New carbon membrane for water desalination via reverse osmosis

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Abstract. The recent development of membrane-based water desalination and purification technologies shows new approaches to meeting global demand for freshwater. Carbon-based nanomaterials have shown great potential in various desalination technologies. Such materials are suitable for membrane separation, offering advantageous structure, mechanical properties and porosity. In the present molecular dynamics study, water desalination via reverse osmosis is simulated using a new sp²-carbon membrane. It is found that the membrane under consideration demonstrates a very good rate of ion rejection and a reasonably good water flux, which grows with increasing temperature.

1. Introduction

The lack of freshwater resources, unevenly distributed in the world, makes researchers move towards the development of new good membranes for the desalination of sea water [1]. Obviously, for a good salt rejection rate, the pore size of a membrane must be smaller than the diameters of Na⁺ (~7.5 Å) and Cl⁻ (~6.5 Å) ions and at the same time must be large enough for a good permeate water flux. The latter can be observed only when the pore diameter is larger than the size of water molecule (~4.0 Å). It is important to find single-layer structures with high strength and proper hole sizes. It is believed that due to strong covalent bonding, graphene membranes can be widely used for water desalination. Unfortunately, there is a drawback of such structure, namely, its hexagonal pore size is too small for the penetration of a water molecule. Therefore, researchers are looking for membranes capable to overcome this problem. For example, in a recent molecular dynamics study by Liu et al. [2] the desalination performance of a single-layer C₂N membrane during forward osmosis was addressed. An unstrained membrane showed a relatively poor water flux due to the insufficiently large size of pores. The authors improved the water flux through the membrane, applying a bi-axial tensile strain up to 12%. Another method is the introduction of holes using techniques such as graphene perforation by
ion beams [3]. It is important to look for membranes that can be used for water desalination, avoiding difficulties such as application of tensile stress or perforation.

In a series of recent theoretical works, new single-layer carbon structures with different hole sizes were proposed [4,5]. We believe that some of these structural carbon modifications may be promising candidates for water desalination. In the present work, we study the water desalination performance of a new sp\(^2\) two-dimensional carbon structure using the density functional theory (DFT) and molecular dynamics (MD).

2. Simulation setup

2.1. Material of study

For the seawater desalination through reverse osmosis, the carbon membrane having a particular new structure is chosen. Figure 1 a shows the membrane structure obtained after optimization of the DFT geometry using the VASP software. This single-layer material is characterized by an intrinsic pore size of 5.2÷5.9 Å. The first-principle calculation using the Bader analysis showed that the charge density is evenly distributed within the structure indicating that the charge of C atoms is equal to zero.

![Figure 1](image_url)

**Figure 1** (a) Structure of carbon membrane after DFT geometry optimization. (b) MD model for water desalination via reverse osmosis. The single-layer carbon membrane is located between the feed solution having Na\(^+\) and Cl\(^-\) ions (on the right) and the pure water box (on the left). Two graphene pistons are placed on the two ends of the model. Here, water molecules are indicated in blue shadow, Na\(^+\) in pink, Cl\(^-\) in yellow, while C atoms are given in grey. In order to distinguish the ions and C atoms of the membrane, their sizes are enlarged.

The simulation model for the water desalination process consists of pure water and the feed solution at two sides of the single-layer carbon membrane, which is located in the middle of the model at \(x=0\). In addition, there are two graphene pistons at the two ends of the model, which are treated as rigid bodies (figure 1 b). To model the seawater, the concentration of Na\(^+\) and Cl\(^-\) ions in the feed solution equal to 0.8 mol/L is chosen. The dimensions of the membrane, the solution boxes and the pistons along the \(y\) and \(z\) directions are 29 and 23 Å, respectively. The lengths of the boxes for the feed solution and pure water along the \(x\)-direction are equal and are set to 50 Å. In order to separate the left and right parts of the model and to avoid atomic interactions between them, a vacuum space having a length of 30 Å along the \(x\)-direction was introduced between the pure water box and the feed solution.

During simulation, atomic interactions between particles of a system are considered as electrostatic and van der Waals ones. The latter interactions are described by the Lennard-Jones (LJ) potential with parameters taken from the AMBER03 force field [6], while the particle-particle particle-mesh (PPPM) method is used to characterize long-range electrostatic interactions. The LJ parameters for the interaction of atoms between different types of atoms are calculated using the Lorentz-Berthelot
mixing rule. In order to create water, the so-called Transferable Intermolecular Potential 3P (TIP3P) water model [7] and the SHAKE constraint algorithm [8] were adopted for the simulation.

2.2. Modeling
The MD simulations are performed using the atomic/molecular massively parallel simulator (LAMMPS) program package [9]. Periodic boundary conditions are applied along the three orthogonal directions \( x, y \) and \( z \) of the simulation model. Initially, the system is equilibrated at a corresponding reverse osmosis temperature, which can be 280, 300, 320, 340 or 360 K in the NVT ensemble for 20 ps. Further, in order to create an osmotic pressure of 100, 200 or 300 MPa, the corresponding forces are imposed on the right graphene piston for 3 ns to compress the seawater box. For visualization of the atomic structure and phase composition at different temperatures, the OVITO and VMD packages are used [10,11].

