ABSTRACT: In this study, we describe the adsorption behavior of water (H$_2$O) in the interstitial space of single-walled carbon nanotubes (SWCNTs). A highly dense SWCNT (HD-SWCNT) film with a remarkably enhanced interstitial space was fabricated through mild HNO$_3$/H$_2$SO$_4$ treatment. The N$_2$, CO$_2$, and H$_2$ adsorption isotherm results indicated remarkably developed micropore volumes (from 0.10 to 0.40 mL g$^{-1}$) and narrower micropore widths (from 1.5 to 0.9 nm) following mild HNO$_3$/H$_2$SO$_4$ treatment, suggesting that the interstitial space was increased from the initial densely-packed network assembly structure of the SWCNTs. The H$_2$O adsorption isotherm of the HD-SWCNT film at 303 K showed an increase in H$_2$O adsorption (i.e., by $\sim$170%), which increased rapidly from the critical value of relative pressure (i.e., 0.3). Despite the remarkably enhanced adsorption capacity of H$_2$O, the rates of H$_2$O adsorption and desorption in the interstitial space did not change. This result shows an adsorption behavior different from that of the fast transport of H$_2$O molecules in the internal space of the SWCNTs. In addition, the adsorption capacities of N$_2$, CO$_2$, H$_2$, and H$_2$O molecules in the interstitial space of the HD-SWCNT film showed a linear relationship with the kinetic diameter, indicating an adsorption behavior that is highly dependent on the kinetic diameter.

INTRODUCTION

Water (H$_2$O) adsorption into porous materials, such as porous silica, metal–organic frameworks, and metal-based catalyst materials, has been studied passionately over a number of years because of its potential applicability in eco-friendly energy devices. Water adsorption into carbon nanotubes (CNTs) can also play a crucial role in carbon nanotubes because of the hydrophobic nature of the CNT surface. In addition, studies into the adsorption/desorption of H$_2$O molecules in these nanoporous materials have been the basis for energy and environmental research in industrial processes, such as H$_2$O purification, desalination, drug delivery, and ion transport. Since the adsorption/desorption behaviors of H$_2$O molecules are altered by the pore structures and properties of such materials, further research is required in this area.

Carbon nanoporous materials mainly possess a hydrophobic surface but show a unique phenomenon in which the adsorption of H$_2$O molecules increases rapidly at a critical value of the relative H$_2$O vapor pressure.$^{11-14}$ The adsorption of H$_2$O through control of the pore structures of these nanoporous carbons has been extensively studied.$^{15-17}$ For example, the mechanisms for stable H$_2$O cluster formation and adsorption in nanoporous carbons with different pore widths were examined through small-angle X-ray scattering measurements, simulations, and in situ molecular adsorption studies for carbon materials with nanopores of various shapes (i.e., activated carbon fibers, carbon nanohorns, and carbon aerosol materials).$^{18-20}$ Single-walled carbon nanotubes (SWCNTs) with one-dimensional hollow structures and high aspect ratios can be divided into their internal spaces and interstitial spaces, which are formed by the networks between the nanotube bundles.$^{21,22}$ In particular, the narrow internal spaces of SWCNTs with diameters of generally $\leq$2 nm can realize the fast transport of molecules (e.g., H$_2$O) with a particularly strong confinement effect.$^{23-27}$ In this context, Holt et al. reported a mechanism for the fast transport of H$_2$O to microfabricated membranes using sub-2 nm SWCNT arrays.$^{24}$ In addition, Tunuguntla et al. reported an enhanced H$_2$O permeability and tunable ion selectivity through the application of 0.8 nm diameter SWCNT porins,$^{27}$ while Ohba et al. studied the formation of H$_2$O clusters in the SWCNT internal space and examined the H$_2$O adsorption mechanism based on...
the nanotube diameter using X-ray diffraction and molecular simulation analyses.\textsuperscript{28,29} Furthermore, a number of studies into the unique $\text{H}_2\text{O}$ adsorption phenomena and mechanisms taking place in the SWCNT internal spaces have been reported.\textsuperscript{30–32}

However, compared to extensive and systematic studies into the internal spaces of SWCNTs, studies into the adsorption behaviors and storage mechanisms of molecules, such as $\text{H}_2\text{O}$, in the interstitial spaces of SWCNTs are rare. The interstitial space formed by the assembly network between nanotubes has the advantage of being able to freely control the nanoporosity through interfacial engineering of a solution-based process, unlike the internal space determined by the nanotube diameter.\textsuperscript{33–36} The study of $\text{H}_2\text{O}$ adsorption in such developed interstitial spaces would therefore be expected to provide a clear understanding of the nanoporous structures of SWCNTs and the adsorption behaviors of different molecules.

