Direct Thermal Fluorination of Single Wall Carbon Nanohorns

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Received: December 18, 2003; In Final Form: April 23, 2004

Single wall carbon nanohorns (SWNHs) were fluorinated to form more attractive nanohorns that have characteristic structural and adsorptive properties. Nitrogen adsorption, XPS, and TEM studies elucidated the surface states and the morphologies of fluorinated SWNHs (F−SWNHs). The XPS results of F−SWNHs showed that the nature of C−F bonds changed from semi-ionic to covalent with an increase in the fluorination temperature. The N_2 adsorption isotherm indicated that the total amount of N_2 adsorption on SWNHs fluorinated at 303 and 373 K was smaller than that of pristine SWNHs. After fluorination at 473 K, nanoorder windows were produced on the sidewalls of SWNHs without a change in the shape of each horn and aggregate. Therefore, the SWNHs fluorinated at 473 K can adsorb N_2 molecules on the internal surfaces of nanohorns through the nanowindows.

Introduction

Nano-structured materials have attracted a great deal of attention in materials science and considerable applications, such as electronic devices and energy-related applications, are being made.[1−4] The Single Wall Carbon Nano Horn (SWNH) is one of the most attractive new forms of nanocarbons and has excellent prospects for a wide range of technological applications because of its unique structural properties.[5] The SWNHs are composed of a rolled graphene sheet and closed by a horn-shaped cap, and form an aggregate of many horn-shaped sheaths. The bulk synthesis of SWNH is possible and high-purity SWNH in sufficient quantities has made it possible to explore the reactivity and properties of the resulting compounds in detail. It has been reported that the aggregate can offer a nanospace, which can adsorb large quantities of gases owing to the attractive potential between horns.[6] It has also been reported that the marked adsorptive properties were given to the nanoporous systems of SWNH by chemical manipulations.[7−17] Therefore, it is expected that the controlled functionalization of SWNH can be achieved by chemical modification.

Fluorination is one of the most effective methods to control physical properties of nanocarbon materials.[18,19] The fluorination of Single Wall Carbon Nanotubes (SWNTs) was performed by several groups under conditions similar to those used for the
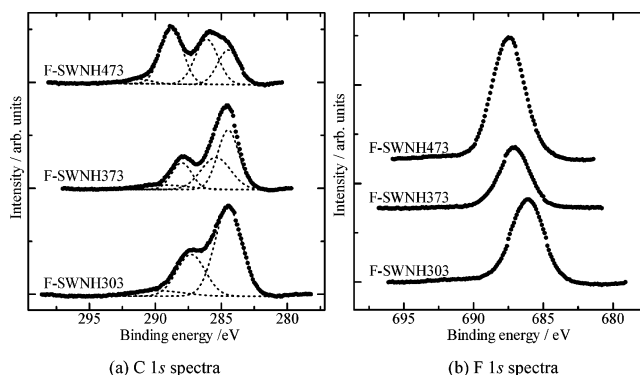

Figure 1. Carbon 1s (a) and fluorine 1s (b) XPS spectra of SWNHs fluorinated at 303, 373, and 473 K.

fluorination of other carbon materials.[20−24] In those investigations, it was clarified that fluorine atoms can be attached on the side wall of SWNTs without the destruction of the tubular structure. The fluorinated carbon nanotubes are useful precursors for nanotube derivatives, because of their solubility in organic solvent. The recent studies also revealed that SWNTs could be shortened through fluorination. Therefore, fluorine chemistry in carbon nanotubes is very interesting for their potential applications.

Fluorine chemistry can also effectively modify not only chemical, but also physical, properties of porous carbon materials. A marked change in adsorptive properties of fluorinated porous carbons has been reported.[25−27] Therefore, the fluorination of SWNH is expected to induce striking changes in their adsorptive properties.

