Rapid Water Transportation through One-dimensional Carbon Nanospaces

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Water transportation through one-dimensional (1D) and quasi-1D internal nanospaces of highly pure single- and double-wall carbon nanotubes (SWCNTs and DWCNTs), respectively, was directly investigated from the experimentally measured rates of water vapor adsorption in these nanospaces as well as those determined by molecular dynamics (MD) simulations. Water was found to be transported more rapidly through 1D nanospaces than through quasi-1D nanospaces. This faster transportation through 1D nanospaces is attributed to the formation of fewer hydrogen bonds between water molecules of water adsorbed in a 1D system. The adsorption rates determined through the MD simulations were in agreement with the experimentally determined rates.

Water is one of the most ubiquitous naturally occurring chemical substances and has anomalous physical properties owing to its constituent hydrogen bonds. Hence, the anomalous properties of water have been studied extensively.[1] Water transportation through a water channel in a biomembrane is another important research topic, because a water channel is involved in many physiological processes. Water channels have narrow hydrophobic nanospaces.[2] As these channels are flexible and complex structures, a nanoporous material having a model structure for a water channel is required in order to understand water mechanism via a water channel. A carbon nanotube (CNT) is believed to be an example of one such material because it has hydrophobic one-dimensional (1D) nanospaces.[3] Thus, the behavior of water in CNTs has recently been studied actively.[4] For example, water permeation through membranes fabricated using CNTs has been demonstrated with the aim of understanding the working of a water channel.[4] However, the mechanism of water transportation through the internal nanospaces of CNTs remains to be elucidated.

Single- and double-walled CNTs (SWCNTs and DWCNTs) were synthesized by Hata et al. and Endo et al., respectively; they were found to have extremely low metal catalysts, high aspect ratios, and hydrophobic internal nanospaces.[5] As mentioned above, they have high potential for being used to conduct fundamental studies on water transportation through their internal nanospaces. Therefore, we directly show water vapor transportation through these SWCNTs and DWCNTs to investigate water transportation through their 1D nanospaces by the adsorption rates of water vapor, and molecular dynamics (MD) simulations.

The SWCNTs and DWCNTs were observed by High-resolution transmission electron microscopy (HRTEM) using JEM-2100F (JEOL Co.) at 120 kV. Adsorption rates of water vapor were measured at 303 K every 50 ms using a custom-designed volumetric apparatus. These CNTs were heated at a pressure of less than 0.1 Pa for 2 h prior to the adsorption rate measurements. MD simulations with the leapfrog time integration scheme were performed for understanding the water transportation mechanism; the simulation model comprised a single SWCNT having an infinite length and diameters of 1 or 2 nm, placed in a unit cell of dimensions $4 \times 4 \times 6$ nm^3. The interaction potentials between water molecules and between a water molecule and a carbon wall were calculated using TIP5P and Lennard-Jones potential models, respectively. The TIP5P potential model is a model that combines dispersion and electrostatic interactions.[6] A complete MD simulation (100 ps) was performed at ~303 K using an integration time of 0.1 fs (see Supporting Information for details of the simulation procedure).

Figure 1 shows the HRTEM images of the DWCNT and SWCNT. The average internal diameters of 1 and 2–3 nm, respectively, which are also shown in the preceding papers.[7] Water vapor can be adsorbed mainly in the internal nanospaces, as these CNTs form bundles. Thus, the SWCNTs and DWCNTs act as typical 1D and quasi-1D systems, respectively, for water. Figure 2(a) shows changes in the fractional filling of water with time. Water vapor is not adsorbed only from 0.1 s onward, and finally, equilibrium fractional filling is achieved. The fractional filling of water vapor for the 1D system increases rapidly

from 0.5 to 10 s, and that for the quasi-1D system increases gradually in the same time. Therefore, we can say that water molecules are transported more rapidly through 1D nanospaces than through quasi-1D nanospaces. The adsorption rates of water vapor were evaluated from the differential fractional filling change, as shown in Figure 2(b); these rates are directly representative of the transportation of water vapor through 1D or quasi-1D nanospaces. Furthermore, we observed extremely fast adsorption of water vapor below 0.2 s, relatively fast adsorption from 0.2 to 10 s, and gradual adsorption above 10 s. Fast adsorption below 0.2 s is caused by diffusion of water into the internal nanospaces. The relatively fast and gradual adsorption behaviors are believed to result from transportation of water vapor through the nanospaces. In comparison with the quasi-1D system, faster adsorption in the 1D system is actually observed from 0.2 to 10 s.

Results of the MD simulation of water in the internal nanospaces are shown in Figure 3; they also clarify the mechanism of water vapor transportation through 1D and quasi-1D nanospaces. This figure also shows the snapshots of water transportation through the 1D and quasi-1D nanospaces. At 0 ps, water molecules are located on the left side of the CNTs, after which they begin moving to the right side. Fractional filling of water is calculated from the number of water molecules on the right side. In the 1-nm diameter DWCNT, water transports rapidly to the right side, in contrast to that in the 2- to 3-nm diameter SWCNTs. The thermal diffusivity of water vapor in the DWCNT increases rapidly with oscillation. In contrast, the increase of thermal diffusivity in the 2-nm diameter SWCNT increases moderately. After 10 ps, the thermal diffusivities are 28×10^{-9} m^2 s^{-1} for the 1D nanospace and 4×10^{-9} m^2 s^{-1} for the quasi-1D nanospace. However, after 70 ps, they become 40×10^{-9} and 28×10^{-9} m^2 s^{-1}, respectively (see Supporting Information). These values agree with the experimental adsorption rates, as shown in Figure 2. The number of hydrogen bonds evaluated from the snapshots in Figure 3 is shown in Figure 4. In the 1D system, the number of hydrogen bonds is constant (0.4) during the calculation time step. In the quasi-1D system, however, the number of hydrogen bonds is increased from 1 to more than 3 in 50 ps. Thus, it is clear that the water molecules are unable to form sufficient hydrogen bonds in the 1D system; this lack of bond formation hinders water transportation through 1D nanospaces, because these nanospaces provide a path for rapid water transportation, as mentioned above. Thus, the experimental and simulation results are in good agreement; the minor difference in the experimental and MD-simulation time scales of water transportation is attributed to the difference in the lengths of the CNTs considered in the experiment and simulation.

