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A Controllable Molecular Sieve for Na^+ and K^+ Ions

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Abstract: The selective rate of specific ion transport across nanoporous material is critical to biological and nanofluidic systems. Molecular sieves for ions can be achieved by steric and electrical effects. However, the radii of Na^+ and K^+ are quite similar; they both carry a positive charge, making them difficult to separate. Biological ionic channels contain precisely arranged arrays of amino acids that can efficiently recognize and guide the passage of K^+ or Na^+ across the cell membrane. However, the design of inorganic channels with novel recognition mechanisms that control the ionic selectivity remains a challenge. We present here a design for a controllable ion-selective nanopore (molecular sieve) based on a single-walled carbon nanotube with specially arranged carbonyl oxygen atoms modified inside the nanopore, which was inspired by the structure of potassium channels in membrane spanning proteins (e.g., KcsA). Our molecular dynamics simulations show that the remarkable selectivity is attributed to the hydration structure of Na^+ or K^+ confined in the nanochannels, which can be precisely tuned by different patterns of the carbonyl oxygen atoms. The results also suggest that a confined environment plays a dominant role in the selectivity process. These studies provide a better understanding of the mechanism of ionic selectivity in the KcsA channel and possible technical applications in nanotechnology and biotechnology, including serving as a laboratory-in-nanotube for special chemical interactions and as a high-efficiency nanodevice for purification or desalination of sea and brackish water.

1. Introduction

With the development of nanotechnology, the demand for techniques that precisely differentiate ions has increased, especially those that distinguish and filter ions.[1−3] Fortunately, nature has already designed such ion-selective machines. Potassium (K^+) channels are composed of tetrameric membrane-spanning proteins and are most remarkable in their ability to differentiate K^+ from Na^+ by more than a thousandfold.[2] The recently solved structure of potassium channels inside *Streptomyces lividans* (KcsA channel) shows that there are precisely arranged arrays of carbonyl oxygen atoms in the entrance of the pore, which play an important role in efficiently recognizing and guiding the passage of K^+ (see more details in the Supporting Information).[4] In each binding site of KscA, a K^+ ion is bound to about eight carbonyl oxygen atoms which mimic the hydration shell of K^+ in solution. Originally, it was thought that K^+ selectivity in KscA arises from the tight fit with these carbonyl oxygen atoms, the geometry matching that of the hydration shell of solvated K^+ in bulk water (the so-called "snugfit" hypothesis) but was too large for Na^+.[4] However, current molecular dynamics (MD) simulation results are contrary to the "snugfit" hypothesis and show that dynamic carbonyl ligands in KscA can collapse around Na^+ and provide an optimal coordination radius.[5] Recently, it was realized that when ions are confined within nanopores (including biochannels or inorganic nanopores), the ionic hydration is much different from that found in bulk solution and has important effects on the ionic selectivity across the biochannel.[6,7] Bostick et al. have utilized a simple theoretical model of K^+ and Na^+ complexation with water (or carbonyl groups),[8] to verify the important effect of the ion hydration number on the selectivity. Their analysis has revealed that K^+- or Na^+-selective environments can be obtained if the coordination numbers of water molecules around the K^+ or Na^+ are constrained to be the same value as that in bulk water, but it is hard to control the hydration number by conventional methods in applications. Nanopores in graphene sheets with different functional units have been applied to sieve cations of alkali metals or anions of group 17 element, respectively.[9] Results have showed that the broken hydroshell around the ions can be compensated by the charged nanopore

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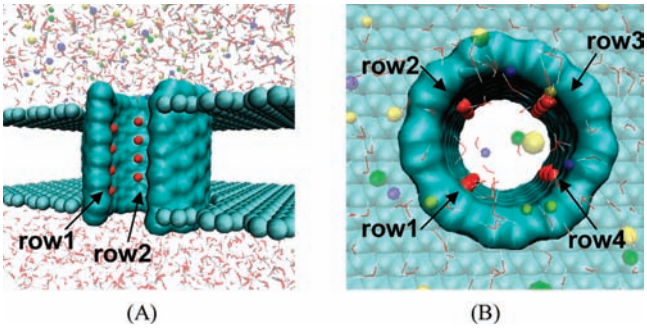
rim. Two kinds of nanopores are designed for K^+ and Cl^- ions. More recently, Shao et al.[10] have also indicated that the ionic hydration within a carbon nanotube presents anomalous change and is critical for the ionic selectivity.

