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Evidence of Water Adsorption in Hydrophobic Nanospaces of Highly Pure Double-Walled Carbon Nanotubes

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The adsorption of water vapor by carbon nanotubes and other narrow channels is receiving increasing attention in physical, chemical, and biological sciences owing to its promise for practical applications such as separation and purification, selective chemical sensing, and the efficient design and operation of micro- and nanofluidic devices. As explained by Sansom and Biggin, one would not intuitively expect water to enter a narrow hydrophobic carbon nanotube, but computer simulations surprise us to show that it can.[1] This adsorption phenomenon can also provide clues about the behavior of biological pores.[1,2] Single-walled carbon nanotubes (SWCNTs) as well as multiwalled carbon nanotubes (MWCNTs) with rigid, chemically simple, and well-defined nanopores provide a model system for investigation into the behavior of nanoconfined interfacial water, and thus water adsorption by SWCNTs and MWCNTs has been extensively investigated by means of molecular dynamics (MD) simulations.[2,3] Recently, nuclear magnetic resonance measurements have been used to construct water adsorption isotherms in SWCNTs.[4] Hummer et al. have found that, within subnanometer-diameter channels of SWCNTs, water undergoes a one-dimensional ordering, which leads to a concerted, pulse-like movement of water molecules within the nanotube channels due to the tightness of the hydrogen bonding network among the water molecules.[3] Wang et al. have reported that the hydrophobicity of nanoconfined SWCNT surfaces should not be considered an absolute property without considering the structure of interfacial water.[4] Their study corroborates the proposal that carbon nanoconfinement favors the formation of clusters of water molecules and that as these clusters grow the SWCNT pores become effectively hydrophilic.[5] These intriguing progresses have given rise to an intensive interest in water adsorption in nanoscale pores of carbon nanotubes (CNTs). We need to obtain new knowledge of water adsorption on different types of CNTs.[5,6]

Double-walled carbon nanotubes (DWCNTs), a relatively new form of CNTs, have attracted great research interest in recent years because of their unique coaxial structure and promising mechanical, electrical, optical, and thermal properties compared with those of SWCNTs.[7] Progress in selective synthesis of DWCNTs has extended their potentially advanced applications for storage of hydrogen and atomic-scale templates for atomic wires.[8] However, lack of a synthetic route to highly pure DWCNTs has inhibited substantial progress in understanding the interfacial science of DWCNTs in comparison with SWCNTs and MWCNTs. Many studies have been focused on DWCNT synthesis and high-resolution transmission electron microscope (HRTEM) observation of DWCNT morphology and nanostructure, but there have been few attempts to understand the interfacial nature of the DWCNTs.[7,8] To study the interfacial nature of DWCNTs, a much larger sample amount than that required for HRTEM studies is needed. However, we have recently developed a catalytic chemical vapor deposition (CCVD) method to synthesize highly pure DWCNTs,[9] and this method allows for the synthesis of an amount of DWCNTs substantial enough for interfacial studies. In this communication, we present data obtained from molecular probe adsorption studies of our DWCNTs that provide, for the first time to our knowledge, direct evidence of water adsorption in hydrophobic nanospaces of highly pure DWCNTs.

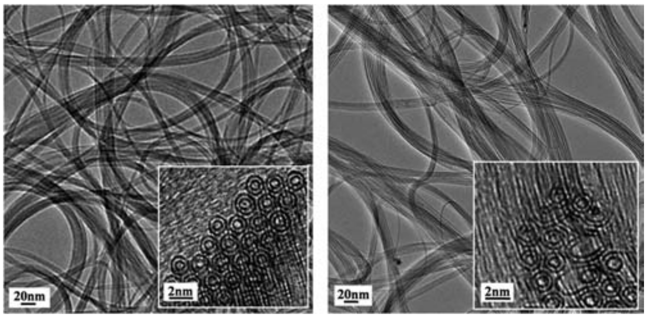

Figure 1. HRTEM images of DWCNTs (left) and HT-DWCNTs (right). Insets show cross-sectional images.

Highly pure DWCNTs were prepared by means of the CCVD method described previously.[9] With an optimized two-step postsynthesis purification procedure using hydrochloric acid to remove the iron catalysts and the magnesium oxide carrier and using oxidation to remove carbon impurities, highly pure (>95%) DWCNTs were obtained. We annealed the DWCNTs at 2273 K in an argon flow for 30 min in a graphite-resistance furnace to obtain heat-treated double-walled carbon nanotubes (HT-DWCNTs). The structural properties of the DWCNTs and HT-DWCNTs were studied by molecular probe adsorption methods using N_2 at 77 K, CO_2 at 273 K, and water at 298, 308, and 318 K, as well as HRTEM.

The morphology and bundle states observed by HRTEM of DWCNTs and HT-DWCNTs are shown in Figure 1. Individual DWCNTs packed hexagonally to form an ordered structure, thus creating a relatively uniform one-dimensional or quasi one-dimensional micropore system. The nanostructured sites within this system can be classified according to their locations as interstitial pores, internal pores, and grooves,[10] and we refer to these pores as nanopores for convenience because of their nanoscale pore widths (insets, Figure 1). For HT-DWCNTs, we observed coalescing among the outer shells and destruction of the bundle state, but the inner tubules of the HT-DWCNTs were mostly preserved during thermal annealing. The HRTEM images in Figure 1 show that the interstitial nanoporosity of the HT-DWCNTs was substantially reduced compared to that of the DWCNTs. Nevertheless, the HRTEM images of both types of CNTs' cross sections clearly show

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Table 1. Pore Structure Parameters of DWCNTs and HT-DWCNTs

	S_{BET} (N_2) ($m^2\ g^{-1}$)	micropore size (N_2) (nm)	micropore vol (N_2) ($cm^3\ g^{-1}$)	total pore vol (N_2) ($cm^3\ g^{-1}$)	total pore vol (H_2O) ($cm^3\ g^{-1}$)
DWCNTs	510	0.68	0.19	1.68	0.18
HT-DWCNTs	350	0.67	0.14	0.97	0.10

empty cavities, suggesting that the CNTs' precise nanopore structures can be studied by means of gas adsorption.

