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Controlled interval of aligned carbon nanotubes arrays for water desalination: A molecular dynamics simulation study

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HIGHLIGHTS

- A fast water filtering method by aligned carbon nanotubes arrays (CNTA)
- Improvement of water permeation by the optimization of aligned CNTA membrane
- Providing a new idea to utilize CNTAs membrane for desalination

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ABSTRACT

Development of high-efficiency and low-cost seawater desalination technologies is critical to solve the global water crisis. Here we report a fast water filtering method with high salt rejection by aligned carbon nanotubes arrays (CNTA). In this study, the effect of interval on the desalination of CNTA was investigated by molecular dynamics (MD) simulation, and our simulation results have shown that water permeation and salt rejection could be greatly improved by the optimization of aligned CNTA membrane. High water permeation could be achieved by specific gap size between highly ordered CNTA, meanwhile, due to high free energy barrier for Na^+ passing through the interval of CNTA, high salt rejection could also be achieved. Our study possibly provides a new idea to utilize CNTA membrane for desalination.

1. Introduction

Although nearly 70% of the earth is covered by water, most of water could not be utilized directly since it is too salty for human consumption or is locked up in ice and snow [1,2]. The growing population in world will have more demand for fresh water in future [3]. To solve the problem of fresh water shortage, desalination of salty water provides one way of boosting fresh water supplies [4,5]. However, the cost of desalination for obtaining fresh water is still very high [6], therefore, cheap desalination method with high efficiency should be developed.

Nanotube and nanopore have demonstrated their promising applications in high-efficiency and low-cost desalination [5,7–14]. Therein, carbon nanotubes (CNTs) have shown excellent water permeation in theoretical [15,16] and experimental studies [17–21]. Hummer et al. found that unfunctionalized CNTs might be exploited as unique molecular channels for water and protons [15], which has been confirmed by experiments [18]. Araki et al. found that the desalination efficiency of CNTs could be improved by adding polyamide [22]. The functionalized CNTs have also shown excellent desalination performance recently [23–27]. Especially, the successful fabrication of aligned CNTs with membrane takes a solid step for practical application of CNTs in desalination [28–30]. Corry reported that the unfunctionalized aligned CNTs could achieve ca. 11.1 L/(cm^2·day·MPa) fresh water with 2.5×10^{11} pores per cm^2 [31]. By using different temperatures in sea water and fresh water, Wu et al. reported that a 10 cm^2 CNTs membrane with 1.5×10^{13} pores per cm^2 could produce freshwater with a flow rate of 186.48 L/day [32]. These studies have greatly enhanced our understanding on applications of aligned CNTs for desalination.

There are lots of factors including radius of CNTs and interval between CNTs etc. could affect the permeation of ion and water molecules, but the mechanism of separation at the molecular level is still obscure. In addition, the thermodynamics and dynamics of water molecules

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Table 1
Details of performed simulations.

Size	Number of atoms	Diameter (Å) C-C internal	NaCl concentration (M)	Simulation time (ns)
Single CNT				
CNT (5, 5)	16,272	6.6	0.5	50
CNT (6, 6)	16,234	8.1	0.5	50
CNT (7, 7)	16,205	9.3	0.5	50
CNT (8, 8)	16,190	10.9	0.5	50
Size	Number of atoms	Distance (Å)	NaCl concentration (M)	Simulation time (ns)
Aligned CNTs				
CNTA (6, 6, 1)	11,560	9.1	0.5	50
CNTA (6, 6, 3)	12,569	11.1	0.5	50
CNTA (6, 6, 5)	13,964	13.1	0.5	50
CNTA (6, 6, 6)	14,155	14.1	0.5	50
Size	Number of atoms	Distance (Å)[a]	NaCl concentration (M)	Simulation time (ns)
PMF calculation				
CNTA (6, 6, 5)	13,964	13.1	0.5	5 × 70
CNTA (6, 6, 6)	14,155	14.1	0.5	5 × 70

[a] Distance represents the distance between the center-of-mass of two most adjacent CNT in *x*–*y* plane. PMF represents potential of mean force.

passing through interval of CNTs at molecular level are also very difficult to explore in experiment, which limits the design and application of water permeable CNTs membrane for desalination. Therefore, in this study we try to understand and answer these fundamental questions via a series of molecular dynamics (MD) simulations on the desalination process of aligned CNT arrays. Although there are a few of reports on similar modelling and simulations [15,16,31], these modelling and simulations are mainly focus on the effects of charge, radius and functionalized groups of CNT etc. on the desalination. To the best of our knowledge, the influence of the interval of CNTA for the desalination has not been studies both in experiment and simulations. Our aim is to find a well-defined interval of CNTs for excellent performance on desalination with high salt rejection and high filtration efficiency. In this study, CNTA was modeled as the permeable membrane. The effects of the arrangement pattern of CNTs in aligned CNTs for desalination were investigated by MD simulations. Our results demonstrated that water molecules could spontaneously move across the interval between CNTs. By utilizing the interval between CNTs, it exhibits promising high-efficiency water permeation. At the same time, high salt rejection could also be achieved while maintaining the high-efficiency water permeation.

