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Capability of charge signal conversion and transmission by water chains confined inside Y-shaped carbon nanotubes

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The molecular scale signal conversion, transmission, and amplification by a single external charge through a water-mediated Y-shaped nanotube have been studied using molecular dynamics simulations. Our results show that the signal converting capability is highly sensitive to the magnitude of the charge, while the signal transmitting capability is independent of the charge signal. There is a sharp two-state-like transition in the signal converting capacity for both positive and negative charges. When the charge magnitude is above a threshold ($|q| \geq \sim 0.7$ e), the water dipole orientations in the main tube can be effectively controlled by the signaling charge (i.e., signal conversion), and then be transmitted and amplified through the Y-junction, despite the thermal noises and interferences between branch signals. On the other hand, the signal transmitting capability, characterized by the correlation between the two water dipole orientations in the two branches, is found to be always larger than 0.6, independent of charge signals, indicating that the water-mediated Y-tube is an excellent signal transmitter. These findings may provide useful insights for the future design of molecular scale signal processing devices based on Y-shaped nanotubes. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4773221]

I. INTRODUCTION

Design nanoscale systems for signal conversion, transmission, and amplification at the molecular level have quickly emerged as an important field with many potential applications, such as molecular switches, nano-gates, biosensors, and artificial neural systems.[1–3] Recently, we have proposed a molecular signal converter and amplifier based on the water chains inside a Y-shaped single-walled carbon nanotube (Y-SWNT).[4,5] Carbon nanotubes have been studied extensively in the past and are known to exhibit a wealth of unique and fascinating properties.[1,6–9] For example, a carbon nanotube with suitable radius can be filled with water molecules forming a densely packed single-file water chain with concerted orientations. This water chain rarely ruptures due to the tight hydrogen bonds.[8,10,11] Previous studies have been focused mainly on the transportation of water (and other small molecules) through the carbon nanotubes as well as ion separations by Y-SWNT;[12–32] while the capability of water (or other polar molecules) mediated carbon nanotubes as potential molecular signal processors has been largely neglected.[4]

Our previous study has shown that a single charge can effectively control the orientation of single-file water chains inside nanotubes due to the strong charge-dipole interactions.[5] Hence, a charge signal can be converted into a water dipole orientation signal using this method, which can be further multiplied into two or more signals with a Y-shaped nanotube.[4,5] The response to the switching of the input charge signal is also very rapid, typically within a few tens of nanoseconds. Moreover, since the key component of the signal processing system, the Y-SWNT, can be fabricated by many different methods nowadays with the advancement of nanotechnology, such as alumina templates, chemical vapor deposition of products generated from a pyrolysis of metallocenes, nano-welding of overlapping isolated nanotubes using high-intensity electron beams, or spontaneous growth of nanotube mats using Ti-doped Fe catalysts,[3,33–36] it is becoming feasible to implement these nanoscale signal processing devices in practice.

However, there still remain some questions, such as how sensitive the water dipole orientation signal conversion and transmission is on the external charge. In other words, is there a critical value (or threshold) for the external charge size, does it depends on the charge sign (positive or negative), and what kind of charge dependence (linear or two-state transition like) does it have? These are all critical questions for the design of the Y-tube based nanoscale devices, since for molecular systems the thermal noises and interferences between the branch signals can play a non-negligible or even dominating role. Therefore, it is important to explore how the size of the external charge affects the water dipole orientations inside the main tube (i.e., the charge signal conversion), and the correlation between the two water chain dipoles in the two branches (i.e., the signal transmission). In this report, we use molecular dynamics simulations to study these effects with atomic detail to better access the capability of signal conversion and transmission in this water-mediated Y-tube system.

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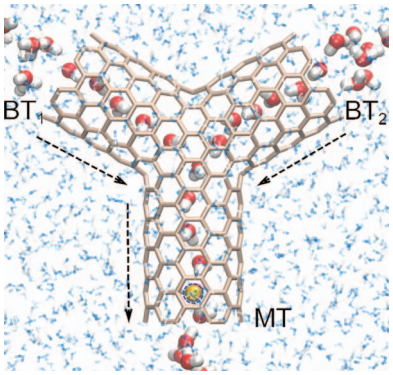

FIG. 1. Side-view of the simulation system. The Y-SWNT nanotube features a main tube (MT) with a length of 1.44 nm and two branch tubes (BT1 and BT2) with a length of 1.21 nm each. They are all uncapped armchair (6,6)-SWNTs. The angle between any two neighboring SWNTs is 120°. The yellow sphere represents the imposed external charge (i.e., external signal), highlighted with a dotted circle around it. The water dipole orientations inside the channel depend on the charge signal size and sign (in this particular case, the external charge is −1.0 e).

