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Influence of curvature on water desalination through the graphene membrane with Si-passivated nanopore

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ABSTRACT

In this study, the water desalination across Si-passivated nanopores graphene has been investigated by using molecular dynamic simulation. The effect of pore size, membrane curvature, and applied pressure on water flow rate is explored. It is shown that the salt ions rejection can be affected by membrane curvature. Furthermore, it is shown that in the pore vicinity, the oxygen density distribution is symmetrical and asymmetrical for the fixed and unfixed membranes, respectively. Finally, it is examined that the shapes of density surface can play an important role in the salt ion rejection.

1. Introduction

In recent decades, the global climate change, is leading to increase dry conditions in many countries. Therefore, water desalination is one of the most promising approaches to supply freshwater for these areas. Several methods of desalination, i.e., reverse osmosis [1,2], and pressure differences [3], are known to filter dissolved solids. The novel two-dimensional graphene sheet, in the recent past, has been proposed as a gas separation [4,5] and desalination membrane [1–3,6–14], because of its unique physical and mechanical properties, i.e., extremely strong, extremely thin, and can be chemically modified [15,16].

Recently, a number of experimental and computational researches have focused on water desalination using graphene membrane [3,6–9,11,14,17–20]. Cohen-Tanugi and Grossman [6], explored water desalination across the graphene membrane with hydrogenated and hydroxylated pores, using molecular dynamic simulation and pressure difference as driving force. They found a critical pore diameter, which allows water flow while blocking salt ions, and beyond this diameter, salt ions can pass through nanoporous graphene. Konatham et al. [8], by using molecular dynamics simulation and reverse osmosis technique, the transport of water and salt ions through pore with diameters ranged from 7.5 to 14.5 Å on a graphene sheet were investigated. They showed that graphene functionalized with COO^- and OH^- groups rejects Cl^-; and NH^{3+} groups reject Na^+ ions from passing through the membrane. In addition, water transport through the two-dimensional nanopores was investigated by Zhu et al. [21]. It was found that in contrast to the conventional continuum theoretical models, nonlinear relationship between the pore area and water flow rate is observed for nanopores smaller than about 15 Å [21–23]. Also, Zhu et al., investigated the water desalination through graphyne membranes [22]. They showed that for γ-graphyne-4 sheet the permeate salinity is zero. Sint et al. [24], designed F-N-terminated and H-terminated graphene nanopores. They found that driving electrical field, optimizes the ion selectivity through these nanopores. Azamat et al. [25], investigated the removal of Zn^{2+} from water using the nanopores graphene and boron nitride nanosheet functionalized with fluoride. They used osmotic pressure technique to filter water molecules. Moreover, very recently, it was experimentally reported by Syrwade et al. [3], that water desalination across one nanoporous graphene using pressure difference as a driving force, increases water fluxes of up to 10^6, which is almost several orders of magnitude larger than fluxes measured using osmotic pressure as a driving force.

Recent studies show that small holes in graphene can be filled by diffusing carbon or other adatoms [26]. The MD simulation results indicate that carbon adatoms interact strongly with H-passivated nanopores, and it leads to fill the pores. Moreover, the density-functional calculations show that, silicone (Si) atoms stabi-

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lize graphene nanopores [26]. On the other hand, Si is one of the known impurities in graphene grown by chemical vapor deposition (CVD) [27,28]. In this study, we report the water desalination across Si-passivated nanoporous graphene. The effect of curvature of membrane and applied pressure as the driving force has been investigated. For this purpose, the MD simulations were implemented. We have found that by increasing the radius of curvature of membrane in contrast with fixed membrane, salt ions passing across the membrane as well as water flow rate, decrease.

2. Materials and methods

The graphene membrane sheet of length 3.0 nm in *x* and width 3.0 nm in *y* directions with a pore in a center was modeled. The Si atoms grafted to the pore rim of graphene. Three structural models, V_6Si_3, $V_{24}Si_6$, and $V_{54}Si_{12}$, where V indicates the number of carbon vacancies, and Si indicate the number of Si atoms were considered. The atomic structures of graphene nanopores which were decorated by Si atoms are shown in Fig. 1. The density functional theory (DFT) calculations show that the binding energy of Si atoms is larger than 5 eV [26]. The pore diameters were, ~2.0, ~6.9 and ~11.0 Å for V_6Si_3, $V_{24}Si_6$, and $V_{54}Si_{12}$ membranes, respectively. The choice of current models was based on the structures of pores which was experimentally studied by Lee et al. [26]. As discussed before, they reported that the Si atoms stabilize nanopores of the graphene sheet in terms of the fact that these atoms prefer tetrahedral coordination. Therefore, adatoms that might bond to them would not fill the pore rim. The simulation systems consist of 1240 water molecules, and the water molecules were presented on the both sides of the graphene membrane. The 8 Sodium (Na^+) ions and 8 chloride (Cl^-) ions were randomly placed within the water on the up side of the membrane. The number of salt ions yields a concentration of ~0.5 M. Simulations were conducted using the LAMMPS software package [27]. The water molecules were modeled using the SPC/E model [29]. Bond length and angles in water were using the SHAKE algorithm [30,31]. Nonbonded interactions were modeled by Lennard-Jones (LJ) potential and electrostatic forces. The membrane atoms potential was based on the use of Tersoff potential [28]. The LJ and charge parameters implemented in the current simulations are reported in Table 1 [27,28].

