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Biomimetic modification of large diameter carbon nanotubes and the desalination behavior of its reverse osmosis membrane

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HIGHLIGHTS

- Inner middle of (10, 10) CNTs was modified to imitate the biological channel.
- Lowest water flux of modified (10 10) CNTs is 9 times of traditional RO membrane.
- 100% salt desalination could be achieved with high water conductance.
- One more group (COO^-, $CONH_2$, OH) at the edge will increase both desalination and water flux.

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ABSTRACT

Based on the fact that wide diameter carbon nanotube (CNTs) has higher water conductance and lower cost than narrow one, this paper built a set of RO membranes with modified 1.35 nm diameter CNTs (10,10) and calculated their desalinating properties by molecular dynamics simulations. Inspired by the structure of biological membrane which has perfect ion selectivity, different charged and polar groups ($CONH_2$, NH_3^+, COO^-, OH) were added to the interior of CNTs. The potential of mean force (PMF), conductance and axial density distributions of water and ions in CNTs were examined under hydrostatic pressure. Results showed that water flux of 1.35 nm diameter (10,10) unmodified CNTs was about 3 times of 1.1 nm diameter (8,8) CNTs (Chen S. and Corry B., 2009) [1]. Compared to CNTs with functional groups at entrance, water flux of CNTs with modified groups in the interior decrease slightly, while salt rejection greatly improved. With certain number, type and position of functional groups ($CONH_2$, NH_3^+, COO^-), 100% salt rejection could be achieved without affecting water conductance evidently. Water flux of 100% salt rejection modified CNTs was from 146% to 167% of unmodified (8,8) CNT (Chen S. and Corry B., 2009) [1]. Compared to four functional groups (COO^-, $CONH_2$, OH) in the interior, one functional group added at entrance and four functional groups added in the interior could obtain both higher desalination and high water conductance.

1. Introduction

Although 71% of the earth is covered by water, most of the water is saline or locked up in ice and snow. Only 2.5% of freshwater can be directly used for human consumption and agriculture [2]. With the development of industry and population expansion, the condition is worsening. To face the challenge of the future, desalination provides an accessible way to increase fresh water supplies.

Carbon materials are used widely in many fields due to their remarkable properties. For example, 3D nanoporous graphitic carbon with high surface has a promising future as catalyst support in electrocatalysis and fuel cells [3]. PtDs on genomic-double-stranded-DNA/reduced-grapheneoxide (gdsDNA/rGO) displays very high oxygen reduction reaction, which would be applied in next generation electrochemical energy devices [4]. While CNTs have attracted much attention since their discovery because of their excellent structural, mechanical and electronic properties [5], its hydrophobic pore is similar to biological ion channel and also owns intrinsic ion selectivity. Some simulation has indicated that water could permeate relatively narrow CNTs [6]. Furthermore, flow rate has been found to be unexpectedly high [7] and almost independent of the length of CNTs [8]. Some simulations [8] have found that only a single file chain of water can pass through the narrow nanotube (5,5) and (6,6), whereas double chains were seen in (7,7) and quadruple chains were seen in (8,8). That means more massive flow rate of water can permeate the larger diameter CNTs in the form of “water chain”. Water flux of (6,6) CNTs is about two times of that of (5,5) CNTs, water flux of (8,8) CNTs is also two times of (7,7) CNTs. Since water flux of unmodified (8,8) CNTs is nine times of the traditional membrane [9], it can be expected that water flux of larger diameter CNTs (such as (10,10)) may be more than ten times of that of traditional membrane.

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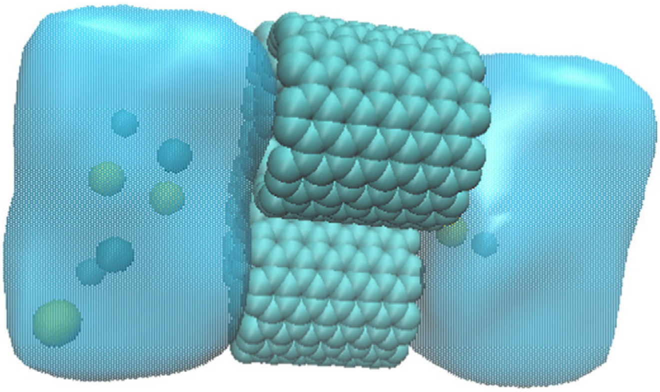

Fig. 1. A model of simulating system, which is formed by hexagonally packing 4 CNTs in a periodic cell and immersing in a solution of NaCl in water.

The ability to fabricate carbon materials is improved rapidly. The present CVD approach is capable of producing large quantities of GNSs with high purity [10] and the graphene films could have the possibility to grow in low vacuum ($5 \times 10 - 1$ Pa) at relatively low temperatures [11] (≤750 °C) by the research of Rajanish N. Tiwari and Jitendra N. Tiwari. Wai-Fong Chan [12] developed a synthesis method used for large scale manufacture of CNT membranes. Ryu [13] provided a new method to produce the carbon nanotube with high transition efficiency under a mild condition with a relatively lower temperature and pressure than those in conventional gas phased-methods without using costly equipment, thereby cost-effectively producing the carbon nanotube in large quantities. Therefore, the cost of manufacturing larger diameter CNTs is hopeful to decrease in the future.