Thus, herein we report the behavior of $\text{H}_2\text{O}$ adsorption in the interstitial spaces of SWCNTs, which are remarkably developed through mild acid treatment. The rates of $\text{H}_2\text{O}$ adsorption and desorption are examined before and after the treatment, and the adsorption capacity of the molecule, which depends on the kinetic diameter of the molecule, is also described.

\section*{RESULTS AND DISCUSSION}

Figure 1a,b shows photographic images of the highly dense SWCNT (HD-SWCNT) film fabricated via mild acid treatment in HNO$_3$/H$_2$SO$_4$ at 298 K and subsequent vacuum filtration (VF). The HD-SWCNT film exhibits a relatively uniform and rigid surface, and the film thickness was determined to be $\sim 30$ $\mu$m. Figure 1c,d shows the field emission scanning electron microscopy (FE-SEM) images of the surface morphologies of the SWCNTs and the HD-SWCNT film, respectively. After HNO$_3$/H$_2$SO$_4$ treatment, the network assembly form of the HD-SWCNT film exhibited a fairly uniform and dense structure (Figure 1d). The dense packing structure of the HD-SWCNT film can be attributed to the following two phenomena: (1) randomly entangled as-grown SWCNT bundles are highly dispensed by oxygen-containing functional groups introduced by the HNO$_3$/H$_2$SO$_4$ treatment, and (2) the individual SWCNTs in the dispersed suspension are densely rearranged through the VF process after sonication. The assembly of SWCNTs through a high dispersion and rearrangement process by the introduction of oxygen-containing functional groups is therefore a simple and effective method for controlling the narrow microporosity in solution-based CNT processes. Such a dense assembly structure of the HD-SWCNT film can provide a remarkably developed adsorption capacity attributed to increasingly narrow micropores.

To determine the surface chemical states of the SWCNTs and the HD-SWCNT film, X-ray photoelectron spectroscopy (XPS) was carried out (Figure 2). The C 1$s$ spectra were fitted with four peaks originating from C$=$C and/or C–H (284.4 eV), C–O and/or C$=$O (286.4 eV), O–C$=$O (288.6 eV), and $\pi$$-$$\pi^*$ shake-up (290.4 eV), as shown in Figure 2a,b.\textsuperscript{39,40} After functionalizing the SWCNTs by HNO$_3$/H$_2$SO$_4$ treatment and thermal treatment at 1173 K (HD-SWCNT film), the content of the oxygen-containing functional groups (i.e., C–O and/or C$=$O) increased by up to 42.4% (Figure 2a,b). Recently, our group demonstrated the peak shifts and the corresponding full widths at half-maximum (fswhm) of the XPS peaks of nanocarbon materials with various defects.\textsuperscript{39,41–43} The XPS peak originating from vacancy defects appears at $\pm 0.7$ eV from the C$=$C and/or C–H main peak.\textsuperscript{39,44} Thus, the fswhm of the peak originating from the C$=$C and/or C–H moiety of the HD-SWCNT film was not increased compared to that of the SWCNTs (Figure 2c), which indicates either that the number of internal pores was small or that no internal pores were introduced.

In Figure 3a, the adsorption isotherms of the SWCNTs are typical IUPAC type II isotherms, whereas the HD-SWCNT film was found to exhibit a type IV isotherm with small hysteresis, especially in the low relative pressure region ($P/P_0 = 0.1$). In addition, the film presented a significantly higher adsorption capacity ($\sim 2x$) than the SWCNTs. In the low relative pressure region ($P/P_0 = 0.1$), the marked increase in the amount of N$_2$ adsorption was associated with the development of narrow micropores, which can be more clearly observed in the adsorption isotherm by plotting the logarithm of $P/P_0$ (see the inset of Figure 3a). The development of this remarkable microporosity can lead to a high micropore surface area and a high micropore volume. The subtracting pore effect (SPE) method determined by the $\alpha_s$-plots is an effective analytical tool for accurately characterizing micropores.\textsuperscript{33,44} Figure 3b shows high-resolution $\alpha_s$-plots of the adsorption of N$_2$ by the SWCNTs and the HD-SWCNT film. A significant increase in the lower regions of the $\alpha_s$-plots ($\alpha_s < 0.5$) indicates the presence of abundantly developed uniform micropores. The pore structure parameters of the SWCNTs and the HD-SWCNT film calculated from the SPE method are summarized in Table 1. After HNO$_3$/H$_2$SO$_4$ treatment, the total surface area of the HD-SWCNT film increased approximately 3 times from 341 to 1048 m$^2$ g$^{-1}$, as shown in Table 1 and Figure 3c. This significant increase in the total surface area is mainly due to the increased interstitial space between nanotubes, which in turn is caused by the formation of tightly packed assembly structures. The micropore surface area of the HD-SWCNT film increased by approximately 10 times from 82 to 859 m$^2$. 