2. Model and simulation

In this study, all simulations were divided into three parts. In the first part, the water permeation and desalination on single CNT were studied. Based on these results, simulations of water and ions permeation in CNTA were performed in the second part. To investigate the mechanism of water permeation in CNTA, the potential of mean force (PMF) of water molecule and ions passing through CNTA were calculated in third part. All simulation details were listed in Table 1.

2.1. Model construction

The 50 Å long CNTs with different diameters varied from armchair (5, 5), (6, 6), (7, 7) to (8, 8) were constructed by visual molecular dynamics (VMD) [33]. The axial direction of CNT was set along *z* axis. The CNTs were immersed in the water molecules box with the dimensions of 40 × 40 × 100 Å^3. NaCl with concentration of 0.5 M were added into the water box to investigate the salt exclusion property of CNT. The aligned CNTs were modeled following the technique of Zhu and Schulten [34]. Based on the results of single CNTs, CNT (6, 6) was select to construct aligned CNT arrays (CNTAs). 9 CNTs (6, 6) with length of 50 Å were hexagonally packed in a regular arrangement, as shown in Fig. 1. Different with their model, the interval between aligned CNTs were thought to be penetrated by water molecules and ions in our simulations. Herein, the interval size (*S*) were defined as follows:

$$S = D - d \quad (1)$$

S is the interval size, *D* is the distance between the centers of two neighboring CNTs (6, 6) in *x*–*y* plane, and *d* is the diameter of CNT (6, 6) in *x*–*y* plane. Aligned CNTs with different interval size varied from 1 Å to 6 Å were constructed, as seen in Fig. 1. These systems are named as CNTA (6, 6, *S*), which is dependent on the interval size (*S*). All different aligned CNTs were immersed into the water box with TIP3P model water molecules, and NaCl with concentration of 0.5 M were added into the water box. The box size in *z* dimension is 100 Å, while the box size in *x*–*y* dimensions depends on the systems. All systems in our simulation were listed in Table 1.

2.2. Simulation details

The parameters of carbon atoms in CNT were taken from our previous work [35–37] and other groups [38,39] in carbon materials (σ_{CC} = 3.85 Å, ε_{CC} = 0.439 kJ/mol), and all atoms in CNTs were set to be neutral. The parameters for Na^+ and Cl^- were taken from CHARMM27 force field. The parameters of the Lennard-Jones potential for cross-interactions (CNT–water, CNT–ion) between nonbonded atoms were obtained from Lorentz-Berthelot combination rule. All carbon atoms in CNTs were frozen during the simulations. All simulations were performed by GROMACS-4.6.3 package [40]. GROMACS is an open-source and free software. It is initially developed by the scientists in Groningen, Netherland under the support of research funding. Currently the development teams of GROMACS are mainly located in Sweden. For carrying out an MD simulation in GROMACS, one has to prepare at least three files: pdb, top and mdp files. Pdb file contains the information of coordinate of all atoms in the system and top file contains the information of force field parameters of all bonded and non-bonded interactions. All parameters that control the protocol of energy minimization or MD simulation are recorded in mdp file.

After energy minimization and pre-equilibration of the system, we performed a constant volume and temperature (NVT) molecular

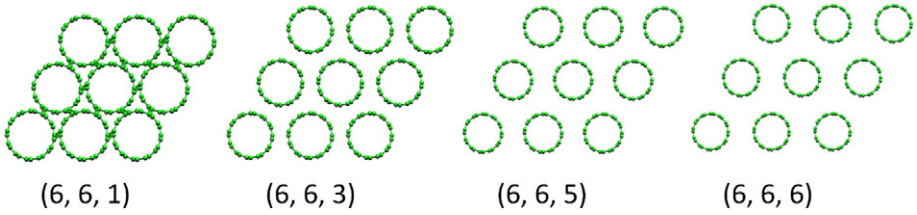

Fig. 1. Schematic of aligned CNTs (6, 6) with different interval between CNTs from top view. These systems are named as CNTA (6, 6, *S*), where *S* is the interval size (please see details in methods section). The carbon atoms in CNTs were shown in green CPK model, and water molecules as well as ions were not shown for clarity.