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Review

Graphene-based membranes for molecular and ionic separations in aqueous environments☆

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ABSTRACT

Graphene-based laminar materials open up to new applications for molecular and ionic separations in aqueous environments due to the atomic thickness, mechanical strength, chemical stability and other fantastic properties. Recent advances on controlling the structure and chemical functionality of graphene-based membranes can potentially lead to new classes of tools for desalination, dehydration, toxicant rejection, specific ionic separation and so on. The recent developments of graphene-based membranes prepared by using a concept to form interlayer space between graphene sheets and creating nanoscale or sub-nanoscale pores in a graphene lattice, together with their mass-transfer mechanisms and potential applications in aqueous environments are reviewed. A summary and outlook is further provided on the opportunities and challenges in this arising field. This article is expected to address the intricate details of mass transport through two distinct graphene-based membranes in aqueous environment and to optimize the fabrication of graphene-based membranes as a fascinating separation system for a wide range of applications.

1. Introduction

In recent decades, membrane technologies show great importance for global sustainable development in myriad fields such as solving resource shortage and environmental pollution [1–3]. Particularly, to improve the decontamination of water, as well as to increase water supplies through the safe re-use of wastewater and efficient desalination of sea and brackish water, membranes and membrane technologies are playing paramount roles [4], because separations based on membranes show fantastic features including no phase change, no additives and low energy consumption in comparison to conventional separation methods [1]. However, most of currently commercial membranes are subject to a trade-off between productivity (*i.e.,* permeability) and efficiency (*i.e.,* selectivity), known as the Robeson's upper bound [2,5]. To address this dilemma, state-of-the-art membrane materials are developed with fantastic ability to distinguish molecules based on size and shape by thickness-reduction approach to maximize their permeability [6,7].

Graphene is a single atomic plane of graphite [8], which presents excellent mechanical strength, high electrical conductivity, superior thermal conductivity and other fantastic properties because of its sp^2 hybridized C atoms arranging in a honeycomb lattice. Rationally, the single-atom-thick graphene is considerable for acting as membrane barrier, but it is confirmed being impermeable to atoms, molecules and ions such as helium [9]. Fortunately, as the derivative of graphene, graphene oxide (GO) contains pristine regions, oxidized regions, and a small fraction of holes, and has drawn great attention for assembling separation membranes with fantastic separation capabilities due to the distinctive transfer channels [10–16]. The passages of the graphene-based membranes for mass transfer are generally built by two approaches. One is stacking the graphene-based sheets to form interlayer spaces, which could connect and form networks of nanocapillaries between the stacked sheets, providing passages for mass transfer. Molecules and ions could diffuse in the direction parallel in the interlayer space from the edge of the stacked sheets. The water molecules can exhibit "hyperlubricity" in the well-defined channels of the graphene-based membranes, similar to the water-permeation mechanism as previously described for small-diameter carbon nanotubes and hydrophobic nanopores [17]. The other one is creating defects on the basal plane of the graphene sheets by ion and electron irradiation [18–21] or chemical routes [10,22–24]. The intrinsic defects in graphene form nanopores, which exhibit selective ionic and water transport due to ion hydration and steric effects that are sensitive to the pore size and functional groups lining the pore, analogous to biological ion channels [25–28]. Conceivably, graphene-based membranes have a great deal to offer over existing technologies for desalination, ionic or

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organic molecular separation in the aqueous environments due to their well-defined channels with an assistance of oxygen-containing groups.

In this review, we will highlight the recent developments of graphene-based membranes for molecular and ionic separations in aqueous environments. The mass-transfer mechanisms of graphene-based membranes in the aqueous solutions and the potential applications for desalination, organic molecular rejection and specific ionic separation are discussed. The discussion is divided into three parts. It is started with the introduction of stacked graphene-based membranes for molecular and ionic sieving and separation. Then, one-atom-thick graphene-based membranes for ionic and molecular separations are introduced. Lastly, an outlook is provided to describe the future challenges in the development and industrial use of graphene-based membranes.

2. Stacked Graphene-based Membranes for Molecular and Ionic Separation and Sieving

2.1. The fabrication approaches and mass-transfer mechanisms

In general, to achieve the stacked structure, the graphene-based membranes could be fabricated by three approaches. One is making the stacked graphene-based membranes by filtration of the graphene sheets through membrane filters. The stacked membranes can be dried in air or vacuum environments, and peeled from the filters [29,30]. This filtration method is not only simple and highly reproducible but also allows precise control over the thickness of stacked membranes. Another method to produce the stacked structure is by spray- or spin-coating of graphene-based sheets suspensions in water due to the intrinsic repulsive edge-to-edge GO sheet interactions and face-to-face attractive capillary forces created by the spin-operation [31]. Furthermore, large-area stacked membranes could be prepared using a gravure printing machine with high concentration of graphene-based sheets (*e.g.*, about 20–60 $mg \cdot ml^{-1}$ of GO sheets), which demonstrates a continuous approach for membrane production [32].

