Supporting Information

Water in Narrow Carbon Nanotubes: Roughness Promoted Diffusion Transition

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1. Rough CNT Models

We constructed rough (6, 6) CNTs shown as follows in Figure S1. The rough surface was demonstrated by a sine function, determined by a wave length (A) and amplitude (λ). Here the amplitude was set to the diameter of CNTs. We also calculated the water diffusion in a larger (10, 10) CNT for comparison.

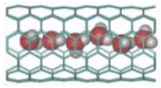
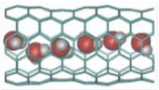
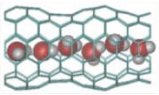
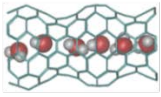
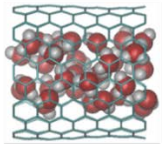
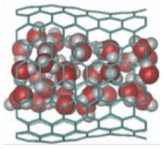
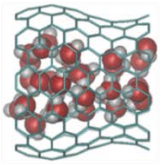
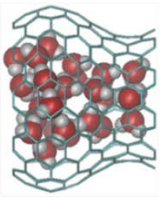
A/R_0	0.01	0.03	0.06	0.1
(6, 6) R_0=0.814 nm				
(10, 10) R_0=1.4 nm				

Figure S1. Calculated rough CNT models in this work.

2. Pore Size Distributions (PSD) of Rough CNTs

Here we utilized a Lennard Jones (LJ) particle as a probe to estimate the pore size distribution (PSD) for each rough CNT model. Figure S2 shows the PSDs for the four models. The average pore size increases with increasing roughness.

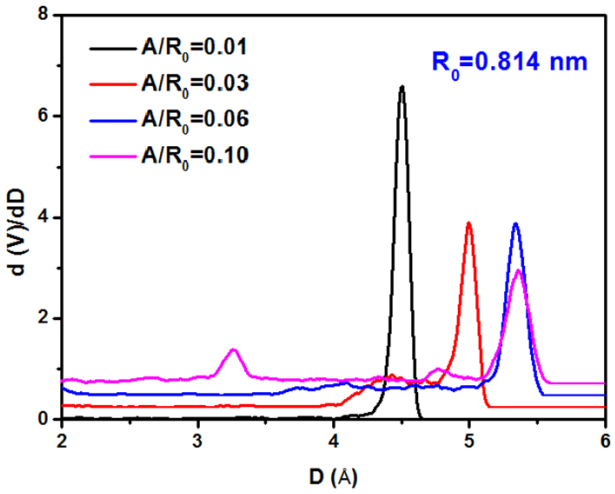


Figure S2. The pore size distributions (PSD) of rough (6, 6) CNTs

3. Temperature and energy in simulations

The temperature of water and energy for water in a smooth (6, 6) CNT in the NVE simulations is shown in Figure S3. The total energy is a constant, and there is no energy drift.

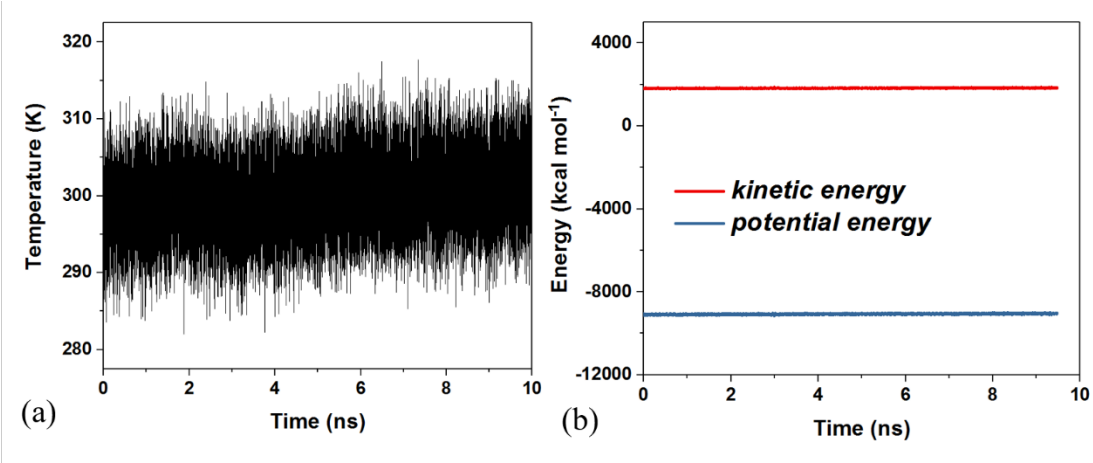


Figure S3. The temperature of water (a) and energy (b) for water in a smooth (6, 6) CNT as a function of simulation time.

