CHARACTERISTIC OF SURFACE OXIDES ON MWNTS INTRODUCED DURING PURIFICATION PROCESS BY XPS

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Introduction

The discovery of carbon nanotubes has attracted much attention on their potential as supports for metals (Zhang et al., 2005), active complex species (Hu et al., 2004) or heterogeneous catalysts (Liu et al., 2001a; Liu et al., 2001b). As a consequence, the development of surface nanostructures has been one of the key issues that drive the modern technology. This rapidly growing area concentrates on tailing the nanomaterial surface for specific and unique properties.

Many techniques have been developed to synthesize carbon nanotubes, such as the arc discharge, laser ablation and catalytic methods (Liu et al., 2002). Methods based on the chemical vapor deposition (CVD) of carbon from molecular precursors, assisted by the catalytic activity of small transition metal particles, have been considered as the method of choice for the mass production of carbon nanotubes, especially for the synthesis of aligned tubes (Laurent et al., 1998). In the case of CVD methods, the pyrolysis temperature, catalyst concentration, solution feeding rate, and carrier gas flowrate all influence the yield of carbon nanotubes (Liu et al., 2002). Metal particles, especially Fe, Co, and Ni, in carbon nanotube synthesis play a crucial role, which can be generated by decomposition of organometallic precursors in the gas phase. Methane (Nerushev et al., 2001), acetylene (Satishkumar et al., 1998), n-butane (Satishkumar et al., 1999), benzene (Sen et al., 1997; Cheng, et al., 1998), xylene (Cao et al., 2001), toluene (Liu et al., 2002), acetonitrile (Yan et al., 2003), or iron (II) phthalocyanine (Wang et al., 2001) has been served as the carbon source. Besides, the addition of thiophene, a growth promoter, to the carbon source has verified to improve the quality of as-grown carbon nanotubes (Cheng, et al., 1998). Moreover, N-doped carbon nanotubes has been found to behave as aligned bundles (Yang et al., 2005).

It is known that the as-prepared carbon nanotubes generally contain an amount of catalyst particles, graphitic particles and amorphous carbon that may degrade the properties of carbon nanotubes. In order to remove these impurities and open the tips of carbon nanotubes, several approaches have been used including oxidation with acid, burning in air/oxygen, or acid oxidation (for instance, by HNO_3 (Rinzler et al., 1998) or H_2SO_4/HNO_3 mixture (Kuznetsova et al., 2000; Kuznetsova et al., 2001), etc.) followed by high temperature treatment in inert atmosphere. It is known that HF (Hernadi et al., 1996), H_2SO_4 (Taberna et al., 2006) or HCl (Rao et al., 1998; Sloan et al., 1998) can be utilized to dissolve the catalyst particles and lead to the selective opening of the tips of carbon nanotubes. $KMnO_4$ (Hernadi et al., 1996) or H_2O_2 (Feng et al., 2003) can be applied to eliminate amorphous carbon and carbonaceous impurities. However, the treatment with boiling concentrated HNO_3 can both eliminate amorphous carbon and other carbon impurities (Rao et al., 1998; Dujardin et al., 1998), as well as open the tips of carbon nanotubes (Tsang and Chen, 1994). The amorphous carbon is known to have a higher reactivity because its structure is highly disordered with many active dangling atomic sites and some weak C-C bonds. Moreover, carbon nanoparticles with a structural pattern of higher curvature are expected to experience higher conformational strain and hence higher reactivity, compared with carbon nanotubes. Therefore, the acid-purified nanotubes might introduce oxidized functional groups in the forms of –COOH, quinine and C-O-C groups (Kuznetsova et al., 2000) on the CNTs surface.

There has been recent interest in the development of nanotube-based polymer composites. Although carbon nanotubes possess several desirable bulk properties, the surface of the carbon nanotubes is generally not ideal for this particular application. Uniform dispersion of carbon nanotubes within the polymer matrix and strong interfacial bonding between carbon nanotubes and polymer matrix are crucial issues in the processing of these nanocomposites. Introduction of surface oxygen-containing functional groups onto carbon nanotubes has been known as a method to improve the interfacial adhesion. Therefore, the objective of this study was to understand the degree of oxidation on the surface of multi-walled carbon nanotubes (MWNTs) during acid purification as well as to determine the types and the proportion of the surface oxides.