II. SYSTEM AND METHOD

Figure 1 shows our simulation system. The Y-SWNT was constructed by joining three (6,6) uncapped armchair single-walled carbon nanotubes symmetrically. Following the previous study,[4] a signal charge q was introduced outside the main tube (at the center of a second layer carbon ring from the edge; see Fig. 1), which is used to control the water dipole orientations inside the main tube. The water dipole orientations inside the channel depend on the charge signal size and sign (in this particular case shown in Fig. 1, the external charge is −1.0 e). To keep the entire system electrically neutral, an opposite charge was assigned at the corner of the simulation box, which is far away from the Y-SWNT to minimize its effect (frozen in simulations). The Y-SWNT was then solvated in a water box of $L_x \times L_y \times L_z = 5.20$ nm × 4.50 nm × 5.60 nm (with 4168 water molecules). The Y-SWNT carbon atoms were modeled as uncharged Lennard-Jones particles with a cross section of $\sigma_{CC} = 0.34$ nm and $\sigma_{CO} = 0.3275$ nm, and a potential well depth of $\varepsilon_{CC} = 0.3612$ kJ/mol and $\varepsilon_{CO} = 0.4802$ kJ/mol.[4] The TIP3P water model was used in our simulations.[37] The magnitude and sign of the external signal charge were varied from 0.0 e to ±1.5 e (0 e, ±0.1 e, ±0.25 e, ±0.4 e, ±0.5 e, ±0.6 e, ±0.7 e, ±0.85 e, ±1.0 e, ±1.25 e, ±1.5 e, respectively), in order to study the sensitivity of this single-charge induced signal transduction (including both signal conversion and transmission).

All the simulations were carried out with the molecular dynamics package GROMACS v.3.3.3[38,39] with a time step of 2 fs. Molecular dynamics simulations have been widely used in the modeling of both biomolecules and nanomaterials[40–44] to complement experiments, which can provide atomic details that are often inaccessible in experiments due to limited resolutions. The NVT ensemble was adopted with a constant temperature of 300 K using the Berendsen thermostat. The Y-SWNT was constrained (frozen) at the center of the simulation box. We first minimized the system with conjugate gradient method for 10 000 steps, and then equilibrated it with molecular dynamics for 5 ns before data collection. The particle-mesh Ewald method[45] was used for the long-range electrostatic interactions with periodic boundary conditions, while a smooth cutoff was used for the van der Waals interactions with a cutoff distance of 12 Å.

III. RESULTS AND DISCUSSION

Our simulation results show that water molecules confined inside the Y-SWNT form three well-defined single-file water chains that join at the Y-junction. Water chains in these nanotubes rarely rupture because of the tight hydrogen bonds between the water molecules under the nanoscale confined environment. Hydrogen bonds are highly oriented and almost perfectly aligned along the nanochannel axis, and only collectively flip in their orientations once a while. According to our previous reports,[4,11] the orientations of the water chains can be quantified by the average dipole angle, denoted $\bar{\phi}$. ϕ_i is the angle between the ith water molecule dipole and the nanotube axis, which can be calculated by the following formula:

$$\phi_i = \text{acos}(\vec{p}_i \cdot \hat{u}/|\vec{p}_i|), \tag{1}$$

where $\vec{p}_i$ is the dipole of the ith water molecule and $\hat{u}$ is the axis unit vector of the nanotube. The averaged dipole angle, $\bar{\phi}$, is thus defined as

$$\bar{\phi}(t) = \sum_i^N \phi_i(t) \Big/ N(t), \tag{2}$$

where $N(t)$ is the number of water molecules inside this tube. We find that, for each nanotube, $\bar{\phi}$ usually falls into two ranges, $10° < \bar{\phi} < 70°$or $110° < \bar{\phi} < 170°$, which were named +dipole and −dipole states,[4] respectively. To describe the state of the dipole orientations of the water molecules at any moment, we introduce an integer variable $s(t)$ defined as

$$s(t) = \begin{cases} 1 & 10° < \phi(t) < 70° \\ -1 & 110° < \phi(t) < 170° \end{cases}. \tag{3}$$

As shown previously,[4] when the external charge is negative, the water dipole orientation inside the main tube is mainly at the +dipole state ($s(t) = +1$), while it is mainly at the −dipole state ($s(t) = -1$) when the charge is positive, due to its different attraction and confinement to the nearest water molecule inside the tube.

There are two key capabilities that need to be addressed for the current molecular signal transduction with the water-mediated Y-tube system. One is the signal converting capability, i.e., how effective it is in converting the external charge signal to the water dipole orientation signal. The other is the signal transmitting capability, which can be described by the correlation between the two water chain dipole orientations in the two branches.