4. Diffusion Coefficient Calculations

To assess the reliability of our results, we repeat all the calculations several times with different initial conditions. Figure S4a shows the three cases for water in smooth (6, 6) CNTs. No significant difference was noticed on the conclusions here reported. We also fitted 3# in this figure using $y=ax^b$. The MSD curve is well fitted, indicating that the MSD is proportional to the square of time and a ballistic diffusion style (see figure S4b).

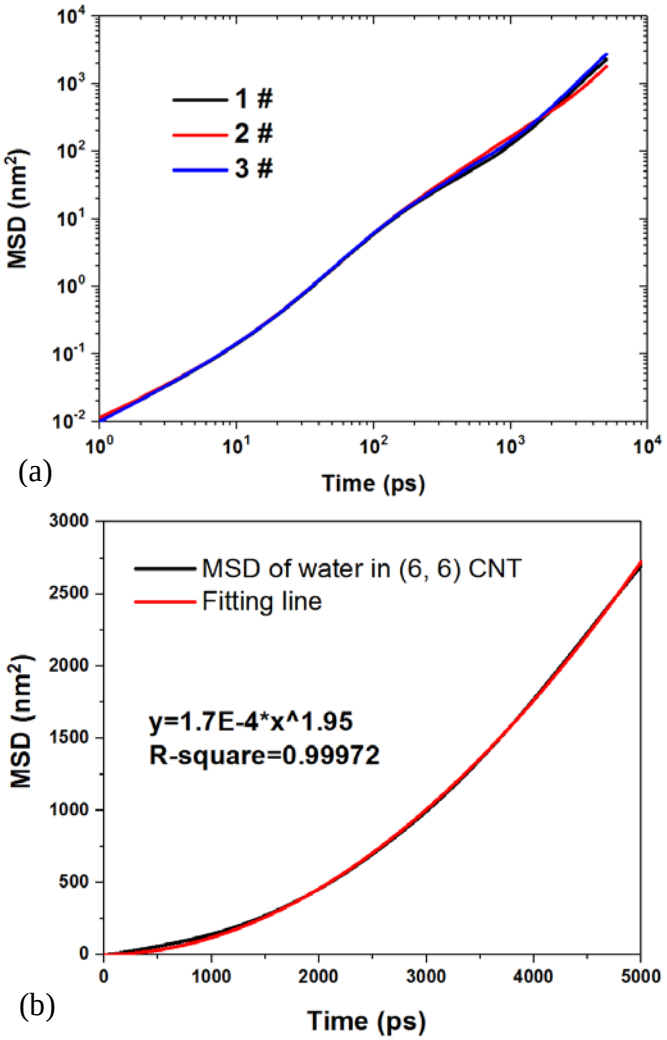


Figure S4. (a). The logarithmic plot of MSDs of single-file water in smooth (6, 6) CNTs. (b). Nonlinear fitting of MSD curve.

5. Center of mass (com) MSDs of confined water

The MSDs of the center of mass (com) of water molecules in CNTs were calculated, as shown in Figure S5. We both calculated water molecules confined in a smooth (6, 6) CNT and a rough CNT with $A/R_0 = 0.1$. From the figure, the total and com MSDs are similar for water in smooth CNTs, indicating that water molecules hardly exhibit self-diffusion. While for water in a rough CNT, the com MSD can be neglected. This means that water molecules are highly confined and diffuse randomly in a small space.

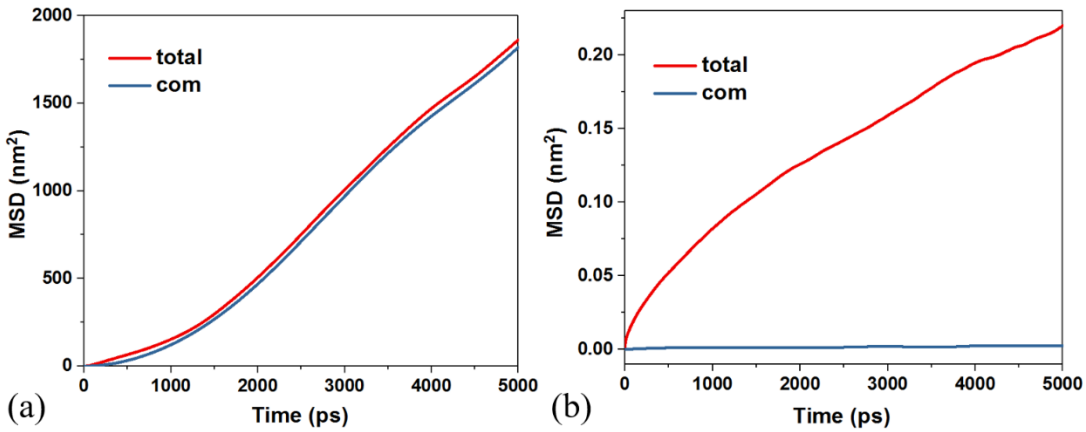


Figure S5. The total and center of mass MSDs of water confined in smooth (a) and rough (b) (6, 6) CNTs with A/R_0 = 0.1.

