An XPS Study of Oxyfluorinated Multiwalled Carbon Nano Tubes

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Abstract

In order to investigate functional groups on the surface of Multi-walled Carbon Nanotubes (MWCNTs) induced by oxyfluorination, XPS (X-ray photoelectron spectroscopy) analysis was carried out. All core level spectra of MWCNTs were deconvoluted to several Pseudo-Voigt functions (sum of Gaussian-Lorentzian functions). Both O1s and F1s binding energy of oxyfluorinated MWCNTs shifted high value as increment of fluorine mixing ratio. The carbon-fluorine covalent bonding concentration increased as increment of fluorine mixing ratio. The shape and intensity of OF10-MWCNTs are similar with those of as-received MWCNTs. However, the intensity and binding energies of main peak position of OF20-MWCNTs and OF30-MWCNTs were dramatically increased by oxyfluorination.

Keywords : MWCNTs, Oxyfluorination, XPS, Pseudo-Voigt functions

1. Introduction

Since the discovery of synthetic methods of carbon nanotubes (CNTs) by Iijima in 1991[1], many research groups have been studying about these structure [2-5], properties [6-8] and application [9, 10]. In specialty, in order to improve dispersibility and reactivity, an attempt to induce functional groups on the surface of CNTs was gone on [11]. Among these methods, fluorination is one of the effective methods [12, 13]. The strongest electronegativity of F⁻ ion leads to strong bonding between fluorine and other elements [14]. The chemical composition, as well as the structure of carbon materials obtained by fluorination is dependent on the structure and characteristics of starting materials and on the fluorination conditions. In addition, using fluorine-oxygen mixed gas can induce the functionalization with oxygen groups even on the surface of CNTs which have high chemical stability [14]. Many studies have been carried out on fluorinated carbon materials and defined the interaction between carbon surface and fluorine atom, which have found important practical applications [12-15]. There are several kinds of interaction between carbon and fluorine (carbon-fluorine covalent, semi-ionic, ionic and van der Waals interaction) [15].

Although some studies about the carbon/fluorine system and the properties of CNTs were carried out by other research groups, the oxyfluorination (fluorination using oxygen-fluorine mixed gas) on CNTs is still fresh ground. Especially, there are few papers reported about the oxygen groups bonded at carbon atoms onto CNT by oxyfluorination.

In the present study, we report and discuss the results obtained by X-ray photoelectron spectroscopy (XPS) analysis of the oxyfluorinated multi-walled carbon nanotubes (MWCNTs) with different fluorine-oxygen mixing ratio.
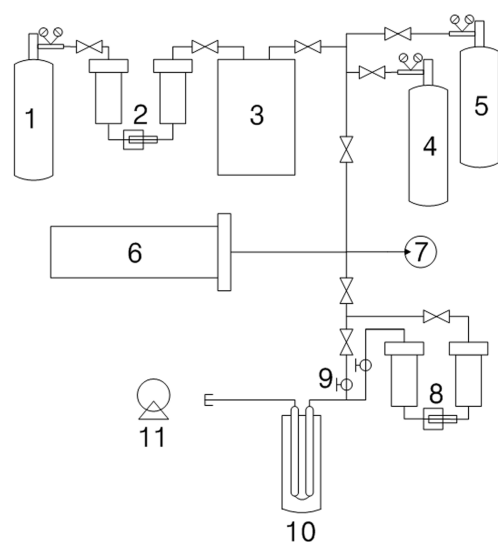
2. Experimental

2.1. Materials

MWCNTs were obtained from NK CNT Co., Korea. It was grown by the vapor growth method using acetylene (C_2H_2) as carbon source and ironpentacarbonyl ($Fe(CO)_5$) as catalyst and purified by chemical and thermal treatment [16]. The nanotubes used in this study are under 20 μm long, and outer and inner diameters are 60-80 nm and 30-50 nm, respectively. Fluorine gas used for oxyfluorination, were supplied by Messer Grieheim GmbH (99.8%). Oxygen (99.999%) and argon (99.999%) gas were used also.

2.2. Oxyfluorination

Fig. 1 shows the schematic diagram of oxyfluorination apparatus. Oxyfluorination apparatus consists of a reactor, vacuum-pump and buffer-tank connected gas cylinders. Prior to oxyfluorination, fluorine and oxygen gas were mixed with

Fig. 1. Schematic diagram of a fluorination apparatus.

