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A comparative study on properties of multi-walled carbon nanotubes (MWCNTs) modified with acids and oxyfluorination

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Abstract

In this study, the surface modification of multi-walled carbon nanotubes (MWCNTs) with acid and oxyfluorination has been examined. Acid treatment of multi-walled CNTs produces many functionalized groups on the surface of MWCNTs, such as C–N stretching and the asymmetric carboxylate group (–COO–). It can be concluded that nitrogen doping of the graphite sheets may take place and a C–N bond identical to the sp^3-bonded carbon nitride may form during the acid treatment process. In addition, oxyfluorinated MWCNTs exhibit higher BET specific surface area and mesopore volume than those of the as-received and acid treated MWCNTs. Therefore, acid and oxyfluorination treatments are more effective methods for enhancing the chemical and textural properties of MWCNTs.

Keywords: Surface modification; Oxyfluorination; Acid treatment; Multi-walled carbon nanotubes

1. Introduction

The discovery of synthetic methods to produce carbon nanotubes (CNTs) [1], structurally built of graphene cylinders, opened the possibility of research opportunities for a variety of applications [2–5]. CNTs seem to hold a promise for energy-related alternative applications such as fuel cell or hydrogen storage. Despite intensive research on CNTs, applications for electronic and energy storage devices are still limited for a number of reasons. CNTs are chemically stable and a mechanically hard material due to their delocalized π electron system. Therefore, researchers have attempted to provide functional properties on the surface of CNTs. Chemical modification such as acid treatment can increase the solubility and purity of CNTs [6].

Recently, there have been several papers discussing surface modification of single-walled CNTs by fluorination [7–9]. Fluorination of new forms of carbon materials is of great interest because it is one of the most effective chemical methods to modify and control physicochemical properties over a wide range. The fluorination was reported for commercially available multi-walled carbon nanotubes (MWCNTs) [10]. Although there are many papers about fluorination of MWCNTs, there are few studies on oxyfluorination of MWCNTs to provide functionalized sites.

In this study, in order to modify the surface properties, oxyfluorination of multi-walled carbon nanotubes (MWCNTs) has been used. MWCNTs have a double resonance band mainly originating from defects in tube walls and graphene layer surrounding the tubes. The functionalized nature resulting from chemical treatment of MWCNTs is discussed.

2. Results and discussion

Fig. 1 shows XRD patterns of MWCNTs. As shown in Fig. 1, as-received MWCNTs display the iron oxide peak used as catalyst, while there are no impurity peaks on the XRD patterns of acid treated and oxyfluorinated MWCNTs. This indicates that acid treatment of MWCNTs is very useful for removing the impurities. Also, comparing the acid treated to oxyfluorinated MWCNTs, there is no difference in crystallinity, a key result.

The chemical treatment increased the sample purity. According to JCPDS cards no. 39-1346 for maghemite (r-Fe_2O_3), diffraction peaks that are at $2\theta = 30.12$, 35.48, 62.64, etc. can be assigned to iron oxides [11]. Fig. 1(a) exhibits the XRD patterns including the maghemite phase, while these

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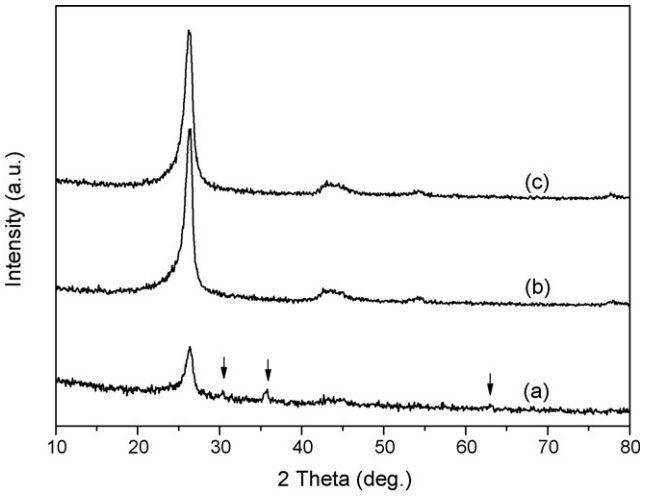

Fig. 1. XRD patterns of (a) as-received; (b) acid treated; (c) oxyfluorinated MWCNTs, arrows denote the peak of iron oxide, maghemite phase.