6. Water Distribution in CNTs

We traced one of the water molecules through calculating the displacement of a water molecule along z direction. The results are given in Figure S4a. As depicted in Figure S2, the average pore size increases in rough CNTs. We analyzed the displacements of three adjacent water molecules (represented by oxygen atoms) in a CNT with A/R_0 = 0.1, as shown in Figure S4b. From the figure we can see that water molecules cannot pass each other.

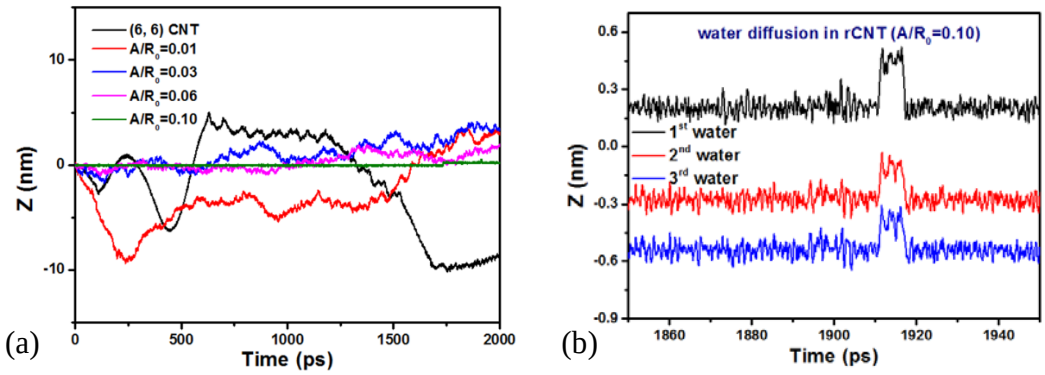


Figure S6. (a) The displacement of a water molecule along z direction. (b) The

displacements of three adjacent water molecules in a CNT with $A/R_0 = 0.1$.

7. Properties of water in CNTs as an effect of density

To understand the diffusion of the water as an effect of water density, the radial density profile (RDP), axial density profile (ADP) and dipole orientation profile (DOP) have been analyzed and shown in Figure S7.

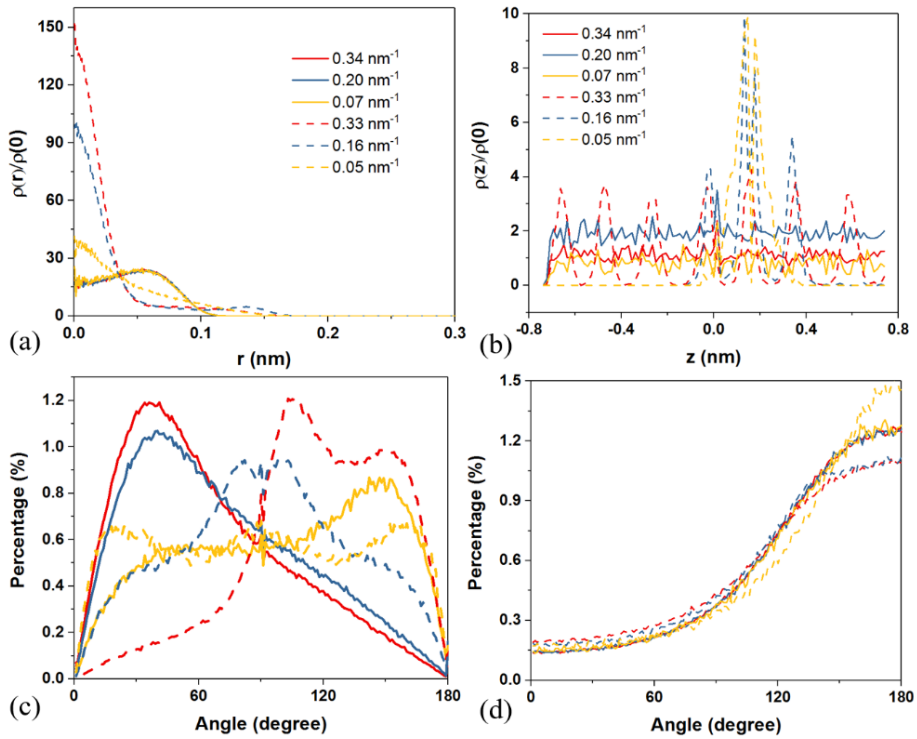


Figure S7. Radial density profile (a), axial density profile (b), and dipole orientation profile along axial (c) and radial (d) of water in CNTs with different water density.

