Angewandte Chemie International Edition

DOI: 10.1002/anie.201408633

Nanochannels

Electromanipulating Water Flow in Nanochannels**

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Abstract: *In sharp contrast to the prevailing view that a stationary charge outside a nanochannel impedes water permeation across the nanochannel, molecular dynamics simulations show that a vibrational charge outside the nanochannel can promote water flux. In the vibrational charge system, a decrease in the distance between the charge and the nanochannel leads to an increase in the water net flux, which is contrary to that of the fixed-charge system. The increase in net water flux is the result of the vibrational charge-induced disruption of hydrogen bonds when the net water flux is strongly affected by the vibrational frequency of the charge. In particular, the net flux is reaches a maximum when the vibrational frequency matches the inherent frequency of hydrogen bond inside the nanochannel. This electromanipulating transport phenomenon provides an important new mechanism of water transport confined in nanochannels.*

Understanding the water transport through nanochannels is essential to uncovering the complex mechanisms of water permeation through biological membranes and porous media and developing advanced nanofluidic systems for various applications. In recent years, water transport through nanochannels and water structures inside the nanochannels were extensively investigated, and some unconventional phenomena were revealed. For example, both molecular dynamics (MD) simulations[1,2] and experiments[3] demonstrated that the flow rate through a carbon nanotube is three to five orders of magnitude faster than that predicted from conventional fluid-flow theory, which compares favorably with those inside the biological channels, proving the necessity to understand water transport in a confined nanochannel.

It was reported that charged residues exist in biological protein channels and play a vital role in water permeation.[4–6] Since water molecules in the carbon nanotube share many characteristics with those inside the biological channels,[1,7] for example, the single-file arrangement, the wavelike density distribution and the wet–dry transition, a number of researchers used nanotubes as a model to study the complex water transport in biological channels.[8] It has been widely reported that water permeation through a nanochannel can be shut down by placing a stationary charge close to the channel wall, so-called electro-gating.[9,10] These studies formed a prevailing view that charges next to nanochannels can greatly reduce and even block the water permeation through the nanochannel. Biological channels are actually exposed to vibrational electrical signals due to metabolism.[5,11] However, how a vibrational charge next to a nanochannel affect the transport of water molecules has not been properly understood.

Herein, we report a surprising finding from molecular dynamics simulations, namely that water flow through a confined nanochannel can be sped up by placing a vibrational charge next to the nanochannel. This unexpected vibration-charge-induced fast flow of water molecules, which can be named electro-propelling, is a result of the disruption of the hydrogen bond of water molecules confined inside the nanochannel. We show that by manipulating the vibrational frequency of the charge as well as the distance between the charge and the nanochannel, the net flux of water in the nanochannel can be regulated over a wide range. We therefore name this phenomenon electromanipulating.

The simulation setup consists of an unperturbed single-wall carbon nanotube (SWCNT) and two graphenes, which are dissolved in a water bath, as shown in Figure 1a. A (6,6) SWCNT of 0.81 nm in diameter and 13.4 nm in length is embedded between two monolayer graphenes with a pore diameter slightly larger than the diameter of SWCNT along the z direction, that is, being vertical to the surface of the graphenes. The choice of the SWCNT is based on the fact that a nanochannel of (6,6) SWCNT can share the properties of biological channels.[1,7] The graphenes are impermeable to water. The space between the two graphenes is vacuum. Water can only be transported between the two graphenes through the SWCNT. To study the behavior of the water permeation through a nanochannel with a vibrational charge, a periodically vibrational positive charge of 1.0 e with a distance d from the nearest carbon atoms of the SWCNT is imposed at the center outside the SWCNT. The charge vibrates periodically along the direction parallel to the SWCNT surface and satisfies the relation $z(t) = A\cos(2\pi f t + \varphi)$, where A is the amplitude, f is the vibrational

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[**] We thank Prof. Ruhong Zhou for critical comments on the manuscript. This work was supported by the NSFC (11405146, 61274099, 51234007, 51404291, and 51490654), NBRPC (2012CB825700), PCSIRT (IRT1294), Shandong Provincial NSFC (ZR2013DL011), Zhejiang Provincial Science and Technology Key Innovation Team (2011R50012-2) and Key Laboratory (2013E10022). J.Y. acknowledge the Climb Taishan Scholar Program in Shandong Province. J.T.F. was supported by the Start-up fund of Cornell University.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201408633.

