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Water and salt permeability of monolayer graph-*n*-yne: Molecular dynamics simulations

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ABSTRACT

As new nanoporous materials, graph-*n*-yne membranes may have several potential applications in water purification and salt rejection. The simulation results from molecular dynamics (MD) method show that graph-*n*-yne membranes exhibit higher salt rejection and water permeability than conventional reverse osmosis membranes. In high salt concentrations, the salt rejection ratio of graph-4-yne and graph-5-yne declines with the augment of hydrostatic pressure, while water flux across graph-4-yne and graph-5-yne membranes increases. However, hydrostatic pressure does not affect the graph-3-yne membrane on the salt rejection. The negative charged graph-*n*-yne membrane can improve the water permeability and prevent ions from passing through the membrane.

1. Introduction

Today, the world faces a new challenge of efficiently gaining lots of freshwater from the ocean, because of a rapidly growing population of the world with environmental pollution and a shortage of freshwater resources. Seawater desalting is one of the most promising solutions to this challenge [1,2]. Currently, reverse osmosis (RO) is the energy-efficient desalination technique to date, with a record of 1.8 kWh/m^3 achieved in a commercial plant [2]. However, traditional seawater reverse osmosis (SWRO) membranes for water purification are still high cost [3]. This issue impedes the widespread use of desalination to relieve the shortage of freshwater in the world. Nanoporous materials were proposed as conventional RO membranes substitutes because of allowing water to fast flow across well-defined channels. This special property can be attributed to its cellular structure, ultrathin thickness, supernormal strength [4], high electrical conductivity and ultra-high thermal conductivity [5]. In recent years, carbon nanotube (CNT) membranes [6–8], boron-nitride nanotubes [9,10] and monolayer graphene [11–14] had been investigated on water purification. Molecular dynamics (MD) simulations suggested that nanoporous graphene and CNTs membranes are able to refuse cations and anions while permitting water molecules to pass [6,11–13]. Fresh water permeability is several orders of magnitude higher than conventional RO membranes. Moreover, it has been reported that nanoporous materials with partial charges have unusual impacts on the water and ions permeability. When partial charges were placed on the rim atoms of the CNT, Joseph [15] found that the ion occupancy increased significantly. Similarly, Majumder *et al* [16] placed negatively charged functional groups at the CNT tips, resulting in the flux of positive ions significantly increases.

Nevertheless, the size and numbers of nanopores in the graphene membranes have to be prefabricated and designed, because water molecules can't pass through perfect graphene membrane. Therefore, perfect techniques for precisely controlling the scale of nanopores in a large area membrane are required. Owing to the successful synthesis of graphdiyne in 2010 [17], one member of carbon allotropes, numerous studies concerning the physical and chemical properties of graphdiyne and its family (including graphyne, graph-3-yne, graph-4-yne, graph-5-yne) have sprung up [18–22]. Unlike graphene, graphyne and its family can be considered as a structure in which adjacent hexagonal rings are connected together by the acetylene linkages (−C≡C−)The presences of these acetylene linkages in such structures introduce the uniform and repeating triangular atomistic pores, with a van der Waals (vdW)

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opening. With increasing the number of acetylene linkages, the size of van der Waals (vdW) pores increases. Naturally, graphyne and its family possess well-defined nanopores with suitable size for highly efficient separation and purification. Jiao *et al* [23] and Cranford *et al* [24]had reported monolayer graphdiyne as a superior separation membrane for hydrogen purification, respectively. This singular property should be attributed to its structure naturally possessing the van der Waals (vdW) pores on the order of ~6.3 $Å^2$. Xue *et al* [25]had investigated α-graphyne, β-graphyne, γ-graphyne, graph-3-yne and graph-4-yne systems on ions (including Na^+, Cl^-, Mg^{2+}, K^+ and Ca^{2+}) rejection. It was concluded that fresh water throughput of α-graphyne, β-graphyne and graphyne-3 is about two orders of magnitude faster than that of conventional RO membranes. In 2014 [26], water molecules can't pass through monolayer (one atom thickness) graph-2-yne had been proved. Shortly after, monolayer graph-*n*-yne (n=3,4,5) had been studied by Kou *et al* [27] and reported that the salt rejection of the graph-3-yne membrane is the best and it can keep a higher water permeability than RO membranes.

In the present work, the operations of desalination of graph-3-yne, graph-4-yne and graph-5-yne membranes were implemented by employing MD simulations. Moreover, water permeability, salt rejection, water diffusion coefficients and the formation of hydration shells were investigated.

2. Methodology

The rectangular graph-*n*-yne (n=3, 4, 5) membranes were modeled, as illustrated in Fig. 1. Density-functional theory (DFT) method was utilized to optimize their geometric constructions (see the supporting information for details). Fig. S1 displayed the optimum structures. Table S1 showed the lattice parameters. SPC/E [28] water molecule model was used in the simulations. Water molecules were filled in the whole reservoirs. Subsequently, graph-*n*-yne membranes were embedded in the middle of reservoirs (Fig. S2), dividing the reservoirs into two equal parts. Sodium chlorides (NaCl) were added into the left bath, creating a high salt concentration. To investigate the impact of the charged membranes on the capacity of water purification of graph-*n*-yne, a neutral system (Fig. S5a) was modeled by embedding two graph-4-yne membranes with $\pm 0.2e$ on carbon atoms, which was located in the left ($-0.2e$) and right ($+0.2e$) edges of reservoir. All the parameters of systems were listed in Table S2.

