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Chemistry

Italicized carbon nanotube facilitating water transport: a molecular dynamics simulation

Jipeng Li · Xian Kong · Diannan Lu · Zheng Liu

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Abstract While the preferential movement of water inside carbon nanotube is appealing for water purification, our understanding of the water transport mechanism through carbon nanotube (CNT)-based membrane is far from adequate. Here we conducted molecular dynamics simulations to study how the alignment of the CNTs in the membrane affects the water transport through the CNT membrane. It was shown that compared to the conventional CNT membrane where the alignment of CNTs was vertical to membrane surface, the "italicized CNT membrane" in which the contact angel between membrane surface and the CNT alignment is not 90° offered a higher transmembrane flux of water. The expanded exposure of more carbon atoms to water molecules reduced the energy barrier near the entrance of this italicized CNT membrane, compared to the vertical one. For water flows through the italicized CNT membrane, the Lennard-Jones interaction between water and nanotube as function of central path of the CNT changes from "U" to "V" pattern, which significantly lowers energy barrier for filling water into the CNT, favoring the water transport inside carbon nanotube. Above simulation indicates new opportunities for applying CNT in water purification or related fields in which water transport matters.

Keywords Carbon nanotube · Water desalination · Molecular dynamics simulation

J. Li · X. Kong · D. Lu (✉) · Z. Liu (✉)
State Key Laboratory for Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
e-mail: ludiannan@mail.tsinghua.edu.cn

Z. Liu
e-mail: liuzheng@mail.tsinghua.edu.cn

1 Introduction

Since Hummer's pioneer work showed the water flux inside a carbon nanotube (CNT) could be three to four orders of magnitude higher than that expected from macroscopic hydrodynamics [1], the molecular dynamics simulations of water flow inside different types of CNTs [2–4] and their derivatives [5–7] have been extensively conducted, showing an attractive potential of CNT-based membranes in desalination. The enhanced water flux is attributed to a velocity "jump" in the depletion region at the water–nanotube interface, as well as water orientation and hydrogen bonds at the interface [8–11].

It is established that nanotube properties such as surface hydrophobicity, charge, composition, shape, and the liquid surrounding the entrance of CNTs significantly affect water transport behaviour. Hummer et al. [1] studied the effect of water–carbon interaction on filling water into pristine CNTs and showed the apparent nonlinear dynamics of filling or emptying water molecules the CNTs was a function of the "hydrophobicity parameter", leading to the transitions from empty to bi-stable filling and full filling of water inside CNT. Aluru and co-workers [12] showed that water flow and transport dynamics are dominated by factors including pore charges, electric fields induced by biomolecules, and the composition of the nanotubes. Raghunathan and co-workers [13–15] firstly simulated the osmotic flux through uncharged, positively charged, and negatively charged semipermeable membranes and found the osmotic flux reached the minimum in an uncharged pore while the maximum in a negatively charged pore. To discover molecular mechanisms of water transport, Granick and Bae [16] and Falk et al. [17] simulated effects of the hydrophobicity of nanotube walls and the smoothen energy landscape on the water flux. Corry [11] showed that

a CNT of 0.9 nm in diameter could give a nearly 100 % salt rejection. In our previous work [18] on the water transport across a charged single-walled CNT (SWCNT), we found the water chains inside the charge nanotube exhibit bipolar properties, leading to inhibition of flipping of water chain and thus enhancement of water flux. In addition, a negatively charged SWCNT accelerated water transport by tuning the single-file flow from a "hopping" to a "continuous" mode, thus decreasing the energy barrier.

Great efforts have also been directed to the fabrication of CNT into membranes for water treatment. Experimentally, Lee et al. [19] achieved a water permeability of 30,000 LMH bar^{-1} for CNT with average diameter of 4.8 nm. This is, however, less than that predicted by molecular dynamics simulation. We also examined the water transport in differently shaped CNTs, such as Y-shaped and "honeycomb" [20]. More recently, Qiu et al. [21] studied the bending of nanotube and observed an accelerated flux of water through CNTs.