Despite these achievements, we are still far from complete understanding of how the hydration shells of Na^+ and K^+ inside the nanopore can be controlled by inner modified functional groups, and there are still few designs for ion-selective nanomachines that use the novel properties of hydration water around the ions. In this paper, we devise a model system in this direction by using inner-wall-modified nanopores to control the ionic selectivity on the basis of molecular dynamics simulations. The uncapped armchair single-walled carbon nanotube is used as the model. Besides its outstanding potential for applications in nanoscale sensors, devices, and machines,[11−26] carbon nanotubes have been accepted as a simple model for the complicated structure of biological water[27−31] or ionic channels.[10]

By changing the pattern of the carbonyl oxygen arrangements inside the channel, we can demonstrate that the selective ability inside the modified carbon nanotube is attributed to the coordination number of the ionic first hydration shell, which can be more easily controlled by the confined environment and precisely tuned by the pattern of the carbonyl oxygens on the wall of the nanotube. That is to say, we can obtain a different ionic selectivity in the modified nanotubes. These results may provide a better understanding for the mechanism of ionic selectivity and also have a wide application for industry, such as purification or desalination of sea and brackish water.

2. Computational Methods

In the present study, the molecular configuration in our arrangement consisted of a (9,9) single-walled carbon nanotube 13.4 Å in length and 6.01 Å in radius, embedded in the vertical direction between two graphite sheets (see Figure 1). Eight or sixteen carbonyl oxygen atoms were modified inside the nanotube, which were connected to the carbon atoms by carbon−oxygen bonds and free to vibrate around the equilibrium sites during the simulation. Recently, experiments have been performed to oxidize only the inner surface of carbon nanotubes,[32] which show the practical feasibility of our design (more details are discussed in Supporting Information).



(A) (B)

Figure 1. The simulation system. (A) Side view of the main system. The solvent-accessible surface of a model pore is shown in light blue (parts of the pore close to the observer are removed for clarity). The two carbon sheets are also in light blue. The carbonyl oxygen atoms inside the nanopore are in red. The K^+, Na^+, and Cl^- ions are represented as green, blue, and yellow balls, respectively. Water molecules are depicted as lines (images created with VMD). (B) Top view of the same arrangement.

As shown in Figure 1A, four carbonyl oxygen atoms are aligned in one row, resulting in four rows of carbonyl oxygen. We designate these four rows as row 1, row 2, row 3, and row 4. Rows 1 and 3, and rows 2 and 4, face each other and are symmetrical about the axis. Figure 1B shows the top view of the modified nanotube. The z axis of four oxygen atoms in row 1 are at 3.03 Å, 0.61 Å, −1.82 Å, −4.24 Å (the center of the nanopore as $z = 0$), and the z axis of the four oxygen atoms in row 2 are at 4.24 Å, 1.82 Å, −0.61 Å, and −3.03 Å, respectively, which is slightly higher than those in row 1. The z axis of the oxygen atoms of row 3 are the same as those of row 1, and the z axis of the oxygen atoms in row 4 are the same as those in row 2. To simplify the discussion, we denote the nanotube with this pattern as type 1, and if we change the modification pattern slightly by setting the z axis of the oxygen atoms in rows 1, 2, 3, and 4 to the same value (i.e., no shifts as the type 1), we designate this model system as type 2. The modified pattern was inspired by the potassium channel which has about sixteen carbonyl oxygen atoms in the selective filter.[4] If there are only eight carbonyl oxygen atoms in the nanotube, i.e., only row 1 and row 3 exit, the model system is denoted as type 3. The nanotube without carbonyl oxygen atoms, namely type 0, was also prepared for purposes of comparison.

