



Water desalination across multilayer graphitic carbon nitride membrane: Insights from non-equilibrium molecular dynamics simulations

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ABSTRACT

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) is a novel two-dimensional, nitrogen-doped carbon material with various applications in many fields. Recently, $g\text{-C}_3\text{N}_4$ has exhibited excellent ability in separations. In this work, mechanisms of water and ion permeation across nanoporous $g\text{-C}_3\text{N}_4$ membranes with different pore diameters were studied using non-equilibrium molecular dynamics simulations. The water conduction rates derived from our simulations are in good agreement with previous experimental data. Due to the nanoscale confinement, we observe a stacked water cluster structure within the narrowest nanochannel. Similar structures are obscure as the increase of the nanochannel sizes. For desalination purposes, we find that the nanoporous $g\text{-C}_3\text{N}_4$ membrane with the desired opening may completely reject calcium and chloride ions, whereas sieve out monovalent cations with acceptable rejection rates (over 70%). This work provides molecular insight into the mechanism of water and ion transport through nanoporous $g\text{-C}_3\text{N}_4$, which strongly supports that this novel material is a promising candidate for developing selective membrane for water desalination.

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1. Introduction

Water covers three-quarters of the earth surface, but 98% of the water is saline, which is impractical to be used directly for life and industry [1]. Because of population growth and industrial development all over the world, the shortage of freshwater resources has become a serious issue for many countries [2,3]. Indeed, more than 2 billion people suffering from freshwater scarcity [2,3]. To address this imminent problem, scientists have paid great attention to developing practical seawater desalination technologies in the past few years [4–6].

Traditional desalination techniques, such as electrodialysis, distillation, and congelation, are difficult for large-scale application due to high energy consumption and production costs [4]. Compared with traditional techniques, membrane-based desalination technology has intrinsic advantages of low energy requirement, ease of operation, and high tenability [4–11]. Notably,

reverse osmosis (RO) membrane separation can remove particles of several Angströms. In an RO process, external pressure is used to overcome natural osmotic pressure so that water can pass through a semi-permeable membrane from a reservoir of seawater to that of freshwater, leaving salts in the feed reservoir. Accordingly, this technique has been well recognized as an applicable and promising solution to supply sustainable freshwater and address the water shortage challenge [12,13].

Two-dimensional (2D) materials were previously believed non-existent in a free state due to thermodynamic instabilities. The discovery of isolated graphene motivates the exploration of many unusual 2D materials and their fascinating properties. Recently, nanoporous 2D materials have attracted considerable interests in designing new classes of RO membrane due to atomic thickness, theoretically allowing high water permeability [5,14,15]. The most commonly investigated 2D materials include graphene, graphene oxide, hexagonal boron nitride, and molybdenum disulfide [4,7,16–23]. Although membranes for water treatment technologies are continuously being developed, the demand for improved membrane materials remains. It is necessary for scientists and engineers to seek for new, efficient materials to maximize the separation performance of the RO membrane.

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Amongst many carbon-based 2D materials, nitrogen-doped materials have received considerable attention during the past few years. The heterogeneous mixture of carbon and nitrogen atoms usually makes 2D materials with interesting electronic features. Because element ratio and atom arrangement may differ, this class of materials possesses many forms such as covalent triazine framework, $g\text{-C}_2\text{N}$, $g\text{-C}_3\text{N}_4$ [24–27]. Specifically, $g\text{-C}_3\text{N}_4$ has been widely used in photocatalysis attributed to its excellent visible-light response and good thermal/chemical stability [28–30]. Moreover, since the strength of the single bonds connecting carbon and tertiary nitrogen is weaker than the conjugated ones in tri-*s*-triazine units, it is feasible to precisely eliminate such units and produce uniform nanopores on the $g\text{-C}_3\text{N}_4$ monolayer [29,31]. It is interesting that the $g\text{-C}_3\text{N}_4$ membrane can be suitable for particle separation and even water desalination. Recently, Wang et al. reported the first application of $g\text{-C}_3\text{N}_4$ in a separation process [31]. They demonstrated that, concerning commercial membranes, the $g\text{-C}_3\text{N}_4$ membrane characterized by artificial nanopores (1.5–3.0 nm) exhibited better performance in separating organic molecules from the aqueous phase. To the best of our knowledge, there are few studies of the desalination process based on a $g\text{-C}_3\text{N}_4$ membrane to date.

It is often a challenge to illuminate detailed mechanisms of 2D-material-based separation experimentally because it is challenging to generate controllable nanopores in practical engineering. With the help of advances in high-performance computing, molecular dynamics (MD) simulations have provided an alternative way to characterize the transport process of different particles across nanoporous RO membranes from an atomic level. In this paper, we simulated the seawater desalination process and investigated the mechanisms of water and ion permeation through the nanoporous $g\text{-C}_3\text{N}_4$ RO membrane using non-equilibrium molecular dynamics (NEMD) simulations. We systematically scrutinized the confined water structures, which is strongly dependent on the dimension of the nanochannel. We discover that it exhibits various hydrodynamic behavior as water permeates across different size of nanochannels. Furthermore, our simulated water conduction agrees well with previous experimental data [31]. We also evaluated the desalination performance of the $g\text{-C}_3\text{N}_4$ membranes with appropriate nanoporous openings. We notice that the desired membrane can prevent calcium and chloride ions from permeating while retaining a significant amount of sodium and potassium ions. Our simulations provide direct theoretical evidence of promising application of nanoporous $g\text{-C}_3\text{N}_4$ membranes in separation and desalination.