It is established that the entrance structure of CNTs also affects water transport [22]. A traditional method is to chemically modify the entrance of CNTs so that electrostatic interaction and stereo-hindrance are employed simultaneously for ion rejection. However, as simulated by Corry [11], an enhanced ion rejection by CNT surface modification is obtained by the expense of compromise of water flux, due to counter-ion occlusion at the entrance of the CNT. More recently, Chan et al. [23] simulated a zwitterion-modified CNT composite membrane and obtained a higher ion rejection and a higher water flux.

Cross-flow is the regular pattern for membrane separation, in which the transmembrane flux is perpendicular to the bulk flow. By far the CNT-based membrane processing is also based on the cross-flow pattern, i.e. the CNT is aligned vertically to the membrane surface. It thus comes to our interest to examine the effect of the CNT alignment on the water transport. Thus, two types of CNT membrane were proposed and simulated. The first one was the conventional CNT membrane in which the CNT is aligned vertically to the membrane surface and thus referred as the vertical CNT membrane hereafter. The second one was the italicized CNT membrane in which the CNT alignment is not vertical to the membrane surface. There are two major differences between above-mentioned CNT membranes: the first was the entrance structure and the second was the orientation of water chain inside CNT. The different water transport performances of above-mentioned CNT membrane were compared, and the underpinned mechanism was discussed.

2 Models and simulation methods

2.1 Models

CNT membrane composed of one CNT(10,0), and two graphene plates were generated using Carbon Nanostructure Build Plugin of VMD [24]. Figure 1 gives all models of CNT membrane used in the present work. Figure 1a, b gives the vertical CNT membrane and italicized CNT membrane, respectively. For all these models, the diameter of CNT is 0.782 nm, which permits only one water chain inside nanotube. A simple point charge-extended (SPC/E) model was used for water molecules, due to its excellent description for bulky water. The Lennard-Jones (LJ) parameters for the carbon atoms are $\sigma = 0.355$ nm and $\varepsilon = 0.086$ kcal/mol, and those for the oxygen atoms are $\sigma = 0.3166$ nm and $\varepsilon = 0.152$ kcal/mol, which are adopted from Hummer's previous work [1].

Here we defined the length of central path (λ) shown in green dashed line in Fig. 1. In order to examine solely on the effects of the entrance structure on the water transport

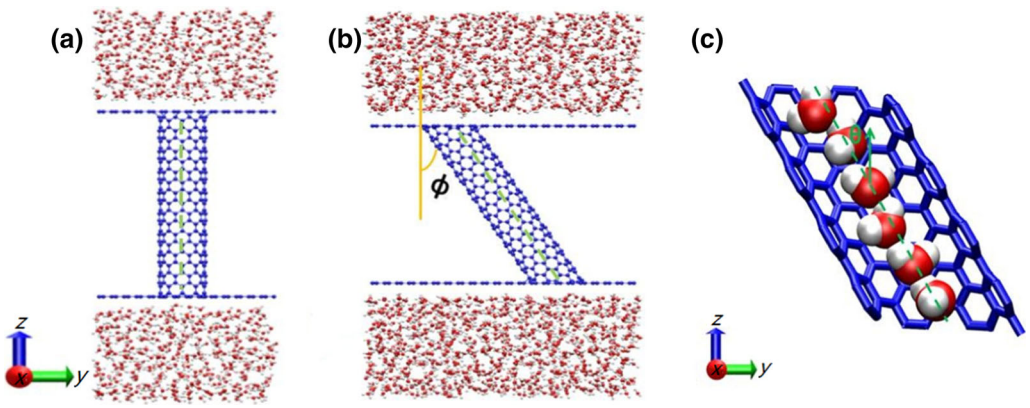

Fig. 1 Different models of CNT membranes. **a** Vertical CNT membrane; **b** italicized CNT membrane; and **c** representation of the water dipole inside the CNT. θ is the angle between water dipole and λ

in different CNT membranes, here the λ is fixed as 3.824 nm for both the vertical and the italicized CNT membranes. The angle between λ and z-axis is defined as ϕ, which reflects the orientation of CNT along z direction.

