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X-ray diffraction (XRD) and electrical resistance measurement on single-walled carbon nanotube (SWNT) samples prepared by the arc-discharge method are reported. The XRD profile of heat-treated sample indicated that air (oxygen, and/or nitrogen and/or water) can be condensed inside the SWNTs. We also found that the electrical resistance of SWNT soot is significantly affected by exposing to the oxygen gas and humid air.

Keywords: carbon nanotube; XRD; adsorption; resistivity; SWNT

INTRODUCTION

Carbon nanotubes have an inner hollow cavity with a diameter that is typically between one and 20 namometers, and can be filled by certain substances[1, 2]. This leads to interesting possible applications, such as for gas cylinders[3, 4] and molds to form one-dimensional (quantum) system[5]. Actually, it has been reported that low-surface-tension liquid is drawn up into multiwalled carbon nanotube (MWNTs) by capillarity[2]. Furthermore, the storage of hydrogen[3] by single-walled carbon nanotubes (SWNTs) and the trapping of argon inside MWNTs by a hot isostatically pressing (HIPing) process[4] have been reported. In this paper, we present X-ray diffraction

(XRD), garavimetric, X-ray photemission spectroscopy (XPS), and electrical resistance studies on SWNT soot. We found an evidence for gas adsorption inside the SWNTs.

EXPERIMENTAL RESULTS AND DISCUSSIONS

The SWNT samples were synthesized by evaporation of composite rods of nickel (Ni), yttrium (Y) and graphite in helium atmosphere by the arc discharge method[6]. Observations by transmission electron microscopy (TEM) confirmed that the soot contains a large quantity of SWNTs, as well as "amorphous" carbons and metal particles.

XRD experiments

The XRD profile for as-grown samples is shown in Fig. 1(a). In the large background signal, we can see rather broad peaks indexed to the triangular lattice of SWNTs, as previously reported[7]. The XRD profiles of the SWNT soot heated in air at 350°C for 20 min were also shown in (b) and (c). We notice that the (10) peak intensity, indicated by an arrow in Fig. 1, drastically decreases from (b) to (c). Here, (b) was taken just after the heat treatment, and (c) was taken after the sample had been left in air for five days. Subsequent heat treatment restored the (10) peak intensity ((d) in Fig. 1). Such behavior was repeatedly observed as shown in Fig. 1 ((e) and (f)).

One possible origin of the above behavior is gas adsorption into the *SWNT soot* after heating and desorption from the soot by heating. In order to confirm this, we made thermogravimetry (TG) analysis and weight uptake experiment. The data gave evidences for the adsorption in the *heat-treated soot*. However, such experiments cannot provide the direct evidence for the adsorption *inside the SWNTs*.

Thus, we performed a simulation of the XRD profile in Fig. 1, taking into account the desorption / adsorption of air from / into the hallow cavities of SWNTs. Figure 2 shows the XRD patterns for SWNT ropes, obtained by subtracting the background signals from the raw data. We examined two

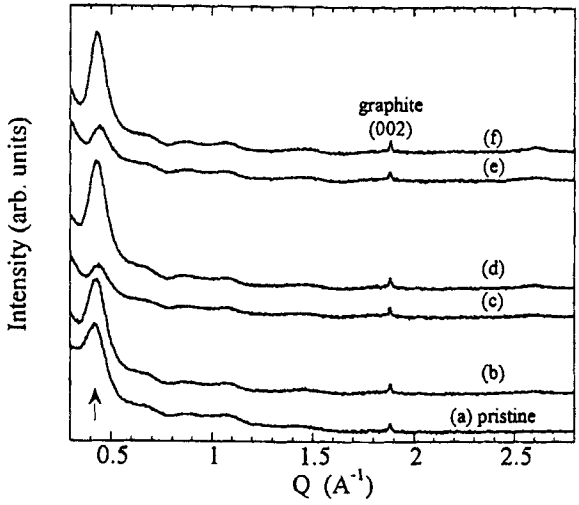

FIGURE 1. XRD profile (total counts versus $Q = 4\pi\sin\theta/\lambda$, where λ is X-ray wave length; ~1.54 A) of a SWNT sample at RT. Measurements were performed on the same sample as a function of time and heat-treatment, sequentially from (a) to (f). (a) for pristine sample; (b) just after heating at 350°C for 20 min in air; (c) after leaving for 5 days in air at RT; (d) just after heating at 350°C for 20 min in air; (e) after leaving for 15 h in air at RT; (f) just after heating at 350°C for 30 min in air.

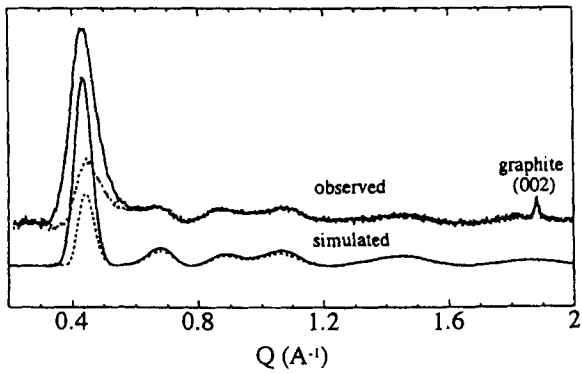

FIGURE 2. Observed and simulated XRD patterns of a SWNT sample. The observed patterns were obtained by subtracting the background signals from the raw data, (d) and (e), in Fig. 1.

possible models of SWNT ropes that adsorb gases. Model I: The gases are adsorbed outside the nanotubes, mainly at intertube sites; model II: The gases are adsorbed inside each SWNT.