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c06302)
and the micropore volume increased by 4 times from 0.10 to 0.40 mL g\(^{-1}\) (Table 1). The Dubinin–Radushkevich (DR) equation was then applied to analyze the precise microporous structure and the isosteric heat of adsorption (\(q_{\text{st,1/e}}\), \(\Phi = 1/e\)) for the SWCNTs and the HD-SWCNT film. Figure 3d shows the DR plot of the N\(_2\) adsorption isotherm at 77 K, where it is apparent that both DR plots of the SWCNTs and HD-SWCNT film are linear in the low-pressure range. The values of \(q_{\text{st,1/e}}\), \(w\), \(W_0^{\text{N}_2}\), and \(W_0^{\text{CO}_2}\) obtained from the DR plots are summarized in Table 2. In addition, the average micropore width of the HD-SWCNT film was found to narrow from 1.5 to 0.9 nm (Table 2). In general, the \(q_{\text{st,1/e}}\) value depends on the micropore width, the chemical state, and the interaction of the pore walls. This implies that the higher the \(q_{\text{st,1/e}}\) value, the stronger the adsorbent–pore interaction. Following mild H\(_2\)SO\(_4\)/H\(_2\)NO\(_3\) treatment, the \(q_{\text{st,1/e}}\) value of the HD-SWCNT film increased by 3.1 kJ mol\(^{-1}\) compared to that of the SWCNTs. These results clearly indicate the remarkable development of micropores with a narrow average width of 0.9 nm, mainly owing to the enhancement of the interstitial space caused by the formation of highly packed SWCNT assemblies.

Subsequently, the enriched narrow interstitial space of the HD-SWCNT film with \(w = 0.9\) nm was analyzed by applying the CO\(_2\) adsorption technology. Since CO\(_2\) molecules (kinetic diameter = 0.330 nm) are smaller than N\(_2\) molecules (kinetic diameter = 0.364 nm) and have a higher kinetic energy, they can easily access the very narrow interstitial spaces of the nanotubes where N\(_2\) molecules cannot be adsorbed (Table 3). Figure 4 shows the CO\(_2\) adsorption isotherms of the

### Table 1. Pore Structure Parameters of the SWCNTs and the HD-SWCNT Film Determined by the SPE Method

| sample             | total surface area (m\(^2\) g\(^{-1}\)) | micropore surface area (m\(^2\) g\(^{-1}\)) | mesopore surface area (m\(^2\) g\(^{-1}\)) | total pore volume (mL g\(^{-1}\)) | micropore volume (mL g\(^{-1}\)) | mesopore volume (mL g\(^{-1}\)) |
|--------------------|----------------------------------------|-------------------------------------------|------------------------------------------|-------------------------------|-------------------------------|-------------------------------|
| SWCNTs             | 341                                    | 82                                        | 259                                      | 1.01                          | 0.10                          | 0.91                          |
| HD-SWCNT film      | 1048                                   | 859                                       | 189                                      | 0.72                          | 0.40                          | 0.32                          |

### Table 2. Isosteric Heats of Adsorption (\(q_{\text{st,1/e}}\)), Average Micropore Widths (\(w\)), and Micropore Volumes (\(W_0^{\text{N}_2}\) and \(W_0^{\text{CO}_2}\)) Determined from DR Plots of the N\(_2\) (77 K) and CO\(_2\) (273 K) Adsorption Isotherms

| sample             | \(q_{\text{st,1/e}}\) (kJ mol\(^{-1}\)) | \(w\) (nm) | \(W_0^{\text{N}_2}\) (mL g\(^{-1}\)) | \(W_0^{\text{CO}_2}\) (mL g\(^{-1}\)) |
|--------------------|-----------------------------------------|-------------|----------------------------------|----------------------------------|
| SWCNTs             | 9.8                                     | 1.5         | 0.10                             | 0.08                             |
| HD-SWCNT films     | 12.9                                    | 0.9         | 0.40                             | 0.32                             |

