Pyridinic nitrogen doped nanoporous graphene as desalination membrane: Molecular simulation study

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ABSTRACT

Functionalized nanoporous graphene has shown great promise as emerging membrane. Herein, we computationally demonstrate the separation performance using pyridinic-like nitrogen doped nanoporous graphene as reverse osmosis desalination membrane. The water permeation and salt rejection of the functionalized graphene membranes with various nitrogen-doping levels were simulated and characterized. We show that all functionalized graphenes investigated in this work exhibit higher water flux and acceptable salt rejection. In particular, the NOH graphene membrane with partial hydroxyl group inclusion shows excellent desalination efficiency. The interfacial properties of water and ions, as well as their free energy landscapes in passing through the graphene nanopores have been simulated in order to explore the desalination mechanism. The moderate free energy barriers for water passages confirm larger water fluxes in the functionalized graphene membranes. It was revealed that the salt rejection for the functionalized graphenes is the pore size exclusion of hydrated ions and the charged repulsion from pore surfaces is not the main factor. Overall, our results indicate that pyridinic-like nitrogen doped graphenes have a significant potential as nanostructured desalination membranes.

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1. Introduction

Reverse osmosis (RO) with semipermeable membranes has become the leading technology for desalination because of its lower energy consumption [1,2]. However, in current RO technology, it is still required to improve water flux rate and increase membrane fouling-resistant ability [1,3], while keeping higher salt rejection level. Because polymeric RO membranes do not have well-defined pores, they generally possess lower water permeability [3]. Nanoporous membranes, such as zeolites [4,5] and carbon nanotubes (CNTs) [6–8], are expected to have great possibility as alternates to existing RO membranes. However, the water permeability of zeolite membrane is still very low due to larger membrane thickness and complex pore architecture [3,9]. For the CNT-based membranes, the fabrication of CNT alignment and CNT tip remains quiet huge challenge [10]. So, developing new membrane materials with high water flux has attracted considerable attention in order to make RO desalination process more economic.

Graphene, as a new-type two-dimensional carbon material [11], has shown potential application as separation membrane material owing to its unique properties [11–14]. In particular, the monolayer thickness of graphene can allow fast molecular penetration [15] and reduce the concentration polarization effect [16]. At present, large-scale monolayer graphene film can be prepared onto copper substrates [17]. However, the perfect graphene sheet is impermeable to molecules as small as He [18]. Therefore, it is necessary to "drill holes" on graphene sheet [18]. Various experimental methods [19–22] for introducing nanopores on graphene surface are in progress, which accelerates the application of graphene membranes. For example, graphene with defined nanoscale pore sizes has been successfully prepared and applied in the gas separation [23]. In recent experimental report , nanoporous single-layer graphene has been successfully fabricated as desalination membrane with tremendously high water transport and almost complete salt rejection [24].

Generally, hole formation in graphene would reduce its thermodynamic stability [25]. As a result, unsaturated carbon atoms at the pore edge of graphene are required to be passivated by functional groups in order to decrease the formation energy of graphene pore and to improve the stability of pore edge [25,26]. Furthermore, functionalization of pore edge might modify pore-size and pore-chemistry, probably improving permeation performance. It was reported that the gas separation performance of porous graphene membranes can be affected by the chemical functionalization on pore rim [27,28]. Hydrogenated and hydroxylated graphenes with fast water transport and acceptable salt

rejection have been simulated as desalination membranes [29]. These studies clearly show the probability of tuning water and ions transport through functionalizing graphene pores as RO desalination membranes.

Nitrogen atom with comparable atomic size is regarded as an excellent element for the chemical doping of carbon material [30]. Three nitrogen doping configurations are commonly used for nitrogen-doped (N-doped) graphene: (1) pyridinic N (N bonding with two C atoms at the edges or defects of graphene); (2) pyrrolic N (forming a five-membered ring); (3) quaternary N or graphitic N (nitrogen atoms replacing the C atoms inside the graphene layers) [31]. Among them, N-doped graphene sheets with pyridinic-like hexagonal hole preserve excellent intrinsic strength, cyclic stability, and thermal stability [32,33]. These properties are in favor of the application of pyridinic-like N doped nanoporous graphene as membrane materials. Up to now, extensive experimental methods [34–38] have been developed to fabricate N-doped porous graphene materials. In addition, the nitrogen atoms on the edge of graphene pore can be easily controlled by tuning experimental conditions [39]. Recently, single layer graphene doped with pure pyridinic N at its edges and defects has been successfully synthesized by thermal chemical vapor deposition of hydrogen and ethylene on Cu foils in the presence of ammonia [40]. Therefore, pyridinic-like nitrogen doped porous graphene membranes have the great possibility of realization as desalination RO membranes. Although limited studies have been carried out for the gas [23] and isotope [41] separations using pyridinic-like N doped graphene

membranes, their performance in water desalination has not yet studied, to our best knowledge.

