

Solvent Effects on Hole-Edge Structure for Single-Wall Carbon Nanotubes and Single-Wall Carbon Nanohorns

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To extend the application fields of single-wall carbon nanotubes (SWNTs) and single-wall carbon nanohorns (SWNHs), their chemical modification is essential. Since their graphene-sheet-based structures are chemically robust, only the edges of the graphene sheets, more specifically the oxygen-containing functional groups at hole edges, are useful sites for chemical modification. However, not much is known about the hole-edges, so the phenomenon reported here, that the hole edges easily react with conventional reagents, was previously unknown. We observed a lowering of the combustion temperature of SWNTs and SWNHs immersed in water; this lowering was induced as a result of the hydrolysis of oxygen-containing functional groups (anhydrides and/or lactones) at the hole edges. We also found that the reactivity of hole edges can be easily controlled through an appropriate choice of solvents. We believe that this study is helpful to our understanding of hole-edge chemistry and will help to enable the production of well-designed carbonaceous materials with high functionality.

Introduction

Carbon nanotubes (CNTs) have attracted a great deal of attention from both the perspective of fundamental interests and with regard to applications in nanoscale electronic devices, hydrogen storage media, polymer composites, and so forth. Since as-synthesized CNTs have a closed structure, paths need to be introduced to use the inherent internal space of CNTs.^{1–5} Heating in air,^{1,2} O₂,⁶ and CO₂^{7,8} or acid-washing^{9,10} causes holes to open preferentially at caps and defects of CNTs,^{2,11–13} and, at the same time, oxygen-containing functional (OCF) groups are attached to the hole edges. The presence of carboxylic acid and quinone groups has been confirmed.^{9,14,15} It was suggested that the OCF groups at the hole edges blocked the entry of Xe for adsorption into CNTs.^{9,16} It has been expected and recently reported that the OCF groups at edges have great potential regarding the chemical modification of CNTs to expand their functionalities.^{17–22} Therefore, a control of states and amounts of the OCF groups is indispensable for producing well-designed CNTs.

In this report, we selected two kinds of CNTs to investigate hole-edge reactivity: single-wall carbon nanotubes (SWNTs) and single-wall carbon nanohorns (SWNHs). SWNHs, a new variety of SWNT, are single-walled graphitic tubes with conical caps and form unique spherical aggregates.²³ They can be produced on a large scale with high purity. We report herein that the reactivity of the functional groups at the hole edges of SWNTs and SWNHs can be controlled through immersion in suitable solvents.

Experimental Section

SWNHs were produced by CO₂ laser ablation of graphite under an Ar atmosphere, as reported elsewhere.^{23,24} As-produced

HiPco SWNTs was purchased from Carbon Nanotechnologies Inc. The HiPco SWNTs were heated under ultrahigh vacuum at 1700 °C for 5 h to reduce the content of metal catalysts (residue amount after the combustion of heat-treated HiPco was ca. 8 wt %). The carbons were heated in an O₂ flow (760 Torr, 200 cm³ min^{−1}) at 350 or 580 °C for 10 min. The samples treated at *T* °C are referred to by a suffix “ox*T*” in this report; for example, SWNHox580. It has been confirmed that oxidation treatment of SWNHs increases the quantity of OCF groups.²⁵ To remove the OCF groups, we heated the oxidized SWNHs at 1200 °C under a H₂ gas flow (300 cm³ min^{−1}) for 3 h.

The oxidized samples were immersed in solvents to investigate the effect of the immersion on the reactivity of carbons. The solvents used here were toluene, benzene, acetone, 2-propanol, ethanol, methanol, deionized water, and deuterium oxide. The carbons were immersed in the solvents for about 5 min at room temperature, followed by overnight drying in an air oven at 110 °C. The samples immersed in solvent are designated as having the name of the solvent used in a prefix.

Thermogravimetric analysis (TGA) was carried out from room temperature to 1000 °C under a pure O₂ gas flow of 100 cm³ min^{−1} with a heating rate of 10 °C min^{−1}. A constant amount (ca. 1.3 mg) of sample was used for the TGA measurements. The gas components evolved at elevated temperature under a He flow (50 cm³ min^{−1}) were analyzed using temperature-programmed desorption mass spectrometry (TPD-MS). The temperature was ramped up to 1000 °C at 10 °C min^{−1}.

The adsorption and desorption isotherms of N₂ at 77 K were measured volumetrically using a commercial apparatus (AS-1-MP, Quantachrome) to examine the effect on porosity of the immersion of the oxidized SWNH in water. The samples were vacuumed at 150 °C for 2 h prior to the adsorption measurement.