### Table 3. Kinetic Diameters of the N\(_2\), CO\(_2\), H\(_2\), and H\(_2\)O Molecules

| molecule          | N\(_2\)     | CO\(_2\)    | H\(_2\)      | H\(_2\)O      |
|-------------------|-------------|-------------|--------------|--------------|
| kinetic diameter (nm) | 0.364\(^{45}\) | 0.330\(^{45}\) | 0.289\(^{45}\) | 0.265\(^{46}\) |
SWCNTs and the HD-SWCNT film at 273 K up to a maximum relative pressure ($P/P_0$) of 0.029. CO$_2$ adsorption by the HD-SWCNT (170 mg g$^{-1}$) film exhibits a Langmuir isotherm, in addition to an approximately 2.9 times higher adsorption than the SWCNTs (59 mg g$^{-1}$). The significant increase in the amount of CO$_2$ adsorption following HNO$_3$/H$_2$SO$_4$ treatment indicates the presence of well-developed and abundant micropores with a narrow size distribution. After HNO$_3$/H$_2$SO$_4$ treatment, the micropore volume ($W_0$) value obtained from the DR plot of the CO$_2$ adsorption isotherm also increased approximately 4 times from 0.32 to 0.08 mL g$^{-1}$, as outlined in Table 2.

The kinetic diameter of the H$_2$ molecule is 0.289 nm, which is smaller than that of the CO$_2$ molecule (0.330 nm), and so can provide accurate information regarding the narrow microporosity of a densely-packed HD-SWCNT film (Table 3). Figure 5 shows the H$_2$ adsorption isotherm and the DR plot analysis of the SWCNTs and the HD-SWCNT film obtained by H$_2$ adsorption at 77 K, respectively. In the H$_2$ adsorption isotherm at a pressure up to 100 kPa, H$_2$ adsorption by the HD-SWCNT film increased approximately 2.5 times from 7 to 18 mg g$^{-1}$ (Figure 5a). This enhancement in the H$_2$ adsorption may be associated with an increase in the narrow interstitial space in the SWCNT assembly network following HNO$_3$/H$_2$SO$_4$ treatment. Supercritical DR plots are primarily used to accurately characterize the interactions of micropores with supercritical gases such as H$_2$. The following supercritical DR equation was therefore applied to analyze the precise microporous structure and the isosteric heat of adsorption for the HD-SWCNT film with an enhanced narrow interstitial space

$$\ln\left(\frac{W}{W_0}\right) = \frac{RT}{\beta E_0} (\ln P_{0q} - \ln P)$$

(1)

where $W_L$ is the amount of saturated H$_2$ adsorption at 77 K, which can be calculated from the Langmuir plot of the H$_2$ adsorption isotherm, $W$ is the amount of gas adsorption at adsorption pressure $P$, $P_{0q}$ is the quasi-saturated vapor pressure, $R$ is the gas constant, and $T$ is the temperature. In addition, $\beta$ is the affinity coefficient, and $E_0$ is the characteristic adsorption energy. The isosteric heat of adsorption at the filling ratio of 1/$e$, $q_{st,1/e}$ can be obtained from the value $\beta E_0$ determined from eq 2

$$q_{st,1/e} = \Delta H_v + \beta E_0$$

(2)

where $\Delta H_v$ is the enthalpy of vaporization ($\Delta H_v$ of H$_2$ = 0.898 kJ mol$^{-1}$). Figure 5b shows the DR plot of a linear H$_2$ adsorption isotherm at 77 K above 10$^{-2}$ kPa. The measured values of $W_L$, $P_{0q}$ and $q_{st,1/e}$ are listed in Table 4. As indicated, the $W_L$ and $P_{0q}$ values of the HD-SWCNT film more than doubled, while the $q_{st,1/e}$ value for the H$_2$ molecule gave almost similar values in the range of 4.5–4.6 kJ mol$^{-1}$. The...
Table 4. Adsorption Parameters Calculated by the Supercritical DR Plots of H₂ (77 K) Adsorption

| sample         | $W_{f}^H$ (mL g$^{-1}$) | $P_{0I}$ (kPa) (mL g$^{-1}$) | $q_{aφ=1/e}$ (kJ mol$^{-1}$) |
|----------------|------------------------|-----------------------------|-----------------------------|
| SWCNTs         | 7.8                    | $3.9 \times 10^3 \pm 0.4 \times 10^3$ | 4.6 ± 0.2                  |
| HD-SWCNT film  | 18.9                   | $1.8 \times 10^3 \pm 0.4 \times 10^3$ | 4.5 ± 0.2                  |