In this paper, fluorination of SWNH has been performed by thermal reaction (303−473 K) with elemental fluorine. The fluorinated SWNH (F−SWNH) was studied by X-ray photoelectron spectroscopy (XPS) and transmission electron micro-

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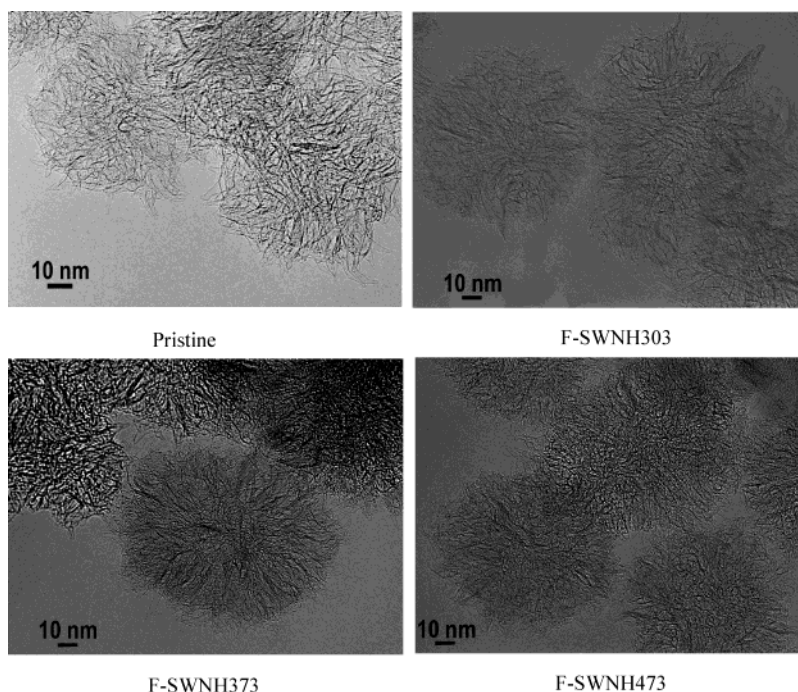*J. Phys. Chem. B, Vol. 108, No. 28, 2004* **9615**

Figure 2. High-resolution TEM images of pristine and fluorinated SWNHs at 303, 373, and 473 K.

TABLE 1: Reaction Temperatures, Peak Positions for XPS Spectra, and F/C Atomic Ratios of F−SWNHs

Fluorination temperature (K)		303	373	473
C 1s (eV)	C=C	284.5[a]	284.5[a]	284.5[a]
	C−CF	−	285.4	286.1
	CF	287.3	288.0	288.8
	CF$_2$	289.8	289.3	292.4
F 1s (eV)		686.1	687.5	688.7
F/C (XPS)		0.35	0.30	0.60
F/C (Gravimetry)		0.25	0.26	0.45

[a] A peak attributable to sp^2 carbon was used as a reference (284.5 eV) for charge correction.

scope (TEM). The detailed analyses on porous structures and adsorptive properties of F−SWNH have been made by means of nitrogen adsorption isotherm in comparison with fluorinated carbon black.

Experimental Section

The SWNH was prepared by the CO$_2$ laser ablation method. The detailed preparation methods of SWNH are described elsewhere.[5] The SWNH and nonporous carbon black (CB, Mitsubishi Chemical Co.) were used for fluorination. The type of carbon black used was furnace black. The SWNH and CB were heat-treated at 573 K in a vacuum prior to fluorination. Fluorine gas (Daikin Industries, Ltd., purity 99.7%, HF was removed by passing the gas over NaF pellets) was performed by direct reaction of SWNH with elemental fluorine. The reaction was run for 24 h in the temperature range from 303 to 473 K with 1 atm of fluorine gas. Hereafter, the F−SWNHs are named as "F−SWNH303". Here, "303" in the sample name indicates the fluorination temperature. XPS measurements were carried out using a Shimadzu ESCA850 with Mg Kα (1253.6 eV) X-rays for the ionizing radiation provided by an X-ray source working at 240 W. Fluorination leads to the change in the electronic structure of SWNHs. It should be noted here that the charging shift up to 1.1 eV was observed in F−SWNH473, while a small charging shift within 0.5 eV was observed in F−SWNH303 and 373. An accurate compensation must be

made for charging shift caused by an electron loss from the surface by photoemission. The following are the methods that are valid for charge correction on the fluorinated SWNHs. The XPS spectra showed a peak attributable to the carbon atoms with the bonded structures of sp^2 configurations. This peak was used as a reference (284.4 eV) for charge correction in this study. High-resolution transmission electron micrographs of the products were taken using a TEM (Topcon, EM-002B) operated at 200 kV. The adsorption and desorption isotherms were measured by means of an automatic volumetric sorption analyzer (Autosorb-1, Quantaqurome) using nitrogen gas as adsorbate at 77 K.