We used molecular dynamics simulations to simulate the nanotube and graphite sheets solvated in a salt solution reservoir containing NaCl and KCl for 305 ns for the different modified patterns. The data from the last 300 ns were collected for analysis. Our simulations were performed with the GROMACS 3.3.3 molecular dynamics program.[33] The solvent used was TIP3P water molecules.[34] In the simulations, the carbon atoms were modeled as Lennard−Jones particles with $\sigma_{CC} = 0.34$ nm and $\sigma_{CO} = 0.3275$ nm and a depth of the potential well of $\varepsilon_{CC} = 0.3612$ kJ mol^{-1} and $\varepsilon_{CO} = 0.4802$ kJ mol^{-1}.[29,35,36] The carbon atoms at the inlet and

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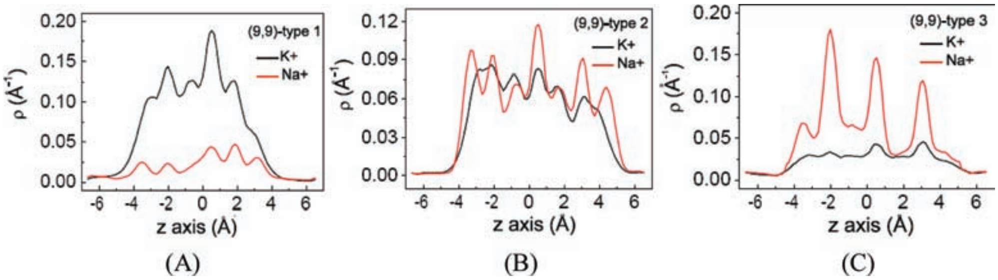

Figure 2. Density distributions of Na^+ (red line) and K^+ (black line) along the nanotube axis are shown: (A) nanopores with the modified pattern type 1; (B) type 2; (C) type 3.

outlet were fixed to prevent the nanopore from being swept away in the simulations, and the other atoms of the nanopore were flexible. Periodic boundary conditions were applied in all directions. The electrostatic interactions were handled by the PME summation method[37] with a cutoff for real space of 1 nm, and we tested the results with a different cutoff value (0.8 nm, 1.2 nm). Little effect on the main results was observed by changing the cutoff value. All simulations were carried out at a constant volume with box size dimensions of $L_x = 5.0$ nm, $L_y = 5.0$ nm, and $L_z = 5.0$ nm, and temperature 300 K. A constant electric field of 0.01 V/nm is applied, which is of comparable order to that of some ion channel membrane potentials.[38] The 30 Na^+, 30 K^+, and 60 Cl^- were randomly placed on the top side. The partial charges on the carbonyl oxygen and the carbon atoms connected to them are −0.51 and 0.51 e, respectively. The whole system is electrically neutral. The parameters for sodium, potassium, and chloride ions are taken from the Gromacs force field. In comparing the results of nonmodified nanotubes with those in ref 10, we found that choosing different parameters of the ion did not alter the main results and conclusions made from the series of simulations.

3. Results and Discussion

For ease of discussion in the later sections, we define the passage rate as the total number of particular ions that exits from the nanotube per nanosecond from one end, after having entered the opposite side.[9] To our surprise, the results show that the passage rate of Na^+:K^+ was 12:55 in the type 1 nanopore, i.e., we can obtain the passage (or flow) rates of K^+ 4.6 times over that of Na^+, while the opposite situation occurs in the type 3 nanopore. The flow rate of Na^+ is 2.2 times that of K^+ (the passage rate is about 39:18). There is no ionic selectivity in the type 2 nanopore (the passage rate is about the same for K^+ and Na^+). From these results one can see that the ionic selectivity is very sensitive to the carbonyl oxygen pattern inside the nanopore. Slight alteration of the pattern of charge arrangement can completely reverse its selectivity.

