Desalination 422 (2017) 83–90

Contents lists available at ScienceDirect

Desalination

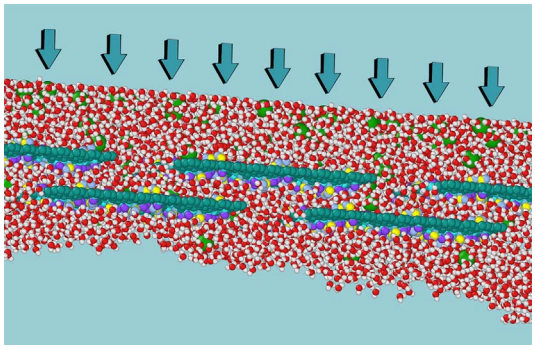
journal homepage: www.elsevier.com/locate/desal

On the design of graphene oxide nanosheets membranes for water desalination

Sina Safaei, Rouhollah Tavakoli*

Department of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Graphene oxide
Desalination
Water
Membrane
Molecular dynamics

ABSTRACT

According to current researches, graphene oxide (GO) membranes show promising desalination properties due to ease of synthesis, low production cost, and high efficiency. There are several experimental works to study ionic sieving properties of GO membranes. However, it is difficult to characterize atomistic mechanism of water permeation and ion rejection by experimental approaches. On the other hand, there exist a few reports in which the atomistic picture of water permeation across GO membranes is investigated by means of molecular dynamics (MD) simulation. In the present work, in addition to water desalination, the atomic scale mechanism of ion rejection is studied using large scale MD simulation. For this purpose, surface color maps based on the potential of mean force (PMF) are computed between GO nanosheets to indicate interaction between functional groups and existing species in saline water. The radial distribution function (RDF) between water molecules and functional groups are measured to study the disordering of water molecules between GO nanosheets. Furthermore, the effect of different layers separation value and applied pressure are examined to explore the optimal design of GO membranes. According to our simulation results, the oxygen atoms in hydroxyl and epoxide groups play an important role in rejection of the Cl ions and attraction of the Na ions. The hydroxyl groups have the most impact on disordering of the water molecules between GO membranes. In addition, our designed GO membrane, showed a water permeability of one to three orders of magnitude higher than commercial reverse osmosis membranes.

* Corresponding author.
E-mail address: rtavakoli@sharif.edu (R. Tavakoli).

http://dx.doi.org/10.1016/j.desal.2017.08.013
Received 21 May 2017; Received in revised form 27 July 2017; Accepted 19 August 2017

1. Introduction

"By 2030 nearly half the global population could be facing water scarcity, with demand outstripping supply by 40 percent", said United Nations Secretary General Ban Ki-Moon [1]. Over 97% of the water on the Earth is saline water, and two thirds of remaining 3%, is frozen [2]. It seems that in the near future, desalination of seawater will be the only way to provide fresh water. The methods based on distillation and reverse osmosis (RO) are common approaches to desalinate seawater [3,4]. In the RO method, an applied pressure is used to overcome natural osmotic pressure such that water passes through a semi-permeable membrane leaving salt behind. In the distillation methods, seawater is evaporated and then condensed to produce freshwater. Both of these methods waste a lot of energy and are very expensive [5].

Recently, nanotube-based and graphene-based membranes have attracted many interests for their potential in water desalination due to high permeability and excellent ion rejection. In spite of these advantages, the synthesis and fabrication are remained as major challenges to produce cost effective membranes [6–15].

Graphene oxide (GO) is a chemical derivative of graphene with several functional groups such as epoxide and hydroxyl that is produced from graphite by the Hummer's method [16]. Recently, it is synthesized and fabricated in the forms of papers and films at the industrial-scale. Functional groups and layers separation of GO membranes can easily optimized during the synthesis process to achieve best performance for desalination [17–19].

Dry GO membranes have a layers separation of ~5 Å which permits only water vapor molecules permeate through the membrane. When a GO membrane is immersed in water, it is swelled so the layers separation is increased to ~10 Å (excluding the thickness of carbon atoms). The Na ions are the smallest in the saline water which has a hydrated diameter of ~9 Å. Therefore, after swelling of the membrane, small ions like Na^+ can permeate easily that leads to reduction of ion rejection property. Several methods such as physical confinement and crosslinking of nanosheets are employed to prevent swelling of GO membranes [20–26].

In the GO membranes, water molecules permeate through the nanochannels between oxidized regions (within pristine regions) provided by the hydrophobicity of functional groups. Particles that have a smaller size than the GO nanochannels can permeate in the membrane with the speed of orders of magnitude greater than conventional membranes [22,26–29].

