A chloride ion-selective boron nitride nanotube

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ARTICLE INFO

Article history:
Received 9 April 2009
In final form 20 July 2009
Available online 24 July 2009

ABSTRACT

Combined density functional theory and molecular dynamics simulations were performed to investigate ionic selectivity of boron nitride nanotubes (BNNTs). A finite-length (10, 10) BNNT with a diameter of 1.356 nm immersed in a reservoir of 1 M KCl solution can selectively conduct Cl− ions, while K+ ions barely reach the center of the nanotube and do not conduct. In contrast, a (10, 10) single-walled carbon nanotube of approximately the same diameter immersed in a 1 M KCl solution can selectively conduct K+ ions through the nanotube. We investigate the potential of mean force analysis, binding energy calculations, the water structure, and its orientation, to explain the selectivity of BNNT.

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1. Introduction

The passage of ions across membranes surrounding all living cells is a fundamental process that governs the electrical properties of the cells, such as, the action potential generation in nerves and muscles, and the membrane potential regulation [1]. The cell membrane, however, is almost impermeable to ions. Thus, an ion channel is needed to allow the transport of ions in and out of the cell through the membranes. Each ion channel can be highly specific for a single ion or conduct a few or several ions. Depending on the selectivity, ion channels are classified as K+ channels, Na+ channels, Cl− channels, etc. The malfunction of ion channels can lead to several diseases. For example, the dysfunction of sodium channels, potassium channels, and chloride channels can cause hypomagnesaemia, long-QT syndrome, and epilepsy, respectively [2]. As a result, in recent years, there has been growing interest in understanding the molecular mechanisms governing ion transport mediated by ion channels [3–5].

During the past decade, several nanotubes or nanochannels have been proposed as artificial ion channels to mimic the selectivity properties of biological ion channels. For example, porous silica has been investigated using both experimental and theoretical studies. Experimental studies have shown that ion permeation can be controlled by surface chemistry and charge distribution of a silica nanochannel [6,7]. In theoretical studies, it has been shown that a functionalized silica channel can strongly attract sodium ions and repel chloride ions [8]. Recently, single-walled carbon nanotubes (SWCNTs) have also been considered as selective ion channels. Using combined ab initio molecular dynamics and grand canonical Monte Carlo simulations, it has been shown that a clean (18, 18) SWCNT is favorable for sodium ions, but not for chloride ions [8]. Joseph et al. demonstrated that an asymmetrically functionalized (16, 16) single-walled carbon nanotube (SWCNT) can be chloride selective over potassium by using molecular dynamics simulation [9]. Potassium and chloride ions in an aquatic solution can be separated by different diameter and surface charge of SWCNT [10]. These and many other previous studies indicate that the ion selectivity can be strongly affected by the surface charge of the channel [6–10] and water properties inside the channel [11].

Boron nitride nanotubes (BNNTs) which have relatively strong nanotube polarization and superior water permeation properties [12] can be promising candidates as ion channels. However, there have been no studies reported so far on ion transport using BNNTs. In this work, we demonstrate that the (10, 10) single-walled BNNT has extraordinary ionic selectivity of Cl− ions over K+ ions, while the Cl− ions are unfavorable in a similar diameter and length SWCNT. The ion selectivity of the BNNT was investigated by using molecular dynamics simulations and density functional theory (DFT). The BNNT's polarization effect arising from its unique bonding nature, a combination of weak ionic and covalent bonding, was captured by the DFT calculations.