$q_{aφ=1/e}$ value of the HD-SWCNT film remained relatively unchanged compared to the corresponding value for the SWCNTs, suggesting that the interstitial space following mild HNO$_3$/H$_2$SO$_4$ treatment was similar to that of the SWCNTs. Therefore, this result indicates that the increase in the adsorption amount of H$_2$ is due to the development of a narrow interstitial space in the HD-SWCNT film.

The SWCNTs have a hydrophobic surface but can exhibit a unique H$_2$O adsorption behavior due to the strong interaction between H$_2$O molecules and the nanotube surface. Figure 6 shows the H$_2$O adsorption isotherm at 303 K for the SWCNT samples. (a,b) Variation in the amount of H$_2$O adsorbed with equilibration time, (c,d) variation in the saturation pressure with equilibration time, and (e,f) normalization of the H$_2$O adsorption amount using the saturated adsorption amounts.

Figure 6. H$_2$O adsorption on the SWCNTs and the HD-SWCNT film at 303 K.

SWCNTs and the HD-SWCNT film. The H$_2$O adsorption of the SWCNTs is classified as IUPAC V-type with a small hysteresis, indicating that the isotherm gradually increases above $P/P_0 = 0.3$. The HD-SWCNT film also exhibited a similar increase at $P/P_0 = 0.3$ but showed a greater hysteresis than the SWCNTs, and its H$_2$O adsorption capacity increased significantly from 188 to 320 mg g$^{-1}$ close to a $P/P_0$ value 0.9. This increased H$_2$O adsorption amount corresponds to a 170% greater quantity compared to that of the SWCNTs and was attributed to an increase in the number of narrow interstitial spaces measuring <0.9 nm. This result is in good agreement with previous studies showing that the amount of H$_2$O adsorption increases as the micropore volume of the nanohorn increases. The inset in Figure 6 shows the adsorption branch of the H$_2$O adsorption isotherm up to $P/P_0 = 0.6$. In both samples, the H$_2$O adsorption amount increased at $P/P_0 = 0.3$, and the H$_2$O adsorption amount of the HD-SWCNT film shows a steeper rise than that of the SWCNTs.

The equilibrium time for H$_2$O adsorption and desorption was then determined to evaluate the H$_2$O adsorption rate of the HD-SWCNT film exhibiting an enhanced interstitial space. Figure 7a shows the equilibration times required for H$_2$O adsorption by the SWCNTs and HD-SWCNT films. More specifically, in the initial 60 min, the H$_2$O adsorption amounts of the SWCNTs and the HD-SWCNT film rapidly increased to 220 and 122 mg g$^{-1}$, respectively, prior to reaching an equilibrium state (Figure 7b). Interestingly, the adsorbed amount of H$_2$O was similar to the result of stepwise H$_2$O adsorption from a low pressure ($P/P_0 = 0.005$), as shown in Figure 6. In addition, Figure 7c,d shows the variations in the $P/P_0$ values of the SWCNTs and HD-SWCNT films. For both samples, the value of $P/P_0$ decreased rapidly during the initial 60 min, with an increase in the amount of H$_2$O adsorption being observed. Furthermore, Figure 7e,f shows the adsorption branches of the normalized H$_2$O adsorption rates. The larger slope observed for the normalized H$_2$O adsorption in this range reflects the more rapid adsorption of H$_2$O molecules in the narrower micropores of the interstitial space. In this system, the adsorption capacity of H$_2$O for the HD-SWCNT film increased by ~180%, and the average micropore width narrowed from 1.5 to 0.9 nm; however, the slope of the adsorption rate was similar to that of the SWCNTs. This result shows that the width of the developed interstitial space in the HD-SWCNT film is not sufficiently narrow to increase the adsorption rate of H$_2$O. These results therefore agree with the unchanged $q_{aφ=1/e}$ value of the isosteric heat value of the HD-SWCNT film during H$_2$ adsorption at 77 K (Table 3).