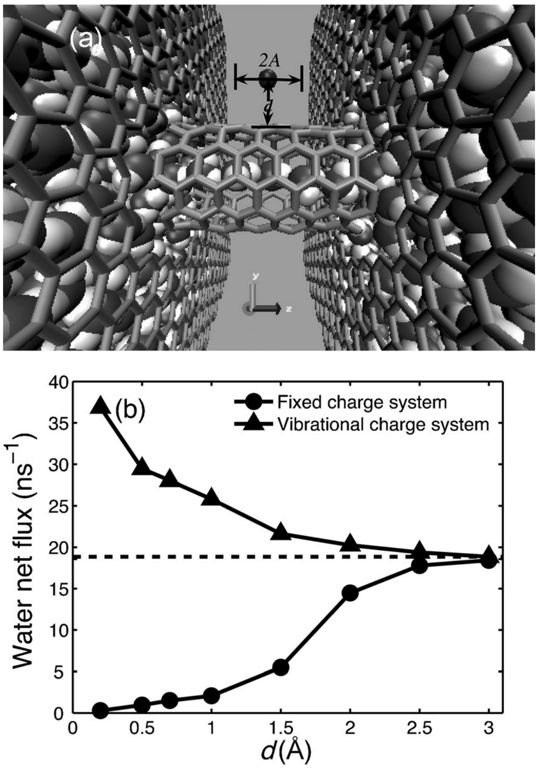

Figure 1. a) Snapshots of the simulation system. The light gray structures are the nanotube and graphite sheets. The black and white spheres are oxygen and hydrogen atoms in water molecules. The single black sphere at the center above the SWCNT is a periodic vibrational positive charge ($q = +1$ e) with an amplitude of A and with a distance of d from the nearest carbon atoms of the SWCNT. b) The water net flux as a function of distance d for fixed-charge system (FCS) and vibrational-charge system (VCS). For the VCS, the frequency is 2500 GHz and the amplitude A is 3 Å. FCS may be considered as a special case of VCS with a frequency of zero.

frequency, and φ is the initial phase. The system with an external vibrational charge is named as vibrational-charge system (VCS), while that with an external fixed (or stationary) charge, namely fixed-charge system (FCS). FCS may be considered as special case of VCS with a frequency of zero. To keep the whole system electrically neutral, a negative charge with the same charge magnitude is assigned close to the boundary of the system.

We performed a series of molecular dynamics simulations with varying systems (the detailed simulation set-up parameters and processes are reported in Section S1 of the Supporting Information). To produce a unidirectional flow, a hydrostatic pressure difference was imposed by applying an additional acceleration of 0.01 nm ps^{-2} to every water molecule along the z direction.[12] For convenience, the net flux is defined as the difference between the number of water molecules leaving from one end and that from the other per nanosecond. The hydrogen bonds are defined as a pair of water molecules simultaneously having an O–O distance of less than 3.5 Å and an angle O–H–O of less than 30°.[13]

The water net flux as a function of the distance d between the wall of the SWCNT and either a fixed or vibrational charge is shown in Figure 1 b. For a fixed charge system (FCS), when d is sufficiently large, the effect of charge on the net flux is almost negligible. When d decreases, the average net flux decreases monotonically. In particular, when d is shorter than 0.5 Å, the net flux is almost zero (that is, the nanochannel is closed to water permeation), which is consistent with the previous findings.[9] It is understood that this outcome is a result of the balance of the competing interaction between the neighboring water molecule in the SWCNT and the imposed charge.[9] To our surprise, for a vibrational-charge system (VCS), the net flux exhibits an opposite behavior to that of the FCS. When the vibrational charge is far away from the SWCNT, the net flux is almost the same as that without any external charge and the same as that with a fixed charge in far distance (mentioned in above). This is reasonable, as water molecules in the confined nanochannel is unlikely to be influenced by the existence of charge in far distance. However, as the vibrational charge moves closer to the nanochannel, the net flux increases and reaches about two times as high as the net flux without any external charge under the present set-up parameters. As an example, at $d =$ 0.2 Å, the net flux for FCS is 0.28 ns^{-1}, while the net flux for VCS is 36.86 ns^{-1}.