2. Simulation methods

First, we considered hydrogen saturated finite-length (9, 9) and (10, 10) BNNTs. The diameters of the BNNTs are 1.220 nm and 1.356 nm for (9, 9) and (10, 10), respectively. The length of the BNNTs is approximately 14 Å. Additional details on initial BNNT geometries can be found in recently reported work [13]. The optimized geometries of the BNNTs were obtained by AM1 semiempirical method using Gaussian 03 [14]. As described in previous study [13], the polarization of BNNTs was captured by DFT, and quantified as fixed partial charges using the CHelpG scheme [15].
Previous ab initio study [16] suggests that water surrounding an ion can prevent electron transfer to or from the nanotube. Our preliminary partial charge calculations showed that an ion surrounded by water molecules in a BNNT gave rise to a negligible change in the magnitude of partial charge on BNNT, compared to the partial charges computed on a BNNT with only water. Hence, we did not include the effect of ions in the determination of partial charges on BNNT. The quantum partial charges obtained from previous study [13] were included in the MD simulation. For the MD simulation, the nanotube is fixed in a slab with electrolyte reservoirs attached on either end. The electrolyte reservoirs contained approximately 4200 water molecules and 1 M of K\(^+\) and Cl\(^-\) ions. The initial simulation box was \(5.6 \times 5.45 \times 6\) nm\(^3\), and periodic boundary conditions were applied in all the three directions. The Lennard-Jones (LJ) parameters for B, N, and H atoms are summarized in Ref. [12], and those of K\(^+\) and Cl\(^-\) ions were taken from Ref. [17]. Water is modeled by using the extended simple point charge (SPC/E) model [18]. The long-range electrostatic interactions were computed by using the Particle Mesh Ewald (PME) method with a 10 Å real-space cutoff, 1.5 Å reciprocal space gridding, and splines of order 4 with a 10\(^{-5}\) Å tolerance. For equilibration, the MD simulation was started without ions. The initial simulations were performed with a constant temperature of 300 K and a constant pressure of 1 bar as described in the previous study [13]. The simulation box size in the z-direction was adjusted to maintain the constant pressure. When the equilibration state is attained, we replaced some of the water molecules with 1 M of K\(^+\) and Cl\(^-\) ions. Next a 1 ns of equilibration with ions is performed and the simulation was continued for another 19 ns with 1.0 fs time step under a constant temperature [19] of 300 K using GROMACS 3.3.1 [20]. The equations of motion were integrated by using a leapfrog algorithm.

3. Results and discussion

To obtain fundamental insights into ion selectivity of K\(^+\) versus Cl\(^-\) ions in BNNTs, we carried out molecular dynamics (MD) simulations (see Fig. 1). The MD simulations were started with empty BNNTs. After the simulations were equilibrated for 1 ns, the nanotube was continuously filled by water during the entire simulation time. The simulations reveal that the K\(^+\) and Cl\(^-\) ions do not go through (size exclusion) the (9, 9) BNNT. Thus, in the rest of the paper we focus on the (10, 10) BNNT. We measured the occupancy of the K\(^+\) and Cl\(^-\) ions in the (10, 10) BNNT. The occupancy of the ions can be quantified by the ion residence time in the BNNT, which is defined as the percentage of time the K\(^+\) and Cl\(^-\) ions were observed in the tube during the entire simulation time. Table 1 shows that both K\(^+\) and Cl\(^-\) ions enter the (10, 10) BNNT, but Cl\(^-\) ions have significantly higher chance of getting into the BNNT, compared to K\(^+\) ions. The Cl\(^-\) ions were found in the BNNT for approximately 10% of the total simulation time, while K\(^+\) ions were observed for approximately 1% of the total simulation time. The higher the residence time of the ion, the higher is the probability for the ion to translocate through the nanotube. During 19 ns of simulation time, a total of three Cl\(^-\) ions passed through the (10, 10) BNNT, but no K\(^+\) ions passed through the tube. Interestingly, the transport of K\(^+\) and Cl\(^-\) ions is quite different in SWCNT. We expected the (10, 10) SWCNT to be K\(^+\) selective over Cl\(^-\) because it has been previously shown that Na\(^+\) is selective over Cl\(^-\) in the case of clean SWCNT [8], and K\(^+\) is favorable than Na\(^+\) in a simple cylindrical