Fig. 2. XPS wide scan spectra of as-received MWCNTs (a); OF10-MWCNTs (b); OF20-MWCNTs (c); OF30-MWCNTs (d).

1. F_2 gas cylinder
2. HF absorber (NaF pellet)
3. Buffer tank
4. O_2 gas cylinder
5. Ar gas cylinder
6. Reactor
7. Pressure gauge
8. F_2 absorber (Al_2O_2)
9. Glass cock
10. Liquid nitrogen
11. Rotary vaccum pump

fluorine partial pressure, in the ratio of 0.1, 0.2 and 0.3 in buffer-tank for 24 h. 1 g of MWCNTs was loaded on nickel boat in the reactor and was degassed at 473 K for 2 h. Oxyfluorination was carried out at 373 K for 1 h after introduction of prepared mixed gas to 1 bar. Non-treated MWCNTs and oxyfluorinated MWCNTs with different mixing ratio of fluorine and oxygen gas were named as follows; as-received MWCNTs, OF10-MWCNTs, OF20-MWCNTs and OF30-MWCNTs, respectively.

2.3. XPS analysis

The XPS spectra of the MWCNTs used in this study were obtained with MultiLab 2000 spectrometer (Thermo electron corporation, England) to the changes of chemical species on the surface of MWCNTs before and after oxyfluorination. Al Ká(1485.6 eV) was used as X-ray source at 14.9 keV of anode voltage, 4.6 A and 20 mA as filament current and
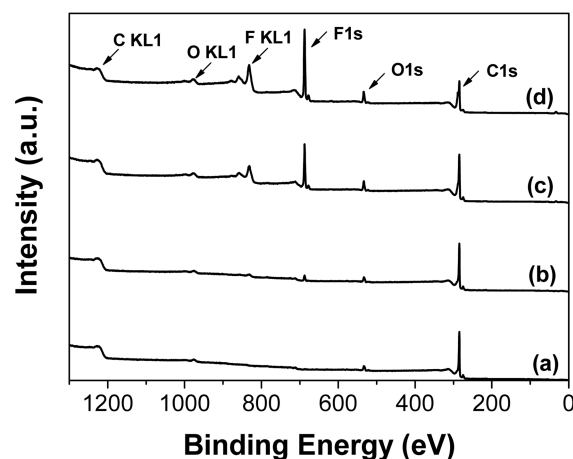
emission current, respectively. All samples were treated at 10^{-9} mbar to remove impurities. The survey spectra were obtained at 50 eV of pass energy and 0.5 eV of step size. Core level spectra were also obtained at 20 eV and 0.05 eV as pass energy and step size, respectively [16].

3. Results and discussion

The survey spectra in the 0-1300 eV of binding energy range were investigated to identify the elements on the surface of samples and perform a quantitative analysis. The survey spectra of MWCNTs oxyfluorinated with different mixing ratio of fluorine-oxygen gas and as-received MWCNTs are shown Fig. 2. All of the survey spectra show distinct carbon and oxygen peaks at around 285.0 eV and 533.0 eV, respectively. And fluorine peaks were found at around 687.7 eV on oxyfluorinated MWCNTs. The atomic ratio and binding energy of each element on the surface of MWCNTs were listed in Table 1. The binding energies of all peaks were corrected as compare with reference peak (graphite C1s, 285.0 eV). The surface carbon concentration of samples dramatically decreased after oxyfluorination with OF20-MWCNTs and OF30-MWCNTs, whereas fluorine atomic ratio of OF20-MWCNTs and OF30-MWCNTs si-

Table 1. XPS surface element analysis parameters of as-received and oxyfluorinated MWCNTs

