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Free-standing graphene slit membrane for enhanced desalination

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This study considers two novel ideas to further explore and enhance the graphene membrane for desalination. Firstly, while earlier molecular dynamics (MD) simulations studies have used frozen membranes, free-standing membrane is considered here. Since 2D membranes are usually embedded on porous support in the experimental reverse osmosis (RO) process, the free-standing membrane can more accurately model the behavior expected during operation. This study showed, using MD simulations, that a free-standing nanoporous graphene membrane can provide a higher salt rejection, but lower water permeability as compared to frozen membrane. Secondly, the performance of a slit membrane as compared to a membrane with circular pore is studied. At a pressure of 268 MPa, the critical diameter of circular pore that can maintain perfect salt rejection is found to be 5 Å and the critical size for a slit is determined to be 2.28 Å. It is shown that a slit membrane at its critical size can achieve water flux 3.5 times higher than a membrane with circular pore at its critical radius. This finding highlights the importance of slits over circular pores which can potentially widen the options for the design and fabrication of 2D graphene membranes for experimental verification of RO.

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1. Introduction

Since the discovery of free-standing graphene in 2004 by Geim and Novoselov, there has been a myriad of potential applications associated with 2D materials [1]. While initial interest in 2D materials was mainly on electronic applications, the use of such materials as membranes for desalination has garnered much attention recently [2–4]. It is believed that 2D materials can revolutionize current desalination membrane technology because of their two unique properties: single atom thickness and high mechanical strength.

Current desalination membranes employ a thin film composite (TFC) design under reverse osmosis based operations [5]. TFC membranes consist of a thin polyamide active layer supported by a porous sublayer. While the thin polyamide active layer in TFC membranes have thickness in the order of 100 nm, the single atom thick property of 2D materials means that membranes made of 2D materials have thickness two orders of magnitude lower than conventional TFC membranes. Since the Hagen-Poiseulle equation predicts that flux is inversely proportional to the membrane thickness, theoretically, in the absence of factors like concentration polarization and fouling, the water flux through such atom thick 2D membrane is expected to be orders of magnitude higher than the current RO membrane [6]. Indeed, in 2012, Cohen-Tanugi & Grossman showed that a graphene based membrane can achieve a flux two to three orders of magnitude higher than conventional RO membranes using molecular dynamics (MD) simulations [3]. Following this, Heiranian, Farimani & Aluru showed in 2015, also through MD simulations, that a membrane based on molybdenum disulfilde (MoS_2) can theoretically boost flux 2 to 5 orders of magnitude higher than conventional RO membranes [4]. Apart from MD simulations, Surwade et al., in 2015 conducted an experimental study on nanoporous graphene membrane [7]. They reported that graphene membrane with nanopores introduced using oxygen plasma can effectively separate salt while maintaining water flux. All these studies prove the potential of 2D materials as a desalination membrane.

Of course, apart from water flux, salt rejection is the other determining factor in membrane-based desalination. One of the

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earliest works which showed that nanopores in graphene can effectively sieve out ions from water is that by Sint, Wang & Kral in [8]. They showed using MD simulations, that by functionalizing the nanopores, selective passage of ions can be facilitated. The MD simulations performed by Cohen-Tanugi & Grossman [3] and Heiranian, Farimani & Aluru [4] also confirmed the salt rejection behavior of nanopores. Depending on the size of the pore and the driving pressure force, the salt rejection ranges from 100% (all salt ions are rejected), to 33% at applied pressure of about 200 MPa [3,4]. There are two known separation mechanisms identified so far: the sieving effect, and the electrostatic effect [9–12]. The sieving effect refers to the retention of solutes due to size exclusion. For charged solutes, one needs to additionally consider the hydrated radius since the charge on the ion will cause a hydrated shell of water molecules to be bounded around it. The bond between the surrounding water molecules and the ion can be sufficiently strong such that the ion behaves like a rigid sphere [10]. According to Wu & Zhao [10], the hydrated radii of sodium (Na^+) and chlorine (Cl^-) ions have been experimentally determined to be 3.72 Å and 4.54 Å, respectively (the crystal ionic radius of Na^+ and Cl^- are 1.02 Å and 1.81 Å respectively [13]). The radii of a water molecule on the other hand is 1.25 Å [14]. This sieving effect is the main mechanism for the water-ion separation by nanopores when the membrane is uncharged. When the membrane is charged or functionalized, one needs to additionally consider the electrostatic interactions between water molecules, the solutes and the membrane. This is collectively considered as the electrostatic effect [11].