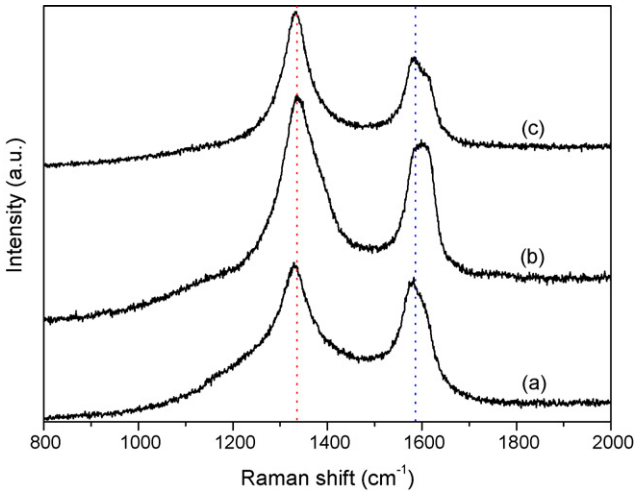

Fig. 2. Raman spectra of (a) as-received; (b) acid treated; (c) oxyfluorinated MWCNTs.

peaks were not shown in Fig. 1(b) and (c) due to acid treatment. These results also indicate that non-crystalline impurities, such as soot, and metal, such as iron oxide used as catalyst, were removed. Raman spectra are in good agreement with XRD patterns. Therefore, acid treatment was more effective in purifying the MWCNTs.

Textural characteristics of MWCNTs are listed in Table 1. As summarized in Table 1, BET specific surface areas of as-received and acid treated MWCNTs were nearly unchanged, while cumulative pore volume increased. These results indicate that acid treatment of MWCNTs removed impurities such as non-porous carbon and iron oxide as catalyst from as-received MWCNTs. Also, the oxyfluorination of MWCNTs treated with acids increased specific surface area and pore volumes. Specifically, BET clearly shows that oxyfluorinated MWCNTs at 423 K have much higher micropore volume than that of as-received and acid treated samples. This result is in good agreement with the study by Touhara et al. [12].

In order to investigate D (disordered) and G (graphitic) bands of samples, Raman spectroscopy was used. Fig. 2 exhibits Raman spectra of the samples. Raman spectra of chemically treated MWCNTs exhibit D and G bands at 1335 and 1570 cm^{-1}, respectively, corresponding to the sp^3- and sp^2-hybridized carbons signifying disordered graphite and the ordered state on the CNTs surface, respectively [13,14]. The shape and relative intensity of Raman spectra were changed due to acid treatment and oxyfluorination. Generally, single-walled and multi-walled CNTs show that the intensity of graphite band (G band) is higher than that of the defects and disordered graphite band (D band) [9]. The smaller I_D/I_G ratio is, the better MWCNTs are. On the other hand, the D band was more highly developed than the G band in our study. This implies that these CNTs are different from other CNTs.

Fourier transform-infrared (FT-IR) spectra were used to identify the functional groups within the samples. Fig. 3 shows FT-IR spectra of MWCNTs. As can seen in Fig. 3(b) and (c), the peak at 1215 cm^{-1} corresponds to C–N stretching vibration bond [13–15] resulting from acid treatment, especially due to 12N nitric acid treatment, while there is no such peak in Fig. 3(a). It can be estimated that nitrogen doping of graphite sheets may be taking place and a C–N bond identical to the sp^3 bonded carbon nitride sample may be forming during the acid treatment process [13]. Also, the carboxylic bond of asymmetric –COO–$_{(as)}$ stretching vibrates at 1580 cm^{-1} [16]. Acid treatment and oxyfluorination of MWCNTs give rise to the functional group on the surface of MWCNTs.

All samples show the peaks of hydroxyl group at 3400 cm^{-1}. The peaks at 2350 cm^{-1} are due to ambient CO_2. The spectra of C=C stretching band are apparent at about 1630 cm^{-1} [17–19]. Additionally, symmetric and asymmetric bands of CH_2 and CH_3 are at 2850 and 2920 cm^{-1}, respectively [20]. Assignments of FT-IR peaks are listed in Table 2.