In this study, we investigated direct water transportation through 1D and quasi-1D nanospaces of CNTs. Water vapor was found to transport more rapidly through 1D nanospaces than through quasi-1D nanospaces, which is in agreement with results of MD simulations. The rapid transport of water molecules in 1D nanospaces is attributed to the restricted formation of hydrogen bonds in water molecules in these 1D nanospaces.

Associated content

SUPPORTING INFORMATION AVAILABLE. N2 adsorption isotherms at 77 K for SWCNT and DWCNT, and analysis of nanospace structure. Water vapor adsorption isotherms at 303 K and thermal diffusivities of water by MD simulation. This material is available free of charge via the Internet at

http://pubs.acs.org.

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Comment [A13]: Again, this expression is slightly confusing. Do you mean "differential change in the fractional filling factor"?

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Comment [A19]: I have deleted this from here because this information has already been given above. Further, the template does not seem to contain the corresponding author details at the end of the manuscript.

Comment [A14]: This part is slightly confusing. Do you mean "taken as"? Or is the fractional filling actually *calculated* from the number of water molecules? If yes, then how exactly is it calculated? Please revise this part suitably according to the intended meaning.

Comment [A15]: Whose oscillation is being referred to here? Oscillation has not been mentioned prior to this in the text. Please clarify.

Comment [A16]: It is not clear what "time step" refers to here. Please explain what time step means in the current context.

Comment [A17]: Please check whether this revision is correct. If yes, then consider specifying the exact value (in decimals) greater than 3 (e.g., 3.4).

Comment [A18]: I have revised this part to make it grammatically correct. However, it does not make sense logically. How can hindering of water transportation result in rapid water transportation? Do you mean "this lack of bond formation promotes rapid transportation of water through 1D nanospaces, as mentioned above"?
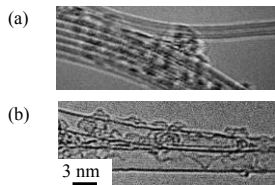
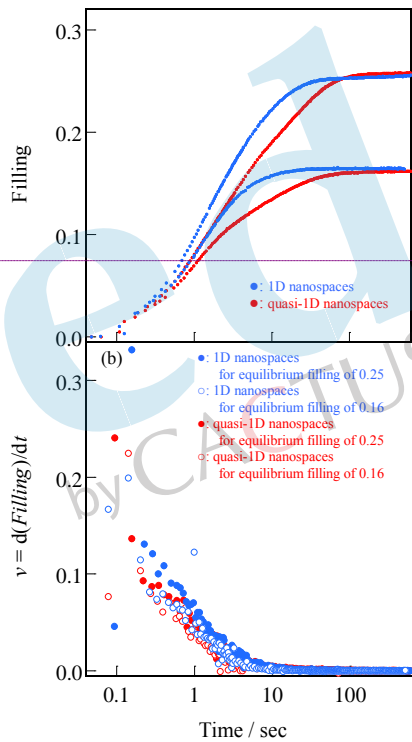**Figure 1.** TEM images of DWCNT (a) and SWCNT (b).

(a)

(b)

Figure 2. Changes in fractional Ffilling changes and rates of water vapor adsorptionbed in the internal nanospaces of CNTs.carbon nanotubes.
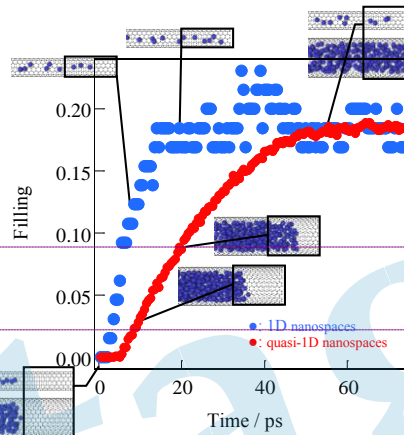

Figure 3. Simulated filling changes in fractional filling of water molecules in internal nanospaces of CNTscarbon nanotubes. The Wwater molecules flow from the left to the right side ofin the CNTscarbon nanotubes to the right side.
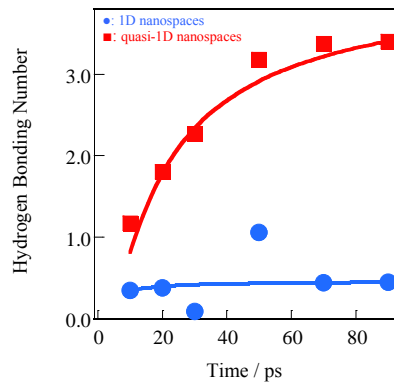

Figure 4. Changes in the number of Number changes of hydrogen bondsing with time progress.

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SYNOPSIS TOC