In order to understand the effect of roughness surface of membrane on water desalination and salt ions rejection, two series of simulations with fixed and unfixed membrane were modeled. In the case of unfixed membrane, to avoid the deformation of nanopores graphene edge, supported boundary conditions (SBCs) were imposed on the end sides in all directions of GRs to prevent the end atoms of the surface to move. Periodic boundary conditions are imposed in all three dimensions. To do these simulations, firstly, the energy minimizations of the structures were performed using the conjugate gradient algorithm. Secondly, the systems were equilibrated within an NPT ensemble to find the optimum value of the volume of the simulation cells. The equilibration phase was performed for 100 ps at a room temperature (300 K) for all simulations. At last, a constant force, $f = \frac{A\Delta P}{n}$ [32], related to the driving force, is applied in the $-z$ direction to a rigid piston during simulation, where n is the number of solvate atoms, A is the cross sectional area of the graphene, and ΔP is the desired pressure difference from 100 to 300 MPa. To do this, the external force was applied to a rigid piston, away from and toward the membrane, and then the system was reequilibrated. By repeating this procedure, the water flow was obtained for all simulations. Initial velocities were sampled from a Maxwell-Boltzmann distribution at the given temperature. To control the temperature during the simula-

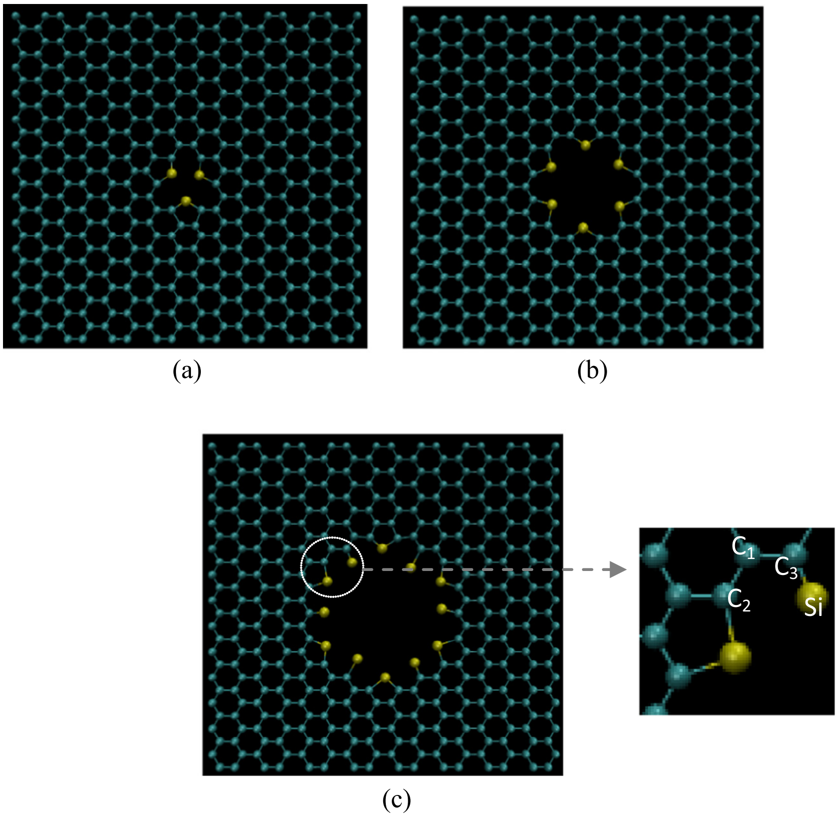
(a)
(b)
(c)

Fig. 1. V_6Si_3 (a), $V_{24}Si_6$ (b), and $V_{54}Si_{12}$ (c) graphene membranes. In this plot carbon atoms of graphene are shown in blue, and silicone in yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)