Figure 2 shows the density distribution of K^+ and Na^+ inside the nanotube in the *z* direction for the three nanopores (types 1−3) with differently modified patterns. The profile shape varies inside the various nanopores. In the type 1 nanopore, the density of K^+ is greater than for Na^+, and in contrast, in the type 3 nanopore, the density of Na^+ is higher than that for K^+. For the type 2 nanopore, the densities of the two ions are very similar.

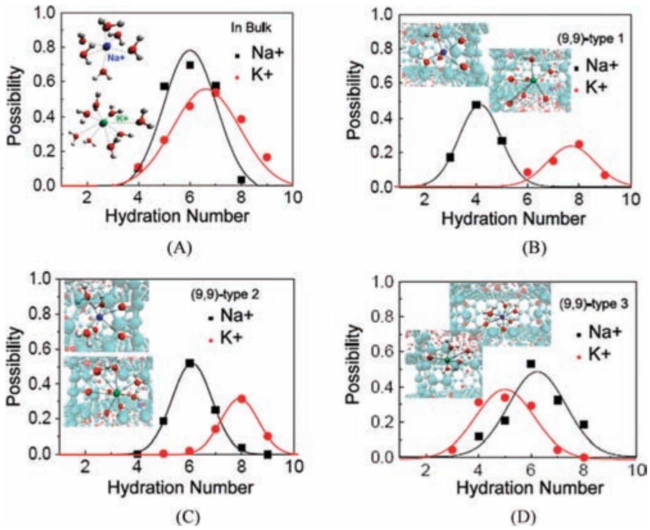

Figure 3. The possible distribution of hydration numbers for Na^+ (black square) and K^+ (red circles). The raw distributions are well represented by Gaussian probability models (solid lines). (A) In bulk, the average coordination numbers of Na^+, and K^+ are 5.6, and 6.8, respectively. (B−D) In the type 1−3 nanopores, the average coordination numbers of Na^+ and K^+ are 4.1, 7.6 for type 1; 6.1, 7.9 for type 2; and 5.1, 6.3 for type 3 nanopores, respectively. The inserted graphs are the snapshots from simulations showing details of the first hydration shell around the ions.

In addition, we performed a series of analyses to examine the mechanism of the controllable ionic selectivity. First, the average hydration number of K^+ and Na^+ ions in the bulk water solution and within the nanopore was calculated. In bulk water, the optimal coordination number ranges from ∼7 for K^+ to ∼6 for Na^+ (Figure 3A), resulting in an absence of selectivity for K^+ and Na^+. The obtained coordination number for K^+ and Na^+ in bulk is in excellent agreement with the data from X-ray diffraction[39] and theoretical simulations.[8] According to these earlier analyses, Na^+ strongly prefers 6-fold coordination. The comparatively softer K^+ ion displays a broader range of satisfactory coordination numbers (six to eight), favoring 7-fold and 8-fold coordination nearly equally. From a plot of the average coordination numbers of Na^+ and K^+ in type 1, type 2, and type 3 nanopores (Figure 3B−D), it is clear that the hydration shell number of the selected ion across the nanopore is similar to that in bulk water. Hence, the selected ion can enter the pore more easily than another ion with a lesser hydration shell number in the nanopore, thereby inducing the ionic selectivity. In the case of the type 1 nanopore, the coordination numbers for K^+ inside the nanopore is ∼8, similar to that in bulk water, and thus K^+ can easily transport across the nanopore with less energetic hindrance. For Na^+ ion, the coordination

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number is only ∼4, which is less than the value in the bulk solution. In this case, Na^+ ions are less hydrated when entering the type 1 nanotube and the transportation of Na^+ across the nanopore is energetically unfavorable. This stripping induces the enthalpic and entropic changes that affect the ionic selectivity inside the narrow nanopore. In the type 2 nanopore, the coordination numbers for K^+ and Na^+ inside the nanopore are about 8 and 6, in the range of the optimal coordination number, and both ions are equally transported across the channels, resulting in no ionic selectivity. As for the type 3 nanopore, the hydration numbers for K^+ and Na^+ inside the nanopores are ∼5 and ∼6, respectively. The hydration number of Na^+ within this type of nanopore is very similar to that of Na^+ in bulk water, while K^+ ions are significantly less hydrated, thereby inducing Na^+ selectivity.