Vertical CNT membrane—there are 1,058 carbon atoms and 1,003 water molecules in simulation box, which has dimension of 3.1 nm × 3.1 nm × 7.2 nm. Italicized CNT membrane—CNT was tilted between two graphene sheets. Adjust the distance between two graphene sheets to make sure the central path was 3.824 nm. Then the CNT atoms outside the sheets were removed to make the surface of CNT smooth. When the ϕ was tuned to 0°, the italicized CNT membrane became vertical CNT membrane. The size of box and the number of atoms differed with different angles ϕ. More information is shown in Table 1.

2.2 Simulation methods

All parameters of carbon atoms were adopted from CHARMM27 force field, while water is presented by SPC/E model. MD simulations were performed using GROMACS [25] simulation package. VMD was used to visualize the system. NVT simulations were conducted with temperature of 300 K which were well controlled using Nose–hoover methods [26]. Periodic boundary condition was applied in all directions. To prevent deformation of CNT, each carbon atom was fixed during all the simulation. LJ potential was shifted smoothly from 0.9 to 1.2 nm with cut-off of 1.2 nm. Particle mesh Ewald (PME) [22, 27] calculation was used for the treatment of the electrostatic interaction with cut-off of 1.2 nm. The LINCS algorithm [28] was used to maintain the geometry of the water molecules. The equilibrium density of the bulk water was around 1.0 g/cm^3. Unless otherwise stated, calculated trajectories were collected every 1.0 ps. All simulations underwent 1,000-step energy minimization before simulations. Each simulation ran 200 ns with a time step of 2 fs. The first 40 ns was discarded, and the rest 160 ns was used for analysis.

Table 1 Detailed information of italicized CNT membranes

ϕ (°)	L_x (nm)	L_y (nm)	L_z (nm)	Number of carbon atoms	Number of water molecules
73	2.8	8.0	5.2	1,898	2,615
60	2.8	6.8	6.0	1,656	2,265
45	2.8	5.7	7.0	1,494	1,923
30	2.8	4.7	8.0	1,254	1,827
15	2.8	3.7	9.0	1,111	1,600

2.3 Analytical methods

When one water molecule penetrated into one entrance of CNT and exited through the opposite outlet, we considered this water molecule to have "flowed through" the CNT. Water flux was defined as the average number of water molecules per nano-second flowing through the CNT. There were no pressure drops from osmosis pressure or other pressure difference during all simulations, i.e. water flow through the CNT was solely achieved by free diffusion.

The description of angle (θ) between the water dipole inside the CNT and the λ direction is shown in Fig. 1c. The value of θ reflects the orientation of water molecules inside CNT. Hydrogen bonds between water molecules inside the CNT were determined with cut-offs for the acceptor–donor-hydrogen angle, which is less than 30°, and the hydrogen-acceptor distance, which is less than 0.35 nm.

The one-dimensional (1D) diffusion coefficient (D) along central path of CNT is calculated according to Einstein equation, as shown in Eq. (1).

$$D = \lim_{t\to\infty} \frac{1}{2t} \left\langle |r_i(t) - r_i(0)|^2 \right\rangle, \quad (1)$$

where $r_i(0)$ is the position of oxygen of water at initial time ($t = 0$) and $r_i(t)$ is the position of oxygen of water at time t.

3 Results and discussions

3.1 Water flux through different CNT membranes

Firstly, we simulated the water flux through a vertical CNT membrane ($\phi = 0°$) and italicized CNT membranes at $\phi = 15°$, 30°, 45°, 60°, and 73° as shown in Fig. 1. The results are shown in Fig. 2.