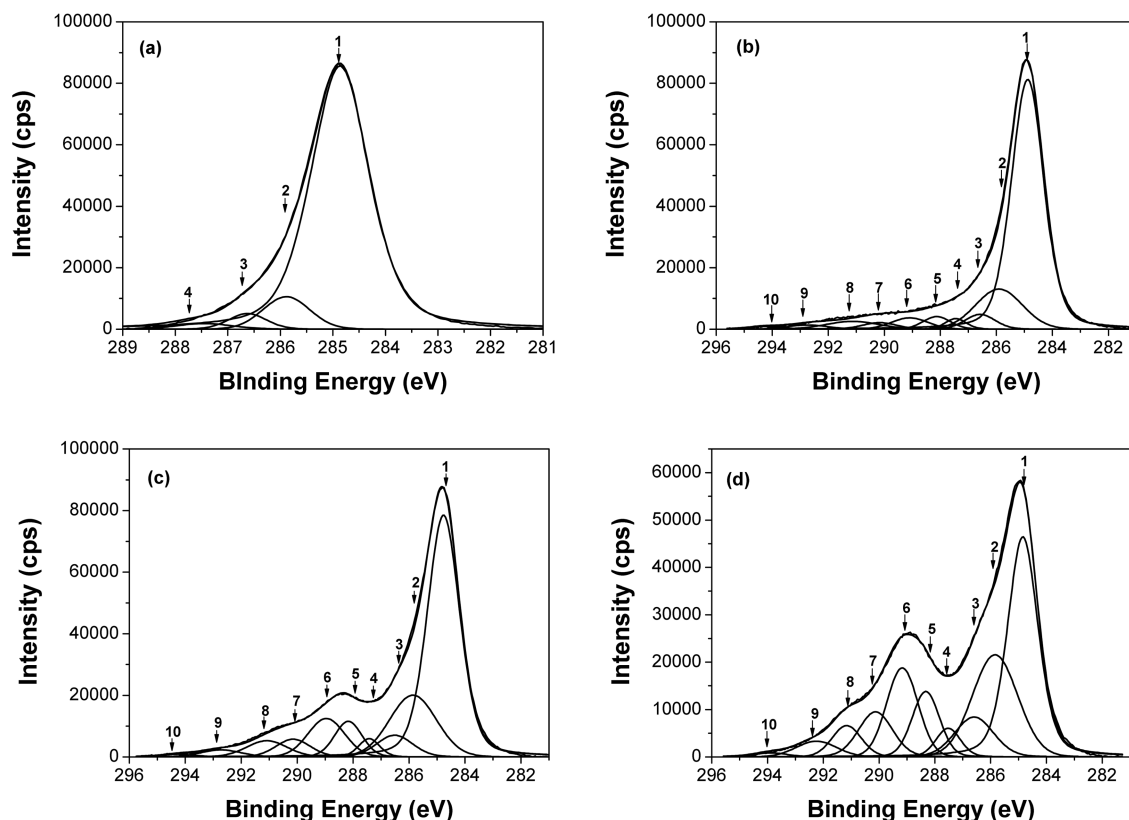| Samples	C1s		O1s		F1s		O1s/C1s (atomic ratio/%)	F1s/C1s (atomic ratio/%)
	Atomic percent (at%)	Binding energy (eV)	Atomic percent (at%)	Binding energy (eV)	Atomic percent (at%)	Binding energy (eV)		
As-received MWCNTs	95.01	285.0	4.99	532.64	-	-	5.25	-
OF10-MWCNTs	91.37	285.0	5.00	532.93	3.63	687.50	5.47	3.97
OF20-MWCNTs	76.86	285.0	6.09	533.42	17.05	687.52	7.92	22.18
OF30-MWCNTs	67.08	285.0	7.34	533.46	25.58	687.60	10.94	38.13

Fig. 3. Deconvolution of the core level C1s spectra: as-received MWCNTs (a); OF10-MWCNTs (b); OF20-MWCNTs (c); OF30-MWCNTs (d).

gnificantly increased. And O1s peaks of oxyfluorinated MWCNTs slightly increased according to increment of fluorine partial pressure. And both O1s and F1s binding energy of oxyfluorinated MWCNTs shifted high value. From the results of table 1, it is clear that oxyfluorination with higher fluorine ratio is more effective to induce functional groups on carbon surface.

