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Molecular dynamics study on water desalination through functionalized nanoporous graphene

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ABSTRACT

Molecular dynamics simulations were employed to investigate water desalination through functionalized nanoporous graphene membranes. Six graphene membranes were considered in which the carbon atoms of the pores were terminated by hydrogen or hydroxyl functional groups. The results demonstrate that water desalination occurs under external pressure and water flux permeating the membranes scales linearly with external pressure and pore diameter. The hierarchy of water flux through the functionalized graphene membranes was explained by potential of mean force. The salt rejection from smallest pore was 100% and decreases as pore diameter increases. Both Na^+ and Cl^- ions permeate through membrane with the largest pore, and the selectivity of the ions permeating exhibits a significant correlation with functional group. The designed graphene membrane shows excellent performance in terms of both salt rejection and water transport. Ultrahigh water permeance of 785.6 L per $m^2 \cdot h \cdot bar$ obtained is two or three orders of magnitude higher than current commercially available reverse osmosis (RO) and nanofiltration membranes. This simulation study provides a microscopic insight into water desalination in various functionalized graphene membranes and reveals governing factor for water flux and also suggests a potential candidate as a RO membrane.

1. Introduction

Recent water crisis has attracted much attention in the globe owing to the rapid growth of world population, accelerated industrialization and environmental pollution [1–6]. Desalination is known to be one of the most promising sustainable approaches for water treatment to supply fresh water. Currently, reverse osmosis (RO) membranes have been prevalent in commercial desalination systems worldwide mainly due to its energy-efficiency, flexible installation, high-resistant and lower cost.

As membrane materials play a key role in desalination performance, carbon structures with various dimensionality such as carbon nanotubes (CNTs) [7–18], graphene [19–31] and covalent triazine frameworks (CTFs) [32–34] as well as metal organic frameworks (MOF) [35–38] have been previously investigated as promising membranes. Although CNTs are expected to possess high water permeability and exhibit a high salt rejection, it is currently difficult to fabricate well aligned and high density CNTs with large lengths [39,40]. Despite the three dimensional networks of zeolites that can effectively reject salt ions, the water permeability is low [35,36]. Furthermore, the CTFs [34] possess a high water permeance of 64.2 $L \cdot cm^{-2} \cdot day^{-1} \cdot MPa^{-1}$ similar to graphene (66 $L \cdot cm^{-2} \cdot day^{-1} \cdot MPa^{-1}$) [19], however, the salt rejection is lower than graphene. To search a potential membrane for desalination, we should consider overall performance in terms of both permeance and salt rejection.

Recently, with the development of experimental technologies, large-area graphene nano sheets have been successfully prepared [41]. In such a two dimensional sheet of sp^2-bonded carbon atoms forming a hexagonal honeycomb lattice, the delocalized electron clouds of π-orbitals take up the voids of aromatic rings in graphene sheet, which is able to prevent the permeation of even atomic helium [42,43]. Nevertheless, heavy ions were reported to bombard monolayer graphene film and produce operated nanopores, which have been more commonly known as nanoporous graphene [44]. Existing studies have already found potential applications of nanoporous graphene in fields such as gas separation [45–56] and

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DNA sequencing [57–61]. Generally, functionalization of pores is associated with the formation of sp^3 carbon network structure through the rehybridization of existing one or more sp^2 carbon atoms accompanied by simultaneous loss of electronic conjugation [28,62]. The functionalizations of nanoporous graphene sheets with various active groups and inorganic nano particles make the properties of the pristine graphene to be engineered as a class of new and exciting materials for specific applications, such as desalination. As is well known, the water flux varies inversely with membrane thickness, so the exfoliated graphene as single atomic layer membrane could be promising for desalination. The first attempt to investigate functionalized graphene as desalination membrane was reported by Cohen-Tanugi and Grossman [19] using molecular dynamics (MD) simulations. They demonstrated that the functionalized nanoporous graphene membranes could perform more than 99% salt rejection and provide water permeance up to 66 $L \cdot cm^{-2} \cdot day^{-1} \cdot MPa^{-1}$ which is 2–3 orders of magnitude higher than that of current commercially available RO membranes and nanofiltration membranes [63]. Therefore, there is a large opportunity to further explore functionalized graphene materials for excellent desalination performance.

In this work, we have performed MD simulations for seawater desalination by further considering three types of nanoporous graphene membranes with hydrogenated (-H) and hydroxylated (-OH) terminations. Thus, the role of pore sizes and pore functionalization under induced pressure can be exclusively revealed. Following this introduction, the models and methods used are briefly described in Section2. In Section 3, salt rejection and water permeance through the graphene membranes are presented and compared with other membranes. Finally, the concluding remarks are summarized in Section 4.