Since the nanochannels are created by pristine areas of GO nanosheets, some molecular dynamics (MD) studies, explored the behavior of water molecules across graphene sheets [21,30]. Other MD researches, examined The velocity profiles for water flow across GO sheets [28,31], density profile of water molecules between GO sheets [28,31–33], the effect of GO surface oxidization degree on water flow and ion rejection [31], the breaking and forming of hydrogen bonds during the passage of water through the membrane [33], potential of mean force profiles for water molecules [31,33], and Alignment of water molecules in graphene and GO nanochannels [31,34,35].

In the present work, we tried to bring molecular dynamics simulation of desalination systems one step closer to the realistic situation that is occurred in practice. For this purpose, we designed a membrane in agreement with experimental reports considering graphene oxide nanosheets orientation and distribution, also the water, flows in perpendicular direction to the membrane as it occurs in reality. The water pressure is considered close to realistic pressures that is used in commercial RO membranes. In addition to water molecules, we studied the interaction of salt ions with functional groups of GO nanosheets. To explore the atomistic mechanism of desalination, we introduced a new way to study the interaction between salt ions and functional groups by using the surface color maps for indicating potential of mean forces, corresponding to each species. The information from surface color maps can help us to decide which functional groups give us better performance for satisfactory water flux and excellent ion rejection ability simultaneously. The radial distribution function (RDF) between water molecules and functional groups are measured to study disordering of water molecules between GO nanosheets. In addition, we show that the membrane antifouling property can be seen in limited timescales of molecular dynamics simulation. Finally, we investigate the effect of layers separation value and applied water pressure on desalination properties.

2. Material and methods

We performed Classical MD simulations using the large-scale atomic molecular massively parallel simulator (LAMMPS) [36]. The visual molecular dynamics (VMD) and the open visualization tool (OVITO) are used for analysis and visualization of results [37,38]. All simulations are carried out in NVT ensemble with a Nosé-Hoover thermostat and a damping constant of 10 femtoseconds. The velocity-verlet algorithm is used to solve motion equations with a time step of 1 femtosecond. The periodic boundary conditions (PBC) are considered in all three directions.

The all-atom optimized potential for liquid simulations (OPLS-AA) is used for GO and salt ions [39]. This potential contains many-body terms, including bond coefficients, angle coefficients, van der Waals parameters, and electrostatic interactions. In addition, OPLS uses a geometric combining rule for the Lennard-Jones coefficients. The extended simple point charge model (SPC/E) is applied for water molecules, following previous studies on similar systems [26,28–34]. The corresponding parameters of these force fields are given in the Table S1 to Table S4 (see supporting information).

The shake algorithm is used to fix the bond distance between oxygen and hydrogen atoms in the water molecules due to high frequency vibrations of hydrogen atoms, so that we can use longer time steps. The interaction between water and GO includes van der Waals and electrostatic terms. The van der Waals forces cut-off is 1.0 nm, and the long-range Coulomb interactions are computed by using the particle-particle particle-mesh (PPPM) algorithm.

As it is illustrated in the Fig. 1 in our model of GO, hydroxyl and epoxide groups are considered on both sides and at the edges of GO nanosheets, following the Lerf–Klinowski model that is the most common GO model [40]. The infrared spectroscopic data for a stack of large-area GO sheets, indicated negligible quantities of carboxylic acid groups [41]. Therefore, we used just hydroxyl groups at the periphery of nanosheets due to limited edges of nanoscale GO model.

The structure of a GO single nanosheet contains 18 epoxide and 25 hydroxyl groups, with dimensions of $1.8 \times 3\ nm^2$. The functional groups are distributed on both sides of GO nanosheets. Furthermore,

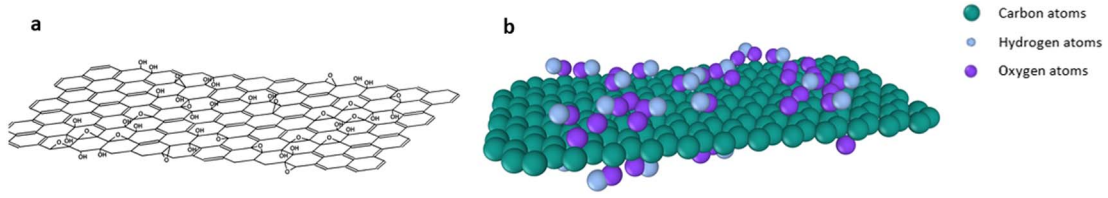


Fig. 1. (a) Lerf–Klinowski GO model [40], (b) our designed model for GO nanosheets.