

# Rapid Water Transportation through One-dimensional Carbon Nanospaces

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**ABSTRACT:** Water transportation through one-dimensional (1D) and quasi-1D internal nanospaces were directly observed by the rates of water vapor adsorption in the 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 that have quasi-1D and 1D nanospaces, respectively. Water is/was found to be rapidly transported more rapidly through 1D nanospaces rather than through quasi-1D nanospaces. Molecular dynamic simulation of water through carbon nanotubes shows the same tendency as the experimental adsorption rates. This faster transportation through 1D nanospaces is attributed to the formation of 1D system, fewer water molecules rarely form hydrogen bonds bonding between water molecules of water adsorbed in a 1D system. The Therefore, the rapid water transportation is a result of less hydrogen bonding formation of water adsorbed in 1D nanospaces. 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 well-known to have anomalous physical properties owing due to its constituent hydrogen bonds hydrogen bonding. Hence, the anomalous properties of water have been continuously studied extensively.<sup>1</sup> Water transportation through a water channel in a biomembrane is another important research topic issue, because a water channel is involved in many physiological processes. Water channels have narrow hydrophobic nanospaces.<sup>2</sup> 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 an ideally model structure of a water channel, because it has due to having hydrophobic one-dimensional (1D) nanospaces.<sup>3</sup> Thus, the behavior of water properties in CNT carbon nanotubes are has recently been studied actively studied recently.<sup>4</sup> For example, the water permeation through membranes fabricated by using CNT carbon nanotube is has been demonstrated to with the aim of understanding study the working of a water channel mechanism.<sup>4</sup> However Nevertheless, the mechanism of water transportation through the internal nanospaces of CNTs carbon nanotubes remains to be elucidated is still not clear.

**Ideal Model** single- and double-walled CNT carbon nanotubes (SWCNTs and DWCNTs) were synthesized by Hata et al. and Endo et al., respectively; these have were found to have extremely low metal catalysts, long-high aspect ratios, and hydrophobic internal nanospaces.<sup>5</sup> As mentioned above, they have high potential for being used to conduct These carbon nanotubes have the great advantage of fundamental studies study on water transportation through the their internal nanospaces. Therefore, we employed Here we directly show water vapor transportation through these SWCNTs and DWCNT carbon nanotubes to investigate water transportation through their 1D nanospaces from by the adsorption rates of water vapor adsorption in SWCNT and DWCNT; and molecular dynamics (MD) simulations.

The SWCNTs and DWCNTs were observed by High-resolution transmission electron microscopy (HRTEM) observations were performed on SWCNT and DWCNT using JEM-2100F (JEOL Co.) at 120 kV. Adsorption rates of water vapor were measured at 303 K every 50 ms using a homemade custom-designed volumetric apparatus. Here these These CNT carbon nanotubes are 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 through carbon nanotubes 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  $4 \times 4 \times 6 \text{ nm}^3$ . The interaction potentials between water molecules and between a water molecule and a carbon wall were calculated by using TIP5P and Lennard-Jones potential models, respectively. Here, †The TIP5P potential model is a combination model that combines of the dispersion and electrostatic interactions, and it was proposed by Mahoney et al.<sup>6</sup> A complete MD simulation (100 ps) was performed conducted at close to ~303 K using with an integration time of 0.1 fs (see The simulation procedures are presented in detail in Supporting Information; for details of the simulation procedure).

Figure 1 shows the HRTEM images of the DWCNT and SWCNT, with The average internal diameters of DWCNT and SWCNT are 1 and 2–3 nm, respectively, which are also shown in the preceding papers.<sup>7</sup> Water vapor vapors can be adsorbed mainly in the internal nanospaces, as these CNTs carbon nanotubes form bundles. Thus, the SWCNTs and DWCNTs act as produce typical 1D and quasi-1D systems, respectively, for water, respectively. Figure 2(a) shows changes in the fractional filling changes of water with time progress. Water vapor vapors are not adsorbed only from below 0.1 s onward, then begin to be adsorbed at that time, and finally, achieve equilibrium fractional fillings is achieved. The fractional filling fillings of water vapor for the 1D system were increases rapidly significantly increased

**Comment [A1]:** You can include the telephone number and fax number of the corresponding author here.

**Comment [A8]:** This expression appears confusing. In particular, it is unclear what "low" means in this context. Are you referring to the small amount of metal catalyst required for their preparation? Or are you referring to metals with a smaller atomic number? Please revise this expression suitably according to your intended meaning.