The equilibrium time for H$_2$O desorption was also measured, as shown in Figure 8. After H$_2$O adsorption by the SWCNTs and the HD-SWCNT film had reached equilibrium (i.e., after 500 min), the H$_2$O desorption process was performed at 303 K from $P/P_0 = 0.97$ to 0.001 under a
vacuum condition of \(10^{-4}\) Pa for 500 min. Figure 8\(a, b\) shows the change in the amount of desorbed H\(_2\)O with equilibration time, \((c, d)\) variation in the saturation pressure with equilibration time, and \((e, f)\) normalization of the H\(_2\)O desorption amount using the saturated desorption amounts.

Figure 8. Effect of the equilibration time for H\(_2\)O desorption at 303 K for the SWCNTs and the HD-SWCNT film. \((a, b)\) Variation in the amount of desorbed H\(_2\)O with equilibration time, \((c, d)\) variation in the saturation pressure with equilibration time, and \((e, f)\) normalization of the H\(_2\)O desorption amount using the saturated desorption amounts.

Figure 9. Relationship between the kinetic diameter and the enhanced adsorption capacities toward H\(_2\)O, H\(_2\), CO\(_2\), and N\(_2\).

CONCLUSIONS

A HD-SWCNT film with a narrow interstitial space was fabricated through the mild H\(_2\)NO\(_3\)/H\(_2\)SO\(_4\) treatment of SWCNTs and a subsequent VF process. The pore structure of the enhanced interstitial space of the HD-SWCNT film was analyzed by adsorption isotherms of N\(_2\), CO\(_2\), and H\(_2\), which indicated a remarkably developed interstitial space with narrow micropores of an \(\sim 0.9\) nm diameter. H\(_2\)O adsorption at 303 K showed that the adsorption capacity of the HD-SWCNT film increased significantly from 188 to 320 mg g\(^{-1}\). However, in the equilibrium time measurements, despite an increase in the adsorption capacity of \(\sim 170\)%, the adsorption rate did not change, which indicated that the developed interstitial space had no effect on the adsorption rate of H\(_2\)O. It also shows that the adsorption behaviors of N\(_2\), CO\(_2\), H\(_2\), and H\(_2\)O within the developed interstitial space are linear with respect to their kinetic diameters. This result suggests that the enhanced interstitial space of the HD-SWCNT film obtained upon mild H\(_2\)NO\(_3\)/H\(_2\)SO\(_4\) treatment can provide the appropriate nanoporosity for the adsorption of larger molecules, such as N\(_2\) and CO\(_2\). We expect that controlling the interstitial spaces of SWCNTs through interface engineering in a scalable solution-based process will lead to their use in energy and environmental applications for selective molecular capture and also in the storage of clean fuel gases.

EXPERIMENTAL SECTION

Fabrication of the HD-SWCNT Film. SWCNTs produced by the high-pressure CO disproportionation (HiPco) process were used for the purpose of this study (Carbon Nanotechnologies, Inc., USA). The as-produced SWCNT powder was stirred in ethanol for 1 h, sonicated for 5 min, and then
dried for 24 h at 383 K. Subsequently, the dried SWCNTs (100 mg) were stirred in a mixed solution of HNO₃ (65%) and H₂SO₄ (98%) (100 mL, 1:3 v/v) for 12 h at 298 K. The resulting acid-treated suspension was filtered through a membrane filter (10 μm pore diameter) and washed several times with distilled water. The washed sample was sonicated with distilled water for 30 min and then subjected to VF once again. The resulting HD-SWCNT film was then dried at 383 K for 24 h and annealed at 1173 K under an Ar atmosphere for 1 h.

Characterization and Gas Adsorption Experiments.

