Porous Graphene for Sea Water Desalination Considering the Effects of Fluorine/nitrogen Modification: A Molecular Dynamic Study

Zhang Fa
College of Chemistry and Chemical Engineering, Chongqing University
zhangfajason@163.com

Abstract. Sea water desalination becomes more and more important as the consumption of fresh water. Forward osmosis (FO) is a novel technology for sea water or brackish water desalination, where a most important device, semi-permeable membrane, are required low resistance, high selection and inexpensive. In this study, based on molecular dynamic simulations, we explored the performance of porous graphene as the semi-permeable membrane for sea water desalination. Fluorine (F) and nitrogen (N) are adopted to optimize the property of graphene pore. We found that although pure pore have highest water flux (indicating lower resistance), N modified pore has the best selection due to the high electronegativity of N atoms. The about 60 L/cm²/h water flux and 100% solute rejection ratio confirm the graphene with N modified pores is good candidate as a semi-permeable membrane for sea water desalination.

1. Introduction
Mixture separation, such as sea water desalination and gas purification, plays an important role in many industrial processes [1-5]. Compared to conventional distillation, solvent adsorption, and solid adsorption, membrane separation system has many advantages, such as energy conservation, high flexibility, and no moving parts and exotic chemicals, especially for small-scale applications [6]. Many carbon materials and their analogues, such as graphene, graphene oxide, fluorine-modified graphene and hexagonal boron nitride (h-BN) have been widely explored as promising membranes for sea water desalination and gas separation [7-8]. The mechanism of membrane separation is the different permeation fluxes for mixtures due to their differences in the adsorption, diffusion, potential energy, and even the size ratio of pore and molecule.

Graphene, as a 2D material with high thermal stability, low dielectric constant and high mechanical strength, exhibits good impermeability and preferential adsorption properties to many molecules and ions, and is deemed as very promising sea water desalination membrane [1-2]. What’s more, the adsorption capacity, interaction energy and selection of graphene to molecules can be significantly improved after the oxidation, fluorination and ion coating treatments, etc. [9-10]. For example, using some other atoms to modify the pore properties can significantly enhance the selection of water molecules and ions [11, 12].

In this work, molecular dynamic simulations are performed to explore the application of porous graphene for sea water desalination under a forward osmosis (FO) technology. To enhance the selection the graphene pore, fluorine (F) and nitrogen (N) atoms are used at the pore edge. A uniform
pore diameter and ion concentration in sea water are chosen to compare the effects of pure pore, F modified pore and N modified pore. The fluxes of water and ions with time are obtained and the solute rejection ratios are quantitatively discussed. Last, the adsorption energies of water molecule and several ions are calculated for the three pores to explain the difference in fluxes and solute rejection ratios.

2. Methods
The establishment of models and calculation are based on the Materials Studio version 7.0 (MS) of Accelrys. We visualize the structures by using the Materials Visualizer in MS, the sea water filling is by the Packing function in Amorphous Cell module, the geometry optimization and dynamic simulations are by the Forcite module. The COMPASS forcefield is used in all the simulations. Van der Waals interactions and Ewald electrostatic interactions were applied with a cutoff distance of 9.5 Å. COMPASS forcefield was developed by an ab initio calculation, and therefore this forcefield can accurately predict many condensed phase properties with covalent models and ionic models, such as graphene and seawater [13-14].

The front, side views of computational model and pores in graphene are shown in Figure 1. The sheet areas of both prefect graphene and graphene with pore are 24.6×25.6 Å2. The pores in this study are with a diameter of ~14.7 Å and N atoms and F atoms are used to modify the pores as the edge atom can significantly affect the molecule permeance [11]. The computational domain in z-axis is 60 Å. Periodic boundary conditions are applied in all directions. Two graphenes with periodic condition divide the region to two parts. The left part of the pore graphene contains fresh water, but the right part with seawater. Sea water part are with 540 H2O, 27 Cl-, 14 Na+ and 13 K+, which makes the density of ~1.05 g/cm³ and salting concentration of ~2.8 mol/L, and the fresh water part only includes 540 H2O.

The prefect and pored graphenes are set as fixed and movable, respectively. Before the dynamic simulation, the system is optimized using the Smart algorithm with a force tolerance of 0.5 kJ/mol/Å, then a Langevin thermostat is used to control the temperature at 298 K. With a 1 fs time step, a 10 ps NVT (constant number of atoms, N; constant volume, V; constant temperature, T) dynamics is run to equilibrate the systems. Next, an NVE (constant number of atoms, N; constant volume, V; constant energy, E) is run more than 1 ns for the systems.

To quantify the flux of water, JW, and solute rejection ratio, R, we define JW and R as,

\[ J_W = \frac{18g \text{ mol} N_W(t)/N_A}{tS}, \quad R = \frac{(N_{Na}+N_{K})R_m}{N_w+(N_{Na}+N_{K})R_m} \]  

where \( \rho \) is the density of water, \( N_W(t) \) is the net number of water molecule through the pore, \( N_A \) is avogadro's number, \( N_{Na} \) and \( N_{K} \) are net number of Na+ and K+, and S is the area of a graphene sheet. \( R_m=20 \) is the molar ratio of salt and water in the seawater side.
Figure 1. Graphical representation of calculation model. (a) are the front view and side view of the modeling region, where two parts are divided by two graphenes and one part with fresh water and the other with seawater. The middle graphene with a pore, and the pore structure are displayed in (b), where N and F atoms are used to modify the graphene pores.

