WATER ADSORPTION ON MICROPOROSITY-CONTROLLED SINGLE WALL CARBON NANOUBE

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Introduction

So called supergrowth single wall carbon nanotubes (SWCNTs) do not form the bundle structure. Therefore, we can obtain the bundle structure-controlled SWCNTs and thereby we can compare the both of the internal tube and external tube surface sites of isolated SWCNTs and the interstitial and grove sites of the bundled SWCNTs. As water adsorption is expected to be sensitive to the small micropores coming from the bundle structure [1,2], we have studied water adsorption on microporosity-controlled SWCNTs.

Experimental

We attempted to control the microporosity of SWCNTs through the bundle formation with the capillary force on drying. SWCNTs of 25 mg were ultrasonically dispersed in methanol or toluene for 12 hrs at water bath of 288 K. Then the SWCNTs deposited after 24 hrs were filtrated and dried at 423 K and below 2 kPa for 24 hrs. The treated SWCNTs using toluene or methanol are named Tol-SWCNT or MeOH-SWCNT, respectively. The N_2 adsorption isotherms of these SWCNTs were measured volumetrically at 77 K after pre-evacuation at 423 K for 2 hrs. Both the surface area and micropore volume were decreased by this treatment (Table 1).

Table 1 Pore structural parameters by N_2 adsorption at 77 K by α_s-plot

	Surface Area	Micropore Volume
	m^2g^{-1}	cm^3g^{-1}
SWCNT	1200	——
MeOH-SWCNT	680	0.35
Tol-SWCNT	680	0.36

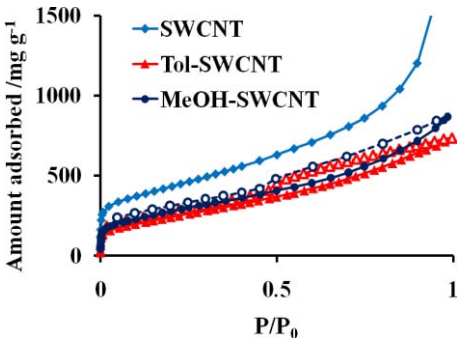

Fig. 1 N_2 adsorption isotherms of SWCNTs at 77 K. Solid symbols: Adsorption, open symbols: Desorption

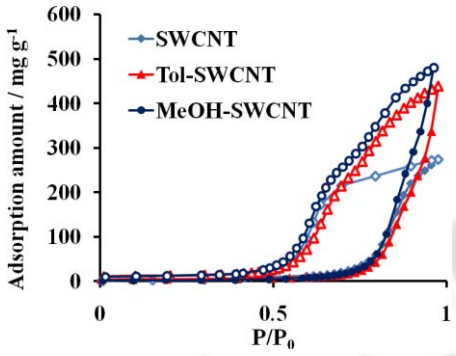

Fig. 2 Water adsorption and desorption isotherms of SWCNTs at 303 K of at least 30 min equilibration time. Solid symbols: Adsorption, open symbols: Desorption.

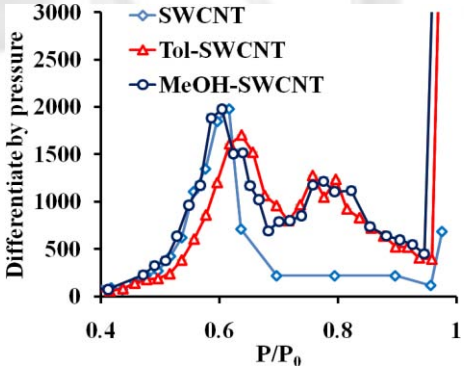

Fig. 3 The differential adsorption with the relative pressure for the desorption branch on Fig.2.

The water adsorption isotherms were measured using the flow-type adsorption equipment (CI Electronics: Cisorp). The SWCNTs samples were pretreated at 338 K for 2 hrs under a flow of N_2 (flow rate: 200 cm^3 (STP) min^{-1}) prior to the adsorption measurement. The structure analysis of the samples was carried out on transmission electron microscope. FTT (Fast Fourier Transform) analysis was used Image J (Image Processing and Analysis in Java).

Results and Discussion

Figure 1 is shown N_2 adsorption isotherms of SWCNT and treated SWCNTs at 77 K. The N_2 adsorption isotherm of SWCNT before the treatment is of IUPAC Type II without an explicit hysteresis.

