Molecular simulation of reverse osmosis for heavy metal ions using functionalized nanoporous graphenes

Yaping Li [a], Zhijun Xu [a], Shuyan Liu [a,b], Jinwen Zhang [b], Xiaoning Yang [a,*]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, China
[b] School of Mechanical and Materials Engineering & Composite Materials and Engineering Center, Washington State University, Pullman, WA 99164, USA

ABSTRACT

Currently, elimination of heavy metal ions from contaminated water resource is an important issue in environmental protection. In this study, we simulated the separation performance of heavy metal ions using nanoporous graphene surfaces as reverse osmosis membranes with functionalized groups (boron, nitrogen and hydroxyl groups). We show these nanoporous graphenes could realize high water permeation and ion rejection for various conditions. The simulated water permeability is 2–5 orders of magnitude greater than that of currently commercial membranes. The interfacial water structures and flow velocity of water molecules within the nanopores were characterized. The calculations of the potential of mean force reveal water molecules generally face lower free energy barrier than ions when passing through graphene pores. The free energy barriers for ions can be explained as the combining contributions from the ion dehydration effect and the surface electrostatic interaction. Overall, the functionalized nanoporous graphene membranes exhibit potential application in the removal of heavy metal ions, and meanwhile our simulation results provide new insights into the ion rejection mechanism.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Heavy metal pollution has become a worldwide environmental concern [1] because industry wastewater containing copper, cadmium, zinc, lead, mercury and manganese etc. is often deliberately or accidentally being discharged to local water resources [2,3]. For example, industrial processes can produce copper wastewater with 0.3 M concentration [4], which is beyond the permitted concentration for human body and brings about serious vomiting, cramps, convulsions, or even death [5]. Moreover, they are not biodegradable and tend to accumulate in living organisms. Various technologies and measures have been proposed for removing heavy metal ions from water [6,7]. However, these existing technologies have inherent deficiencies and limitations [7]. Among them, reverse osmosis (RO) with semipermeable membranes has been considered as effective ion-removing approach because of its lower energy consumption and environmentally benign feature [8,9]. However, conventional RO membranes still have lower water permeable ability [10,11], and meanwhile, they are prone to degrading and fouling in actual operation conditions [12].

In current years, nanoporous graphenes have attracted great interest for their potential application in desalination and purification of contaminated water [13–15]. Perfect graphene sheet is impermeable to molecules [16]. It is necessary to introduce nanoscale pores on graphene sheet through modern experimental techniques [17,18]. Very recently, nanoporous single-layer graphenes have been fabricated as selective ionic transport membrane [19] and desalination membrane with high water transport and almost complete salt rejection [20].

During the hole formation in graphene, the unsaturated carbon atoms at the pore edge of graphene need to be passivated by functional groups in order to improve structure stability [21,22]. Functionalized graphene sheets have been prepared and used for removal of high concentrations of metal salt ions [23]. Recent study of transport of various ions across graphene-oxide shows that decorated oxygen-containing functional groups on graphene can control the ion transport [24]. In general, heavy metal ions could produce enhanced interaction with pore edge of functionalized graphene and thus affect ion rejection. Generally, heavy metal ions have strong ion hydration due to enlarged Coulombic interaction [25], thereby leading to a weak dehydration effect when ion passing through graphene pores. As a result, the previously accepted dehydration mechanism [14,15] of ion rejection in graphene membranes is probably no longer suitable for heavy metal

ions. Therefore, it is of highly scientific interest and practical value to investigate the separation performance of functionalized graphene pores for heavy metal ions.

In this work, molecular dynamics (MD) simulations were conducted to investigate the water permeation and ion rejection for $CuCl_2$ aqueous solution using three types of functionalized porous graphene membranes. We firstly considered the Boron (B)-doped graphene pore. Due to the small mismatch in atomic sizes, B is often considered as one of the most popular doping elements in carbon materials [26,27]. The B-dopant defect on graphene has been investigated on the atomic adsorption [28–30] by using first-principle study, which indicates the B-dopant could improve the adsorption property. It has also been demonstrated that the larger water-boron interaction might promote the water conduction across B-doped graphene pores [31]. In addition, porous graphene modified by hydroxyl group (OH-graphene) [14] and doped by nitrogen (NH-graphene) [15] were chosen because of their excellent performance of seawater desalination. For the three types of functionalized graphene pores, we explored the effect of pore chemistry and various conditions on water permeability and ion rejection by computing the interfacial properties and the corresponding potential of mean forces (PMFs) through the graphene pores. Finally, we evaluated the separation behavior of other heavy metal ions by using the B-doped graphene membrane.

2. Methodology and simulation details

At first, the geometric structures of three types of functionalized nanoporous graphenes were optimized by the quantum chemical computation using ADF package [32]. The Perdew-Burke-Ernzerh including dispersion correction (PBE-D) level of theory with the localized double-ζ plus polarization (DZP) basis sets was adopted. The atomic charges (shown in Fig. S1) were represented by the Hir-

shfeld charges [33,34] for each functionalized nanoporous graphene. The optimized nanoporous graphene structures will be employed in the following MD simulations.

