Fluorination of CN_x Nanotubes

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ABSTRACT

Multiwall CN_x nanotubes have been prepared by thermal decomposition of acetonitrile over Co/Ni catalytic particles. The fluorination of nanotubes was performed at roomtemperature by using a gaseous mixture of BrF_3 and Br_2. Transmission electron microscopy (TEM) and x-ray diffraction (XRD) indicated that only the outer shells of CN_x nanotubes were fluorinated, whereas the inner shells remained intact. X-ray photoelectron spectroscopy (XPS) showed an oxidation of pyridinic-type nitrogenwith tube fluorination.

Key Words: Fluorination; CN_x nanotubes; Binding energy.

INTRODUCTION

Single-wall and multiwall carbon nanotubes (SWNTs and MWNTs) were demonstrated to have higher reactivity towards fluorine and fluorinating agents than graphite.[1,2] The moderate or even low temperature should be held during synthesis to preserve a tubular morphology of the fluorination product. Fluorination of catalytic MWNTs using a gaseous mixture of F_2, HF, IF_5 was shown to proceed at room temperature yielding CF_x compounds with a limited fluorine content $x \leq 0.4$.[2] Arc-produced MWNTs were fluor inated with volatile BrF_3 and Br_2 up to $C_1F_{0.3}Br_{0.02}$ composition.[3,4] Rather low fluorination degree MWNTs is due to attaching of fluorine atoms to the surface layers mainly. N-doping of carbon nanotubes yields electron-rich strictures[5] characterized by metallic behavior and high density of field emission current.[6] In this work, we studied the reactivity of CN_x nanotubes towards the fluorinating agent BrF_3.

EXPERIMENTAL

CN_x nanotubes were obtained using a chemical vapor deposition (CVD) process described in details elsewhere.[7] Ni/Co particles were produced in result of bimaleate decomposition and used as a catalyst for CN_x nanotubes growth via pyrolysis of acetonitrile in an argon flow (3 L/min) at 850° C and atmospheric pressure. The CVD process resulted in the formation of a dark gray material consisting of MWNTs with average diameter of ~ 40 nm. The CNx tubes have a conical arrangement and contain about 3% of nitrogen as it was estimated by x-ray photoelectron spectroscopy (XPS).

Fluorination of CN_x nanotubes was carried out following a procedure previously applied to arc-produced MWNTs.[3,4] The sample placed in a teflon flask was held in a vapor of liquidBr₂ for 24 hr and then in a vapor over a solution BrF_3 (2 g) in Br_2 (5 g) for 7 days. Thereafter the flask content was dried by a flow of N_2 up to the termination of Br_2 evolution (~ 48 hr). Characterization of the samples produced were

performed by using transmission electron microscopy TEM, Phillips CM200 LaB6 electron microscope operated at an accelerating voltage of 200 kV equipped with an energy dispersive elemental x-ray analysis DX-4)], x-ray diffraction (XRD, DRON-SEIFERT-RM4 instrument, Cu Kα radiation), and XPS (VG ESCALAB spectrometer with the Al Kα excitation).

RESULTS AND DISCUSSION

The typical TEM image of the fluorinated product is shown in Fig. 1(1). The applied fluorination procedure leaves the tubular morphology almost unchanged. The arrows points to the most destroyed nanotube parts. One can see the tube ends and interfaces between compartments of CN_x nanotube have higher reactivity towards the fluorinating agent due to the large concentration of defects. In some cases, catalytic particles attached at the tube ends were etched while metal located in the tube cavities remained intact. From analysis of TEM pictures of the fluorinated CN_x nanotubes it seems that the tubes having large diameter are more readily broken into separate compartments with fluorination. The large diameter CN_x tubes are characterized by larger inclination angle of stacked graphitic layers respect to the axial direction that could increase imperfection of tube surface. The high-resolution TEM image of tube bending demonstrates the inner graphitized shells separated by ~ 3.4 Å and the fluorinated surface layers with increased spacing between them [Fig. 1(2)]. The estimated distance between fluorinated layers is about 4.2 Å.
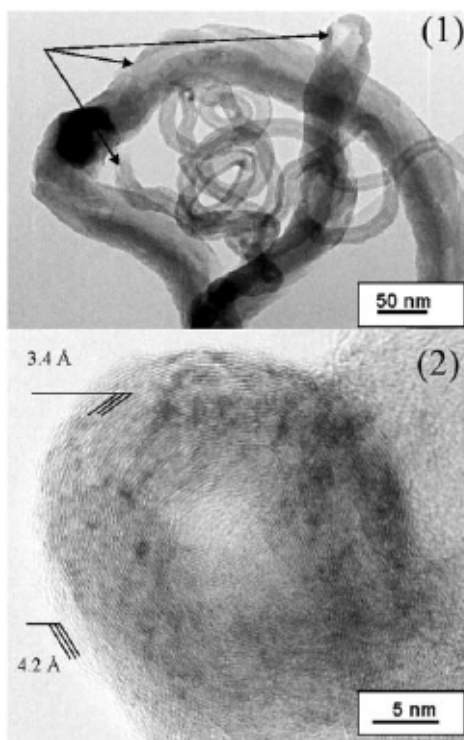

Figure 1. Low-resolution (1) and high-resolution (2) TEM images of fluorinated carbon nanotubes.