2. Models and methods

Fig. 1 shows the atomistic structure of three types of graphene nanopores. It is clear that the nanoporous graphene membranes are different in terms of pore size and chemical functional group. Two different functionalized nanopores named hydrogenated pore (P_H pore) and hydroxylated pore (P_OH pore) were used in this work. For practical purposes of the real liquid, hydrogen bonds will be formed if the separation of the oxygen atoms on neighboring water molecules is less than 3.5 Å, and about 3.58 hydrogen bonds per water molecule are obtained at ambient conditions [64]. Thus, the diameter of the water molecular cluster is about 5.0–6.5 Å. On the other hand, to effectively reject ion transport across graphene membrane, the pore diameters should be chosen to be similar or smaller than the diameters of hydrated Na^+ and Cl^- ions which are 6.4 and 7.7 Å respectively [65]. Because the pore diameter plays a key role in governing water transport through the nanoporous graphene membrane, the pore diameters are appropriately chosen as 8.2, 5.6, 5.2, 6.6, 4.6 and 3.8 Å for membranes of Fig. 1(a)–(f), respectively. In-plane dimensions of the functionalized nanoporous graphene membranes are 29.8 × 29.5 $Å^2$ with a pore density of 1.1×10^{13} cm^{-2}.

Water desalination through each graphene membrane was simulated in a system schematically illustrated in Fig. 2. The membrane was located at the center of a simulation box at 30 Å since simulation box length is 60 Å along z dimension. The simulation box was filled with 0.5 mol/L NaCl aqueous solution, corresponding to a salt concentration of 33 g/L which is slightly lower than seawater of 35 g/L. Each system was initially subjected to energy minimization using the steepest descent method, then velocities were assigned according to the Maxwell-Boltzmann distribution at 300 K. Finally,

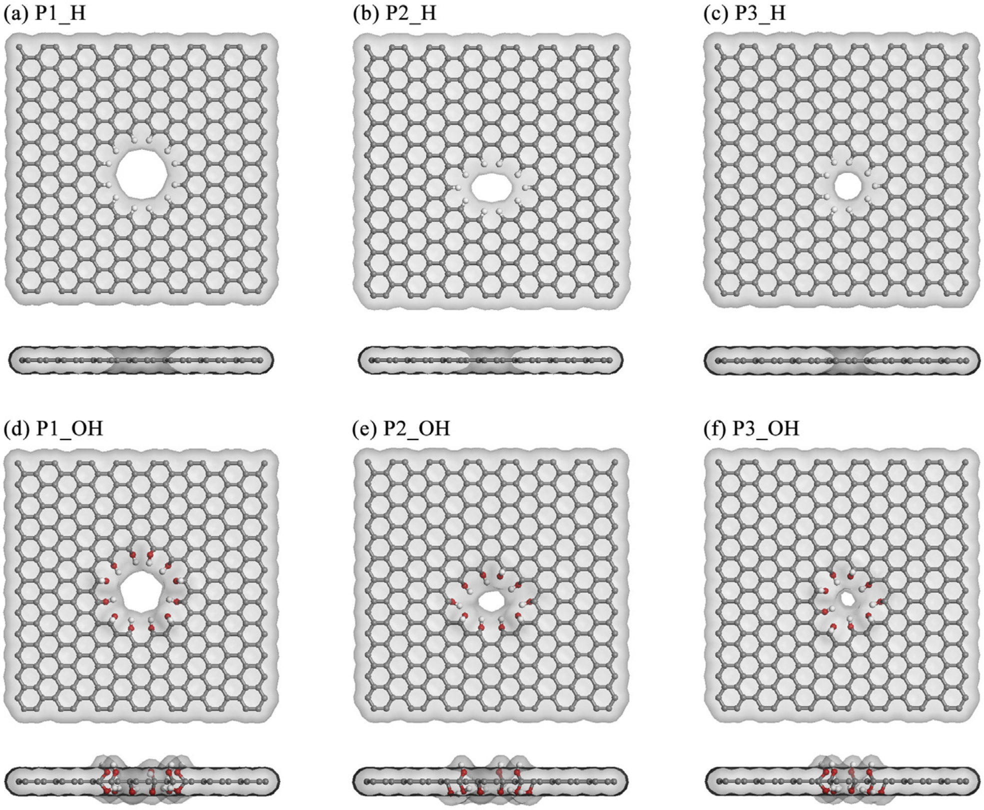

Fig. 1. Functionalized pores in graphene membranes: (a) P1_H pore, (b) P2_H pore, (c) P3_H pore, (d) P1_OH pore, (e) P2_OH pore, and (f) P3_OH pore. (A colour version of this figure can be viewed online.)