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News & Views

Two-dimensional graphitic carbon nitride based membranes for separation

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Energy crisis, resulting from growing population and emerging progress in modern society, has received global concern over the past decades. Among these, feasible ways that can well address task-specified issues, such as available fresh water, are highly desired. In this regard, separation membranes consisting of two-dimensional (2D) materials with abundant nano-pores, show great potential for water purification and seawater desalination, by virtue of their low transport resistance, high permeability and tailorable interlayer spacing (*d*). Recently, we reported graphitic carbon nitride (GCN) based 2D membrane for selective permeation at sub-nanometer scale [1]. The chemically inert GCN was functionalized via synergetic effect of protonation and anion intercalation using sulfuric acid (SA). The decorated GCN-SA membrane exhibits amphiphilicity and thus high permeability for water and organic solvents, showing application potential of separation membranes in both aqueous and organic solutions. More importantly, sulfate anion intercalation resulted in enlarged *d* value by 10.8 Å, which allowed selective permeation of a diverse class of solutes with varied hydrated radii, thus realizing ionic/molecular sieving with high accuracy. Further functionalization with chiral organic acid (camphorsulfonic acid, CSA) simultaneously tailored the *d* value and interlayer chemical environment by creating chiral sites in-between the protonated GCN layers. The GCN-CSA membrane shows high enantiomeric excess (*ee*) for various racemates, 89% towards limonene racemate, for example.

It is well acknowledged that 2D graphene oxide (GO) are featured with easy-to-make process, nanoporous structure and tunable physiochemical properties. GO based membranes are outstanding examples to realize ultrafast solute separation from aqueous solution (Fig. 1a), showing great promise in water treatment technologies [2,3]. More recently, Quan Yuan's group [4] in Wuhan University has greatly promoted the mechanical strength of large-area graphene nanomesh/carbon-nanotube hybrid membranes, resulting from the strong π-π interaction between two components (Fig. 1b). The high water permeability and precise size selectivity endowed centimeter-scale GO based membrane with a step closer to practical applications. The randomly distributed oxygen-containing groups on GO, however, weaken the stability when GO membranes are exposed to ambient atmosphere with fluctuated humidity (Fig. 1c). The *d* value of GO changes accordingly, which fails to guarantee reliable ionic and molecular sieving. On the other hand, extensive efforts have been devoted towards the sieving performance of GO in aqueous solution, with less attention on the potential use in organic solutions, which is of great importance for practical biomedicine applications.

Distinguishing from GO with randomly distributed oxygen-containing groups, GCN with uniformly distributed nitrogen atoms, on which the long-pair electron can be protonated, facilitates its dissolution in strong acid (SA). We found that the protonated GCN layers separated by intercalated anions form stable sandwich structure via electrostatic interaction (Fig. 2a and b). Using vacuum filtration method, GCN-SA membranes with adjustable thickness can be obtained. Note that SA functionalized GCN renders the membrane improved hydrophilicity, which also allowed permeation of organic solvents with high permeability, demonstrating its amphipathicity and extending the potential use in organic solutions. More importantly, sulfate intercalation effectively enlarged the *d* value by 10.8 Å (increased from 3.26 to 14.06 Å), which kept unchanged with varied humidity and temperature. Using an isobaric U-shaped device (Fig. 2c), the sieving performance of GCN-SA membrane was evaluated towards a series of solutes with different sizes and charges. It was found that the solutes with hydrated radii smaller than 5.4 Å (hydrated diameter: 10.8 Å) can permeate through the membrane with different rates, while larger solutes were blocked (Fig. 2d). The overall results demonstrated the precise sieving effect of Brønsted-acid-functionalized GCN, which is anticipated to offer new avenue to realize water purification technology using this functionalized 2D membrane [1].

On the other hand, chiral membranes for enantioselective separation featuring low energy consumption, high capacity and continuous operation, is of great importance in pharmacy and biomedical industries. To achieve highly efficient separation of enantiomers, the key issue lies in the precise control of pore size, structure and chiral sites. Crystalline nanoporous materials with unambiguous crystal structure and pore size distribution, such as metal–organic framework (MOF), covalent organic framework (COF), are promising candidates. Although the chiral sites and pore sizes can be precisely controlled, while the membrane-formation ability is always challenging due in large part to the cracks among