Fig. 3 showed core level C1s spectra of as-received and oxyfluorinated MWCNTs with different fluorine-oxygen mixing ratio. The C1s peaks were obtained in the range of binding energy from 281 to 296 eV. The C1s peaks of oxyfluorinated MWCNTs were deconvoluted to several Pseudo-Voigt functions (sum of Gaussian-Lorentzian function) by peak analysis program obtained from Unipress Co., USA [17]. The Pseudo-Voigt function is given by

$$F(E) = H\left[(1-S)\exp\left(-\ln(2)\left(\frac{E-E_0}{FWHM}\right)^2\right)\right.$$

$$\left. + \frac{S}{1+\left(\frac{E-E_0}{FWHM}\right)^2}\right] \tag{1}$$

Where, F (E) is intensity at energy E, H is peak height, E_0 is peak centre, FWHM is full with at half maximum and S is

shape function related with symmetry and Gaussian-Lorentzian mixing ratio. The assignments for the different components of C1s were listed in Table 2 [12, 15, 18, 19]. The C1s spectra of oxyfluorinated MWCNTs have been fitted into 10 components in order to evaluate the components induced by oxyfluorination. The main peak of all samples is C(1) corresponding to non-functionalizes sp^2 and sp^3 carbon atoms. In this case, because MWCNTs have rolled graphite structure, we assumed that the C(1) component is sp^2 carbon atoms. The C(1) component concentrations of samples are 88.1% (as-received MWCNTs), 68.1% (OF10-MWCNTs), 51.8% (OF20-MWCNTs) and 33.8% (OF30-MWCNTs), respectively. It suggests that high concentration of fluorine lead to destruction of sp^2 structure. Touhara et al[20] reported that sp^2 carbon atoms reformed to sp^3 carbon atoms after fluorination. We confirmed similar result in XPS results. C(2) component assigned to aliphatic sp^3 carbon atoms, are 7.3% (as-received MWCNTs), 14.1% (OF10-MWCNTs), 17.0% (OF20-MWCNTs) and 20.5% (OF30-MWCNTs), respectively. According to component concentration of C(1) and C(2), C(1) concentrations decreased, whereas C(2) concentration increased as increment of fluorine concentration. As shown in Table 2, higher numbers of carbon components from C(6) to C(10) correspond to carbon-fluorine covalent bonding. Nansé et al. suggested two

Table 2. Energy shifts and assignments of the different component of C1s spectra

Component	$\Delta C(i)-C(1)$ (eV)	Assignment
C(1)	-	Non-functionalized sp^2 and sp^3 C atoms, not affected by fluorination
C(2)	1.0	Aliphatic non-functionalized sp^3 C in a non-fluorinated environment
C(3)	1.8	Non-functionalized sp^2 C in a position to one F atom Non-functionalized sp^2 C or sp^3 C in a position to one or two F atom(s), respectively sp^2 C bound to an oxygen atom (phenol, phenyl ether)
C(4)	2.6	Non-functionalized sp^2 C or sp^3 C in â position to two or three F atoms, respectively Oxygenated sp^3 C in a non-functionalized environment (CH_x–OH, or C–O–C)
C(5)	3.3 ± 0.1	Oxygenated sp^3 C in a position to a F atom Non-functionalized sp^3 C in a position to at least three F atoms sp^2 C 'semi-ionic', bound to intercalated F atom
C(6)	4.2 ± 0.2	sp^2 C covalently linked to an F atom in Type I structure
C(7)	5.4 ± 0.3	CF groups of Type I structure in a position of CF_2 groups
C(8)	6.3 ± 0.4	CF_2 groups of Type I structure CF groups of Type II structure
C(9)	7.9 ± 0.4	CF_3 groups of Type I structure CF_2 groups of Type II structure
C(10)	9.6 ± 0.4	CF_3 groups of Type II structure

Table 3. C1s peak parameters of as-received and oxyfluorinated MWCNTs

Component	As-received MWCNTs			OF10-MWCNTs			OF20-MWCNTS			OF30-MWCNTs		
	Peak Position (eV)	FWHM (eV)	Concentration (%)	Peak Position (eV)	FWHM (eV)	Concentration (%)	Peak Position (eV)	FWHM (eV)	Concentration (%)	Peak Position (eV)	FWHM (eV)	Concentration (%)
C(1)	284.86	1.31	88.1	284.88	1.37	68.1	284.77	1.37	51.8	284.85	1.29	33.8
C(2)	285.89	1.04	7.3	285.91	1.96	14.1	285.86	1.96	17.0	285.84	1.90	20.5
C(3)	286.63	0.84	3.0	286.58	1.26	3.5	286.52	1.51	4.8	286.60	1.64	7.2
C(4)	287.45	1.24	1.6	287.45	0.88	1.7	287.43	0.88	2.4	287.52	1.03	3.3
C(5)				288.13	1.15	2.7	288.17	1.15	5.9	288.33	1.15	8.2
C(6)				289.09	1.54	3.1	288.96	1.54	8.3	289.17	1.32	12.4
C(7)				290.17	1.44	1.7	290.15	1.44	3.7	290.13	1.44	7.1
C(8)				291.13	2.22	3.2	291.09	1.70	3.9	291.16	1.24	4.1
C(9)				292.75	1.70	1.3	292.73	1.70	1.7	292.25	1.70	2.8
C(10)				294.25	1.42	0.7	294.25	1.42	0.6	293.89	1.42	0.7