The capillary force aggregation treatment varies the N_2 adsorption isotherm remarkably; the adsorption isotherms are close to ICPAC type I, suggesting the increase in the micropores and they have an adsorption hysteresis loop of which shape is nearly horizontal and parallel over the wide relative pressure. The N_2 adsorption isotherms were analyzed by the subtracting pore effect (SPE) method for the high resolution α_s-plots [3]. The surface area and pore volume are listed in Table 1. The surface area of SWCNT is 1200 m^2g^{-1}, being quite close to a half value of the surface area of grapheme (2630 m^2g^{-1}). Therefore, SWCNT is almost close and mutually isolated. However, the capillary force–aggregation treatment reduces intensively the surface area by almost 50 %, which is caused by decrease in external surface area of SWCNT due to the bundle formation. The interstitial and groove sites of the bundled SWCNT should lead to the observed type I characteristic. The unique hysteresis loop also indicates the presence of slit-shaped mesopores which are formed by the bundle-bundle association. Accordingly, the capillary force-aggregation treatment can provides both of interstitial and groove sites as micropores and interbundle gaps as mesopores.

The water adsorption on hydrophobic carbons is indispensable to the presence of micropores below the relative pressure of 0.8[4].

Figure 2 shows water adsorption isotherms of SWCNT and treated SWCNT samples at 303 K. All adsorption isotherms have a predominant hysteresis loop. However, the water adsorption amount of the treated SWCNT at $P/P_0 = 0.96$ is about twice of that of the non-treated SWCNT. The micropore volume can be evaluated from the adsorbed amount of water around the relative pressure of 0.9. If the density of adsorbed water is 1 gcm^{-3}, the micropore volumes of SWCNT, Tol-SWCNT and MeOH-SWCNT are 0.27 mlg^{-1}, 0.44 mlg^{-1}, and 0.48 mlg^{-1}, respectively.

Although we assumed the perfect closed SWCNT before the treatment, the water adsorption data indicate partial opening of the non-treated SWCNT. The micropore volume (0.27 mlg^{-1}) of the non-treated SWCNT from water adsorption should originate from the internal tube spaces of partially open SWCNTs. Therefore, the excess water adsorption amount of the treated SWCNT stems from the micropores produced by the bundle formation; the produced micropore volumes of Tol-SWCNT and MeOH-SWCNT are 0.18 mlg^{-1} and 0.21 mlg^{-1}, respectively.

This is supported by the presence of the step in the water desorption isotherm of the treated SWCNT near the half of the total adsorption amount. Figure 3 shows the differential adsorption with the relative pressure for the desorption branch. The SWCNT has only single peak at $P/P_0 = 0.62$, whereas the

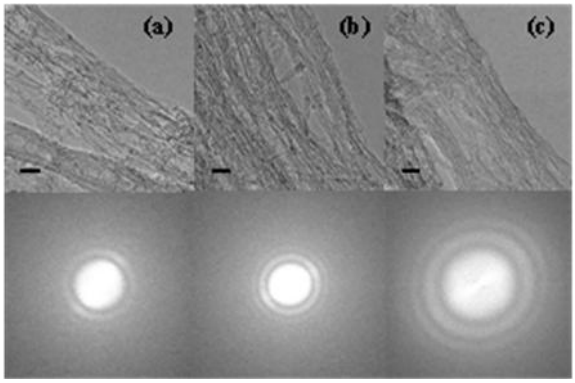

Fig. 4 TEM image and power spectral density (PSD) by FFT: (a) SG-SWCNT, (b) MeOH-SWCNT, and (c) Tol-SWCNT. Scale bar is 20 nm.

treated SWCNTs have another peak at $P/P_0 = 0.8$ in addition to that at $P/P_0 = 0.6$. Thus, the differential adsorption isotherms explicitly evidence the pressure of two kinds of adsorption sites for treated SWCNTs.

Figure 4 shows TEM images and their power spectral densities (PSDs) by FFT analysis for three SWCNT samples. The TEM images of the treated SWCNTs have a clearer bundle structure and distinct rings in the PSD which is indicative of the long range-order.

Conclusions

The capillary force-aggregation treatment can control both of micropores and mesopores of SWCNTs. The differential water adsorption isotherm is efficient for determination of the micropores of different sizes. Hence a combination analysis of water adsorption at 303 K and N_2 adsorption at 77 K can elucidate more accurately the pore structure of SWCNTs.

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