The morphologies of the SWCNTs and the HD-SWCNT film were observed by FE-SEM (JEOL JSM-6330F). The chemical states of the SWCNTs and the HD-SWCNT film were analyzed by XPS (ESCALAB 250Xi, Thermo Fisher Scientific Inc.) using an Al Kα gun at 10 mA and 15 kV with a pass energy of 10 eV. A flood gun was used as a charge neutralizer. The C 1s peaks of the SWCNTs and the HD-SWCNT film were set to 284.4 eV for calibrating the binding energy values. All C 1s spectra were normalized by adjusting the maximum intensities of the C 1s spectra to 1.0. The pore structures of the SWCNT samples were analyzed from the adsorption isotherms of N₂ (77 K), CO₂ (273 K), and H₂ (77 K) using volumetric equipment (Quantichrom AS-1-MP) after preheating at 423 K under 10⁻⁶ Pa for 2 h. The parameters of the pore structures were calculated by the SPE method and the DR method. The SPE method was derived using high-resolution α₃-plots constructed for standard adsorption data for highly crystalline non-porous carbon black. Adsorption isotherms of H₂O in the SWCNTs and the HD-SWCNT film were measured gravimetrically at 303 K after prevacuum treatment at 10⁻⁴ Pa and 423 K for 2 h. H₂O was introduced into the adsorption cell after repeated purification via freeze–pump–thaw cycling. For the H₂O adsorption and desorption equilibrium time measurements of the SWCNT samples, distilled water was injected at a pressure P/P₀ of ~0.97 (corresponding to an equivalent H₂O vaporization of 31.8 Torr at 303 K) after pre-evacuation at 423 K and 10⁻⁴ Pa for 2 h. The changes in the adsorption amount and in P/P₀, with the equilibrium time were recorded.
(18) Yang, C.-M.; Kaneko, K. Adsorption properties of iodine-doped activated carbon fiber. *J. Colloid Interface Sci.* 2002, 246, 34–39.

(19) Obha, T.; Kanoh, H.; Kaneko, K. Affinity transformation from hydrophilicity to hydrophobicity of water molecules on the basis of adsorption of water in graphitic nanopores. *J. Am. Chem. Soc.* 2004, 126, 1560–1562.

(20) Kaneko, K. Water capture in carbon cuboids. *Nat. Chem.* 2015, 7, 194–196.

(21) Hiraoka, T.; Izaei-Najafabadi, A.; Yamada, T.; Futaba, D. N.; Yasuda, S.; Tanaka, O.; Hatori, H.; Yumura, M.; Ijima, S.; Hata, K. Compact and light supercapacitor electrodes from a surface-only solid opened carbon nanotubes with 2200 m² g⁻¹ surface area. *Adv. Funct. Mater.* 2010, 20, 422–428.

(22) Chen, Z.; Kim, D. Y.; Hasegawa, K.; Noda, S. Methane-assisted chemical vapor deposition yielding millimeter-tall single-wall carbon nanotubes of smaller diameter. *ACS Nano* 2013, 7, 6719–6728.

(23) Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. Water conduction through the hydrophobic channel of a carbon nanotube. *Nature* 2001, 414, 188–190.

(24) Holt, J. K.; Park, H. G.; Wang, Y.; Stadlermann, M.; Artyukhin, A. B.; Grigoriopoulos, C. P.; Noy, A.; Bakajin, O. Fast mass transport through sub-2-nanometer carbon nanotubes. *Science* 2006, 312, 1034–1037.

(25) Joseph, S.; Aluru, N. R. Why are carbon nanotubes fast transporters of water? *Nano Lett.* 2008, 8, 452–458.

(26) Kipper, A. C.; da Silva, L. B. Water filling of carbon nanotubes membranes: Porosity and temperature effects. *Chem. Phys. Lett.* 2012, 552, 84–87.

(27) Tunuguntla, R. H.; Henley, R. Y.; Yao, Y.-C.; Pham, T. A.; Wanunu, M. Enhanced water permeability and tunable ion selectivity in subnanometer carbon nanotube porins. *Science* 2017, 357, 792–796.

(28) Obha, T. Size-dependent water structures in carbon nanotubes. *Angew. Chem., Int. Ed.* 2014, 53, 8032–8036.

(29) Obha, T.; Taira, S.; Hata, K.; Kanoh, H. Mechanism of sequential water transportation by water loading and release in single-walled carbon nanotubes. *J. Phys. Chem. Lett.* 2013, 4, 1211–1215.

(30) Wang, H.-J.; Xi, X.-K.; Kleinhammes, A.; Wu, Y. Temperature-induced hydrophobic-hydrophilic transition observed by water adsorption. *Science* 2008, 322, 80–83.

(31) Lee, B.; Baek, Y.; Lee, M.; Jeong, D. H.; Lee, H. H.; Yoon, J.; Kim, Y. H. A carbon nanotube wall membrane for water treatment. *Nat. Commun.* 2015, 6, 7109.

(32) Hassan, J.; Diamantopoulos, G.; Homouz, D.; Papavassiliou, G. Water inside carbon nanotubes: Structure and dynamics. *Nanotechnol. Rev.* 2016, 5, 341–354.