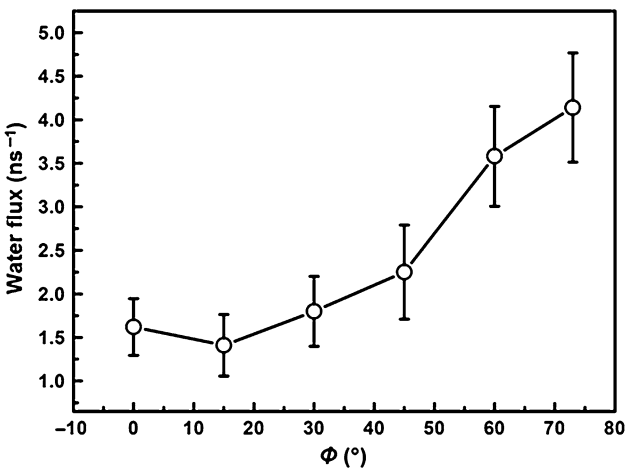

Fig. 2 Water flux through italicized CNT membranes at various values of ϕ (°)

As shown in Fig. 2, the average of water flux through the vertical CNT is about 1.6 water molecules per nano-second. Due to no pressure difference or osmosis difference between two sides of membrane, there is no net water flux. Here, "average of water flux through the CNT" means total number of water molecules per nano-second flowing through from both ends of CNT. That is, the total number of water molecules through the CNT is the summation of water number passing through from upper membrane to bottom membrane and water number in opposite direction. As shown in Fig. 2, the increase in ϕ from 0° to 15° appears no effects on the water flux that is around 1.6 water molecules per nano-second. The further increase in ϕ to 73° leads to a monotonous increase in water flux up to 4.1 water molecules/ns. These results imply a new possibility of enhancing water transport by tuning the alignment of CNTs in CNT membrane, in addition to chemical modification of CNTs [11, 18].

It is interesting to note that, different from our previous simulation studies of water transport in charged CNT, the changes of CNT alignment inside membrane will not result in the accumulation of ions and thus get rid of the blockage of CNT channels [18, 20]. This suggests the opportunity of an improved desalination using CNT with well-designed entrance structure.

3.2 Free energy analysis of water along flow path at different ϕ

Figure 2 shows that when water flows through the italicized CNT membrane, the water flux also increases when the ϕ increase from 0° to 73°. Here we calculated free energy as function of λ at different ϕ, as shown in Fig. 3.

It is shown in Fig. 3a that the free energy profile inside the italicized CNT membrane is different to that of the vertical CNT membrane. Firstly, with the increase in $\boldsymbol{\phi}$, the area of the high energy status inside CNT is reduced. This favours the transport of water molecules towards italicized CNT membrane. Secondly, with increase in $\boldsymbol{\phi}$, as shown in Fig. 3b, the free energy barrier, i.e. the free energy difference of water molecules entering into CNT at the entrance of CNT decreases, which favours water "enters" the CNT.

3.3 The interaction between water and CNT along flow path at different ϕ

To account for the changes of free energy inside the italicized CNT membrane, we calculated the changes of LJ potential between one water molecule and CNT when moving water molecule along flow path λ. The results are shown in Fig. 4.

It is shown in Fig. 4 that at $\phi = 0°$ which is the case of the vertical CNT membrane, the LJ interaction between water and CNT quickly increases when water moves into nanotube. The curve of LJ interaction exhibits a "U" pattern. The further increase in ϕ value changes the LJ profile from the "U" pattern to a "V" pattern. Above results indicate the decrease in the interaction between water molecules and the italicized CNT facilitated not only the movement of water inside nanotube as shown in our previous studies and reports from others [18, 21, 24], but