2. Methods

A schematic representation of the simulation cell was illustrated in Fig. 1a. A nanoporous $g\text{-C}_3\text{N}_4$ membrane, which was frozen during MD simulations, separated the cell into two reservoirs. The dimension of the cell in the xy -plane was 7.25×6.27 nm. The thickness of the aqueous phase was 2.50 nm for the feed reservoir and 2.00 nm for the permeate reservoir. The thickness of the membrane was dependent on the number of $g\text{-C}_3\text{N}_4$ monolayers in the simulated cell. In this work, the distance between two neighbor monolayers was 0.33 nm, which is consistent with previous experiment measurement [32]. The dimension in the z -direction of the cell was eventually ranging from 4.50 to 5.82 nm (corresponding to from one to five $g\text{-C}_3\text{N}_4$ monolayers).

We filled two reservoirs with either pure water or electrolytic salt solutions. If reservoirs were filled with water, the density of the liquid was maintained at 0.99 g/cm^3 . The concentration of NaCl solution was set as the average concentration of seawater (0.55 M); the same concentration was applied to KCl and CaCl_2 solutions for

the convenience of comparison. The whole simulation cell contained approximate 6000 water molecules. Nanopores of different sizes were created by removing different numbers of tri-*s*-triazine units from $g\text{-C}_3\text{N}_4$ monolayers. The porosity of our model membranes resembled that of the real nanoporous $g\text{-C}_3\text{N}_4$ membrane, whose two neighbor nanopores were approximately 5 nm away from each other [31].

The molecular geometry and Mulliken partial charges of the $g\text{-C}_3\text{N}_4$ monolayer were determined by Gaussian 09 software at the B3LYP/6-31G* level of theory [33,34]. The coordinates of the optimized tri-*s*-triazine unit were tabulated in Table S1. Water molecules were represented by the TIP4P/2005 model, as suggested in previous studies [35–37]. Otherwise, the Lennard-Jones (LJ) parameters of the AMBER99SB force field were employed [38]. In the present study, we used the Lorentz-Berthelot combination rule to calculate the LJ interactions. The force field parameters used in this work were listed in Table S2.

All NEMD simulations were performed in the canonical ensemble (NVT) using GROMACS 4.6.7 package [39]. The periodic boundary conditions (PBC) were employed on all three dimensions. The temperature was maintained at 300 K using a refined velocity rescaling algorithm [40]. A 1.2 nm cut-off was used for calculating LJ interactions as well as for real-space electrostatic interactions of the particle mesh Ewald (PME) scheme [41]. Each NEMD simulation was performed for 21 ns with a time step of 2 fs. The first 1 ns was required to achieve a steady state flow; the remaining 20 ns was used for data collection. For each system considered, three parallel simulations with different initial particle velocities were performed in order to estimate statistical uncertainties. The results reported below were the averages of individual results from three replicas.

In order to maintain a steady state flow across the $g\text{-C}_3\text{N}_4$ membrane, a well-established algorithm was employed to generate a pressure difference along the z -axis [42]. In this method, a constant force, whose direction was perpendicular to the $g\text{-C}_3\text{N}_4$ membrane, was exerted to a subset of water molecules. It should correspond to a pressure difference of

$$\Delta p = nf/A, \quad (1)$$

where Δp is the pressure difference, n is the total number of water molecules in the subset, f is the constant force, and A is the area of the $g\text{-C}_3\text{N}_4$ membrane. The subset was defined as the region located at the top of the feed reservoir with a thickness of 0.5 nm in the z direction (see Fig. 1a). We updated the list of water molecules in the subset for every 10 ps, rather than every time step, to speed up simulations. A previous study has confirmed that the simulated results are insensitive to the choice of update frequency [35]. On average, the subset contained about 550 water molecules. All results we discussed in this work were obtained under a pressure difference of 100 MPa. Note that a high magnitude of external pressure is usually required in simulation studies so that we can observe desirable phenomena within an acceptable real-world timescale. The water permeability is still meaningful if it is normalized by dividing the magnitude of the applied pressure difference.

In this work, water structures within the nanochannel were revealed by investigating hydrogen bonds. With respect to a given O–H···X pair, where O–H represents oxygen-hydrogen covalent bond of one water molecule and X represents either oxygen of another water molecule or nitrogen at the nanopore rim, a hydrogen bond was defined as follows: (1) $d_{\text{OX}} < 0.34$ nm, (2) $d_{\text{HX}} < 0.24$ nm, and (3) $\theta_{\text{H-O}\cdots\text{X}} < 30^\circ$ [43,44]. In order to calculate the likelihood of different ions passing through the nanoporous $g\text{-C}_3\text{N}_4$ membrane, we calculated the potentials of mean force (PMF) for ions [45,46]. The PMF were obtained using the umbrella

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