Experimental

Synthesis and Purification
The MWNTs were synthesized by CVD method through an iron catalyzed reaction. The samples were obtained in the temperature of 760 ^{o}C under a flow of argon with a surface velocity of 4 cm/min by a solution injection method in a horizontal reactor using benzene as carbon source and ferrocene as catalyst precursor. The temperature was maintained at the target temperature for 1 hour under flowing argon with injection of mixture of ferrocene/benzene (1/9 by weight) at a rate of 1.2 cc/hr by a syringe pump (Kd Scientific, Model 100). The yield of as-grown MWNT from this system was about 50-80 mg/h. The as-prepared MWNT samples, denoted by CNT hereafter, then were washed by refluxing in the mixture of 4M HNO_3/HCl (1:1 by volume) for 2, 4, 8, 16 or 24 hours to remove the amorphous carbon, catalysts or other impurities. The purified sample was denoted by CNT-NC*x* hereafter, where *x* represents the reaction time.

Characterization
The properties of the MWNTs were probed using a number of surface analytical methods. The high resolution transmission electron microscopy (HRTEM, Tecnai G2, 200kV, high resolution) was carried out to gain insight into the interior microstructure of MWNTs. The thermogravimetric analysis (TGA, Dynamic TGA 2950 in TA Instrument 5100) was used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. The loss in weight over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability.

X-ray photoelectron spectroscopy (XPS, also called electron spectroscopy for chemical analysis, ESCA) was employed to study the composition as well as the number and type of functional groups present on the surface region of a sample. The XPS spectra of all samples were obtained with a spectrophotometer (VG Scientific ESCALAB 250). Al Kalpha (hν = 1486.68 eV) was used as the photon energy for this analysis, at a power of 15 kV at 400 W. The survey scans were collected from the binding energy of 0 to 1200 eV, and the high resolution scans were acquired over 280-296 eV. For calibration purposes, the C 1s electron binding energy corresponding to graphitic carbon was referenced to 284.5 eV (Biniak et al., 1997). The spectral deconvolution was conducted using the XPSPEAK software. A Shirley type background was chosen to be subtracted prior to quantification. After the base line was subtracted, the curve-fitting was performed using an asymmetric Gaussian-Lorentzian sum function fitting program under an optimized peak shape. This peak-fitting procedure was iterated until an acceptable fit was obtained. It was assumed that the surface composition does not vary significantly along the nanotubes, and that its heterogeneity is present but at a much smaller scale than the analysis area probed by the X-ray beams.

Results and Discussion

HRTEM Images
The HRTEM examination could give a more clear insight into the changes in the interior structure of MWNTs, which were illustrated in Figure 1. As seen from Figure 1a, a catalyst particle appeared at the tip of nanotube. The number of graphene layers of as-grown MWNTs varied about from 6 to 36 with an interplaner spacing of 0.34 nm. It has been found that the inside diameters of as-grown MWNTs were approximately a third of the outer diameters, and a length over than 15 μm were observed. Purification of MWNTs by an acid mixture could result in the tip opening of nanotubes or the etching on the surface of graphene layers. In spite of the tip opening or the generation of defect sites, the reaction time of 2 or 4 hrs seemed not effective to remove the catalysts in the tube interior. In addition, the structure integrity still remained even though the reaction time extended to 24 hrs.