First, we simulated the case in which there are no adsorbed gases, using a uniformly charged cylinder model for each tube[7]. The best result is denoted by solid lines in Fig. 2, in which a triangular lattice with a lattice constant of 17.1 Å and a nanotube radius of 7.11 Å were used. These values are slightly larger than those estimated by Thess *et al.*[7]. Next, we simulated the case in which gases are adsorbed in the ropes. It became clear that the gases at intertube sites (model I) significantly increases the first (10) peak, in contrast to the experimental observations. Therefore, we conclude that model I cannot explain the observed XRD profile. In model II, on the other hand, it was found that the XRD pattern is successfully explained, as denoted by dotted lines in Fig. 2. Here, the lattice constant and the nanotube radius are the same as those used in the nonadsorbed sample, and air (oxygen, and/or nitrogen and/or water) of ~20 wt% per SWNT filled the inner hollow cavity of a radius of 5 Å. In the case of an oxygen molecule, with the dimension of 2.8 Å in diameter and 4 Å in length, each SWNT can be filled up by oxygen of 27 wt% per SWNT. So, the estimated value is not unrealistic. The gas adsorption inside the nanotube is probably possible as a result of opening the SWNT by heating in humid air.

Electrical resistance

It is interesting to know how the physical properties change on the gas adsorption. So, we studied the resistance of SWNT soot, as one example. First, we found that the soot resistance gradually drops in air with time at room temperature (RT) *after heating* in humid air up to ~350°C. Next, we examined the same measurements in nitrogen (N_2), oxygen (O_2), and helium (He). These results are shown in Fig. 3, where the RT resistance of the heat-treated soot is shown as a function of time in different atmosphere. In the case of O_2 and humid air, clear resistance drops were observed, indicating that O_2 and H_2O molecule can be absorbed into the SWNT soot, while the reason for the change is not clear. Interestingly, the resistance changes in the opposite direction to the case of C_{60} solid on "O_2 doping"[8].

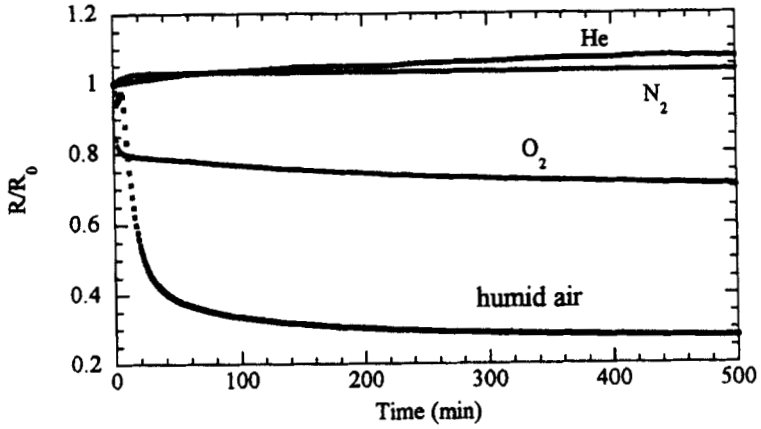

FIGURE 3. The electrical resistance of heat-treated SWNT soot as a function of time in different atomosphere; N_2, O_2, He, and humid air.

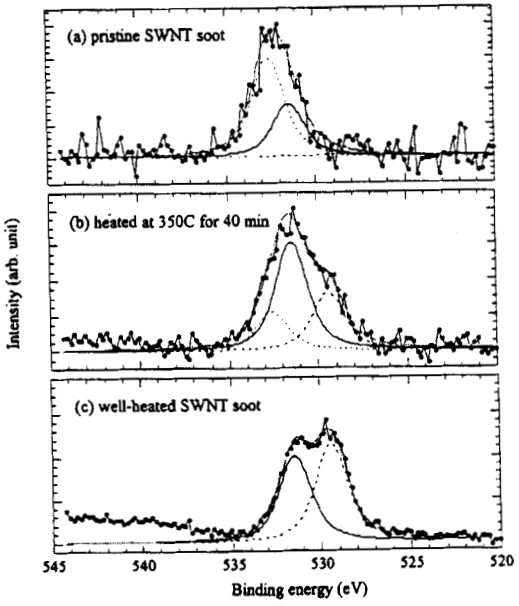

FIGURE 4. XPS spectra of O-1*s* level in pristine and heat-treated SWNT soots. The observed spectra can be decomposed into three components with the peak position of 532.5, 531.5, and 529.5 eV.

XPS measurements

Finally, we present X-ray photoemission measurements of oxygen 1*s* level and carbon 1*s* level for the pristine and heat-treated SWNT soots. From O-1*s* XPS spectra, we found three different oxygen states with binding energies of 532.5 eV, 531.5 eV and 529.5 eV, as shown in Fig. 4. The binding energy and the heat-treatment dependence of the intensity suggested that the peaks observed at 532.5 eV, 531.5 eV and 529.5 eV are assigned to carbonyl carbon (C=O), Y_2O_3 and NiO, respectively. We also estimated O/C ratio in the samples from the relative intensity for O-1*s* and C-1*s* levels; 2.5 % for the pristine soot, 6.44 % for the soot heat-treated at 350°C for 40min, and 34.6 % for the well heat-treated soot. The presence of C=O group may be responsible for sensitive adsorption to polar molecules such as water.

Acknowledgments

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