To find out why water transport behave so differently with respect to the condition of external charge and what happens to the water molecules inside the SWCNT, we calculated the average number of water molecules, $\langle N \rangle$, and the number of hydrogen bond of water molecules, $\langle N_{\mathrm{Hbond}} \rangle$, inside the SWCNT with varying distances between the charge and the nanochannel, as shown in Figure 2.

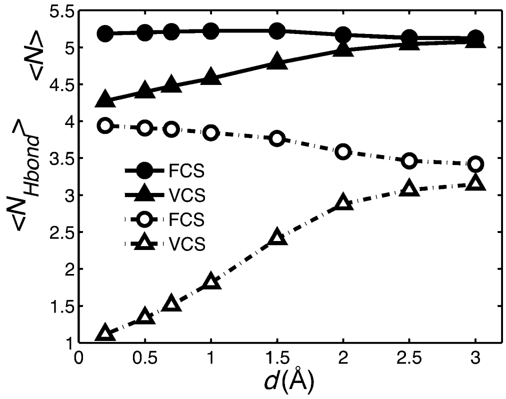

Figure 2. Average number of the water molecules (——), $\langle N \rangle$, and the hydrogen bonds (-----), $\langle N_{\mathrm{Hbond}} \rangle$, inside the nanochannel as a function of distance d for the fixed-charge system (FCS) and vibrational-charge system (VCS).

For the FCS, the average number of water molecules is little affected by the distance between the charge and the SWCNT, while the average number of hydrogen bonds tends to decrease with the increase of the distance, reaching the number of hydrogen bonds of a no-charge system when the charge is far away from the SWCNT. This verified the previous finding that the static charge will attract the negatively charged oxygen in water molecules by electrostatic interaction, immobilizing the motion of water molecules.[9,15] Here, we calculated the average angle between the water dipoles and the nanotube axis over all water molecules inside the tube, ϕ. When the charge is close to the water molecules inside the SWCNT, ϕ is about 90° (that is, bipolar water orientation), which resembles and is consistent with the bipolar water orientations in the central region of the aquaporin water channels.[5] The bipolar orientation enables more hydrogen bonds to be formed, leading to the closure of water permeation through the nanochannel. This confirms the previous finding that water molecules are not easy to move when the fixed charge is close to the SWCNT.[9] When the distance between the charge and the SWCNT increases, the electrostatic interaction between the charge and water molecules weakens. Understandably, the number of water molecules and hydrogen bond approaches to those of the system without any charge. For the VCS, both the number of water molecules and the number of hydrogen bonds increase with increasing distance between the charge and the SWCNT, reaching their maximum, which is almost equal to those of a system without any charge, when the charge is far from the SWCNT. It is interesting to realize from the above discussion that the net flux is the maximum when the number of hydrogen bonds is the least. It has been recognized that the tight hydrogen-bonding network plays a key role in the continuous transport of water molecules through nanochannel and the hydrogen bonds exhibit an elastic characteristic.[16] As reported previously and discussed above, when a charge outside the SWCNT is moving, water molecules inside the SWCNT will be dragged to move.[17] This means that an external charge can interfere with the water molecules inside the SWCNT. If the kinetic energy of water molecules movement is low, the water molecule with hydrogen bonds will move with the charge movement. When the kinetic energy of water molecules induced by the vibrational charge is greater than the binding energy of the hydrogen bond, water molecules are dragged and the hydrogen bond is easily broken. Consequently, the number of hydrogen bonds decreases with the reduction of the distance d. After water molecules are released from the constraints of hydrogen bonds, water molecules inside the nanochannel escape from the channel and enter into the bulk water. Therefore, with a shorter distance d, the number of water molecules as well as the number of hydrogen bonds in the nanochannel decrease, as shown in Figure 2.