Our statistical results show that the carbonyl oxygen atoms can provide an average of one or two ligands with the ions, which seems that the special modification mode in our system will affect the hydration shell of ions and help to compensate the broken ion hydration shell. In the confined environment, the competition between the space confinement for water and the attracting effect on water by carbonyl oxygen plays an important role in determining which ion can be better hydrated. The first hydration shell is highlighted in the inset of Figure 3. The radius for determining the first hydration shell of Na^+ and K^+ is 0.3 nm and 0.35 nm, respectively, which is obtained from the first minimum value along the profile of radial distribution functions of ion−oxygen in bulk. It is easy to see that both K^+ and Na^+ can obtain an optimal hydration number of ∼ 8 and 6, respectively, in bulk (see Figure 3A). As shown in the inset of Figure 3B and 3D, the less favored ion has a broken hydration shell, i.e., the hydration number is smaller than the bulk value. Taking the type 1 system as an example, inside the nanotube there is one carbonyl oxygen atom and three water molecules in its first hydration shell for Na^+, and two carbonyl oxygen atoms with five water molecules for K^+. The space confinement combined with this arrangement of carbonyl oxygen atoms decreases the shell order of Na^+ and maintains the shell order of K^+ while in the type 2 system (seen in the inserted graph of Figure 3 C) the special arrangement of carbonyl oxygen atoms and water molecules forms a fit cage for both K^+ and Na^+ ions. So if the first hydration shell of the ions (e.g., K^+) can be maintained intact, the ion will fit and pass through the channel without an additional cost of energy; on the other hand, if the first hydration shell is broken and not compensated by carbonyl oxygen atoms inside the carbon nanotube, the total energy will rise and result in unfavorable transport through the channel.

Although the modified patterns in the type 1 and type 2 nanopores are very similar, the slight differences between them can lead to various selective properties, which are reflective of the situation in biological systems. The KcsA channel and NaK channel have similar structures for the selective filters, but interestingly, the KcsA channel can precisely select K^+ ions, while the NaK channel allows transport of both Na^+ and K^+.[40] Whether these biological channels are well represented in our model systems is still an open question. Our results may provide some insights for the mechanism of complicated biological systems.

Table 1. Average Interaction Energy between the Cation and the Water Molecules in the Coordination Shell in the (9,9) Type 1−3 Nanotubes and in the Bulk Solution

modified pattern	E_{Na} (kJ/mol)	E_K (kJ/mol)	E_{Na-K} (kJ/mol)
type 1	−68.4	−60.3	34.1
type 2	−92.0	−48.1	∼0
type 3	−115.3	−53.6	−19.5
bulk	−91.1	−48.9	0

According to the above results, the coordination number in the hydration shell is a critical factor for which ions will be selected for transport across the nanotube. To further investigate the underlying mechanisms, we have calculated the average interaction energy E between the ion and ligands (including water molecules or carbonyl atoms) in its coordination shell for Na^+ (E_{Na}) and K^+ (E_K) within the nanopores and also in the bulk solution. We have defined these physical properties as the following: for each snapshot, taking Na^+ ion as an example, if there is Na^+ inside the carbon nanotube, we calculated the interaction potential of this Na^+ with its ligands (water molecules or carbonyl oxygen atoms) in the first hydration shell, and then all Na^+ hydration shells were accumulated and averaged. The average interaction potential of Na^+ is the ratio of the accumulated interaction potential to N, where N is the number of ligands appearing in the first hydration shell. Then we accumulate the average interaction potential of each Na^+ ion during all snapshots from simulation and assign as $E_{Na\text{-}total}$, and the final average interaction potential E_{Na} is the ratio of $E_{Na\text{-}total}$ to total numbers of Na^+ inside the tube during the simulation. The calculation method for E_K is the same as that of $E_{Na.}$