TGA Data

TGA was carried out to obtain the overall information on the crystalline perfection of nanotubes. CNT and CNT-NC24 were cited as examples to compares the TGA data measured in flowing air, shown in Figure 2. The onsets of burning for CNT were approximately 500 ^{o}C; however, the purified CNT-NC24 degraded gradually over the whole temperature range. This reveals the resistance to oxidation of purified samples was slightly deteriorate than CNT, which is also verified by their maximum rate and maximum temperature of weight loss. It should be noted that both CNT and CNT-NC24 exhibited a high total ash content (~ 20 %), which was supposed to be contributed from catalyst particles. As a result, the purification of nanotubes has degraded their crystallinity and resulted in structural heterogeneity, but the removal of metal catalysts was not effectively.
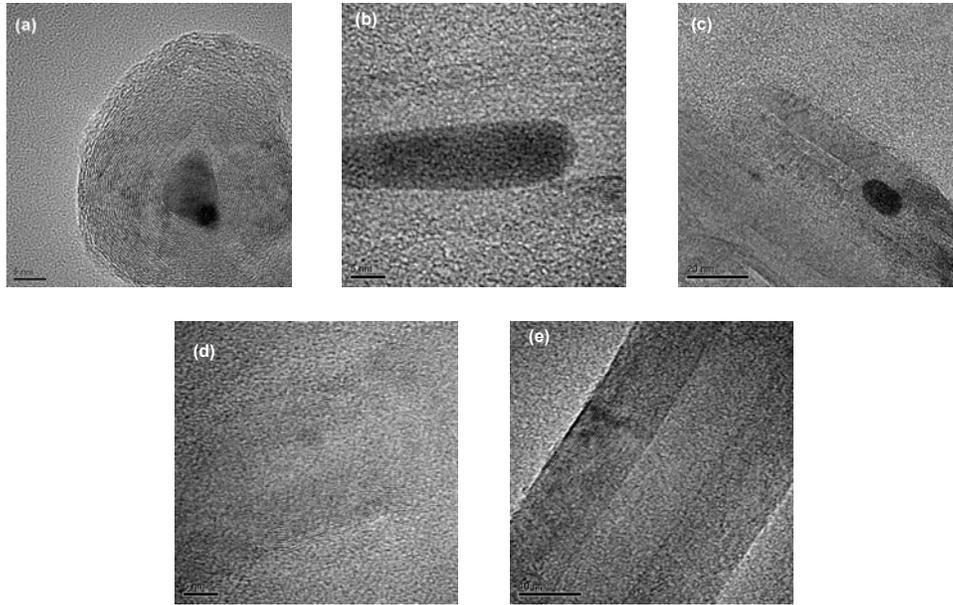

Figure 1. HRTEM Images with a High Magnification of (a) as-prepared CNT, (b) CNT-NC2, (c) CNT-NC4, (d) CNT-NC8, and (e) CNT-NC24.
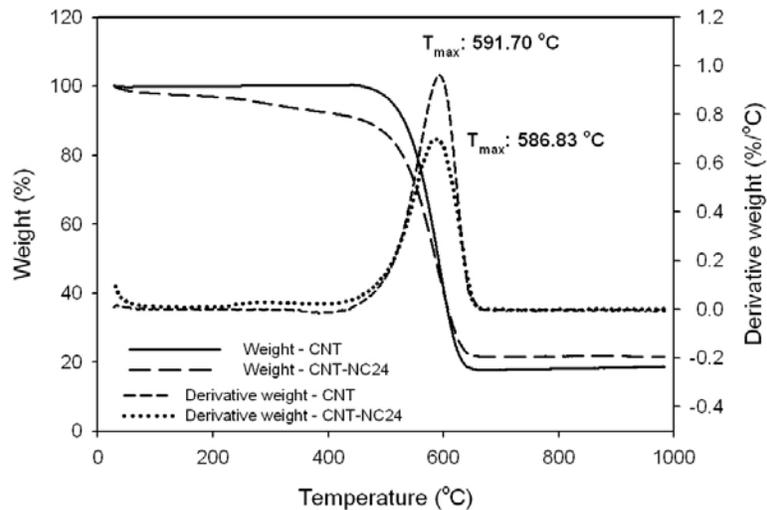
Figure 2. Thermogravimetric Analysis of CNT and CNT-NC24 Samples Showing Weight Loss and Differential Curves at a Heating Rate of 10 °C/min in Air (50 cm³/min).