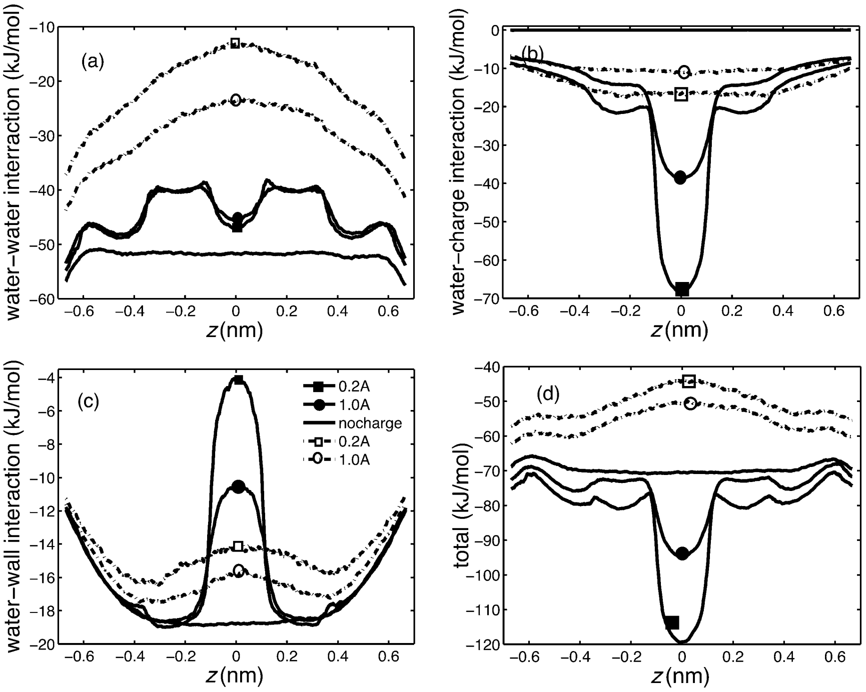

Figure 3. The interaction energies along the z direction of a water molecule with the neighboring water molecules (a), with the imposed charge (b), with the SWCNT (c), and total interaction energy (d) for a vibrational charge system (dotted lines with hollow sign), a fixed charge system (solid lines with solid sign), and without a charge system (black solid line). Only two typical distances ($d = 0.2$ Å (squares) and 1.0 Å (circles) are shown.

To better understand the fracture of hydrogen bonds, average interaction energies at different positions along the z axis inside the nanochannel are calculated, and the results are plotted in Figure 3. As shown in Figure 3a, the average interaction energy between neighboring water molecules is little changed with increasing distance of d in the FCS, which is consistent with the previously results.[9] This explains why the numbers of water molecules and hydrogen bonds do not vary significantly with varying distances of d in the FCS. However, with the reduction of the distance d in the VCS, the energy increases and becomes closer to 0 kJ mol^{-1}, which means that the hydrogen bond inside the SWCNT can be broken more easily. We further traced single-file water chain using the molecular visualization program[18] at varying distances d. A more perfect single-file water chain can be observed in the FCS than that in the VCS. Figure 3b shows that the average interaction energy between the water molecules and the charge is for attraction, and the valley in the FCS[9] disappears in the VCS. This means that the vibration charge drags water molecules to move, revealing the fact that water molecules in the VCS possess greater kinetic energy than those in FCS. The average interaction energy between the water molecules and the wall of SWCNT is shown in Figure 3c. It shows that water molecules are attracted to the wall of SWCNT over longer lengths in the VCS than in the FCS, revealing the fact that the single water molecule is attracted to move closely to the channel wall in the FCS. Figure 3d plots the total interaction energy of water molecules, charge, and nanochannel wall. Because the vibrational charge offers kinetic energy to the water molecule in the SWCNT, the total interaction energy of VCS is greater. As it is difficult for water molecules to enter into and stay in the SWCNT, greater kinetic energy of water molecules result in a dramatic reduction in number of hydrogen bonds, leading to a more efficient water transport or large net flux.

The motions $z(t)$ of individual water molecules inside the SWCNT as a function of time are shown in the Supporting Information, Figure S1. For the no-charge system (Figure S1 a), owing to the filling and emptying kinetics of water in SWCNT, water molecules have a strong tendency to enter into the nanochannel to form a single-file water chain through hydrogen bond. The conduction of the single-file water chain in the nanochannel behaves as a burst-like movement.[1,14] The same takes place in the charged systems when the distance between the charge and the SWCNT is sufficiently far. When the charge is close to the SWCNT, the movement of water molecules is constrained in the FCS, yet propelled in the VCS. As can be seen in Figure S1 c, the water molecules are drifted along the nanotube direction. Figure S1 clearly shows that the movement of water molecules inside the nanochannel is different in three kinds of systems.