In order to obtain information about surface chemical properties of binding characteristics of the element, XPS measurements were carried out. The full range XPS spectra of the samples are shown in Fig. 4. It shows that there are oxygen and fluorine (only oxyfluorinated C) on the surface of MWCNTs.

Table 1
Textural properties of the samples modified by acid and oxyfluorination

	BET surface area[a] (m^2/g)	Micropore surface area (m^2/g)	Mesopore surface area (m^2/g)	Micropore volume (cm^3/g)	Cumulative pore volume (cm^3/g)
As-received	80.4	19.7	60.7	0.0084	0.26
Acid-treated	85.0	19.9	65.1	0.0085	0.45
Oxyfluorinated	119.0	31.5	87.5	0.0138	0.51

[a] Surface area was measured N_2 adsorption at 77 K in the range of $P/P_0 = 0.01$–0.30.

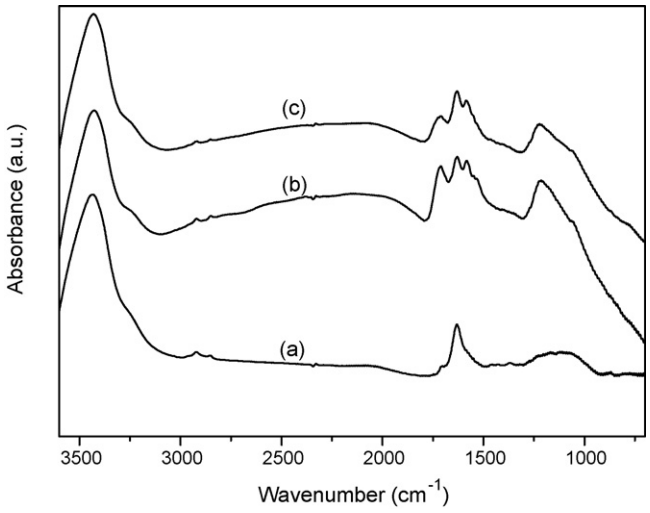

Fig. 3. FT-IR spectra of (a) as-received; (b) acid treated; (c) oxyfluorinated MWCNTs.

Table 2
Assignment of infrared spectra obtained from various carbon nanotubes

Wavenumber (cm^{-1})	Configuration
3400	Hydroxyl
2920	$CH_2 + CH_3$ symmetric
2850	$CH_2 + CH_3$ asymmetric
1710	Carbonyl
1630	Aromatic C=C
1580	Carboxlylic asymmetric
1215	C–N
1100	C–O

Fig. 5 shows the XPS C 1s curve-fitted spectra for the as-received, acid treated, and oxyfluorinated MWCNTs. Three spectra of the as-received MWCNTs are shown in Fig. 5(a), which represent sp^2- and sp^3- carbon (peak 1, 284.6 eV), oxygen related C–O (peak 2, 286.1 eV), and oxygen related COO group (peak 3, 289.2 eV). After acid treatment, sp^2- and sp^3-carbon (peak 1, 284.6 eV), oxygen related C–O (peak 2, 286.1 eV) were not changed, while C=O (peak 4, 287.4 eV) and O–COO (peak 5, 289.6 eV) appeared due to the oxidation resulting from nitric and sulfuric acids [21]. As shown in Fig. 5(b), there are more functionalized groups on the surface of acid treated MWCNTs than that of as-received MWCNTs. It clearly shows that the two kinds of acids functionalized the surface of MWCNTs. On the other hand, comparing oxyfluorinated with acid-treated MWCNTs, oxygen related peaks were converted to carbon–fluorine peaks. The spectra of oxyfluorinated MWCNTs exhibit semi-ionic C–F, nearly covalent C–F, and covalent CF_2, respectively. These peaks at high binding energy, therefore, indicate the existence of various carbon species bonded to fluorine [9,22,23].