X-ray diffraction patterns of the pristine CN_x nanotubes and those after fluorination are compared in Fig. 2. The former pattern exhibits the (002), (100), and (004) reflections from the graphitic layers and strong peaks corresponded to the cubic Ni/Co solid solution [Fig. 2(1)]. The x-ray diffraction pattern of the fluorinated CN_x nanotubes preserves all these lines and shows additional reflection at $2\theta = 14.3°$ attributed to the fluorinated graphite layers [Fig. 2(2)]. This reflection was estimated to be formed by about 30 fluorinated layers, which could constitute the walls of compartments from the large diameter tubes. A halo around $2\theta = 20.0°$ is likely to correspond to the XRD from the fluorinated surface layers detected in the HRTEM image of fluorinated CN_x tube [Fig. 1(2)]. The broadening of graphite (002) reflection in the product indicates decrease of layers number involved in the diffraction. This fact suggests that the thick CN_x tubes have higher reactivity to the fluorinating agent applied.
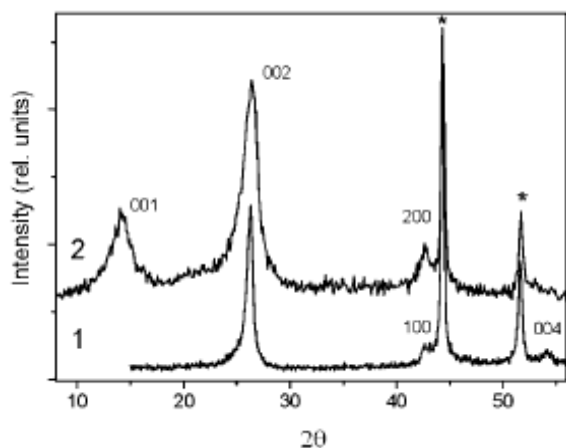
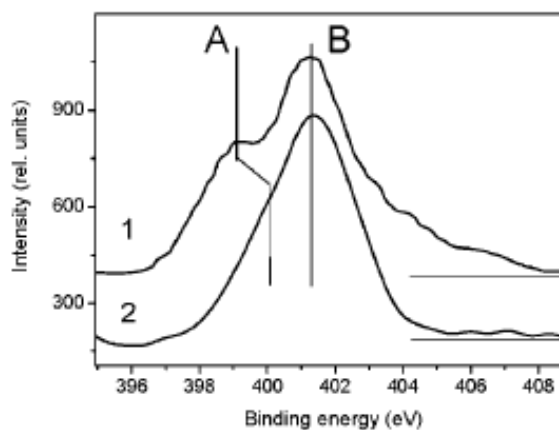Figure 2. XRD patterns for pristine (1) and fluorinated (2) samples.

Figure 3. N 1s XPS spectra for pristine (1) and fluorinated (2) samples.

The C 1s XPS spectrum measured for the fluorinated CN_x nanotubes is similar to that for the fluorinated arc-produced MWNTs.[3] The binding energy centered at 289.5 eV corresponds to the carbon atoms bonded to the fluorine ones and the signal obtained at 286.2 eV is assigned to the bare carbon. Fitting of C 1s spectrum to two Gaussian-shaped curves gave a C_3F composition of the product however, due to the limited depth of photoelectrons yield the carbon atoms from only 3–4 surface shells of nanotubes participate in spectrum formation. The N 1s XPS spectra of the pristine sample of CN_x nanotubes and that after fluorination are compared in Fig. 3. The CN_x nanotube spectrum shows two lines centered at 399 and 401.2 eV. According to the interpretation given in Ref.[5], the former line A can be attributed to pyridinic nitrogen and the latter line B corresponds to highly coordinated nitrogen atoms replacing carbon ones within the graphitic shells [Fig. 3(1)]. The fluorinated material has a low conductivity and to take into account sample charging during the measurement the N 1s spectrum was shifted to lower binding energies by 2.7 eV. The shift value was determined from comparison between the O 1s spectra of the pristine and fluorinated CN_x nanotubes. The N 1s XPS spectrum of the product shows alone asymmetric line B. The keeping of energy position of line B with fluorination indicates inertness of three-fold coordinated nitrogen atoms towards the fluorinating agent. At the same time, the spectral intensity associated with the pyridinic nitrogen is considerably lowered. Nevertheless, the deconvolution of N 1s spectrum of the fluorinated CN_x nanotubes with Gaussian curves gives almost the same ratio between two components while the line A is shifted to higher binding energies by ~ 1.3 eV. This shift indicates an oxidation of pyridine-like nitrogen with fluorination. The nitrogen atoms substitutional in graphite are likely to be incorporated into inner tube shells that exclude their contact with fluorinating agent.

CONCLUSION

The reactivity of multiwall CN_x nanotubes towards volatile BrF_3 was found to depend on a tube diameter. The CN_x tubes with outer diameter of > 50 nm are almost completely fluorinated that could be caused by peculiarities of tube morphology. The TEM investigation showed that the thick CN_x tubes consist of compartments and interfaces between them could provide a penetration of BrF_3 inside of nanotube. For nanotubes with relatively small diameter, the surface shells are fluorinated and the inner shells remain graphitized. Fluorination of CN_x nanotubes was detected to cause oxidation of pyridinic nitrogen and has no effect on chemical state of nitrogen replacing carbon atoms within the graphitic shells. Probably, the latter nitrogen atoms are incorporated into inner shells of thin CN_x nanotubes.

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