copyright 2013, Macmillan Publishers Limited. (b) UV-vis absorption spectra and photographs of the filtrates obtained by the filtration of different volumes of methyl orange (10 ppm) solutions over GO-TiO₂ films. (c) Retention rates and adsorption capacities using different volumes of methyl orange dye solutions. Panel b and c reprinted with permission from ref 63. Copyright 2013, Elsevier Ltd.

interactions are absent.⁵⁴ The permeance difference between alkali and alkaline earth cations was explained by the difference in their ion- π interactions with the sp² clusters on GO sheets. The molecular sieving performance of GOMs in aqueous solutions has also been studied in a similar way by Geim et al.⁵⁵

GOMs acted as molecular sieves, blocking all solutes with hydrated radii larger than 0.45 nm (Figure 6c). According to their elucidation, the effective thickness of each GO sheet was 0.34 nm and GOMs soaked in water had an interlayer space of approximately 1.3 nm, yielding a pore size of about 0.9 nm.

Surprisingly, it was found that solute species with hydrated radii <0.45 nm could permeate through GOMs with approximately the same speeds, without notable dependence on their sizes and charges. For example, AsO_4^{3-} ions showed a permeation rate close to those of K^+ and Mg^{2+} ions (Figure 6c). This is incredible and inconsistent with the observation of Zhu et al.^{53,54} According to the hindered diffusion theory, the permeation rate of a solute through a pore with comparable size should relate to the solute size and the interaction between the solute and the pore wall.⁵⁶ In addition, the GOMs prepared by Geim et al. were contaminated by Al^{3+} ions, which were released from the Anodisc alumina membranes used for filtrating GO dispersions.^{55,57} These interlayer contaminants possibly induced the abnormal phenomena observed by Geim et al., though the actual reason is still unclear.

For Practical Applications in Water Separation, GOMs Must Be Stabilized by Reduction or Chemical Cross-Linking. The instability of GOMs in water is the major issue for using them in aqueous media as separation membranes because they will disintegrate over time.⁵⁷ Although many papers have reported that GOMs could be used for molecular separation or sieving in water,^{43,53,54} stabilizing GOMs is necessary to make them have practical importance. Two methods have been developed to stabilize GOMs in water: reducing and chemical cross-linking. Reducing GOMs can improve their stability in water by enhancing the $\pi-\pi$ interactions between GO sheets. GOMs can be reduced by thermal annealing or with reducing agents. Choosing a proper reduction method is crucial to maintain the high water permeation property of GOMs. For example, Geim et al. reduced a GO membrane by annealing it at $250\text{ }^\circ\text{C}$ in a hydrogen–argon atmosphere and found it became 100 times less permeable to water.⁴³ In contrast, the high water permeation of GOMs were still partially kept when reducing them with base-refluxing⁵⁸ or HI vapor.⁵⁹ On the other hand, the hydroxyl and epoxy groups on the basal plane of GO sheets can be used to covalently cross-link adjacent sheets, thus stabilizing GOMs. Mi et al. fabricated GOMs cross-linked by 1,3,5-benzenetricarbonyl trichloride via layer-by-layer deposition (Figure 7a and b).⁴¹ Cross-linking not only provided GOMs with a good stability in water, but also tuned the charges, functionality, and sizes of GO nanochannels. These cross-linked GOMs showed relatively low rejection for monovalent and divalent salts (6–46%); however, they exhibited high water fluxes ranging from 80 to $276\text{ L m}^{-2}\text{ h}^{-1}\text{ MPa}^{-1}$ (Figure 7c and d), 4–10 times higher than those of most commercial nanofiltration membranes.

Nanochannel Sizes of GOMs Can Be Engineered by Intercalating Nanoparticles or Nanowires between GO Sheets. Separation membranes with tunable pore sizes are highly expected.⁴ Although cross-linking GO sheets with molecules of different sizes can finely tune the nanochannels, the adjustable range is relatively limited (<several nanometers).^{41,60} In contrast, nanoparticles or nanowires with various sizes can be easily synthesized, and intercalating them between GO sheets is a more straightforward technique to modulate the nanochannel sizes of GOMs. For this purpose, copper hydroxide nanostrands (CHNs) channeled GOMs were prepared by mixing negatively charged GO sheets with positively charged CHNs and filtrating their mixed dispersion (Figure 8a).⁶¹ CHNs adsorbed tightly onto GO sheets via electrostatic interaction and a network of nanochannels is formed after removing CHNs with an ethylene diamine tetraacetic acid (EDTA) solution. Compared with pristine GOMs, the water flux of treated

GOMs increased 10-fold without sacrificing the rejection rate. Wang et al. also fabricated GOMs with tunable permeability by embedding carbon dots (CDs).⁶² The structural similarity between GO and CDs makes them compatible with each other to form uniform composites. The interlayer space between GO sheets can be controlled by the size of CDs, thus tuning the selectivity and permeability of GOMs. A GO-TiO₂ composite film has also been prepared and its rejection rate for dye molecules varied with the volume of filtrated dye solutions (Figure 8b).⁶³ This is mainly due to the fact that the GO-TiO₂ composite film can adsorb a considerable amount of dye molecules (Figure 8c). This observation is quite instructive because graphene-based materials were reported to have high capacities of adsorbing dye molecules. Therefore, when testing the rejection rate of dye molecules through graphene-based membranes, it is very important to exclude the contributions of physical adsorption.