**Comment [A9]:** This expression appears to be written more commonly as simply "TIP5P model." Please check whether this is indeed correct. If yes, then make this revision here.

**Comment [A10]:** This information does not seem to be relevant here; simply giving the citation number here is sufficient. Therefore, I have deleted this part from here.

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**Comment [A2]:** Here, it would be helpful to give a few examples of the physiological processes being referred to. This would aid readers' understanding.

**Comment [A3]:** The meaning of this part is not entirely clear to me. Do you mean "it is essential to use a nanoporous material having a model water channel structure to determine the mechanism of water transport through the channels"?

**Comment [A4]:** I have made this revision to avoid repetition of text. Please ensure that the revision is correct.

**Comment [A11]:** This part appears slightly ambiguous. Do you mean "as determined previously"?

**Comment [A5]:** For better clarity, I suggest that this part be revised as "hydrophobic one-dimensional (1D) nanospaces that water can permeate."

**Comment [A6]:** I have added this introductory term here to improve the flow from the previous sentence to this one.

**Comment [A7]:** I have edited this part to make it grammatically correct. However, should it appear as "CNT membranes"?

**Comment [A12]:** Here, it is not entirely clear what "equilibrium fractional filling" means. Do you mean "fractional filling factor stabilizes after approximately 10 s"?

from 0.5 to 10 s, and that for while these for the quasi-1D system increases gradually in the same timewere gradual increased. Therefore, we can say that water molecules are transported more rapidly through 1D nanospaces rather 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 which are directly representative of show the transportation of water vapor transportations 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 progress of adsorption above 10 s were observed. Fast adsorption below 0.2 s is caused by diffusion of a result of water diffusion into the internal nanospaces. The relatively fast and gradual adsorption process should behaviors are believed to result from water vapor transportation of water vapor through the nanospaces. In comparison with the quasi-1D system, faster adsorption in the 1D system nanospaces 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 demonstrate also clarify the mechanism of water vapor transportation through 1D and quasi-1D nanospaces, as shown in Fig. 3. The absolutely different time scale between the experiment and MD simulation is due to different length of carbon nanotubes. This Figure 3 also shows the snapshots of water transportations through the 1D and quasi-1D nanospaces. At 0 ps, water molecules are located situated in on the left side of in the CNT carbon nanotubes, after which at 0 ps and then they begin moving to flow to the right side. Fractional filling of water is calculated from the number of water molecules per number in on the right side. In the 1-nm diameter DWCNT, water transports rapidly transports to the right side in the carbon nanotube of 1-nm diameter, in contrast to while water transportation for that in the 2- to 3-nm diameter quasi-1D nanospace SWCNTs is considerably slow. The thermal diffusivity of water vapor in the DWCNT for 1-nm diameter increases rapidly quickly increased with oscillation. On the other hands in contrast, the increase of thermal diffusivity for in the 2-nm-diameter SWCNT increases moderately is moderate. After 10 ps, the thermal diffusivities of water vapor are  $28 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for the 1D nanospace and  $4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for the quasi-1D nanospace in 10 ps. However, after 70 ps, the thermal diffusivities for 1D and quasi-1D nanospaces become  $40 \times 10^{-9}$  and  $28 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  in 70 ps, respectively (see Supporting Information). These values tendencies agree correspond with the experimental adsorption rates, as shown in Figure 2. The number of numbers of hydrogen bonds bonding are evaluated from the snapshots, in Figure 4 as shown in Figure 4. In the 1D system, the number of hydrogen bonds bonding is constant at (0.4) during the calculation time step. In the quasi-1D system, however, the number of hydrogen bonds bonding is increased from 1 bond to more than over 3 in 50 ps. Thus, that is, it is clear that the water molecules are unable to cannot form sufficient adequate hydrogen bonds bonding in the 1D system; this lack of bond formation Hence, hydrogen bonding formation hinders prevents from water transportation through 1D nanospaces, because these 1D 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 paper, we investigated direct water transportation through 1D and quasi-1D nanospaces of CNTs were observed. Water vapor was found to transport more rapidly transports through 1D nanospaces rather than through quasi-1D nanospaces, which is in agreement with supported by results of MD