One way to quantitatively describe the signal converting capability of the water-mediated Y-tube system is to examine the effect of the charge quantity (charge signal) on the

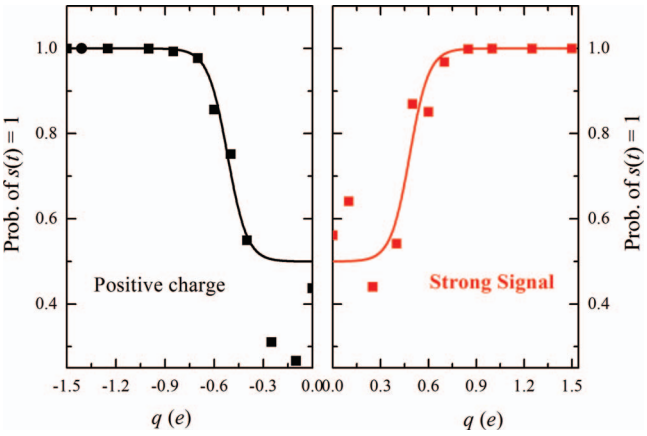

FIG. 2. The occurrence probability of $s(t) = +1$ for different negative charges (left panel), and the probability of $s(t) = -1$ for different positive charges (right panel). The solid lines are from the Boltzmann sigmoidal fit. A sharp two-state-like transition is seen in both cases, with transition charge values near $|q_c| = \sim 0.5$ e.

state of the water dipole orientation inside the main nanotube. Figure 2 shows the occurrence probability $P(t)$ of $s(t) = +1$ for the negative charge, and $s(t) = -1$ for the positive charge, with the change of the charge magnitude. As shown in Figure 2, there is a sharp transition in the occurrence probability $P(t)$ (more below), with it approaching to 1.0 when $|q| \geq \sim 0.7$ e for both positive and negative charges. This indicates that there is a threshold magnitude of ~0.7 e, above which the system can effectively control the water dipole orientations inside the main tube. In contrast, P decreases sharply and approaches to 0.5 when $|q| < 0.5$ e, indicating that water orientation angle $\bar{\phi}$ falls into these two different ranges with an approximately equal probability, hence, the capability of the control from the external charge on the state of the water dipole orientation is lost. Our simulation data can be well fitted with the Boltzmann sigmoidal (see Figure 2),

$$y - y_0 = \frac{C_1}{1 + e^{C_2(x - x_0)}}, \tag{4}$$

where $y_0 = 0.5$, $C_1 = \pm 0.5$ (positive value for the negative charge and negative value for the positive charge), and $x_0 = -0.52$ for the negative charge system, +0.48 for the positive charge system, and $C_2 = 1/0.06$. According to the above fitted formula, x_0 represents the transition point (−0.52 e and +0.48 e, respectively), i.e., there is a transition charge value near $|q_c| = \sim 0.5$ e, where sharp transitions occur. These observations suggest that the transition induced by the charge strength is a typical two-state-like transition, with one state having water highly ordered (controllable state) and the other state having water random (uncontrollable state). In the controllable state, the large charge (strong charge signal) can control the water dipole orientations, suggesting the charge signal can be effectively converted into the ordered water dipole signal (and then transmitted and amplified). In the uncontrollable state, the small charge (weak charge signal) cannot control the water dipole orientations, and the random flippings of water dipoles indicate that the charge signal cannot be converted.

To further characterize the water-mediated signal transmission, we define a correlation function C_s to measure the water dipole orientation correlations among the three channels of the Y-SWNT,

$$C_s = \frac{1}{T} \sum_{t=1}^{T} s_{\mathrm{MT}}(t) s_{\mathrm{BT1}}(t) s_{\mathrm{BT2}}(t), \tag{5}$$

where T is the total number of time steps in the molecular dynamics trajectories, and $s_{\mathrm{MT}}(t)$, $s_{\mathrm{BT1}}(t)$, and $s_{\mathrm{BT2}}(t)$ are the water dipole orientation states $s(t)$ in channels MT, BT1, and BT2, respectively.

The correlations between the two water chains are listed in Table I. We note that the influence of the external charge on the correlation between the two water chains is weak. Despite some fluctuations with the charge value, all the water chains are correlated strongly ($C_s > 0.6$) for -1.5 e $< q <$1.5 e. These results suggest that the state of the dipole orientation in the main tube can be transmitted effectively to the other two branches at the Y-junction, no matter the water dipole signal itself is ordered (controllable state) or random (uncontrollable state).