To further understand water transport behavior in a variety of conditions of external charges, we calculated the potential of mean force (PMF). It has been well-known that energy barrier plays a crucial role in water transportation through CNT membranes.[9,19] In the equilibrium system, the energy barrier can be obtained by calculating the PMF of water. Our calculation shows that the energy barrier for the vibrational charge system is lower than that of the fixed charge system (Supporting Information, Figure S2). For example, the energy barrier is 0.29 k_BT in the VCS at $d=$ 0.2 Å, while that in the FCS is 3.02 k_BT. The relatively lower energy barrier of the VCS helps allow the water molecules to enter into the nanochannel and pass through it more easily. This may be another reason why the system with a vibrational charge possesses much better water transport ability.

As mentioned above, the vibration of charge breaks the hydrogen bond, leading to the decrease of the number of hydrogen bonds and a resultant high net flux. To characterize the dependence of the net flux on the motion of the charge, we calculated the net flux under different vibrational frequencies of the charge. The results are shown in Figure 4. We can see the net flux is almost independent of the vibrational frequency when the frequency is lower than 3000 GHz. With increasing vibrational frequency f from 3000 GHz to 30 000 GHz, the net flux first increases sharply to reach a maximum, then decreases monotonically and reaches a value that is even smaller than that at the low frequency. The number of hydrogen bonds has an opposite trend to that of the net flux and less hydrogen bonds results in higher net flux. The maximum net flux, which is about three times of that at the low frequency, and the minimum number of hydrogen bonds occurs at the frequency of 14 400 GHz, which is approximately equal to the inherent frequency of hydrogen bond oscillation of the single-file water chain. This phenomenon is named as electrical resonance[20] (detailed discussions are presented in Section S2 of the Supporting Information). This means when the vibrational frequency of charge is equal to the frequency of hydrogen bond, hydrogen bonds are easily broken and the permeation of water molecules in the nanochannel is maximum. In a nanoscale pump designed by Rinne et al.,[21] they found that there were two peak pumping velocities when the frequency is proper. The difference and relation between our present finding and that of Rinne et al. are discussed in Section S5 of the Supporting Information.

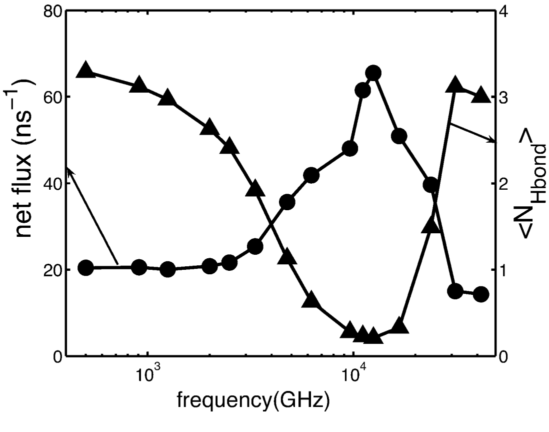

Figure 4. The net flux and average number of hydrogen bonds $\langle N_{Hbond}\rangle$ inside the SWCNT as a function of vibrational frequency for $d=1.5$ Å and $A=3$ Å.

In summary, we have found an unexpectedly high water net flux confined in a nanochannel as a vibrational charge approaches to the nanochannel by MD simulations. The water transport is a result of the vibrational charge-induced disruption of the hydrogen bond inside the nanochannel and the success for the vibration charge-induced movement of water molecules in competition with the strong water–water interaction-induced single-file chain of the confined water. This novel transport process, which can be referenced as electro-propelling, is in sharp contrast to the well-known electro-gating of water and should be important for understanding the transport of water confined inside nanochannels. Furthermore, this work demonstrates that water transport through nanochannels can be regulated through manipulating the vibrational frequency of the charge and its distance from the nanochannel.

Received: August 28, 2014
Revised: November 9, 2014

Keywords: electromanipulation · nanochannels · water transport

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