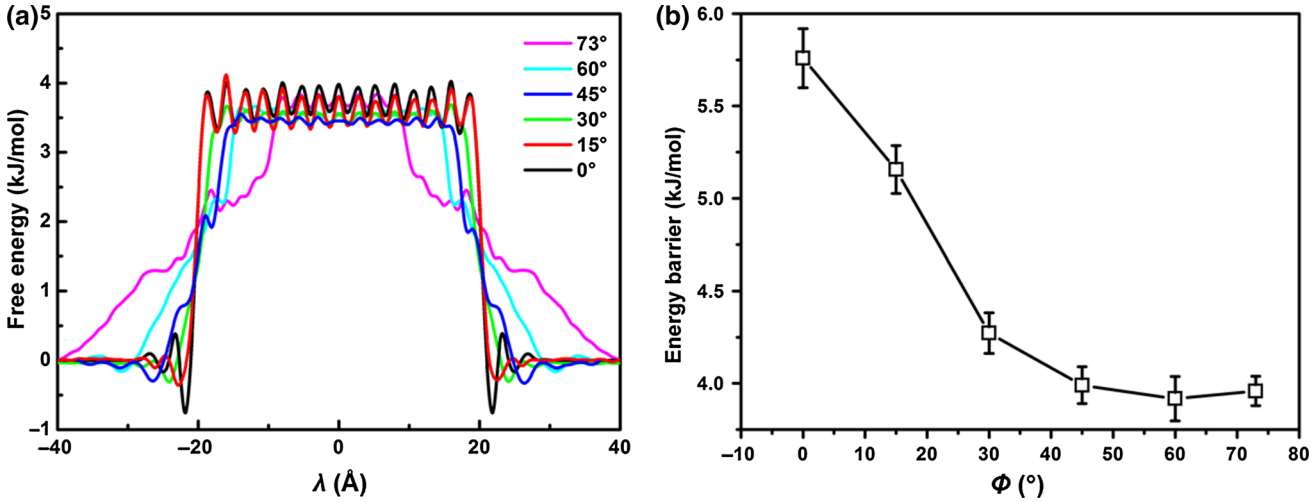

Fig. 3 Free energy analysis of water inside italicized CNT membranes. **a** Free energy profiles along the λ inside italicized CNT membranes; free energy is calculated by $-k_BT\ln(p)$, where p is probability of water molecules occupied along the λ direction. **b** Free energy barrier, which is calculated according to free energy difference between highest free energy of water inside nanotube and lowest free energy of water outside nanotube

also reduced the energy barrier of water filling into nanotube.

3.4 Water orientation inside italicized CNT membranes

We further studied the dipole orientation of water inside italicized CNT membranes as shown in Fig. 5.

It is shown in Fig. 5 that for the vertical CNT ($\phi = 0°$), angle of water dipole and λ have two concentrated ranges, i.e. 40° and 140°. When the ϕ increases, the orientation of water dipole has broader distribution. When the $\phi = 73°$, for example, angle of water dipole and λ mainly at 40° and 140° in the middle of nanotube ($|\lambda| < 4.0$ Å), while that in near two ends of CNT ($|\lambda| > 4.0$ Å), are ranged from 20° to 160°, favouring water filling.