![Fig. 1. Visualization of Cl\(^-\) ion inside a (10, 10) BNNT.](image-url)
To investigate this further, we considered a (10,10) SWCNT of similar diameter as the (10,10) BNNT. Fig. 2 shows the axial location of the K⁺ and Cl⁻ ions in the (10,10) BNNT and SWCNT as a function of simulation time. Consistent with our expectation, K⁺ ions are favorable in the (10,10) SWCNT with about 28% of ion residence time and five translocation events. Cl⁻ ions are barely observed in the (10,10) SWCNT and they can hardly reach the center of the SWCNT (see Fig. 2).

The contrasting ion selectivity of (10,10) BNNT and (10,10) SWCNT can be explained by the potential of mean force (PMF) [21] and binding energy calculations. The PMF for an ion i, denoted $W_i(z)$, is computed by integrating the mean force, $\langle F_i(z) \rangle$, acting on the ion along the tube axis, $z$, due to all other atoms in the system averaged over all the configurations, i.e., $W_i(z) = W_i(z_0) - \int_{z_0}^{z} \langle F_i(z') \rangle dz'$, where $z_0$ is the reference position (taken as the end of the simulation box) where the PMF is zero [22]. The mean force distribution was obtained by sampling the force experienced by the ions placed at various positions along the nanotube axis. The energy barrier is then obtained from the PMF. The energy barrier of Cl⁻ was found to be approximately 6.68 k_BT for the (10,10) BNNT case, which increases markedly to 11.79 k_BT for the (10,10) SWCNT case. For K⁺ ions, the energy barrier is 12.08 k_BT for the (10,10) BNNT and 5.99 k_BT for the (10,10) SWCNT. Because of the lower energy barrier for Cl⁻ ions in the (10,10) BNNT case, the Cl⁻ ion has a relatively higher chance to enter the (10,10) BNNT, compared to the K⁺ ion.

The interactions between the nanotube and the K⁺/Cl⁻ ions were further evaluated by computing the binding energy. Since the binding energy is defined as the energy required to separate a particle from a system of particles, the binding energy of an ion in the nanotube was calculated as follows: $E_i = E_{i+\text{water}} - E_{\text{water}} - E_{\text{bare ion}}$, where $E_{i+\text{water}}$ is the potential energy experienced by water and ion in the nanotube, $E_{\text{water}}$ is the potential energy of water in the nanotube, and $E_{\text{bare ion}}$ is the energy of bare ion. We also computed the binding energy of an ion in the electrolyte reservoir using a similar approach. In the binding energy calculations, we used the cutoff method with 1 nm of cutoff distance to compute the long-range electrostatic interactions, and we disregarded the binding energy of an ion when the ion was at the nanotube entrance, i.e., when the ion is ~0.3 nm from each end of the tube. The average binding energies of K⁺ and Cl⁻ ions in the reservoir were found to be approximately $-355.70 k_BT$ and $-204.54 k_BT$, respectively. The binding energy for Cl⁻ ion in the reservoir is in reasonable agreement with previous binding energy calculations for a Cl⁻ ion in water cluster [16].

Table 1: Translocation of ions and percentage of ion residence time in a (10,10) BNNT with and without polarization effect. For comparison, the results for a (10,10) SWCNT are also shown.

<table>
<thead>
<tr>
<th>Tube type</th>
<th>Ion</th>
<th># of translocation events</th>
<th>Ion residence time (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10,10) BNNT with</td>
<td>K⁺</td>
<td>0</td>
<td>1.05</td>
</tr>
<tr>
<td>polarization effect</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10,10) BNNT with</td>
<td>Cl⁻</td>
<td>3</td>
<td>10.9</td>
</tr>
<tr>
<td>no polarization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10,10) SWCNT</td>
<td>K⁺</td>
<td>1</td>
<td>0.027</td>
</tr>
<tr>
<td>(10,10) SWCNT</td>
<td>Cl⁻</td>
<td>0</td>
<td>0.024</td>
</tr>
</tbody>
</table>