Results and Discussion

Figure 1 a shows the C 1s XPS spectra of pristine and fluorinated SWNHs at 303, 373, and 473 K. The spectrum of the pristine sample indicates an asymmetric peak centered at 284.5 eV, which is characteristic of the C−C bonded carbon atoms with sp^2 configurations. In addition to this peak, the spectra of fluorinated SWNHs exhibit a peak originating from a carbon bonded to a monofluorinated carbon (C−CF, 285−286 eV), a carbon bonded to a single F atom (C−F group, 288−290 eV), and a carbon bonded to two F atoms (C−F$_2$ group, 291−292 eV). In contrast with the C 1s spectra, the F 1s spectra have a symmetric shape as shown in Figure 1b. The F 1s peak of SWNHs fluorinated at 303, 373, and 473 K was observed at 686.1, 687.5, and 688.7 eV, respectively. With increasing fluorination temperature, the C 1s and F 1s peaks assigned to the fluorine functional groups shift to the higher binding energy side. It indicates that the C−F bonding nature has changed from semi-ionic to covalent C−F bonds with the increase in fluorination temperature. The semi-ionic C−F bonds are found in fluorine-graphite intercalation compounds. It is used to describe a C−F bond between those of ionic and covalent bonds of fluorine to graphite matrix. Comprehensive reviews have been published on these subjects.[28−30] The areas of the peaks for each of the elements were calculated, and the relative concentration of each element was deduced taking their relative atomic cross-sections into account. Table 1 shows the results of the

TABLE 2: Pore Structural Parameters of Pristine and Fluorinated SWNHs at 303, 373, and 473 K

	a_{total}, m²/g	a_{ext}, m²/g	W_0, cm³/g	βE_0, kJ/mol	S_{BET}, m²/g	W_{total}, cm³/g
Pristine	399	196	0.136	6.22	355	0.473
F-SWNH303	192	125	0.058	5.37	172	0.324
F-SWNH373	71	90	0.033	3.09	76	0.261
F-SWNH473	280	98	0.078	5.82	236	0.316

[a] Total: total surface area; a_{ext}: external surface area; W_0: micropore volume; β: affinity coefficient (0.33); E_0: characteristics energy; S_{BET}: BET surface area; W_{total}: total pore volume.

deconvolution of C 1s and F 1s spectra for the resulting compounds, and the atomic F/C ratios of the SWNHs obtained from the area of XPS peaks and from the gravimetric method. The F/C atomic ratio of F−SWNH303 was almost the same as that of F−SWNH373. On the other hand, the F/C of F−SWNH increased with the increase of the fluorination temperature from 373 to 473 K. The F/C of F−SWNH473 was 0.60 (XPS) and 0.45 (gravimetry). It is close to the stoichiometry of hypothetical fluorination of one side of a single graphene sheet (CF$_{0.5}$). These results suggest that the nanohorns can be fluorinated thermally with fluorination levels reaching 50%.

Figure 2 shows the TEM photographs of pristine and fluorinated SWNHs at 303, 373, and 473 K. The photograph of the pristine sample showed that the pristine sample consists of spherical particles that are of about 80 nm in diameter. The TEM image of spherical particles shows the radiating forms from the center of the particles, so that these particles are called dahlia (flower) type SWNHs. The photograph also showed that the individual particles were aggregates of nanohorn structures. The photographs of F−SWHNs reveal that the resulting compounds consist only of nanohorn structures and that the dahlia-like structures are preserved after fluorination. In addition, no other carbon forms were found in these photographs of F−SWNHs. These results suggest that structural properties are preserved after fluorination.