As seen from the studies done to date, MD simulations have been used as an enabling tool to understand the process of desalination with 2D membranes. Nevertheless, all these MD simulations are mainly on 2D membranes with circular nanopores held rigid during the simulation run [3,4,15,16]. Based on current reported fabrication strategies [7,17,18], these 2D materials are typically fixed on microporous support. Within a micro-pore, the graphene membrane sheet is only held rigid at the edges where the graphene sheet is in contact with the micro-porous support, while the other areas of the graphene sheet are allowed to deform according to the forces acted on by the water molecules and salt ions. As such, a free-standing membrane, that is one with only the edges fixed, can more accurately model the behavior of such 2D membranes since the dynamic deformation of the membrane is accounted for. Thus, in this work, we carried out MD simulation of nanoporous graphene as a free-standing membrane. The difference between free-standing and frozen configurations are examined and discussed in detail. This study can provide insights to the interactions of membrane with water and salt molecules, and the impact of these interactions on the membrane performance. For the second aspect of this work, we propose slits over circular pores (in the earlier works above) for enhanced filtering of the salt ions while maintaining high flux. MD simulation is carried out to verify this. Since the fabrication of slit membranes do not require the introduction of nanopores on 2D materials, this can potentially lead to simpler fabrication processes for actual application.

Graphene was selected as the membrane material in this study, as it has been relatively well studied as compared to other 2D materials. In this study, the membrane is not functionalized or charged. Hence, it can be expected that the sieving effect will dominate. This is validated via the results of the simulation, and will be further deliberated.

2. Molecular dynamics (MD) simulation method

The methodology used in this work is similar to that adopted by Cohen-Tanugi & Grossman and Heiranian, Farimani & Aluru [3,4]. MD simulations were performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) [19] and results were visualized using Visual Molecular Dynamics (VMD) [20]. The size of the simulation domain is 90.17 Å by 25.56 Å by 24.60 Å. The feed and permeate water are bounded by a two pistons, with initial position in the x direction at 20.00 Å and 43.17 Å respectively. The membrane is located at an *x*-position of 31.56 Å, and the simulation domain is set up to ensure the density of water is close to its standard value of 1 g/cm^3 at standard conditions and that there will be sufficient space for the piston to move through the simulation.

In the feed water zone, a total of 729 water molecules were initially placed, together with 12 Na^+ and 12 Cl^- ions. This amounts to a salinity of 1.0 mol s/L. At the permeate zone, 162 water molecules were initially positioned. A periodic boundary condition is employed throughout the simulation. In this case, it indicates periodicity in the *y* and *z* directions, since the elongated *x* direction ensures each period box is independent of the neighboring cells.

The structure and interactions of water molecules were modeled using the TIP4P water model [21] with a long-range coulombic solver. The particle-particle particle-mesh solver (PPPM) [22] long-range coulombic solver was employed for this study. At each step of the simulation, the bond lengths and angles within each water molecule is held rigid. The carbon atoms that made up the pistons and membrane are bonded together with the AIREBO potential [23]. The rest of the interactions are implemented via the Lennard-Jones and columbic interactions. The wall depth and radius of Na^+ and Cl^- ions that define the Lennard-Jones interactions are obtained from the work by Joung and Cheatham [24]. The intermolecular interactions are then modeled using mixing rule for the Lennard-Jones potential [25,26]. The actual parameters used are detailed in the Supporting Information (SI). The global cutoff distance for Lennard-Jones and Coulombic forces are both specified to be 8.5 Å for the implementation.

The graphene membrane is constructed by removing atoms from a pristine sheet of graphene. Two configurations are studied here, namely, the membrane is either frozen in space or free-standing. In the first case, the entire membrane is held rigid throughout the simulation. In the latter, the edges of the membrane in the simulation domain is held fixed, and the rest of the membrane are allowed to move with respect to the force fields already defined above.

Before each simulation run, the water molecules and salt ions are given a random initial velocity at 300 K and the entire simulation is subjected to energy minimization using conjugate gradient algorithm. Subsequent steps performed compute the positions and velocities at each time step using time integration on Nose-Hoover style non-Hamiltonian equation of motions. The time step is kept constant at 1fs. The pistons and membrane is first kept rigid, while the system undergoes a further energy minimization in isothermal and isobaric conditions (NPT ensemble) for 100 ps, and then in canonical NVT ensemble for a further 100 ps The pistons were then allowed to move at a differential pressure of 0Pa and the entire system undergoes an additional energy minimization of 100 ps Finally, the membrane is either kept frozen or allowed to free-stand, and differential pressure is applied across the pistons at NVT conditions for a period of 2ns–10 ns, depending on the pore size and shape involved in that simulation. For each configuration, the process is repeated for 10 different sets of initial velocity and the results are averaged for statistical reasons. Results are written to a data file at every 50 time steps.

3. Results and discussion

Quantities of interest for membrane desalination are the water permeability and salt rejection. In this work, water permeability is defined as the number of water molecules that cross the membrane

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