8. Interaction Energy Analysis

The interaction energies of water-CNTs (U_{aw}) and water-water (U_{aa}) as a function of CNT roughness. $\alpha_w = U_{aw}/U_{aa}$ denotes the wetting ability of fluids on a solid surface.

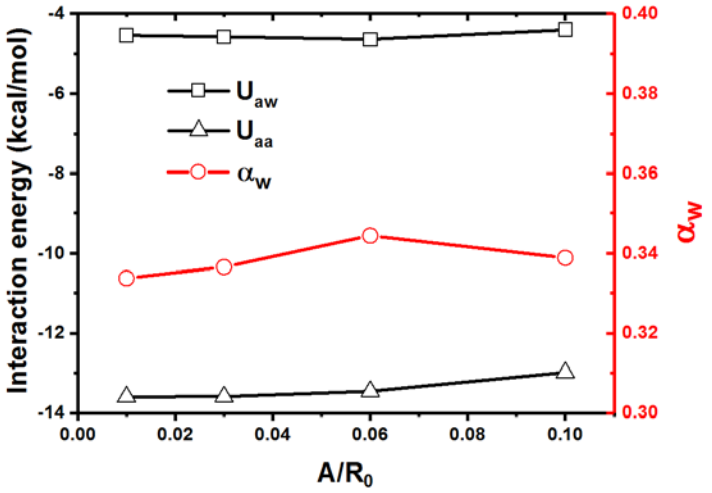


Figure S8. The interaction energies of water-CNTs (U_{aw}), water-water (U_{aa}), and weting parameter (α_w) as a function of CNT roughness.

9. Interaction and hydrogen bond (H-bond) network of water as an effect of water density

To further understand the diffusion of the water as an effect of water density, the interaction energies of water-CNT and water-water and H-bonding network have been analyzed, as shown in Figure S9.

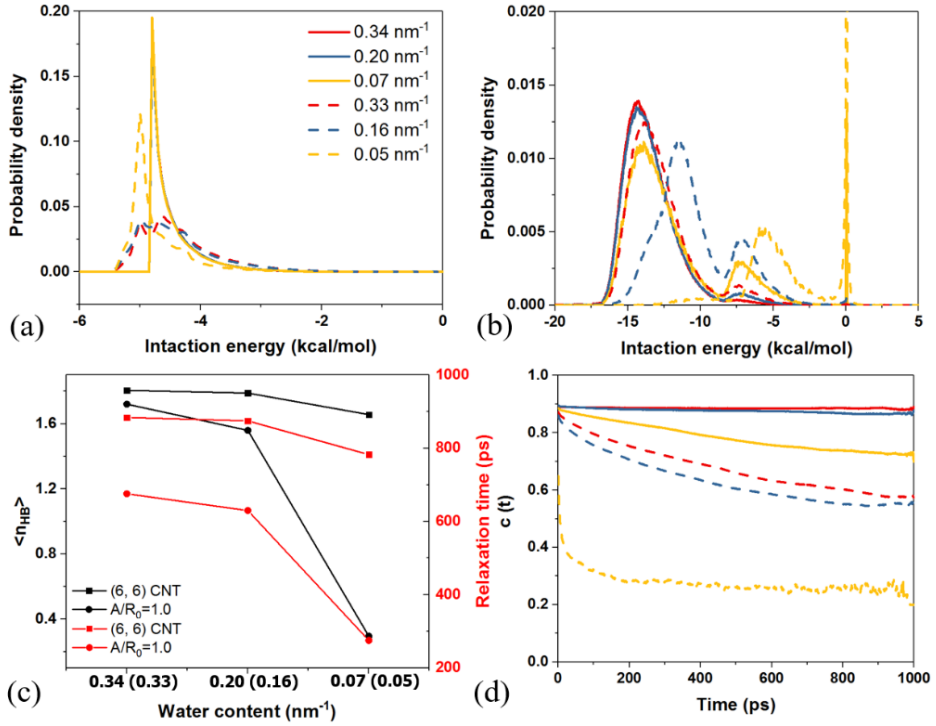


Figure S9. The distribution of water-CNT (a) and water-water interactions (b) of water in various (6, 6) CNTs; (c) Average number of hydrogen bonds (black) and relaxation time (red) per molecule as a function of tube roughness; (d) the intermittent hydrogen bond correlation function of water as a function of time in various CNTs.