With the above in mind, in this paper, molecular dynamics (MD) simulations were conducted to investigate the water permeation and salt rejection using single-layer porous graphene membranes with pyridinic N doped functionalization on the pore rims. Various nitrogen doping levels were considered in this work. Meanwhile, it is postulated that the neutral charged feature of the pyridinic N graphene pores will be effective for the rejection of both positive and negative ions. In order to understand the desalination mechanism, we further compute the potentials of mean forces (PMFs) for water and ions transferring through the graphene pores. The pore size effect and the distribution of water molecules in the vicinity of the functionalized pores are discussed.

2. Methods

2.1. Models and simulations details

The simulation system was illustrated in Fig. 1 (top panel), where the functionalized graphene was positioned at the cell center and two chambers were on both sides of the graphene sheet. The right chamber was designed as the feed side, representing 0.6 M NaCl aqueous solution, which is equivalent to the salt concentration in seawater. The left chamber is the permeate side, containing pure water molecules. The solution density was fixed to be ~ 1 g/cm^3 on
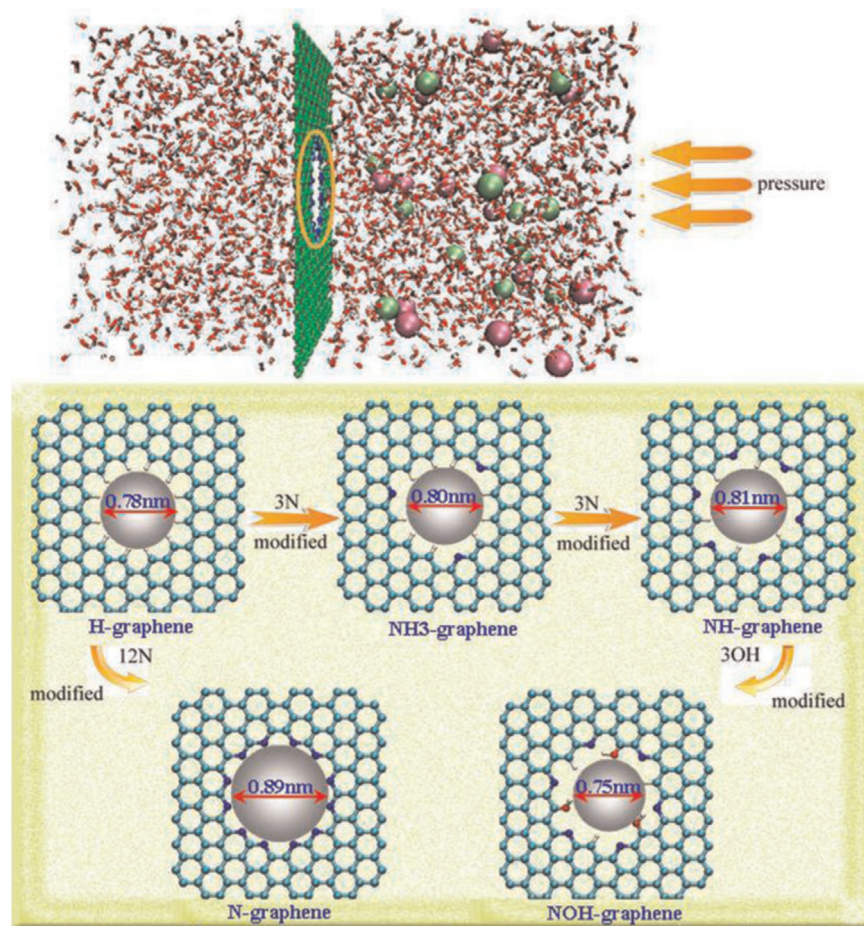
Fig. 1. (Top panel) Lateral view of the simulation system, showing a functionalized graphene membrane placed in the center of the box and two chambers on the both sides of the functionalized graphene. The right chamber contained NaCl solution, while the left chamber was pure water. (Bottom panels) Top view of five functionalized graphene membranes. Carbon atoms in functionalized graphenes are shown as cyan spheres, nitrogen in blue, hydrogen in white, oxygen in red, Na$^+$ in green, and Cl$^-$ in purple. The pore diameters (red line) in the graphene membranes were defined as the diameters of a gray ball fitting the pores. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)