Results

Figure 1 shows the effect of immersion in water on the TGA and derivative TGA (DTGA) curves for SWNHox580. Two

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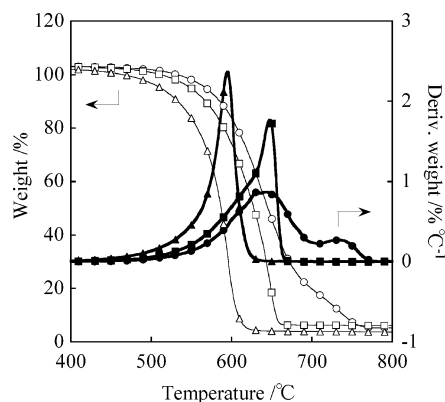


Figure 1. TGA and DTGA curves in O_2 for SWNHox580 and immersed SWNHox580 samples in water: (circle) SWNHox580; (square) H_2O -SWNHox580; (triangle) D_2O -SWNHox580. Open and closed symbols denote TGA and DTGA curves, respectively.

TABLE 1: Amounts of Evolved Gases from TPD-MS Analysis for Oxidized SWNHs before and after Immersion in $H_2^{18}O$ (wt %)

mass no., m/z	possible molecular species	SWNHox580	$H_2^{18}O$ -SWNHox580
20	$H_2^{18}O$	0.00	0.03
30	$C^{18}O$, etc.	0.05	0.33
46	$CO^{18}O$	0.00	0.21
48	$C^{18}O_2$	n.d. ^a	0.01

^a Not detected.

DTGA peaks are observed for SWNHox580; we attributed the main DTGA peak at lower temperature to combustion of the horn-like structure of SWNHs and assigned the peak at 700–800 °C to combustion of rugged graphitic particles.^{24,26} The combustion temperature of graphite has been found to be about 750 °C.²⁷ Thus, we focus solely on the former DTGA peak in this report. Immersion of SWNHox580 in H_2O caused a change in the shape of the DTGA curve, and D_2O -SWNHox580 showed a sharp DTGA peak at a temperature about 40 °C lower than that for H_2O -SWNHox580. The change in DTGA profiles was much less for as-grown SWNHs than oxidized SWNHs (not shown).

The TPD-MS technique using isotope-labeled species is often used to follow a reaction. Here, we chose $H_2^{18}O$ as a probe molecule, because the isotope-labeled element ^{18}O in thermally decomposed products (e.g., $C^{18}O$, $CO^{18}O$, and $C^{18}O_2$) can be easily identified. Table 1 summarizes the amounts of gas components evolved during heating from room temperature to 1000 °C under a He flow for SWNHox580 before and after immersion in $H_2^{18}O$. The amounts of evolved gases containing ^{18}O for SWNHox580 were negligible, whereas they apparently increased for $H_2^{18}O$ -SWNHox580. Because of the low concentration of OCF groups, we could not identify them through either infrared spectroscopy or X-ray photoelectron spectroscopy.

To decrease the amounts of the OCF groups, we treated SWNHox580 in H_2 atmosphere at 1200 °C for 3 h (H_2 -SWNHox580). TPD-MS analysis of H_2 -SWNHox580 showed suppression of the evolved CO ($m/z = 28$) and CO_2 ($m/z = 44$), as shown in Figure 2. After the hydrogen treatment, the D_2O - H_2 -SWNHox580 did not show a significant shift of combustion temperature as was observed for D_2O -SWNHox580 (Figure 3).

Figure 4 shows the adsorption and desorption isotherms of N_2 at 77 K on SWNHox580 and H_2O -SWNHox580. The

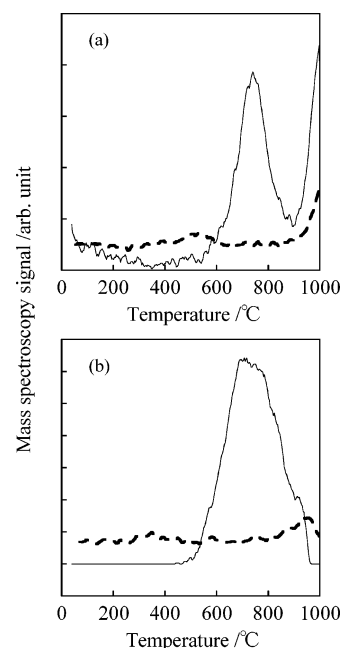


Figure 2. TPD-MS profiles of (a) $m/z = 28$, and (b) $m/z = 44$ for SWNHox580 and H_2 -SWNHox580 in He: (solid line) SWNHox580; (broken line) H_2 -SWNHox580.