The difference (E_{Na-K}) in interaction energy cost between Na^+ and K^+ in the three types of nanopores is defined in eq 1.[10] A negative value of E_{Na-K} indicates that the interaction energy cost of confining a hydrated Na^+ is less than that of confining a hydrated K^+, thereby inducing Na^+ selectivity. Conversely, a positive E_{Na-K} leads to K^+ selectivity.

$$E_{Na-K} = (E_{nanopore} - E_{bulk})^+_{Na} - (E_{nanopore} - E_{bulk})^+_K \quad (1)$$

In a comparison of E_{Na-K} data for the three types of nanopores (Table 1), we observed differences in the energy costs between hydrated K^+ and Na^+ confined within the different nanopores. These variations in energy costs were dependent on the type of modified patterns within each nanopore. For the type 1 nanopore, E_{Na-K} is positive, while for the type 3 nanopore, E_{Na-K} is negative. E_{Na-K} is almost 0 for type 2, which is the same value as that in bulk water. These results indicate that the energy cost of ionic hydration induced by confinement is critical to the ionic selectivity. From Figure 3 and Table 1, we conclude that the higher the loss of order in the coordination shell of the ion, the lower the interaction energy between the ion and the ligands, and the entry of the ion into the nanopore becomes less favorable.

Furthermore, we also simulated nanopores with a larger radius of 6.68 Å (chiral index 10,10). We found that for the (10,10) type 1−3 nanopores, all show Na^+ selectivity, with a Na^+/K^+ ratio of 45:18, 70:12, 96:31, respectively (the same Na^+-selectivity trend as type 0). That is to say, for the large nanotube diameter, Na^+ ions pass through more easily than K^+ ions, regardless of the pattern of charge arrangement, indicating that the confined environment is the predominant factor for the ionic selectivity. In fact, as we knew, the biological sodium channels are generally wider than potassium channels. In case of the (10,10)-type 1 and (9,9)-type 1 nanotubes, although the size of K^+ is larger than that of Na^+, the (10,10)-type 1 nanotube selects

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Na^+ while the (9,9)-type 1 nanopore selects K^+, the phenomenon is very much similar to that observed in biological ionic channels.

4. Conclusions

By using molecular dynamics simulations we have demonstrated that controllable Na^+ or K^+ selectivity can be obtained by using different modified patterns of carbonyl oxygen inside the nanopore. Their positions in the carbon nanotube mimic the arrangement of amino acids in the filter structure of potassium channels. The remarkable selectivity is attributed to the hydration structure of Na^+ or K^+ ions confined in the nanochannels, which can be precisely tuned by different modified patterns of carbonyl oxygen and by the diameter of the nanopore. We also find that the confined environment is the most important factor for ionic selectivity. More interestingly, we can change the Na^+ selectivity into K^+ selectivity or to no ionic selectivity by adding the appropriate inner modified pattern of carbonyl oxygen groups in an unmodified nanotube.

An unresolved issue is how to extract large quantities of a complex biomolecule and keep it intact and fully functional for industrial use in a non-natural context.[41] The inorganic channel may have more advantages in real application and provide a similar but structurally less complicated system to exploit primary characteristics shared by biological ionic systems. Our findings offer a new insight into different ionic selectivity across biological channels and provide possibilities for developing new kinds of devices/machines to separate K^+ and Na^+ in the inorganic nanopore without the use of chemical separation methods, which may have wide technical applications in nanotechnology or biotechnology, including the laboratory-in-nanotube for special chemical interactions and highly efficient nanodevices for purification or desalination of sea and brackish water.

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Supporting Information Available: Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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