(33) Yang, C.-M.; Kaneko, K.; Yudasaka, M.; Iijima, S. Effect of purification on pore structure of HiPco single-walled carbon nanotube aggregates. *Nano Lett.* 2002, 2, 385–388.

(34) Yang, C.-M.; Kim, D. Y.; Lee, Y. H. Formation of densely packed single-walled carbon nanotube assembly. *Chem. Mater.* 2005, 17, 6422–6429.

(35) Landi, B. J.; Ganter, M. J.; Schauerman, C. M.; Cress, C. D.; Raffaele, R. P. Lithium ion capacity of single wall carbon nanotube paper electrodes. *J. Phys. Chem. C* 2008, 112, 7509–7515.

(36) Kim, D. Y.; Yang, C.-M.; Yamamoto, M.; Lee, D. H.; Hattori, Y.; Takahashi, K.; Kanoh, H.; Kaneko, K. Supercritical hydrogen adsorption of ultramicropore-enriched single-wall carbon nanotube sheet. *J. Phys. Chem. C* 2007, 111, 17448–17450.

(37) Kim, D. Y.; Yang, C.-M.; Noguchi, H.; Yamamoto, M.; Obha, T.; Kanoh, H.; Kaneko, K. Enhancement of H₂ and CH₄ adsorptivities of single wall carbon nanotubes produced by mixed acid treatment. *Carbon* 2008, 46, 611–617.

(38) Niu, Z.; Zhou, W.; Chen, J.; Feng, G.; Li, H.; Ma, W.; Li, J.; Dong, H.; Ren, Y.; Zhao, D.; Xie, S. Compact-designed supercapacitors using free-standing single-walled carbon nanotube films. *Energy Environ. Sci.* 2011, 4, 1440–1446.

(39) Kim, J.; Yamada, Y.; Suzuki, Y.; Ciston, J.; Sato, S. Pyrolysis of epoxidized fullerenes analyzed by spectroscopies. *J. Phys. Chem. C* 2014, 118, 7076–7084.

(40) Yamada, Y.; Yasuda, H.; Murota, K.; Nakamura, M.; Sodesawa, T.; Sato, S. Analysis of heat-treated graphite oxide by X-ray photoelectron spectroscopy. *J. Mater. Sci.* 2013, 48, 8171–8198.

(41) Kim, J.; Lee, N.; Min, Y. H.; Noh, S.; Kim, N.-K.; Jung, S.; Joo, M.; Yamada, Y. Distinguishing zigzag and armchair edges on graphene nanoribbons by X-ray photoelectron and Raman spectroscopies. *ACS Omega* 2018, 3, 17789–17796.

(42) Kim, J.; Yamada, Y.; Kawai, M.; Tanabe, T.; Sato, S. Spectral change of simulated X-ray photoelectron spectroscopy from graphene to fullerene. *J. Mater. Sci.* 2015, 50, 6739–6747.

(43) Kim, J.; Han, J.-W.; Yamada, Y. Heptagons in the basal plane of graphene nanoflakes analyzed by simulated X-ray photoelectron spectroscopy. *ACS Omega* 2021, 6, 2389–2395, in press.

(44) Obha, T.; Kaneko, K. Internal surface area evaluation of carbon nanotube with GCMC simulation-assisted N₂ adsorption. *J. Phys. Chem. B* 2002, 106, 7171–7176.

(45) Methio, N.; Dai, S.; Jiang, D.-e. Quantum mechanical basis for kinetic diameters of small gaseous molecules. *J. Phys. Chem. A* 2014, 118, 1150–1154.

(46) Luo, Y.; Funke, H. H.; Falconer, J. L.; Noble, R. D. Adsorption of CO₂, CH₄, C₂H₆, and H₂O in SSZ-13, SAPO-34, and T Type Zeolites. *Ind. Eng. Chem. Res.* 2016, 55, 9749–9757.

(47) Kaneko, K. Effect of temperature on micropore filling of supercritical NO on Fe₂O₃-dispersed activated carbon fibers. *Colloids Surf.* 1989, 37, 115–124.

(48) Kaneko, K.; Murata, K.; Shimizu, K.; Camara, S.; Suzuki, T. Enhancement effect of micropore filling for supercritical methane by magnesia dispersion. *Langmuir* 1993, 9, 1165–1167.

(49) Kaneko, K.; Murata, K. An analytical method of micropore filling of a supercritical gas. *Adsorption* 1997, 3, 197–208.