Fig. 2. Position of K⁺ and Cl⁻ ions inside a (10,10) BNNT (top) and a (10,10) SWCNT (bottom). The axial distance is scaled with the length of the nanotube.
inside the BNNT is about $-18.35 k_BT$. Fig. 3c shows that a Cl$^-$ ion inside the BNNT has more attractive interaction with the BNNT and water molecules compared to a K$^+$ ion. Hence, BNNTs are selective to Cl$^-$ ions. Similarly, for the (10, 10) SWCNT case, a K$^+$ ion with a lower binding energy inside the SWCNT is more favorable compared to the Cl$^-$ ion (Fig. 3d).

We decomposed the total force field in the BNNT case into Lennard-Jones (LJ) and electrostatic force fields. MD simulations were also performed without including the nanotube polarization effects, i.e., by assigning zero partial charges to all the atoms of the BNNT. Both K$^+$ and Cl$^-$ ions are barely observed inside the BNNT with zero charge. Surprisingly, we found that K$^+$ ions are more favorable than Cl$^-$ ions, i.e., K$^+$ ions in the zero charged (10, 10) BNNT have four times higher ion residence compared to the Cl$^-$ ions (Table 1). During 19 ns of simulation time, one K$^+$ ion passed through the nanotube, while no Cl$^-$ ions crossed the tube. Therefore, the Cl$^-$ selectivity in BNNT is primarily due to the strong surface potentials arising from the polarization effects.

To further understand the BNNT polarization effects on Cl$^-$ selectivity, we examined the water structure inside the BNNT as the water structure and ion selectivity are closely connected to each other [11,23,24]. The water structure can be affected considerably by the BNNT polarization effect [13], thereby having a significant influence on the Cl$^-$ selectivity of the (10, 10) BNNT. Fig. 4 shows the radial water charge density distribution, $\rho(r)$, in the (10, 10) BNNT and SWCNT. The radial water charge density distribution was computed with only water molecules in the nanotubes. Water charge distribution due to water orientation near the center of the tube can play an important role in determining ion selectivity as our radial density calculations of K$^+$ and Cl$^-$ ions inside the nanotube indicate that ions are mostly located near the center of the nanotube. Fig. 4 shows that when polarization effects are included, the water molecules at the center of the BNNT are oriented such that the charge density is positive. This leads to the interpretation that hydrogen atoms of the water molecules at the center of the nanotube have a higher chance of pointing towards the center with the oxygen atom pointing towards the wall of the nanotube (see Fig. 4). Therefore, the water charge distribution at the nanotube center results in attraction of Cl$^-$ ions to the BNNT, and repulsion of K$^+$ ions. When the BNNT polarization effects are removed, the charge density of water at the center of the nanotube is approximately zero. Thus, neither K$^+$ nor Cl$^-$ ions are attracted by water molecules inside the BNNT, and extremely low ion residence time of both K$^+$ and Cl$^-$ ions inside the BNNT is observed. In the case of (10, 10) SWCNT, the averaged water charge density near the tube center is negative. Therefore, the water charge distribution at the nanotube center results in attraction of Cl$^-$ ions to the SWCNT, but attracts K$^+$ ions into the nanotube.