To further illustrate this, we show two representative cases with charge $q = -1.5$ e and -0.1 e in Figure 3. For the larger charge $q = -1.5$ e, the dipole orientation of the water chain in the main tube falls into $10^\circ < \bar{\phi} < 70^\circ$ due to the strong charge-dipole interactions, resulting in the occurrence probability $P(t)$ of $s(t) = 1$ approaching to 1.0 (i.e., the system is in the controllable state). Correspondingly, the state of the other two water chains in BT1 and BT2 adopt the same state as in the MT synchronously (see Figure 3). The two water dipole orientation states in the two branches correlate very well through the Y-junction. Thus, the charge signal can be effectively converted, transmitted, and also amplified (one signal in MT amplified into two signals in BTs) despite the thermal noises and interferences between branch signals. For the smaller charge $q = -0.1$ e, on the other hand, the dipole orientation of the water chain in the main tube is under the uncontrollable state due to the weak charge-dipole interactions, with $\bar{\phi}$ switching frequently between those two ranges $10^\circ < \bar{\phi} < 70^\circ$ and $110^\circ < \bar{\phi} < 170^\circ$. Interestingly, even though the state of the water chain in the MT is unstable (random), the states of the other two water chains can still follow what happens in the MT through the Y-junction (see Figure 3), indicating that the water-mediated Y-SWNT is an excellent signal

TABLE I. The correlation between the water dipole orientations in the two branches of the Y-SWNT for different charge signal q.

q (e)	0.00	0.10	0.25	0.40	0.50	0.60	0.70	0.85	1.00	1.25	1.50
C_s	0.89	0.84	0.72	0.82	0.79	0.88	0.92	0.94	0.89	0.87	0.91
q (e)	0.00	−0.10	−0.25	−0.40	−0.50	−0.60	−0.70	−0.85	−1.00	−1.25	−1.50
C_s	0.89	0.85	0.86	0.82	0.77	0.66	0.72	0.77	0.77	0.76	0.76

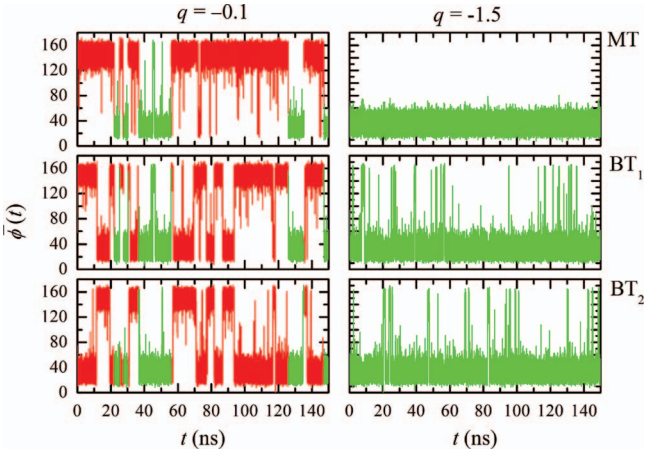

FIG. 3. The time evolution of the average dipole orientation angle $\bar{\phi}$ of the single-file water chains inside the MT, BT1, and BT2, for charge $q = -0.1$ e and -1.5 e, respectively. For the green portion, the state of the water chain in the MT is $s(t) = +1$, whereas for the red portion, $s(t) = -1$. It is clear that when $q = -1.5$ e the occurrence probability $P(t)$ of $s(t) = +1$ approaches to 1.0 (controllable state); and when $q = -0.1$ e $P(t)$ approaches to 0.5 (uncontrollable state). However, interestingly, in both cases, the water dipole orientation states in the two branches follow the MT very well, indicating that the water-mediated Y-SWNT is an excellent signal transmitter.

transmitter. It should be noted, of course, that there is a limit in the tube lengths for the Y-SWNT to be an excellent transmitter, since the correlation in the concerted water dipoles decays with the carbon nanotube length.[31]

IV. CONCLUSION

In summary, we have shown that a single external charge with large enough magnitude ($|q| \geq \sim 0.7$ e, threshold value) can effectively control the dipole orientations of the water chain inside the Y-SWNT main tube (i.e., signal can be readily converted). We also reveal that the signal converting capability is highly sensitive to the magnitude of the charge, while the signal transmitting capability is independent of the charge signal. There exists a sharp two-state-like transition in the signal converting capacity for both positive and negative charges, with transition charge values near $|qc| = \sim 0.5$ e. When the charge magnitude is below this transition value, no effective signal conversion can be achieved. The correlation between the two dipole orientations of the water chains in the two branches of Y-SWNT, on the other hand, is always larger than 0.6, independent of charge signals, indicating that the water-mediated Y-SWNT is an excellent signal transmitter. With large enough charge values, the water-mediated Y-SWNT can thus display remarkable signal converting, transmitting, and amplifying capabilities, which may have significant potential applications in molecular-scale electronic devices.

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