The adsorption/desorption isotherms of N_2 at 77 K on both DWCNTs and HT-DWCNTs were IUPAC type II isotherms, exhibiting a steep uptake of N_2 below a relative pressure (P/P_0) of 0.05 and a gradual uptake of N_2 at higher P/P_0 (Figure S1).[11] The increase in N_2 adsorption at $P/P_0 < 0.05$ corresponded to the volume filling of micropores in the tubule structure. This volume filling of micropores was also confirmed with CO_2 adsorption at subatmospheric pressure at 273 K (Figure S2), for which the isotherms also were type II, indicating pore filling in the narrow micropores.[12] The gradual increase in N_2 adsorption at $P/P_0 > 0.05$, which corresponded to multilayer adsorption on pores with widths larger than 2 nm and to adsorption on the external CNT surface, suggested that the bundles of both DWCNTs and HT-DWCNTs contained some arbitrary mesopores and macropores. Plots comparing the amounts of N_2 and CO_2 adsorption on the HT-DWCNTs against those on the DWCNTs were almost linear, indicating that adsorption sites for the probe molecules on the two types of CNTs were similar to each other for the pressure ranges tested here (Figure S1 and S2). The pore structure parameters determined from N_2 adsorption at 77 K are summarized in Table 1. Both DWCNTs and HT-DWCNTs had ultramicropores of less than 0.7 nm widths.

Figure 2 shows the water adsorption/desorption isotherms for DWCNTs and HT-DWCNTs at 298, 308, and 318 K. All the water adsorption isotherms for DWCNTs were S-shaped, showing two adsorption steps for $P/P_0 = 0.3$ to 0.65 and for $P/P_0 = 0.65$ to $\sim$1. This observed water adsorption behavior on DWCNTs suggests that two types of pores were filled consecutively. The total pore volume determined from the amount of adsorbed water at 318 K near saturation ($P/P_0 = 0.99$) was 0.18 $cm^3\ g^{-1}$. This volume is in agreement with the micropore volume determined by N_2 adsorption at 77 K, indicating that the full volume of the micropores was filled with water. In contrast, all the water adsorption isotherms for HT-DWCNTs showed only a single adsorption step for $P/P_0 = 0.65$ to $\sim$1, but the total pore volume determined from water adsorption in that case was 0.10 $cm^3\ g^{-1}$, also close to the micropore volume determined by N_2 adsorption. The agreement of the pore volumes determined by water adsorption with those micropore volumes determined by N_2 adsorption, which are much less than the total pore volumes, strongly suggests that water was adsorbed in the hydrophobic nanospaces of highly pure DWCNTs. For HT-DWCNTs, the smaller pore volume determined by means of water adsorption was attributed to a reduction in interstitial porosity caused by the destruction of the ordered CNT bundles during thermal annealing, as evidenced by HRTEM observation (Figure 1). Plots comparing the amount of water adsorbed on the HT-DWCNTs against that adsorbed on the DWCNTs showed a correlation near zero, followed by an almost linear correlation (Figure S3), suggesting that the nanopores responded to the filling with water molecules. Thus, comparison of water adsorption on DWCNTs with that on HT-DWCNTs indicates that pore-filling with water in DWCNTs occurred consecutively, first by filling the interstitial nanopores, and then by filling the interbundle nanopores.

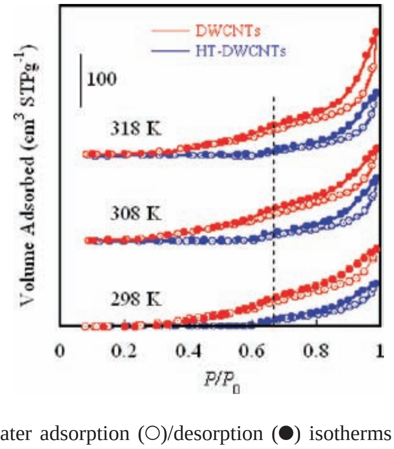

Figure 2. Water adsorption (○)/desorption (●) isotherms for DWCNTs and HT-DWCNTs at 298, 308, and 318 K.

Lastly, none of the water adsorption isotherms for either DWCNTs or HT-DWCNTs exhibited a relative pressure shift with increasing temperature, and the adsorption capacity at $P/P_0 = \sim 1$ was higher for adsorption at a higher temperature. This phenomenon is not adequately described by the Kelvin equation.[11] However, one would expect the formation and filling up of loose unstructured quasi one-dimensional water clusters in the nanospaces of the DWCNTs.[6]

In conclusion, this study demonstrates that water can be adsorbed in the hydrophobic nanospaces of CNTs, particularly within ultramicropores of highly pure DWCNTs. These results should provide insight into the mechanism of water adsorption on carbon pores with sizes between those of supermicropores and ultramicropores.

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Supporting Information Available: Sample preparation and characterization methods, figures with N_2 adsorption isotherms at 77 K, CO_2 adsorption isotherms at 273 K, comparison plots, and table of water adsorption/desorption data at 318 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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