simulations. The rapid transport of water molecules in 1D nanospaces is attributed to the restricted formation of hydrogen bonds bonding formation of in water molecules in these restricted by 1D nanospaces. Therefore, as a result of restriction of hydrogen bonding formation water molecules rapidly transport through 1D nanospaces.

#### Associated content

**SUPPORTING INFORMATION AVAILABLE.** N<sub>2</sub> adsorption isotherms at 77 K for SWCNT and DWCNT, and the analysis of nanospace structure analysis. 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 [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"?

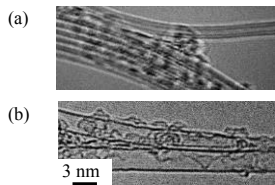


Figure 1. TEM images of DWCNT (a) and SWCNT (b).

(a)

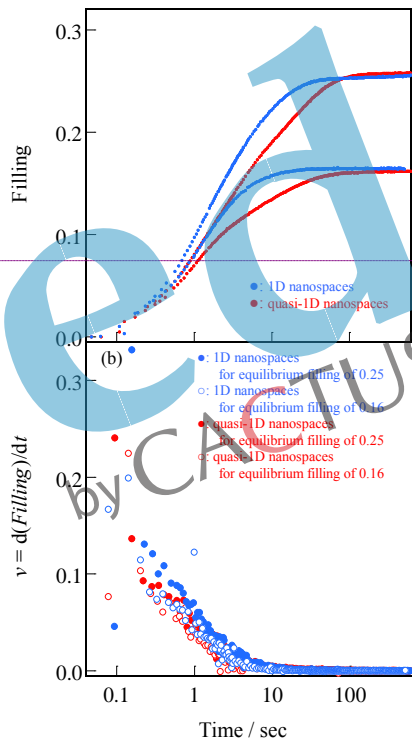


Figure 2. Changes in fractional filling and rates of water vapor adsorption in the internal nanospaces of CNTs carbon nanotubes.

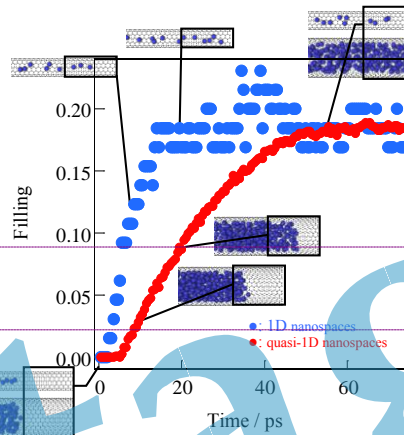


Figure 3. Simulated filling changes in fractional filling of water molecules in internal nanospaces of CNTs carbon nanotubes. The water molecules flow from the left to the right side of the CNTs carbon nanotubes to the right side.

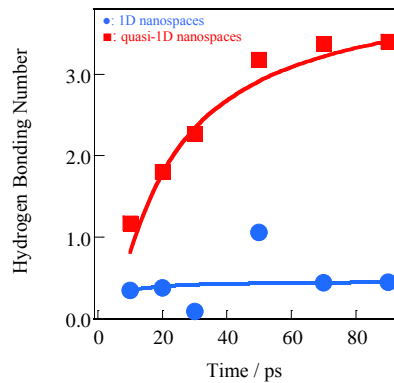


Figure 4. Changes in the number of hydrogen bonds with time progress.

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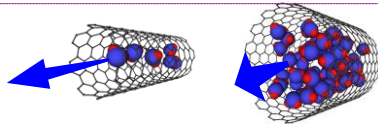
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