In the work, molecular dynamics simulations were implemented via using LAMMPS package [29]. Followed minimizing the system through Langevin dynamics, isothermal-isobaric (NPT) ensemble was utilized to relax the initial systems. With enough relaxations in NPT ensemble (Fig. 1d), the potential energy of reservoirs reached to equilibrium state (Fig. S3). The equilibrium states were transferred into the canonical (NVT) ensemble (details in the supporting information). External force along the z-axis direction was applied to the oxygen atom of each water molecule in the reservoir to generate the hydrostatic pressure [30]. The desired hydrostatic pressure was controlled by $\Delta = pnf/A$ is the area of the graph-*n*-yne membrane. Every simulation was carried out for 4 ns with a time step of 1 fs. The data was collected every 10 ps for analysis.

3. Results and discussion

3.1. Analysis of water passing through membranes

Graph-3-yne, graph-4-yne and graph-5-yne reservoirs were composed of 1200, 1820 and 1700 water molecules and 27, 48 and 45 NaCl in the left bath, respectively. The corresponding salinity in the left bath of each reservoirs is 68 g/Kg, 79 g/Kg and 79 g/Kg, respectively, higher than the average value (35 g/Kg) in seawater of the world [31]. Desalination was performed under diverse hydrostatic pressure with high salt concentrations. Water flow across graph-*n*-yne membranes as a function of time is depicted in Fig. 2. The results show that the percentages of water passing though graph-4-yne and graph-5-yne membranes are more than that through graph-3-yne membrane. Additionally, the flow rate was calculated as the slope of each curve (Fig. S4), increasing with the augment of the number n in the graph-*n*-yne (Fig. 2a). This phenomenon was attributed to bigger van der Waals (vdW) in graph-4-yne and graph-5-yne than that in graph-3-yne. As shown in Fig. 2c and d, water flow rates across monolayer graph-4-yne and graph-5-yne membranes increase with the augment of hydrostatic pressure, in good agreement with the reported literature [25]. However, water flow rate across graph-3-yne membrane is indistinctively influenced by different hydrostatic pressures. All the results showed that water flow rates gradually slow down with the time passed by and eventually reaches to a saturation point, indicated that water molecules in the left bath have become “depleted” before the end of the simulation. VMD [32] software was used to carefully trace the trajectory of water molecules. It is interesting that water molecules in the left bath are not really depleted, bonding with ions (Na^+ and Cl^-) to form a hydration ion. In the hydration structure, ions (Na^+ and Cl^-) work as the core, while water molecules serve as the hydration shells. Since the size of the hydration ion is bigger than one water molecule, these hydration ions nearby the membrane lead to a jam for water molecules across the vdW pores.

To analyze the ‘jam’, the coordination numbers of H atoms and O atoms centered on Na^+ and Cl^- ions in bulk solution were also calculated. We adopted a cutoff radius of 3 Å nearby the radius of first coordination shell [33] to count coordination neighbors. Fig. 3a shows that the relationship of the coordination numbers of oxygen and hydrogen atoms around the ions with the increase of time. The results were collected from the reservoir embedded with graph-4-yne membrane under a hydrostatic pressure of 0 MPa. The data indicated the coordination numbers of hydrogen and oxygen atoms are constant. The average coordination number of oxygen and hydrogen atoms centered on Na^+ is 5.7 and 3.6, respectively. While the average coordination number of oxygen and hydrogen atoms centered on Cl^- is 0 and 6.4, respectively. Additionally, the orientation of water molecules in the first hydration shells of Na^+ and Cl^- ions is different (Fig. 3a). In the distribution of the orientation of water molecules induced by Na^+, 61.3% of oxygen atoms point to the Na^+, while 38.7% of oxygen atoms point away from Na^+ (hydrogen atoms point to the Na^+). In the distribution of the orientation of water molecules induced by Cl^- ion, 100% of hydrogen atoms point to the Cl^- ion. It is speculated that ~8 water molecules surround one Na^+ to form a stable hydration structure in the entire simulations. It has been proved [27] that the diameters of one water molecule, one Na^+, and one pore in the graph-3-yne are about 0.5 nm, 0.2 nm and 0.69 nm, respectively. Therefore, the diameter of hydration ions structures is far bigger than the pore size in the graph-*n*-yne membrane, especially in graph-3-yne system. In other words, the presences of hydration ions undoubtedly prevent water from passing through the graph-*n*-yne membranes.

Water flux across graph-*n*-yne membranes was quantitatively analyzed as shown in Fig. 3b. Owing to the linearity of each subsection (every 0.5 nm) in the water passing curves (Fig. 2a), the water flux per vdW pore across the graph-*n*-yne membrane was piecewise fitted in the each section. The results showed that the water fluxes (#/ns/pore) in graph-4-yne and graph-5-yne purification systems are higher than that in graph-3-yne systems,