We also investigated the water and ion interactions inside the BNNT, and compared with the SWCNT case. The ion–water radial distribution function (RDF) was computed, and the hydration number, defining the number of water molecules in the first hydration shell (n) of the ion, was obtained by integrating the RDF to its first minimum. Fig. 5 shows the comparison of K$^+$–water and Cl$^-$–water RDF in the (10, 10) BNNT, (10, 10) SWCNT, and bulk. The location of the first maximum and the first minimum is similar in all cases. However, the magnitude of the first peak is different in each case which indicates that the hydration number of the ions is different. In the (10, 10) BNNT, the relative hydration number of Cl$^-$ ion with respect to that of in bulk, $n_{Cl}^{BNNT}/n_{Cl}^{bulk}$, was found to be 0.32. This is
about 1.4 times higher than that of $K^+$ ion in the tube. This indicates that the $Cl^-$ ion in the BNNT is closer to a bulk-like state, compared to the $K^+$ ion in the BNNT. For the (10, 10) SWCNT, $K^+$ ions have more number of water molecules in their first hydration shell compared to $Cl^-$ ions. $K^+$ ion has approximately 1.3 times higher relative hydration number compared to the $Cl^-$ ion. When the BNNT polarization effects are removed, the relative hydration number of $Cl^-$ ion is found to be less than that of $K^+$ ion ($\eta_{Cl}/\eta_{bulk} = 0.18$, $\eta_{K}/\eta_{bulk} = 0.34$). Therefore, the polarization effect in the BNNT plays a critical role for the $Cl^-$ ion to have a relatively higher hydration number compared to that of $K^+$ ion.

Finally, we also investigated ion selectivity in the wider (12, 12) BNNT with a diameter of 1.627 nm. As the nanotube diameter is wider, (12, 12) BNNT can no longer exclude $K^+$ ions from the nanotube. During 19 ns of simulation time, the percentage of ion residence time of $K^+$ and $Cl^-$ ions were observed to be 12.74 and 29.80, respectively. A total of eight $Cl^-$ ions passed through the (12, 12) BNNT while only three $K^+$ ions crossed the BNNT. Similar to the (10, 10) BNNT case, $Cl^-$ ions have a significantly higher chance of ion residence time and translocation in the (12, 12) BNNT compared to the $K^+$ ions. In the case of (12, 12) SWCNT, $K^+$ ion selectivity over $Cl^-$ ion is observed. $K^+$ ions were dominantly observed in the SWCNT for about 72.58% of the total simulation time, while the $Cl^-$ ions were observed for only 8.31% of the total simulation time. A total of nine $K^+$ ions crossed the (12, 12) SWCNT while only two $Cl^-$ ions translocated during the entire simulation time.

The effect of flexibility of the water model on the ion selectivity was also investigated since this effect is not included in the rigid nonpolarizable SPC/E water model. The flexibility is included by adding internal (bond stretching and angle bending) conformational change to the SPC/E water model [25]. With the flexible water model, we observed similar ion selectivity as with the rigid nonpolar SPC/E water models even though the translocation events and the residence time are modified.

4. Conclusions

In summary, by combining DFT and molecular dynamics simulations, we investigated ion selectivity in BNNTs of various diameters and compared the results with similar diameter SWCNTs. A (10, 10) BNNT selectively transports $Cl^-$ ions while $K^+$ ions barely enter the nanotube. In contrast, a (10, 10) SWCNT selectively transports $K^+$ ions. PMF analysis indicates that the $Cl^-$ ions experience a lower energy barrier at the entrance of the BNNT compared to the $K^+$ ions. These observations suggest that a (10, 10) BNNT can be a strong candidate for many applications including an ion sensor and artificial ion channel. We found that the $Cl^-$ ion in the BNNT has an average binding energy of $-110.57k_B T$ which is considerably lower than that of a $K^+$ ion ($-18.35k_B T$). The total force field of the BNNT was decomposed into LJ and electrostatic force fields to determine the force component that is primarily responsible for the ion selectivity. The electrostatic force field arising from the BNNT polarization was found to cause the selectivity of $Cl^-$ ions. The effect of water structure on the ion selectivity was also examined. The water molecules inside the BNNT are oriented to have a net positive charge at the center of the nanotube. The positively charged central region of the BNNT attracts $Cl^-$ ions, and repels $K^+$ ions.

Acknowledgments

We thank Prof. Eric Jakobsson for helpful discussions. This research was supported by NSF under Grant Nos. 0328162, 0120978, 0506660, and 0801294.

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