By the research of Chen Song [1] water faces low PMFs (under 1.5 kcal/mol) both in narrow nanotubes (5,5) and (6,6) and wide nanotubes (7,7), (8,8) and (9,9). However, ions can face high PMFs of about 20 kcal/mol more in narrow nanotubes (5,5) and (6,6) and 6 kcal/mol lower in (8,8) and (9,9). These studies have demonstrated that ions can pass through wide nanotubes such as (8,8) and (9,9) with improvement of water permeation. Peter and Hummer [14] found that Na^+ can pass through (10,10) CNTs spontaneously, while Cl^- can't. Another simulating work by Ben Corry [9] also demonstrated that for (8,8) CNTs, Na^+ faced lower free energy barriers than Cl^- with its smaller radius and can pass through nanotubes. Only the inclusion of positive charges and a large number of negative charges at entrance managed to refuse the Na^+ ion [10]. Thus, it is more difficult to achieve a high salt rejection to the large diameter nanotubes (10,10) by adding functional groups at entrance.

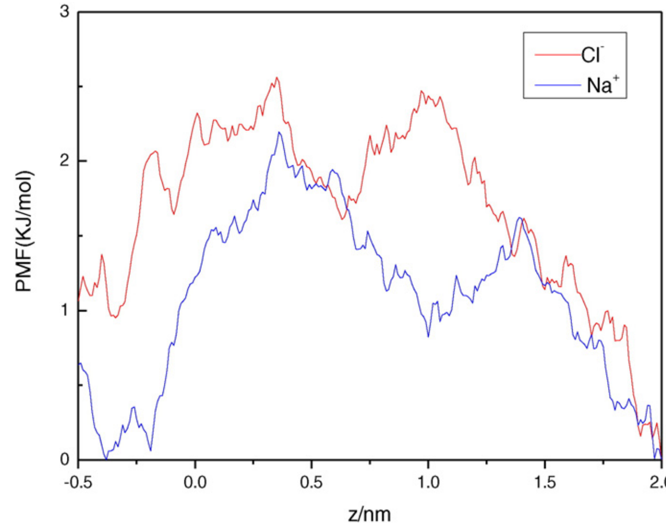

Fig. 3. PMF profiles for Na^+ (blue lines), Cl^- (red lines) within unmodified CNTs, the CNTs are located from $z = 0$ to $z = 1.4$ nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Recent studies have suggested that the hydrophobic pores of CNTs is similar to the water channel of protein Aquaporin-4 [15]. Aquaporin-4 is the predominant water channel to repel all of the ions inclusion protein. The morphology of Aquaporin-4 channel was dumbbell [16]. The throat of the channel is composed of four amino acids — His 182, Arg 197, Phe 58 and Cys 191 [17] in the channel. The diameter of the throat is only 0.28 nm which can prevent ion from passing through. The hydrophilic groups distributed in the channel could also decrease the barrier of water in the channel.

Some simulations indicated that functional groups added interior of CNTs could reveal some interesting phenomena. Zhu Yudan [18] discovered that –COOH groups modified interior of CNTs could control the flow direction of water molecules. Zheng [19] found that adding –COOH functional groups to the interior of CNTs could alter the whole hydrophobic wall into hydrophilic one and found that fluid movement through hydrophilic CNTs was faster than that through hydrophobic ones. Allen and co-workers [20] found that ion diffusion was higher in hydrophobic channels than that in hydrophilic ones for large pores (diameter > 0.4 nm). Gong Xiaojing [21] studies suggested that carbonyl oxygen atoms modified inside the (9,9) CNTs were capable to separate K^+ and Na^+ similar to KcsA channel.

Based on the above conclusions, interior modification of CNTs is hopeful to be applied in water desalination. However, is it feasible in

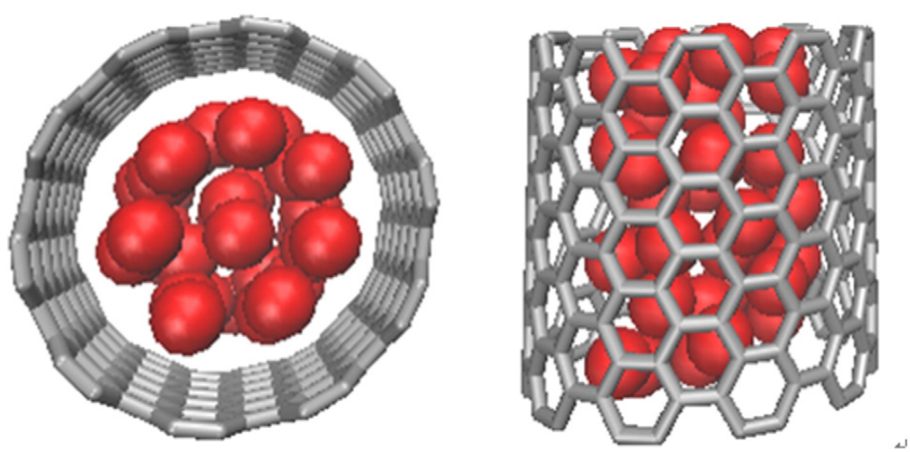

Fig. 2. Eight water chains in 1.4 nm diameter (10 10) carbon nanotube, the red ball represent O^{2-}.