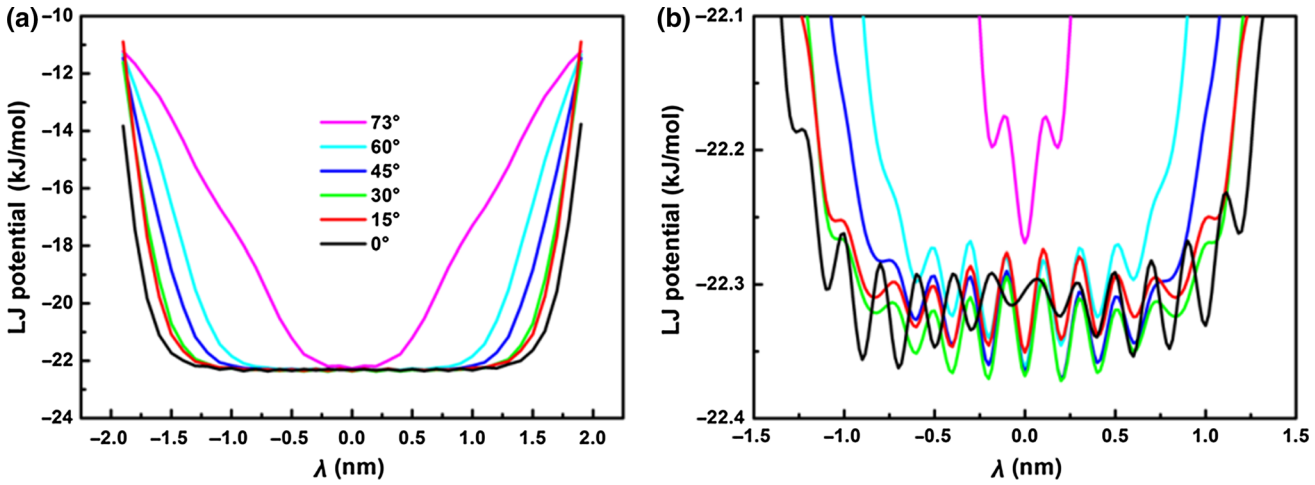

Fig. 4 LJ interaction between water and italicized CNT membrane. **a** Full view and **b** local view