XPS Analysis

The nature of surface functionalities fixed on the surface or over the sampling depth of several atomic layers from the surface of all MWNT samples was studied by XPS, which revealed the composition of the most external surface of the MWNTs. Data from the XPS survey spectra shown in Figure 3 indicate that the major peaks in the spectra were due to the C 1s and O 1s photoelectrons. On as-prepared CNT sample only a small O1s peak was discernible, while it became remarkable after acid purification. The O/C atomic ratios obtained from the survey scan spectra are summarized in Table 1, where the data responded to the above observations. The O/C ratios after purification increased to about eight times of that for as-prepared CNT. In addition, the O/C ratio was not enhanced until the reaction time extending to 24 hrs, approximately a promotion of 60 %.
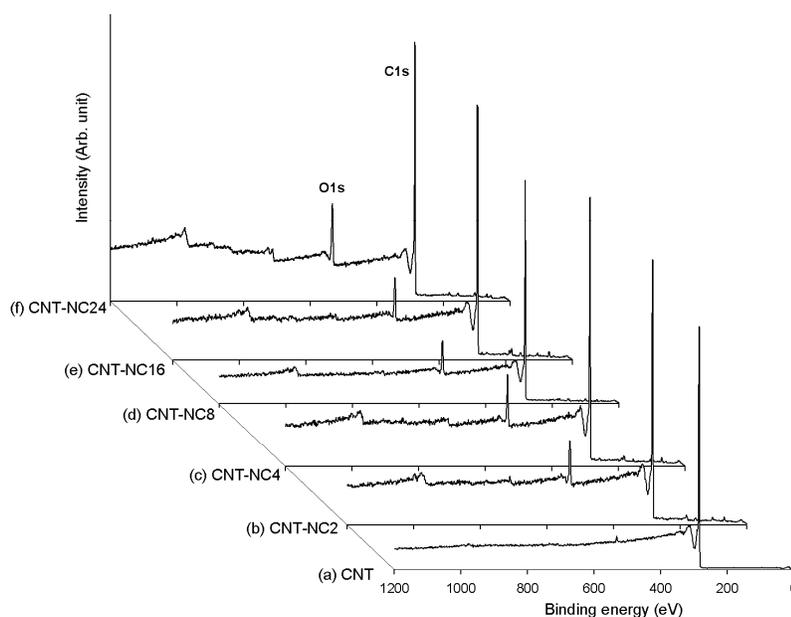

Figure 3. XPS Survey Scan Spectra for All MWNT Samples.

Table 1. Results of the Fits of the XPS C 1s Region, Values Given in Atomic % of Total Intensity.

| | | Binding energy (eV) | | | | | |
| | | 284.5 | 286.1 | 287.3 | 289.1 | 290.6 | 291.6 |
Sample	O/C*	Graphite	C-OH	C=O	C-OOH	CO_3^{2-}, CO, CO_2	$\pi \leftrightarrow \pi^*$
CNT	0.011	73.5	20.1	—	—	4.5	1.9
CNT-NC2	0.087	74.5	16.2	—	4.7	—	4.6
CNT-NC4	0.082	73.3	16.7	—	5.8	—	4.2
CNT-NC8	0.088	67.7	13.5	—	12.8	—	6.0
CNT-NC16	0.082	75.6	14.5	—	5.7	—	4.2
CNT-NC24	0.134	73.8	16.5	—	5.5	—	4.2

* The ratio of O/C is from survey scan spectra, dimensionless.