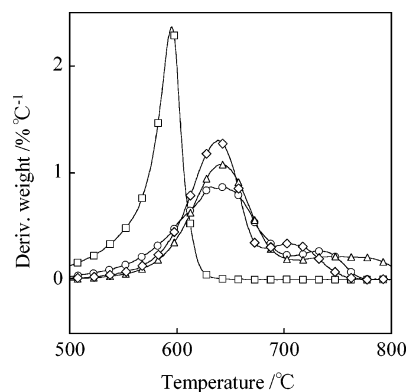


Figure 3. DTGA curves in O_2 of SWNHox580 (circle); D_2O -SWNHox580 (square); H_2 -SWNHox580 (triangle); D_2O - H_2 -SWNHox580 (diamond).

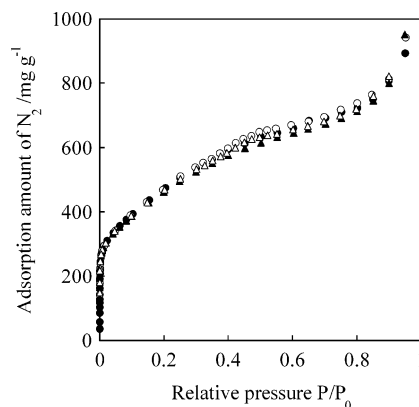


Figure 4. Adsorption and desorption isotherms of N_2 on SWNHox580 (circle) and H_2O -SWNHox580 (triangle) at 77 K. Closed and open symbols denote the adsorption and desorption branches, respectively.

isotherms were closely overlapped, indicating that the specific surface area and pore volume were not affected by the immersion in water. Powder X-ray diffraction and transmission electron microscopy (TEM) examinations also showed that

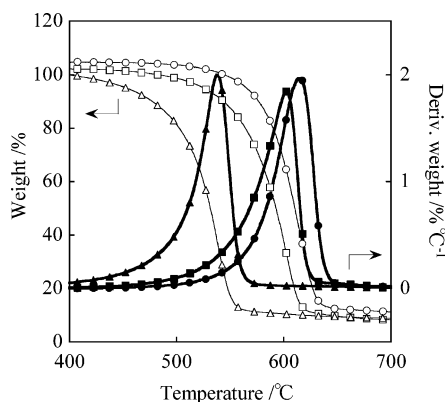


Figure 5. TGA and DTGA curves in O_2 of HiPco SWNTox580 and immersed SWNTox580 samples in water: (circle) SWNTox580; (square) H_2O -SWNTox580; (triangle) D_2O -SWNTox580. Open and closed symbols denote TGA and DTGA curves, respectively.

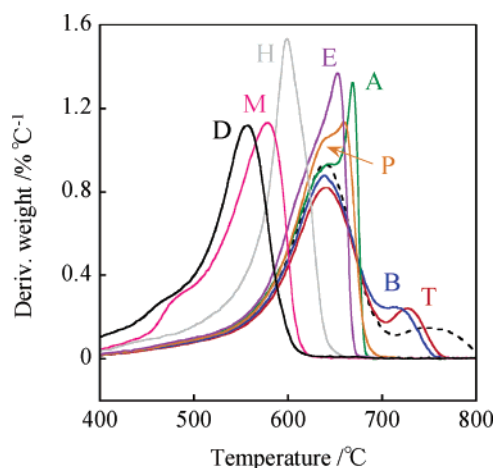


Figure 6. DTGA curves in O_2 of SWNHox350 (broken line) and immersed SWNHox350 samples in various solvents (solid lines): (T) toluene-SWNHox350; (B) benzene-SWNHox350; (A) acetone-SWNHox350; (P) 2-propanol-SWNHox350; (E) ethanol-SWNHox350; (H) H_2O -SWNHox350; (M) methanol-SWNHox350; (D) D_2O -SWNHox350.

immersion in water did not induce any noticeable structural changes in the SWNHs (not shown).

A lower combustion temperature due to immersion in H_2O or D_2O was also observed for oxidized HiPco SWNTs, SWNTox580 (Figure 5). The combustion temperature of D_2O -SWNTox580 fell by about 70 °C from that of SWNTox580.

Figure 6 shows the influence of the immersion of SWNHox350 in various solvents on the combustion temperature. When nonpolar liquids, such as benzene and toluene, were used, the DTGA curves were almost the same as those of SWNHox350. Acetone induced a shift of the DTGA peak at higher temperature, though the main peak was unchanged. For methanol, ethanol, or 2-propanol, SWNHox350 showed different combustion behavior. Among the solvents investigated here, D_2O had the greatest effect with respect to lowering the combustion temperature.