Our simulation system was illustrated in Fig. 1(a). Functionalized nanoporous graphenes were placed in z = 0 Å to divide the cell into two chambers: a feed chamber in the +z region (0–65 Å), representing $CuCl_2$ aqueous solution, and a pure water chamber in the −z region (−30 Å–0). Unless otherwise stated, we will use the concentration of 1.5 M in the simulation. The dimension size of the graphene sheet is 42.608×44.28 Å^2. The pore was obtained by removing 24 carbon atoms in the center of sheet (as shown in Fig. 1(b)), then the pore edge was functionalized using B, NH and OH functional groups, respectively. As shown in Fig. 1, the pore diameters of graphene sheets were estimated as the minimum distances between the ends of two opposite atoms. Each simulation system was equilibrated firstly, and then the pressure-driving permeation was simulated where a rigid graphene sheet as the piston was placed at the rightest side of the simulation cell and external force was imposed to the piston. The external force (f) applied to each atom of piston is based on the equation, $f = \Delta p \cdot A/n$, where Δp is the desired pressure, A is the area of piston and n is the total number of atoms of piston. All MD simulations were conducted by the LAMMPS package [35], using the canonical ensemble (NVT) with 1 fs time step. In order to keep the reasonability of the simulation system, an additional NPT ensemble simulation was conducted firstly. The solution density can be obtained under atmospheric pressure and this obtained solution density was used to construct the simulation system, including the system geometry, in the feed side of non-equilibrium NVT simulation. The Nose-Hoover thermostat was used to keep the temperature (298 K) constant. To accelerate the MD simulations and gather enough statics in the nanosecond timescale simulations, high hydrostatic pressures ranging from 50 to 300 MPa were considered in this work.
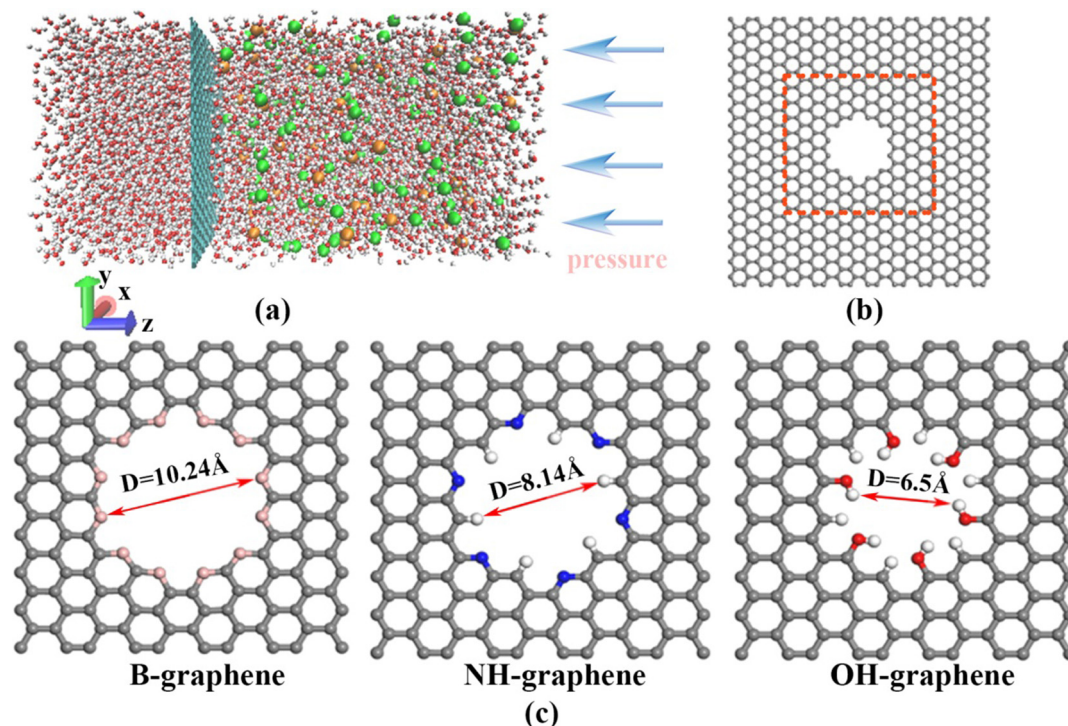

Fig. 1. (a) Lateral view of the simulation system illustration, consisting of a graphene membrane (in cyan) and two chambers on the both sides of the graphene. The right chamber contained cations (in orange) and anions (in green), while the left chamber was pure water (oxygen in red and hydrogen in white). (b) Nanoporous graphene membrane. (c) Top view of three types of functionalized graphene pores. The carbon atoms in membrane are shown as gray, boron in pink, nitrogen in blue, oxygen in red and hydrogen in white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)