Figure 3 shows the nitrogen adsorption isotherms (77 K) of pristine and fluorinated SWNHs. Table 2 summarizes the pore structural parameters calculated by BET, α_s method, and DR analysis.[31] The isotherm for the pristine sample consists of the combination between types I and II.[31] A type I isotherm indicates the presence of micropores or small mesopores where adsorbate molecules are adsorbed by micropore filling. A type II isotherm is indicative of the multi-layer adsorption process that obeys the adsorption theory of BET, suggesting the presence of macropores or external surfaces. A steep increase in adsorption isotherms was observed at very low relative pressure, indicating the presence of microporous structures that arise from the assembly structure of SWNHs. Then, the isotherm shows the continuous increase of the amount adsorbed at a higher relative pressure region and it follows the path as the corresponding type II isotherm, indicating that nitrogen molecules are adsorbed on the external surfaces of SWNHs. The diameter of SWNH was calculated from pore parameters with geometrical model shown in Figure 4 a. The arrangement of triangle arrays of SWNHs was used in this work. The interstice in SWNH arrays with a van der Waals gap (0.335 nm) forms the interstitial pore. The calculated diameter of SWNH is 4.4 nm, which is close to the result of TEM observation. The amount of nitrogen adsorbed on F−SWNH303 in mg per g-adsorbent was smaller than that on pristine SWNHs owing to the narrowing of micropores and the weight increase by fluorination. The βE_0 value is calculated by using DR analysis.[31] As the βE_0 value is associated with the adsorption energy, the change in the βE_0 value indicates change in surface free energy by fluorination. The βE_0 of F−SWNH303 is smaller than that of pristine SWNH, but the decrease in the βE_0 of F−SWNH303 is smaller than that of
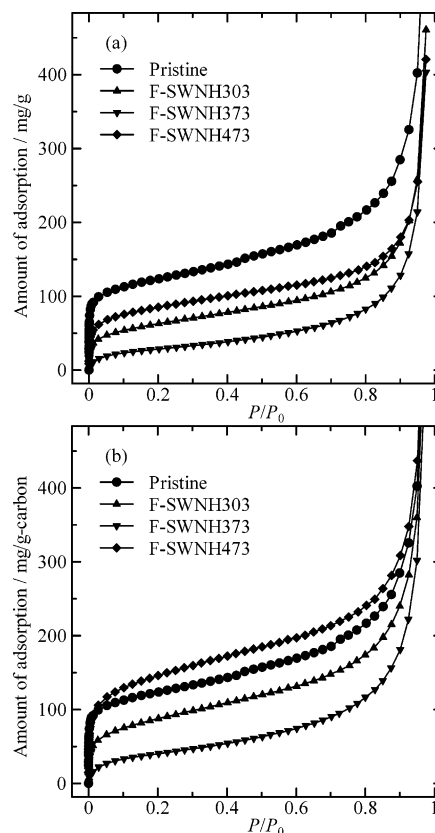

Figure 3. Nitrogen adsorption isotherms at 77 K for pristine and fluorinated SWNHs at 303, 373, and 473 K. The isotherms are based on (a) the sample mass and (b) the carbon mass.

fluorinated ACF.[25,26] This result suggests that the surface of the interstitial pore is not completely covered with covalent C−F bonds. We assume an idealized arrangement of nanohorns as shown in Figure 4b to estimate the array of nanohorns fluorinated at 303 K. The model consists of the arrangements of a triangle lattice of nanohorns having a spacing of x nm. The calculated x for F−SWNH303 was 0.24 nm, corresponding to the diameter of the intercalated species observed in the graphite intercalation compounds of fluorine (C_xF) with a semi-ionic bond. The F 1s binding energy of F−SWNH303, 686.1 eV, is close to that of the semi-ionic C_xF compound. These results suggest that fluorine atoms diffuse into the van der Waals gap between adjacent horns and the charge-transfer interactions between horns and fluorine atoms occurred.

The surface area and pore volume of F−SWNH373 are much smaller than that of pristine SWNH, which should be caused by the narrowing of pores and the weight increase by fluorination. The narrowing of the pore width leads to the decrease in pore volumes and to the blocking effects in very narrow pores. The very small βE_0 suggests that the interstitial surfaces of nanohorns are fluorinated with covalent C−F bond.