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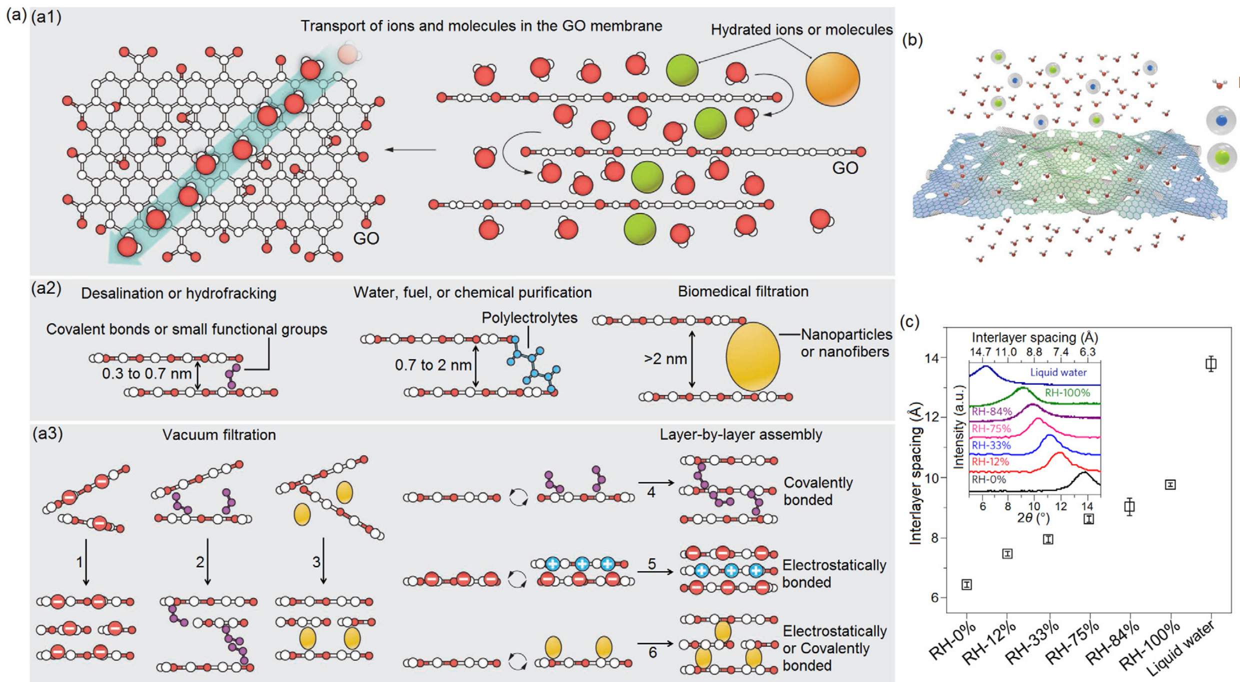

Fig. 1. (Color online) GO membranes for tunable sieving. (a) Water and ions/molecules with small sizes permeate through GO membrane, while larger species are blocked (a1); Control of *d* value of GO membrane for separation of different species (a2); Available strategies for GO membrane synthesis (a3). Reproduced with permission from Ref. [3]. Copyright 2014 The American Association for the Advancement of Science. (b) Schematic illustration of the graphene nanomesh/single-wall carbon nanotube (SWCNT) hybrid membrane for precise sieving. Reproduced with permission from Ref. [4]. Copyright 2019 The American Association for the Advancement of Science. (c) Varied *d* values of GO membranes with changing humidity, as evidenced by XRD patterns (inset). Reproduced with permission from Ref. [5]. Copyright 2017 Nature Publishing Group.

