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Review

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Recent advances in nanoporous graphene membrane for gas separation and water purification

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Abstract Graphene is a one-atom-thick sheet of graphite comprising sp^2-hybridized carbon atoms arranged in the hexagonal honeycomb lattices. By removing the honeycomb lattices and forming nanopores with specific geometry and size, nanoporous graphene has been demonstrated as a very high-efficiency separation membrane, due to the ultrafast molecular permeation rate for its one-atom thickness. This review focuses on the recent advances in nanoporous graphene membrane for the applications of gas separation and water purification, with a major emphasis on the molecular permeation mechanisms and the advanced fabrication methods of this state-of-the-art membrane. We highlight the advanced theoretical and experimental works and discuss the gas/water molecular transport mechanisms through the graphene nanopores accompanied with theoretical models. In addition, we summarize some representative membrane fabrication methods, covering the graphene transfer to porous substrates and the pore generation. We anticipate that this review can provide a platform for understanding the current challenges to make the conceptual membrane a reality and attracting more and more attentions from scientists and engineers.

Keywords Nanoporous graphene · Gas separation · Water purification · Molecular permeation mechanism · Membrane fabrication

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1 Introduction

Graphene [1–3] is a two-dimensional one-atom-thick sheet of sp^2-bonded carbon atoms packed in the honeycomb crystal lattices, exhibiting good chemical stability [4, 5], excellent thermal conductance [6–8], strong mechanical strength [9, 10], and remarkable electronic properties [11–13]. The unique property of graphene, i.e, one-atom thickness, results in many promising applications in a wide range of fields [14], especially in separation science. It is demonstrated that the pristine graphene is permeable to proton [15, 16], but impermeable to any molecules, even the smallest helium atoms [17–19]. However, the graphene sheet featuring nanopores formed by selectively removing carbon atoms, called as nanoporous graphene (NPG) [20, 21], has been proposed as a very promising size-selective separation membrane based on the molecular sieving effects. As said by the editors of *Nature Nanotechnology* [22], "Graphene opens up to new applications—Effective separation membranes could be created by etching nanometer-sized pores in two-dimensional materials". Owing to the one-atom thickness of graphene itself, the transport rates of molecules through the NPG membranes are expected to be extremely high. Several studies [23–26] numerically and experimentally suggested that the NPG membranes can exhibit high permeability and selectivity exceeding those of existing state-of-the-art polymer membranes by orders of magnitude. Meanwhile, high-quality graphene fabrication [27–30], transfer to porous substrates [31–33], and pore generation [25, 34–39] methods are being developed very well, making the NPG separation membranes very promising in the near future. Recently, another graphene-related material—graphene oxide—was also demonstrated as an efficient separation membrane [40–51]. Graphene oxide is an analogue of graphene by

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asymmetrically modified with oxygen-containing functional groups (hydroxyl, epoxy groups, carboxyl, carbonyl, phenol etc.) on the edges and planes. The separation of hybrid molecules using graphene oxide membranes is realized by the selective molecular diffusion in the interlayer spacing between the oxygen-containing groups on the graphene sheets, the structural defects within graphene oxide flakes, etc. The advantages of graphene oxide membranes include ease of synthesis, ease of scale-up and easy of reassembled into large-area film, but at the cost of permeance that is much smaller than those predicted for the single-layer NPG membranes. Therefore, NPG membrane is the limit of membranes, and its permeance can achieve the theoretical maximum, deserving the attentions from scientists and engineers.

In 2009, Jiang et al. [24] firstly proposed that the NPG with specific pore size and geometry would be a very efficient gas separation membrane using first principle calculations (Fig. 1a). They found a high selectivity on the order of 10^8 through an N-functionalized pore and an extremely high selectivity on the order of 10^{23} through an all-H passivated pore for separating H_2/CH_4 mixtures with a high H_2 permeance. Afterward, several theoretical works were conducted to further confirm that the NPG membranes could achieve high permeability and selectivity for gas separations [23, 52–55]. Due to the difficulties in experimental works,