The stacked inter-layer spacing has been proven to play a significant role in molecular transport. The stacked sheets are usually GO or chemically converted/reduced graphene. For the GO sheets, the pristine region has the similar structure as graphene, while the oxidized region has plentiful of oxygen-containing functional groups such as hydroxyl, epoxy and carboxyl groups [33]. When a membrane is stacked with GO [Fig. 1(a)], the oxidized groups that tend to cluster and leave large, percolating pristine regions support interlayer spaces considering as nanocapillaries of *ca.* 0.6–0.7 nm under dry conditions [34–36]. The oxidized groups could strongly hydrate with water molecules. Accordingly, when the GO membranes are immersed in aquous solution or high humidity environment, the intercalating water molecules prop up a large interlayer space to 1.2–1.3 nm, which has been confirmed by X-ray diffraction (XRD) or neutron scattering [36,37]. Considering the GO sheets with a thickness of 0.34 nm, the interlayer space can be considered an empty space of highth of 0.8–1.0 nm [36]. Water molecules with ~0.3 nm in size can accommodate to form a monolayer or multilayer between pristine-graphene sheets due to the increased space (>0.6 nm) [Fig. 1(b)], which are expected to be highly mobile [36,38]. While due to hydrogen bonding and a narrower space available for diffusion, water is expected to be less mobile within the oxidized regions, which are unlikely to contribute to water permeation. Because of the network of nanocapillaries that enables to open up in the hydrated state and accept only species that fit in, GO membrane enables to separate the molecules and ions according to their hydrated radius in the aqueous environment. The intercalating water blocks the nanocapillaries, as a result, small species with a hydrated radius of <0.45 nm, such as Na^+, K^+ or Mg^{2+}, could permeate through the membranes with fast rates accompanied by the assistance of intercalating water layer. Whereas, large ions and organic molecules, such as acetone, hexane, ethanol, and propanol, exhibit no detectable permeation [36,39]. Thus, the GO membranes present a kind of valuable material candidates for separation and filtration technologies, *e.g.*, desalination, organic compounds-containing wastewater treatment, or dewatering.

With partly or mildly reduced graphene stacking a membrane [40], the mass-transfer mechanism of such membrane is analogous to the GO membrane beacuese of the existence of the oxidized groups on the sheets [36,40]. When the GO sheets is reduced under violent condition, the chemically converted graphene (CCG) is corrugated due to the presence of some sp^3 hybridized carbon atoms and topological defects [41]. Thus, stacking of CCG sheets would result in the formation of fuzzy nanochannels through the membrane, making the membrane permeable [Fig. 1(c)]. The amplitude of corrugation of CCG sheets can be controlled, and they become more corrugated in water simply by hydrothermal treatment at elevated temperatures [41]. The water permeation rate increases with increasing the corrugation degree [41,42].

2.2. The stability in aqueous solutions and space adjustment

The stacked GO membranes may suffer from instability in the water due to the high hydrophilicity of GO sheets, and even could disintegrate in water. Recently, Yeh *et al.* [43] investigated the origin of the structural

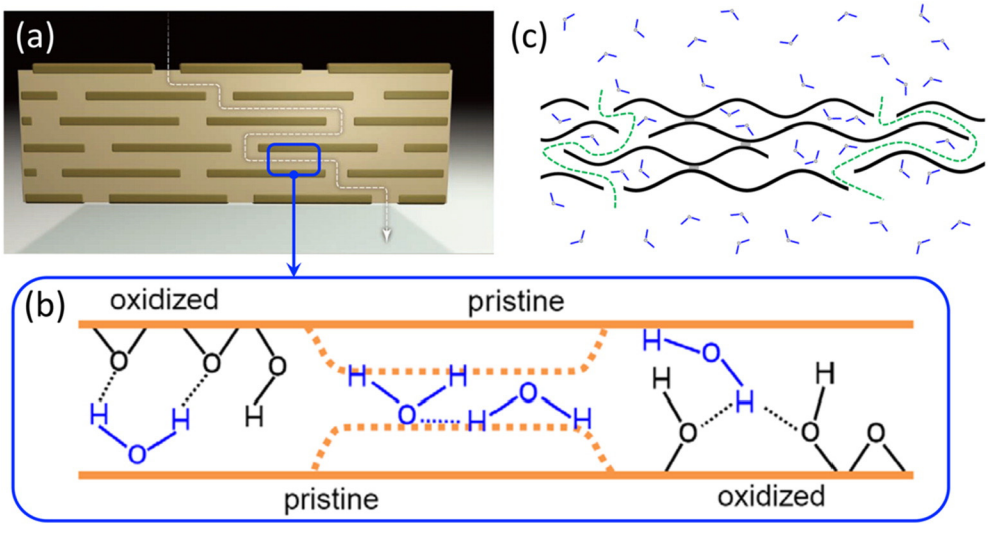

Fig. 1. Schematic diagram for the structures of graphene-based membranes stacked with GO sheets (a, b) and CCG sheets (c) [36,41].

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