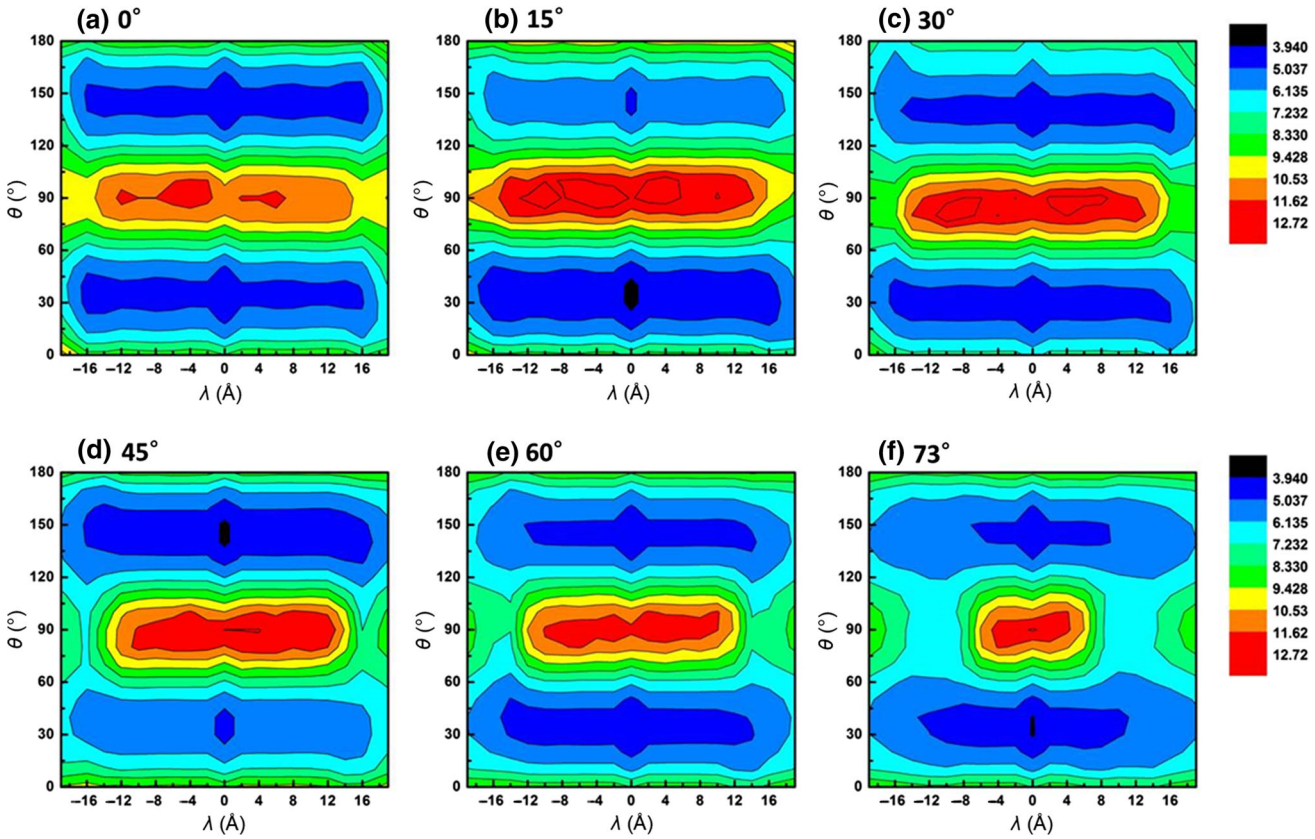

Fig. 5 Free energy of occupancy of a water dipole inside italicized CNT membranes

3.5 Diffusion coefficients of water inside italicized CNT

Finally, the 1D diffusion coefficients of water inside nanotube along the central path of are calculated at different ϕ, which are shown in Fig. 6.

The diffusion coefficient reflects the movability of water inside CNT. The increase in diffusion coefficient indicates that water molecules are easier to pass through CNT, resulting in a higher water flux. Figure 6 shows that the increase in ϕ values results in the increase in water diffusion coefficients inside CNT. Thus, an increase in water flux can be obtained, as shown in Fig. 2. Figure 6 shows that the error bar of diffusion coefficient is not significantly different at $\phi = 60°$ and $\phi = 73°$. The increase in diffusion coefficient is one reason for the increased water flux. Another important factor is, as shown in Fig. 3a, the highest free energy status of water inside italicized CNT at $\phi = 73°$ is reduced, indicating a lower energy barrier for water transport.

4 Conclusions

In this work, molecular dynamics simulation was applied to examine the effect of CNT membrane structure on the water administration and transport. Compared to the conventional vertically aligned CNT membrane, the italicized alignment of CNT in membrane reduces the energy barrier and facilitates administration of water by the CNT. Moreover, a different profile of LJ interaction ("V" pattern) and the unstable water chain near the bulky water were displayed for the italicized CNT membrane. A shallower energy barrier, in comparison with that of the vertically aligned CNT, the italicized CNT also favours the water transport. In summary, the italicized CNT membrane is advantageous over the vertical one in water transportation. The molecular insight into the water transport as function of the structure of the CNT, as shown by above-described molecular dynamics simulation, is helpful for the design and operation of CNT-based membranes for water desalination.

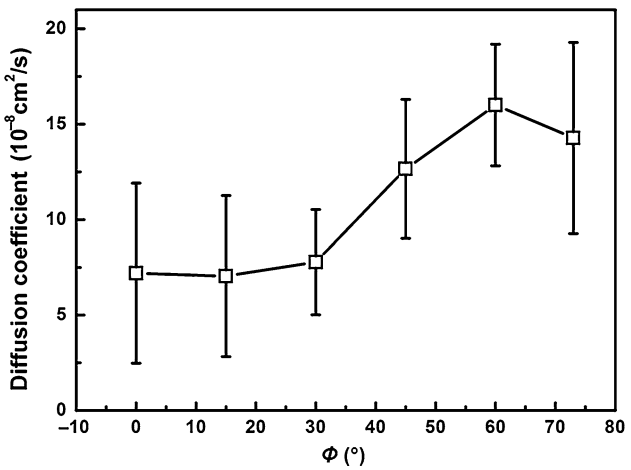

Fig. 6 Diffusion coefficient of water inside italicized CNT membranes

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Conflict of interest The authors declare that they have no conflict of interest.

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