Figure 4 selectively illustrates the high-resolution XPS spectra of the C 1s region for MWNT samples. The C1s signals exhibited an asymmetric tailing skewed to the high binding energy, which was partially due to the intrinsic asymmetry of the graphite peak or to the contribution of oxygen surface complexes. The C1s spectra for all MWNT samples have each been resolved into four individual component peaks that represent graphitic carbon (B.E. = 284.5 eV), and carbon present in phenolic, alcohol, ether or C=N groups (B.E. = 286.1 eV), carboxyl or ester groups (B.E. = 289.1 eV), carbonate groups (B.E. = 290.6 eV), and shake-up satellite peaks due to π-π* transitions in aromatic rings (B.E. = 291.6 eV). The B.E. is an abbreviation of binding energy. The carbonyl or quinine groups (B.E. = 287.3 eV) were not resolved on MWNT samples as usual. The calculated percentages of graphitic and functional carbon atoms are shown in Table 1. The results indicated that phenolic groups were the intrinsic and the primary surface oxides on carbon nanotubes. The chemically adsorbed carbonate groups on as-prepared CNTs were emitted when treated with the acid mixture. The introduction of carboxyl groups onto the surface could be achieved by acid purification. Moreover, the shake-up satellite peaks due to π-π* transitions in aromatic rings could be promoted after treatment. The data reveals that CNT-NC8 could be the most unstable sample under the transition state, where it possessed the most abundant C-OOH groups and active π-π* transitions. As the reaction time was prolonged, the samples would restore back to more stable conditions.
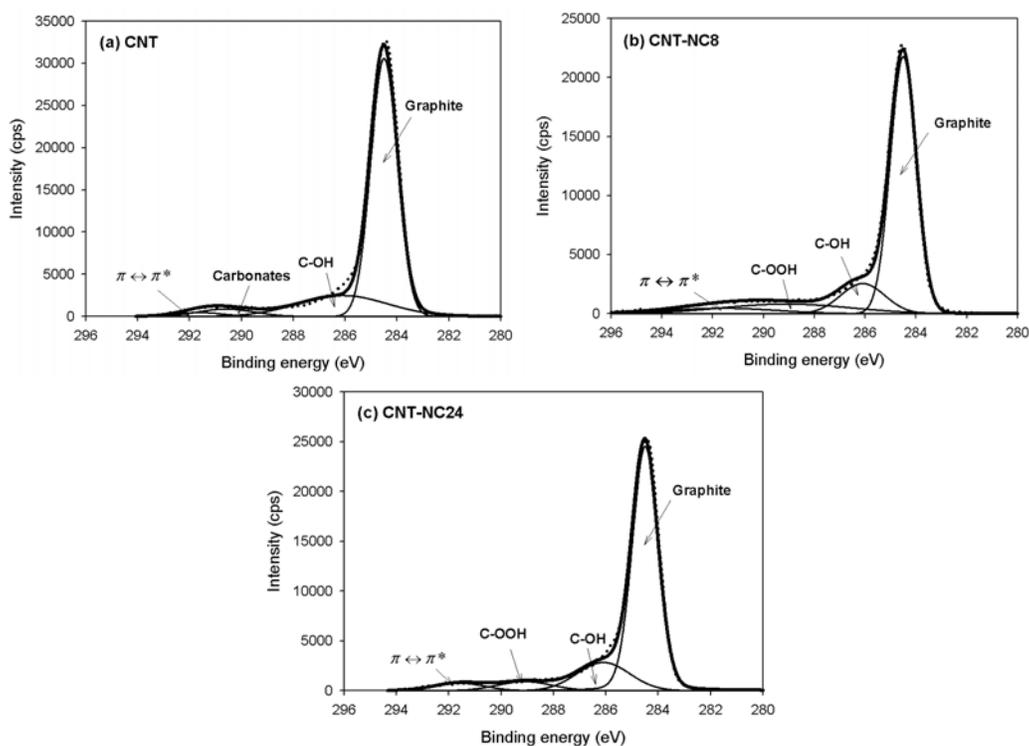

Figure 4. High Resolution Fitted XPS C1s Spectra of MWNT Samples.

Conclusions

An appropriate purification with acid mixtures on as-prepared carbon nanotubes could enhance their crystallization, introduce the surface functional groups, open the tube tips but generate several defect sites. Although the temperature for maximum rate of weight loss of purified MWNTs was inferior to that of as-prepared samples, the purification process appeared to be effective for the formation of carboxyl groups. However, the carbonyl groups commonly present on carbon surface were not resolved on the surface of carbon nanotubes. Acid purification of carbon nanotubes has significantly modified their surface to become active due to the presence of carboxyl groups and π-π* transitions in aromatic rings. This implies the purification process is beneficial to their application on nanotube-based polymer composites

Acknowledgements

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