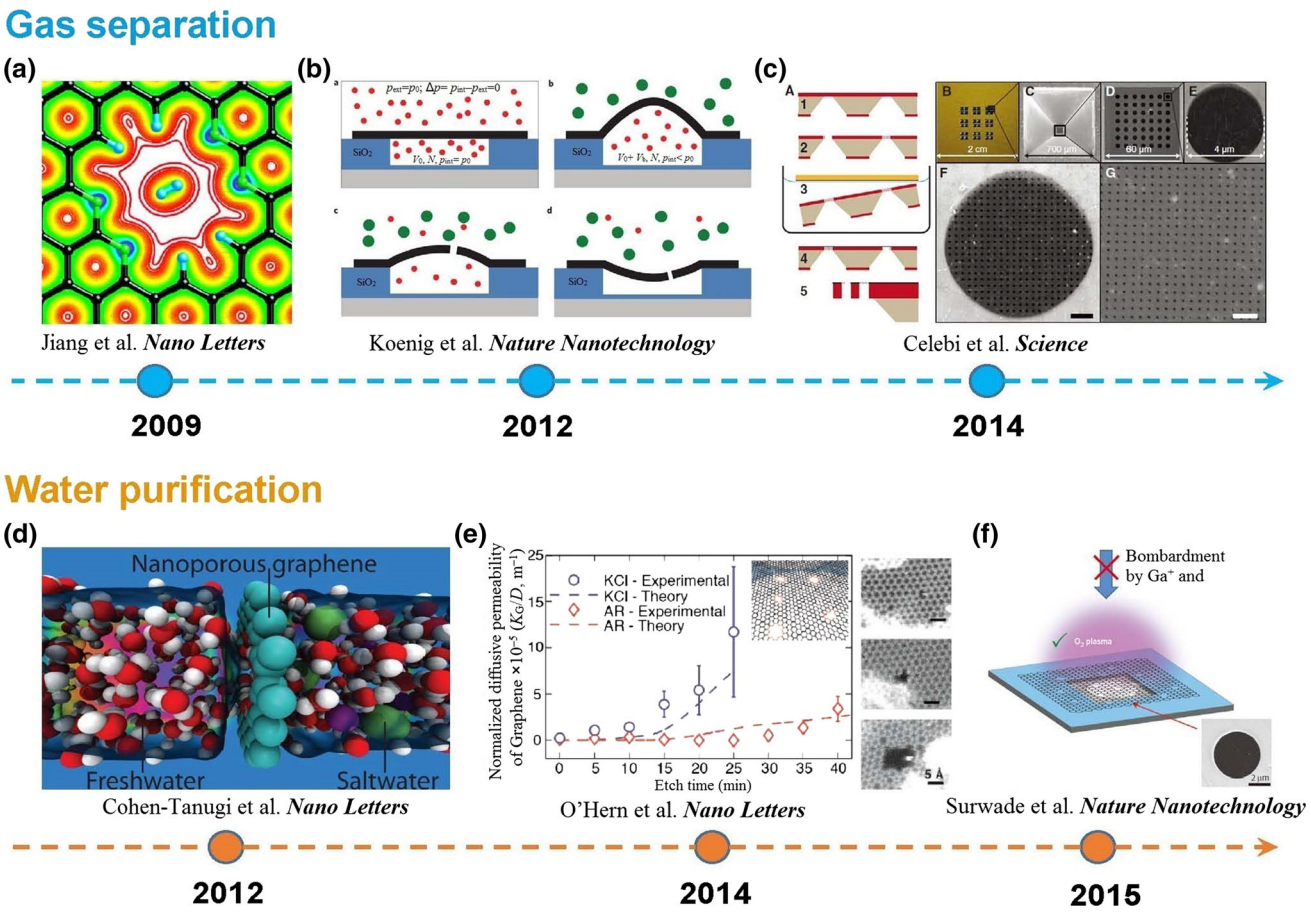

Fig. 1 (Color online) Development history for NPG membranes in the applications of gas separation and water purification. **a** Electron density isosurface of the all-H pore edge passivated NPG. Reprinted with permission from Ref. [24], Copyright 2009, American Chemical Society. **b** Measurement system of the gas transport through micrometer-sized NPG membranes. Reprinted with permission from Ref. [25], Copyright 2012, Nature Publishing Group. **c** Fabrication procedure of the NPG membrane for gas separation. Reprinted with permission from Ref. [56], Copyright 2014, American Association for the Advancement of Science. **d** Atomic view of water desalination by a NPG membrane. Reprinted with permission from Ref. [57], Copyright 2012, American Chemical Society. **e** Permeability of different molecules versus the pore etching time. Reprinted with permission from Ref. [58], Copyright 2014, American Chemical Society. **f** Schematic of single-layer graphene suspended on a 5-μm-diameter hole. Reprinted with permission from Ref. [59], Copyright 2015, Nature Publishing Group