3. Results and discussion
Figure 2a shows the permeation water flux through the membrane as a function of temperature for the three considered applied pressures. It was revealed that at a pressure of 300 MPa, the water flux monotonously increases from 30 to 140 L/(h cm\(^2\)). For pressures of 100 and 200 MPa, similar to 300 MPa, the flux increases from 2 to 70 L/(h cm\(^2\)) and from 20 to 95 L/(h cm\(^2\)), respectively. It should be noted that in these two cases, the general trend of increasing water flux with increasing temperature slows down in the temperature range close to 340 K. The permeation water flux for 100 MPa at 340 K is even lower than at 320 K. The reason for such non-monotonic behavior of water flux with increasing temperature at relatively low pressures remains to be explained in the next more detailed study. At this stage of the study, we can speculate that a decrease in the permeate water flux at 340 K can be explained by the temperature effect on the pressure of the feed solution. It is known that the latter decreases with increasing temperature. This behavior obviously leads to the reduction of the overall reverse osmosis pressure and the reduction of the flux that is especially noticeable at a lower applied pressure (100 MPa), while in the case of high external pressures the temperature effect is not so pronounced (figure 2a). Normally, reverse osmosis systems are designed in such a way that the feed pressure is adjusted to compensate the water flux changes caused by an increase in temperature.

It was revealed that in all the considered cases the studied carbon membrane demonstrates 100% salt rejection. The Na\(^+\) and Cl\(^-\) ions cannot go through the membrane pores.
In order to investigate the diffusion behavior of water molecules in the feed solution, their mean square displacement (MSD) \( \langle \Delta s^2(t) \rangle \) was calculated for the considered temperatures and reverse osmosis pressures. This parameter reflects the deviation of the position of the particles with respect to the reference position over time. From the obtained MSD curves, the diffusion coefficient \( D \) can be found as \( \langle \Delta s^2(t) \rangle \approx 6Dt \), where \( t \) is the simulation time. Figure 2 b shows the dependences of \( D \) for water molecules in the salt water on temperature of reverse osmosis process for differed pressures. Overall, the diffusion coefficient increases with increasing temperature from \( \sim 5.0 \times 10^{-6} \text{ cm}^2/\text{s} \) at 280 K up to \( \sim 1.75 \times 10^{-5} \text{ cm}^2/\text{s} \) at 360 K. The applied reverse osmosis pressure affects insignificantly the diffusion coefficient. Thus, the curves for 100 MPa and 200 MPa are very close to each other, while \( D \) values for the case of 300 MPa are slightly lower especially at higher temperatures.

Temperature determines the rate of diffusion of water molecules. Its increase leads to activation of diffusion (see figure 2 b) and, obviously, to an increase in water flux through the membrane, as can be seen in figure 2 a.

4. Conclusions

The obtained results demonstrate that the carbon membrane having the structure shown in figure 1 a can be successfully used for water desalination via reverse osmosis. The material demonstrates a high water flux and perfect salt rejection rate, which can be explained by the fact that the size of its intrinsic pores are permeable to water molecules, unlike those of the conventional graphene structure, and at the same time, the pores are not big enough for the Na\(^+\) and Cl\(^-\) ion penetration. Such a membrane does not require the application of tensile deformation or the introduction of holes (defects) to increase the water flux.

In the following studies it is important to analyze the theoretical strength of the considered carbon membrane, e.g., in line with the MD study performed earlier for graphene [12] or using the DFT approach.

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References

[1] Hebbar R S, Isloor A M, Inamuddin and Asiri A M 2017 Environ. Chem. Lett. 15 643
[2] LiuB, LawA W-K and Zhou K 2018 J. Membrane Sci. 550 554
[3] Buchheim J, Wyss R M, Shorubalko I and Park H G 2016 Nanoscale 8 8345
[4] BelenkovE A and Greshnyakov V A 2013 New Carbon Mater. 28 273
[5] BelenkovE A and Kochengin A E 2015 Phys. Solid State 57 2126
[6] Duan Y, Wu C, Chowdhury S, Lee M C, Xiong G M, Zhang W, Yang R, Cieplak P, Luo R, Lee T, Caldwell J, Wang J M and Kollman P 2003 J. Comput. Chem. 24 1999
[7] JorgensenWL, ChandrasekharJ, MaduraJD, ImpeyRW and KleinML 1983 J. Chem. Phys. 79 926
[8] Ryckaert J P, Ciccotti G and Berendsen H J C 1977 J. Comput. Phys. 23 327
[9] Plimpton S 1995 J. Comput. Phys. 117 1
[10] Stukowski A 2010 Modelling Simul. Mater. Sci. Eng. 18 015012
[11] Stukowski A, BulatovVV and Arsenlis A 2012 Modelling Simul. Mater. Sci. Eng. 20 085007
[12] Baimova JA, Dmitriev SV, Zhou K and Savin AV 2012 Phys. Rev. B 86 035427