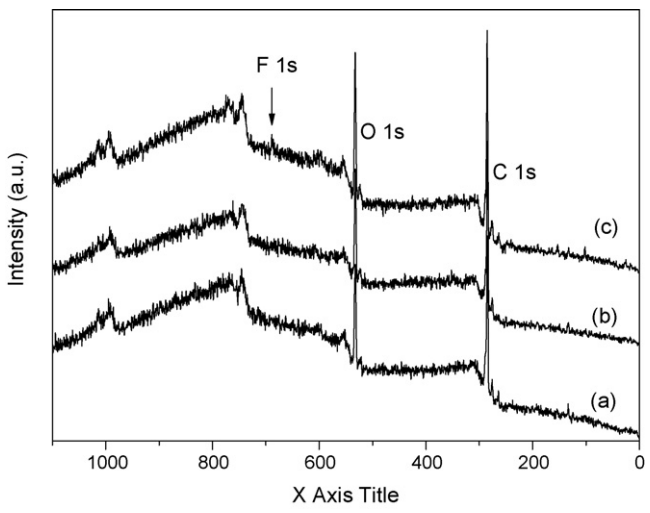

Fig. 4. Full range XPS spectra of (a) as-received; (b) acid treated; (c) oxyfluorinated MWCNTs.

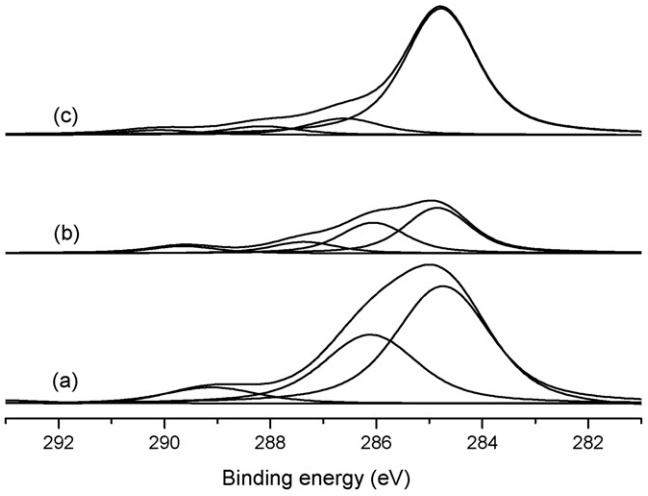

Fig. 5. XPS C 1s spectra (a) as-received; (b) acid treated; (c) oxyfluorinated MWCNTs.

Fig. 6 shows the spectra of XPS O 1s. As can be seen in Fig. 6, there is no difference of binding energy between the as-received and acid treated MWCNTs. However, the spectra of oxyfluorinated MWCNTs were shifted to a higher binding energy position. It clearly indicates that the carbon of the oxyfluorinated sample was bonded to oxygen under fluorine.

Fig. 7 shows XPS F 1s spectra of various MWCNTs. As known in Fig. 7(c), it is natural that only oxyfluorinated

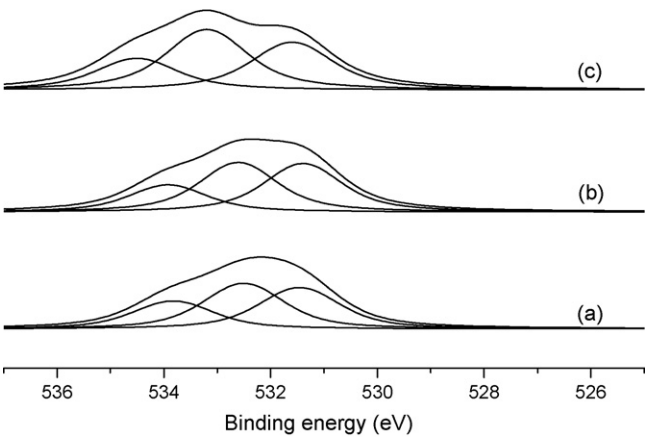

Fig. 6. XPS O 1s spectra (a) as-received; (b) acid treated; (c) oxyfluorinated MWCNTs.