To date, however, the selectivity of GOMs has been mostly limited to relatively large organic molecules or hydrated ions, rendering such membranes only comparable to ultrafiltration or nanofiltration membranes. Controlling the channel sizes in the subnanometer range to obtain high salt rejections remains highly challenging.¹⁶ On the other hand, the direction of permeation is perpendicular to the nanochannels of a GOM; thus, there will be a trade-off between its thickness (or mechanical stability) and separation performance. The reduction of film thickness facilitates to improve the separation performance of GOM while decreasing its mechanical stability. In addition, GO sheets are thermally unstable, undergoing dramatic structural change at elevated temperatures.⁶⁴ Therefore, the long-term stability of GOMs is a crucial issue for their practical applications.

Good Stability of GOMs in Various Organic Solvents Makes Them Promising for Molecular Separation in Organic Solvents. Although GOMs are unstable in aqueous media, we recently found that they exhibited excellent stability in most organic solvents.⁶⁵ Furthermore, the nanochannels between adjacent GO layers can be narrowed by thermal annealing or widened by solvating with different solvents. Thus, the semipermeability of GOMs is tunable for molecular separation in organic solvents. Solute molecules with sizes larger than the nanochannels of GOMs can be entirely blocked. However, the solute molecules smaller than the nanochannels encounter hindered diffusion; their permeation rates depend not only on their sizes but also on their interactions with GOMs. Lately, a GO hollow fiber membrane was prepared by depositing GO sheets on a ceramic hollow fiber and it could reject molecules larger than 300 Da in acetone and methanol, though its solvent flux was relatively low.⁶⁶ So far, organic solvent nanofiltration (OSN) membranes are mostly based on polymeric materials and one kind of OSN membrane is operable only in few specific solvents.² The stability of GOM in a wide range of organic solvents will certainly make it attractive in OSN, especially when considering the tunability of the solvent flux and molecular weight cutoff by intercalating appropriate sized nanoparticles.

Conclusions and Outlook. Graphene-based materials can be applied for membrane separation in two ways: drilling holes in single or few-layer graphene membranes and fabricating GOMs with layered structures. Both theoretical and experimental studies have demonstrated that nanoporous graphene membranes are highly efficient for molecular separation, mainly due to their atomic thicknesses. But the fabrication of large-area single-crystal graphene monolayer is very expensive. Further-

more, the defect-free transfer of large-area CVD graphene and generating high density pores with precisely controlled sizes are still technically challenging. Before these problems are cheaply and properly addressed, GOMs are a good compromise choice. GOMs can be cheaply fabricated at large scale and the nanochannels between GO sheets can act as a precise molecular sieve by blocking all the species with larger sizes. The rich oxygen-containing functional groups endow GO sheets with good dispersibility and processability in water but also make GOMs unstable in aqueous media. Therefore, GOMs without modification are not suitable for water separation. Fortunately, controlled reduction or chemical cross-linking enable the application of GOMs for water separation. More importantly, the sizes of GO nanochannels can be engineered by intercalating nanoparticles or nanowires between GO sheets, thereby tuning the selectivity and permeability of GOMs. Finally, the good stability of GOMs in various organic solvents makes them promising for molecular separation in organic solvents.

Nanoporous graphene membranes showed excellent separation performances; unfortunately, their durability and scalability seem to be intractable challenges.

Although graphene-based membranes have showed potential in molecular separation, there are several unaddressed intrinsic problems in this field. Nanoporous graphene membranes showed excellent separation performances; unfortunately, their durability and scalability seem to be intractable challenges. GOMs are scalable and relatively cheap, but their water fluxes are greatly restricted by the tortuosity of nanochannels. A thinner GOM possesses smaller channel tortuosity, providing a higher water flux; however, its mechanical stability will also be reduced. In addition, the long-term stability of GOMs is unsatisfactory for practical applications because of the unstable chemical structures of GO sheets. Last but not least, the intrinsically complex microstructures of GOMs make some claims given by different groups inconsistent with each other, and it is also difficult to provide reliable explanations for reported abnormal phenomena.

AUTHOR INFORMATION

Corresponding Author

*E-mail: gshi@tsinghua.edu.cn.

Notes

The authors declare no competing financial interest.

Biographies

Liang Huang is a Ph.D. student at Tsinghua University. He joined Professor Shi's group in 2011. His current research interests are the fabrication of graphene-based membranes and their applications.

Miao Zhang is a Ph.D. candidate at Tsinghua University, mentored by Professor Chun Li. His current research interests are the fabrication of graphene-based membranes with high strength and toughness.

Chun Li received his Ph.D. in 1998 from Nanjing University under the supervision of Prof. Yingqiu Liang. He then joined Nanjing University as a lecturer. From 2001 to 2003, he was a postdoctoral fellow with Prof. Toyoko Imae at Nagoya University. In 2003, he moved to

Kyushu University as a postdoctoral research associate with Prof. Seiji Shinkai for two years. Now, he is an associate professor in Tsinghua University. His research interests focus on conjugated polymers and graphene. http://www.chem.tsinghua.edu.cn/publish/chemen/2141/2011/20110403140528221722408/20110403140528221722408_.html

Gaoquan Shi received his B.S. degree (1985) and Ph.D. degree (1992) at the Department of Chemistry, Nanjing University. Then he joined Nanjing University and was promoted to full professor in 1995. In 2000, he moved to Tsinghua University as a Professor of Chemistry. His research interests are focused on synthesis and applications of graphene materials and conducting polymers. He received the Second Grade Award of Natural Science of China and the Youth Knowledge Innovation Prize of the Chinese Chemical Society and BASF Company in 2004, and the First Grade Award of Natural Science of Chinese Education Ministry in 2013. http://www.chem.tsinghua.edu.cn/publish/chemen/2141/2011/20110404224112834413063/20110404224112834413063_.html

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