Discussion

In our recent research, we directly observed through TEM that heating in O_2 caused the opening of holes in SWNHox580 samples and found that such holes acted as paths to the spaces within the SWNHs.²⁸ SWNHox, therefore, was able to adsorb a larger quantity of N_2 than as-grown SWNHs (which had almost no holes).²⁹ The edges of the holes are likely to be

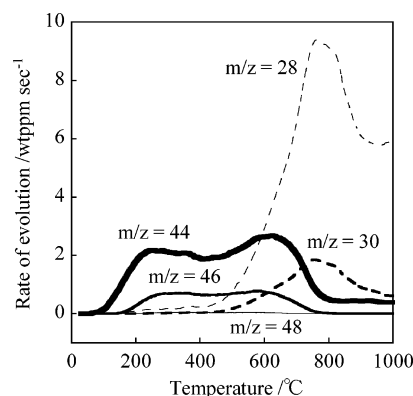


Figure 7. TPD-MS profiles of $H_2^{18}O$ -SWNHox580 in He.

terminated by OCF groups, such as carboxyl ($-COOH$), carbonyl ($-C=O$), and hydroxyl ($-OH$). Upon heated condition, these OCF groups can form anhydrides or lactones through dehydration. The existence of the OCF groups on SWNHox was previously reported.²⁵ We showed in this paper that the OCF groups were removed by exposure to hot hydrogen gas (Figure 2).

We found a curious behavior of SWNHox that the combustion temperature was lowered by immersion in water, and more remarkably by immersion in D_2O (Figure 1). A different degree of combustion-temperature lowering may be explained as the isotope effect. The vibration energy of the O–H bond is lowered by a substitution from H to D, and a cleavage of the weakened O–D bond would be a trigger for further thermal decomposition. We deduced from the TPD-MS analysis of $H_2^{18}O$ -SWNHox580 (Table 1) that this lowering of combustion temperature was brought about by chemical changes in the OCF groups (located most likely at the hole edges) caused by reaction with water molecules.³⁰ A similar combustion-temperature lowering was observed in the case of HiPco SWNTox580 (Figure 5), so we think that the OCF groups of SWNTox580 also chemically reacted with water.

Interestingly, the degree of combustion-temperature lowering differed when various solvents were used instead of water (Figure 6). Methanol caused the greatest lowering of the combustion temperature, followed by ethanol, 2-propanol, and acetone; there was almost no lowering, though, for benzene and toluene. These results suggest that the chemical reactions between the OCF groups and each solvent are characteristic of the solvent molecules, as we discuss in more detail below.

The most likely reaction between water molecules and the OCF groups is hydrolysis of anhydrides and/or lactones. As shown in Figure 2b, SWNHox580 desorbed CO_2 ($m/z = 44$) in the temperature region from 500 to 900 °C; this CO_2 evolution can be assigned to anhydrides and/or lactones.^{31,32} After the immersion in water, a new CO_2 evolution peak appeared in the lower temperature region for $H_2^{18}O$ -SWNHox580 (Figure 7). This new TPD-MS peak corresponded to the reported CO_2 evolution by decomposed carboxylic acids (100–400 °C).^{31,32} This suggests that water opens the rings of anhydrides or lactones of SWNHox580, giving rise to carboxylic acids.

We would also expect the reaction between alcohols and the anhydride or lactone groups to occur during the immersion of SWNHox in solvents. It is reasonable that the shift of the DTGA peaks was largest for methanol, followed by ethanol and 2-propanol. Fischer's esterification starts from a nucleophilic attacking step by an alcohol molecule toward an electrophilic carbon of anhydride (or lactone). The bigger size of an alkyl substituent would cause a stronger steric hindrance effect, giving

rise to lower reactivity for esterification. In the case of acetone, the reaction with anhydrides or lactones is unlikely, but acetals might be formed as a result of the reaction with phenolic functional groups. The CO evolution from the oxidized SWNHs suggests a presence of phenolic functional groups.^{31,32} Reactions for nonpolar solvents, such as benzene or toluene, with oxygen-containing functional groups are also unlikely. Indeed, immersion in benzene or toluene had little effect on the combustion temperature (Figure 6).

We interpret the combustion-temperature lowering as a measure of the chemical reactivity of the chemically modified OCF groups with oxygen gas, and also probably with the other materials. In other words, the chemical reactivity of chemically modified OCF groups at the hole edges can be controlled by selecting the solvents. We believe that this simple method of controlling the edge reactivity might not be restricted to novel carbonaceous materials (SWNTs or SWNHs); it would also be applicable to conventional carbonaceous materials.

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