3. Results and discussions
If the pored graphene has solute rejection ability, the osmotic pressure (salinity in seawater is higher) can drive the fresh water into the seawater part. As the pored graphene is movable in the simulation, the equivalent pressure in the two parts can be guaranteed in the molecule migration process [15]. Figure 2 shows the net number changes of (a) water molecule and (b) Na\(^+\) and K\(^+\) ions in fresh water part with the increase of time for the systems of pure pore, F modified pore and N modified pore. We found the water number in fresh part is reduced and the Na\(^+\) and K\(^+\) and Cl\(^-\) ions are increasing, which is consistent with the forward osmosis.

In detail, with the increase of time, the changes of water number in 200-1000 ps are almost linear in all the three cases. That is due to the stable salinity difference between the seawater and fresh water parts in the simulation, although there is slight variation in concentration. It can also be found that Nw of the system with pure pore are higher than those with F and N modified pores, even the pore diameters are same. The reason might be the destruction of electroneutral C-C bond by F and N atoms. In the pure pore edge, C atoms are zero valent. However, F and N atoms have higher electronegativity, thus F and N atoms in pore edge are with negative valent [16-17], which may enhance the adsorption of the pore to water molecules. Similar trends of NNa+NK vs. t are found in Fig. 2(b). However, the values of NNa+NK are much smaller than Nw, which implying a solute rejection effects of the pores.
Figure 2. Net number changes of (a) water molecule and (b) Na+ and K+ ions in fresh water part with the increase of time for the systems of pure pore, F modified pore and N modified pore.

According to Eq. (1), we obtained the flux of water changing with time for the systems of pure pore, F modified pore and N modified pore, and the solute rejection ratio for the three pores, which are shown in Fig. 3 (a) and (b). Jw for pure pore, F and N modified pores are about 150, 90 and 60 L/cm²/h, indicating lower resistance of those pores. Meanwhile, the significant difference means the F and N modifications have obvious effects on the water permeation. Other than flux, solute rejection ratio, R, is also an important parameter for sea water desalination application. As shown in Fig. 3(b), R of pure pore is only ~0.6, representing a very weak solute rejection effect. However, R of F modified pore is larger than 0.7, and that of N modified case is 1 in all the simulation time. The use of F and N atoms remarkably increased solute rejection ratio, especially for the N modified case.

Figure 3. (a) Flux of water changing with time for the systems of pure pore, F modified pore and N modified pore, and (b) solute rejection ratio for the three pores.

To explain the effects of N and F modification to pores, we calculated the adsorption energy, Ea, of water molecule, Na+ and K+ in the pure pore, F modified pore and N modified pore, the approximate adsorption structure and Ea in the unit of kcal/mol are shown in Fig. 4. When bonding with C atoms, the valence of N is less than F by 0.35 [12], i.e. N atom is more negatively charged than F atom. Then, when molecules or ions through the pores, the charged N and F atoms have electrostatic force because the polar H₂O and +1 valences of Na+ and K+. Electrostatic effects is clearly shown in the adsorption energy values. For instance, Ea of pure pore for H₂O, Na+ and K+ are only ~2.42~1.22 kcal/mol due to the zero valent C atoms. However, the existence of F atoms increases Ea (see the absolute values) to ~17.6~13.7 kcal/mol. More remarkably, N atoms increase the Ea to ~29.1~48.6 kcal/mol, much higher than pure and F modified pores.

Higher Ea indicates higher energy barrier for molecules and ions through the pore. The values of Ea can explain Fig. 1 and Fig. 2 (a), where Nw, NNa+NK and Jw of pure pore are higher than F and N modified cases. Then, comparing Ea of H₂O, Na+ and K+ in a same pore can find the reason of...
selective rejection. In pure and F modified pores, $E_a$ of H$_2$O are similar with Na$^+$ and K$^+$, thus inducing lower R as shown in Fig. 3 (b). However, the high negative valences of N atoms significantly enhances $E_a$ of Na$^+$ and K$^+$, and the $E_a$ improvement for H$_2$O is lower. The large gap between ions and H$_2$O lead to the 100% solute rejection ratio for N modified pore. Our study indicates that pure graphene pore is not good candidate for water desalination, but using high electronegative atoms, such as N, modifying the pore edge can significantly improve the performance of graphene pore.

**Figure 4.** The adsorption energy, $E_a$, of water molecule, Na$^+$ and K$^+$ in the pure pore, F modified pore and N modified pore (kcal/mol), which is obtained by calculating the difference of the total energies of optimized structure and the structure of molecule or ion far from the pore. The negative sign of $E_a$ suggests that the adsorption process is exothermic.

### 4. Conclusion

In this study, we explored the possible application of porous graphene for sea water desalination using molecular dynamic simulations on the Forcite module of Materials Studio. COMPASS forcefield is used in all the simulations due to the satisfactory accuracy. The pore in graphene is 14.7 Å and F and N atoms are adopted as the pore edge to modify the chemical property. Water flux and solute rejection ratio are calculated and compared for the pure, F modified and N modified pores. Results show pure pore has the highest flux (~150 L/cm$^2$/h), and F modified and N modified pores only with fluxes about 90 and 60 L/cm$^2$/h. Although flux of pure pore is favorable, the solute rejection ratio is only ~0.6, much lower than ~0.7 and 1 of F and N modified cases. The adsorption energies of H$_2$O, Na$^+$ and K$^+$ in the three pores are obtained to explain the differences in flux and solute rejection ratio. Due to the negative valences of F and N, the adsorption energies in F and N modified pores are higher than the pure pore. Na$^+$ and K$^+$ have greater adsorption energies than H$_2$O in the N modified pore, which induces a higher energy barrier for Na$^+$ and K$^+$ through the N pore. Our study demonstrate that N modified porous graphene is a good candidate for sea water desalination.

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