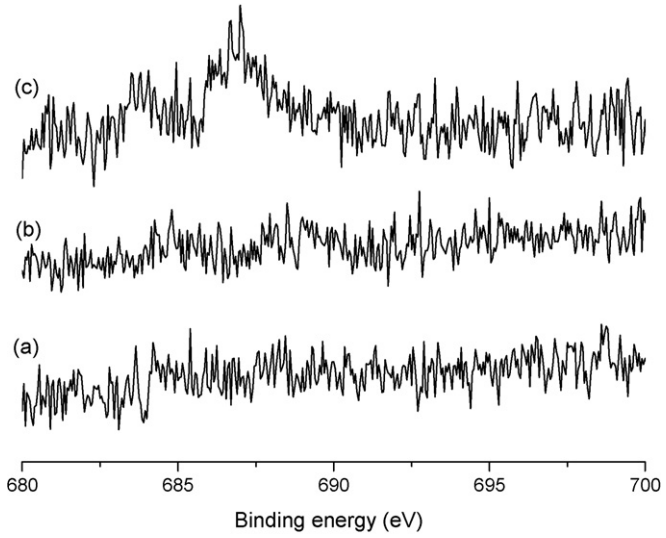

Fig. 7. XPS F 1s spectra (a) as-received; (b) acid treated; (c) oxyfluorinated MWCNTs.

Table 3
XPS analysis of the elemental composition of various MWCNTs

	Elemental content (at.%)				
	C	O	F	Fe	Total
As-received	73.93	23.38	–	0.69	100.00
Acid-treated	74.98	24.67	–	0.35	100.00
Oxyfluorinated	72.72	23.93	2.96	0.40	100.01

MWCNTs exhibit the peak of F 1s. Covalent CF appear at 687.5 eV (peak 2), while another small peak observed at 683.5 eV (peak 1) is corresponding to ionic fluorine, which is probably derived from FeF_2 or FeF_3. As can be seen in Table 3, small amount of Fe exists in MWCNTs after acid treatment, however, there is no peak indicating Fe in X-ray diffractogram shown in Fig. 1.

3. Conclusion

In conclusion, acid treatment of multi-walled CNTs produces many functionalized groups on the surface of MWCNTs, such as C–N stretching and the asymmetric carboxylate group (–COO–). It can be concluded that nitrogen doping of the graphite sheets may take place and a C–N bond identical to the sp^3-bonded carbon nitride may form during the acid treatment process. In addition, oxyfluorinated MWCNTs exhibit higher BET specific surface area and mesopore volume than those of the as-received and acid treated MWCNTs. Consequently, acid and oxyfluorination treatments are more effective methods for enhancing the chemical and textural properties of MWCNTs.

4. Experimental

Multi-walled carbon nanotubes (MWCNTs) were prepared by the vapor-grown method using iron metal as catalyst. This sample was denoted to ‘‘as-received’’ MWCNTs.

4.1. Acid treatments

In order to remove the impurities like metals and soot from MWCNT and provide functional groups such as –COOH, –OH and –CO, etc. on the MWCNT surface, MWCNT powder was immersed in 12N HNO_3 and 12N H_2SO_4 solutions in series. These solutions were boiled for 5 h under refluxing conditions. After boiling, these solutions were filtered with a membrane filter and sufficiently washed by deionized water. MWCNTs obtained by filtration were dried at 110 °C for 2 h.

4.2. Oxyfluorination

After acid treatment, MWCNTs were fluorinated at 423 K for 30 min with oxygen and fluorine. The reaction was carried out following the process described in detail elsewhere [24–26] known to be efficient for the oxyfluorination of CNTs. MWCNTs were exposed to the fluorine–oxygen mixtures with the mole fraction of fluorine set at 0.1. The total pressure of mixture gas was 1 atm. Prior to oxyfluorination of samples, all traces of oxygen had been removed at room temperature with a vacuum system at 423 K for 2 h. Fluorine gas (99.8% purity) was supplied by Messer Griesheim GmbH. The major impurities were nitrogen and hydrogen fluoride under 0.01 mol%. Hydrogen fluoride gas was removed by sodium fluoride pellets heated at 373 K used before the fluorine gas was introduced to the chamber.

4.3. Materials characterization

In order to estimate the crystallinity of the samples, X-ray diffraction (XRD, Rigaku, D/Max III) analysis was used. The specific surface area and pore volume were measured by the BET method (Micromeritics Co., ASAP 2020) using nitrogen adsorption at 77 K. The changes of chemical species on the surface of MWCNTs before and after oxyfluorination were analyzed by X-ray photoelectron spectroscopy (XPS, ESCA-LAB). The XPS spectra were fitted using Gaussian-Lorentzian function. The binding energies of the C 1s and F 1s for surface fluorinated samples were measured from the relative binding energy of C 1s spectra of graphite. In addition, functional groups on the surface of samples were characterized using Fourier transform-Infrared (FT-IR).

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