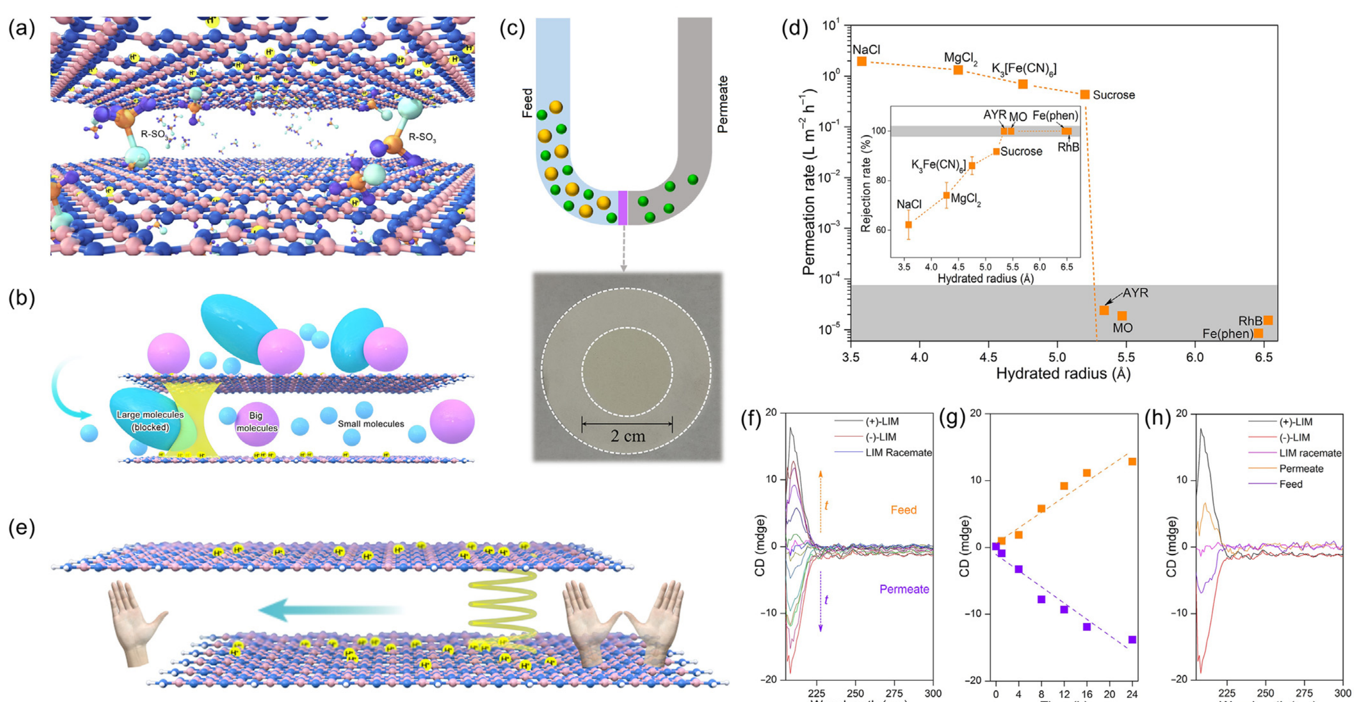

Fig. 2. (Color online) GCN-based membranes for ionic/molecular sieving and enantioselective permeation at sub-nanometer scale. (a, b) Structure model of GCN functionalization. (a) Control of *d* value of protonated GCN with different anions. R-SO_3 denotes the anion of Brønsted acid or chiral organic acid. (b) Solutes with different sizes that transport through GCN-SA membrane. The yellow spring represents the newly created interlayer space. (c) U-shaped isobaric device for permeation test and the digital image of membrane on substrate. (d) Permeation rates of varied solutes as a function of their hydrated radii, using 700 nm-thick GCN-SA membrane. Inset: rejection rates of these solutes (Fe(phen): $[Fe(phen)_3]Cl_2$, AYR: alizarine yellow R, MO: methyl orange, RhB: rhodamine B). (e) Structure model of chiral GCN-CSA membrane for enantioselective permeation. The yellow spiral represents the created chiral site. Under isobaric condition, the variation of CD spectra (f) and signal intensity (g) with prolonging permeation time, using LIM racemate that permeates through 600-nm thick GCN-CSA membrane. (h) CD spectra changes with permeation time when the setup was applied with pressure (LIM: limonene).

micro-sized grains. Alternative methods using chiral macromolecule-based membranes can address this concern, while the wide distribution of pore size fails to realize chiral resolution with high efficiency. 2D materials based chiral membranes can avoid the conflict between pore size control and membrane-formation ability. Being similar with the functionalization strategy adopted in GCN-SA membranes, the use of chiral organic acid (CSA) was found to simultaneously tailor the *d* value and chemical environment in-between GCN layers, forming stable GCN-CSA membrane with successfully intercalated chiral sites (Fig. 2e). As a consequence, the GCN-CSA membrane displayed a molecular weight cutoff around 150 over a series of enantiomers in different solvents, ranging from nonpolar to polar ones. Among these, high enantioselective permeation of limonene and glutamic acid was achieved. Further permeation of limonene racemate over GCN-CSA membrane using the isobaric setup renders a high *ee* value of 89% within 24 h (Fig. 2f and g). Applying pressure for the permeation resulted in significantly shortened enantioselective permeation time (within 3 min), despite of the decreased *ee* value to 75% (Fig. 2h). The chiral decoration strategy extends the potential application range of 2D materials in biomedical fields, such as the separation of drug molecules with high added value [1].

Since the pioneering work by Wang et al. [6] in 2009, GCN-based materials have received considerable attention in terms of photocatalytic H_2 evolution, CO_2 photo-reduction, photo-degradation of pollutants [7], etc. Beyond that, recent advances in GCN-based membranes will further advance the development of highly efficient separation membranes, which are promising candidates for producing fresh water and realizing efficient chiral resolution. Using different intercalators to continuously tailor the *d* value and chemical environment in-between GCN layers, remains challenging yet desirable. These proposals, together with the suitable scaling-up methods for centimeter membrane fabrication, hold great promise for extending the application range of 2D based materials by taking full advantage of the tailorable sub-nanometer-sized interlayer space.

Conflict of interest

The authors declare that they have no conflict of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scib.2019.07.023.

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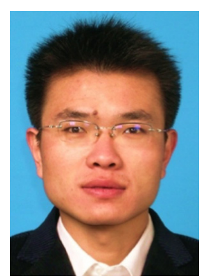

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