The amount of adsorption, surface area, and pore volumes of F−SWNH473 increased despite the weight increase by fluorination. The steep increase at the low relative pressure is
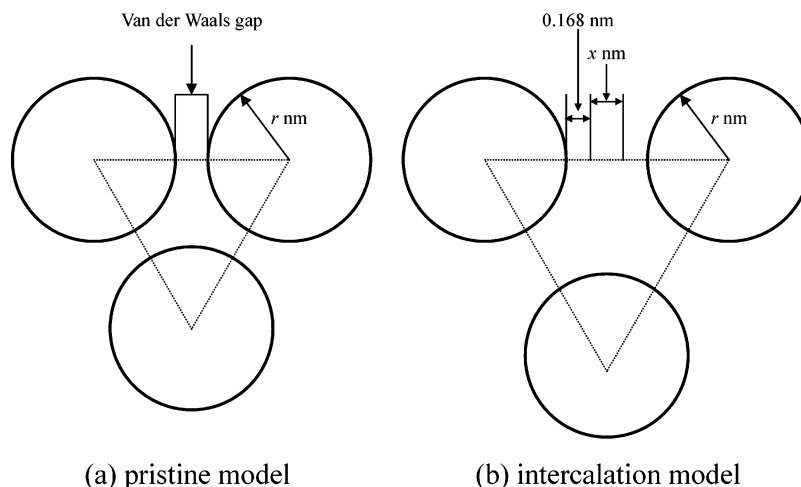
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(a) pristine model   (b) intercalation model

Figure 4. Cross section of the arrangements of the SWNH models: (a) pristine model and (b) intercalation model.

also observed, suggesting that F−SWNH has micropores and small mesopores. The F/C atomic ratio of F−SWNH473 is close to that of the presumed saturation stoichiometry of $CF_{0.5}$, indicating that the outside walls of the SWNHs are completely covered with covalent C−F bonds. Nevertheless, the βE_0 of F−SWNH473 is almost the same as that of F−SWNH303. These results suggest that some parts of the walls of SWNHs are opened by fluorination and that the nitrogen molecules can be adsorbed on the inside walls of SWNHs through the opened gates (nanowindows). The weight increase by fluorination must be taken into account in determining the increase in the amount adsorbed due to the opening of nanowindows on SWNH. Therefore, Figure 3b shows the adsorption isotherms based on the carbon contents in the F−SWNHs. The carbon contents of F−SWNHs were calculated from an F/C atomic ratio determined by gravimetry. The fluorination of inside the horns will not be favorable for smaller horns due to the anticipated repulsive fluorine−fluorine interactions.[21] Therefore, the reaction between the outside surface of SWNH and fluorine gas is the most predominant process in the nondestructive thermal fluorination. Thus, the results of the XPS and the N_2 adsorption isotherm elucidate that F−SWNHs with nanowindows can be prepared by thermal direct fluorination of SWNHs. The studies showed that oxidation with O_2 requires the treatment at the temperature higher than about 600 K. Hence, the production of nanowindows of F−SWNHs473 indicates the unstable nature of the F−SWNH structures.

Conclusions

Single wall carbon nanohorns (SWNHs) were fluorinated in the temperature range of 303 to 473 K and their structural and adsorptive properties were characterized by means of N_2 adsorption isotherm, XPS, and TEM. The C−F bonds of the SWNHs fluorinated at 303 K were similar to those in so-called semi-ionic C_xF, indicating that the charge-transfer interactions occurred on the van der Waals gaps between adjacent carbon nanohorns. The SWNHs fluorinated at 473 K have a $CF_{0.45}$ stoichiometry, close to the limiting stoichiometry for fluorination without destroying the nanohorns. The total amount of N_2 adsorption on SWNHs fluorinated at 303 and 373 K decreased in comparison with pristine SWNHs, owing to the narrowing of pore width and the weight increase by fluorination. On the other hand, the amount of N_2 adsorption on the SWNHs fluorinated at 473 K was larger than those of other fluorinated SWNHs. The result showed that nanoorder windows were

produced in the sidewalls of SWNHs and that the N_2 molecules can be adsorbed on the internal surfaces of SWNHs through the opened windows. These results suggest that the fluorination of SWNHs is one of the effective ways to the functionalization of SWNHs.

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