Table 4. F1s peak parameters of as-received and oxyfluorinated MWCNTs

Component	10 F1s			20 F1s			30 F1s		
	Peak Position (eV)	FWHM (eV)	Concentration (%)	Peak Position (eV)	FWHM (eV)	Concentration (%)	Peak Position (eV)	FWHM (eV)	Concentration (%)
F(4)	685.00	2.65	17.1	685.02	2.13	8.2	685.16	2.01	6.5
F(5)	686.73	2.05	55.1	686.79	2.05	64.6	686.79	1.83	40.5
F(6)	687.70	1.59	17.7	687.74	1.59	18.1	687.72	1.59	37.1
F(7)	688.62	1.45	6.6	688.60	1.45	4.1	688.60	1.45	10.6
F(8)	689.52	1.58	3.0	689.52	1.58	2.9	689.60	1.45	4.2
F(9)	691.02	0.98	0.5	691.02	2.11	2.0	690.87	1.71	1.1

types of carbon-fluorine bonding structure (Type I and Type II of fluorinated carbon structure). The surface fluorinated carbons in which carbon-carbon skeleton and the carbon-carbon length do not significantly changed from those of as-received carbon structure are Type I structure. Whereas, Type II structure is fluorinated carbons where sp^2 carbon sheets of planar conformation are reformed to sp^3 puckered structure. In the results from Table 3 and Fig. 3, the
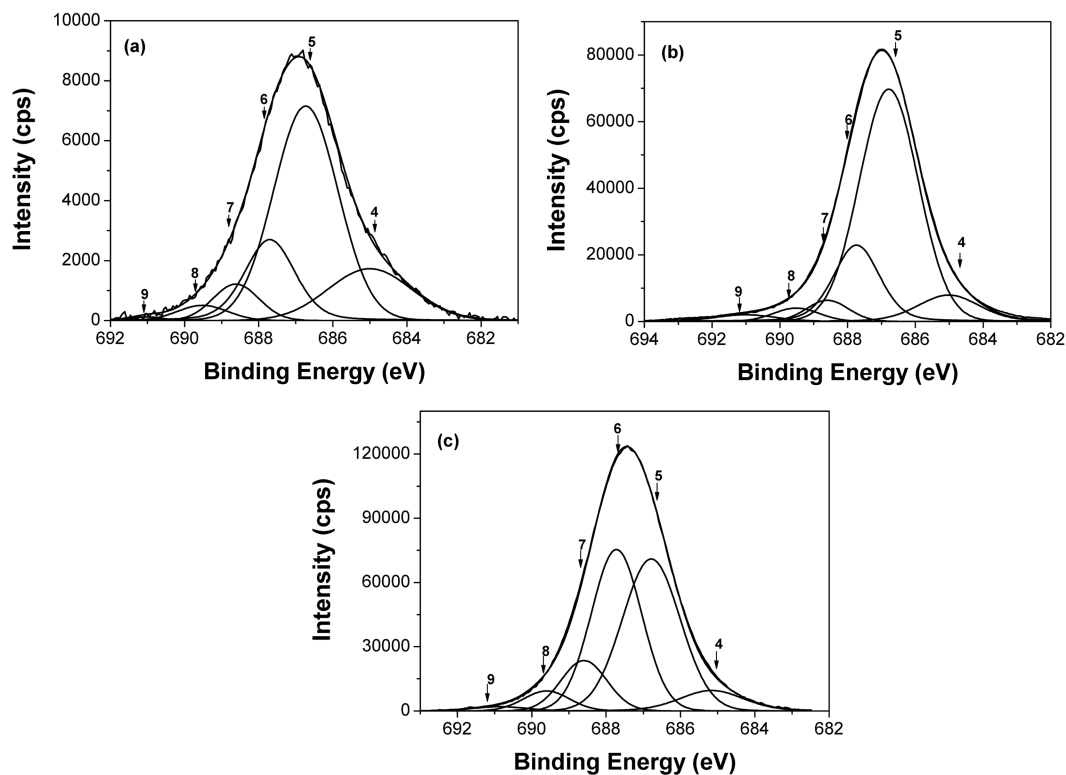
Fig. 4. Deconvolution of the core level F1s spectra: OF10-MWCNTs (a); OF20-MWCNTs (b); OF30-MWCNTs (c).
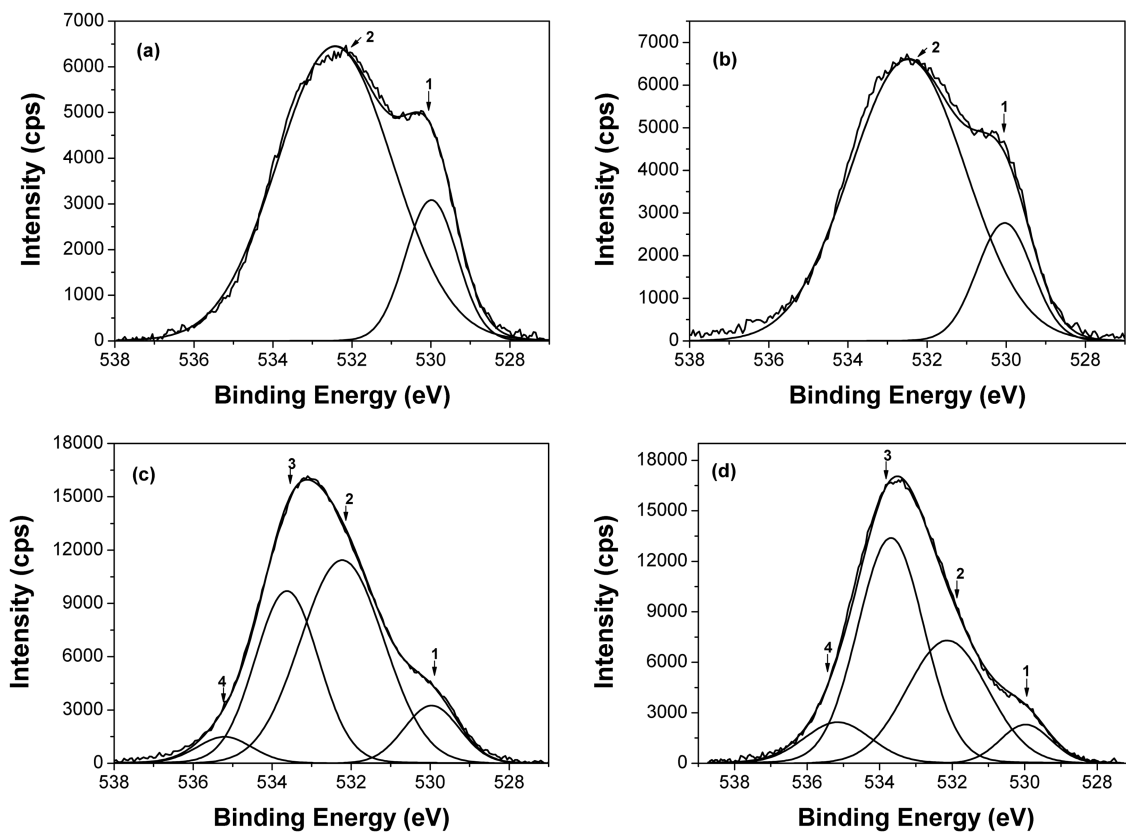

Fig. 5. Deconvolution of the core level O1s spectra: as-received MWCNTs (a); OF10-MWCNTs (b); OF20-MWCNTs (c); OF30-MWCNTs (d).

Table 5. Energy shifts and assignments of the different component of F1s spectra

| Component	$\Delta F(i) - F(1)$ (eV)	Assignment
F(4)	-2.6	Physical adsorbed and entrapped fluorine
F(5)	-0.9	Semi-ionically bound fluorine
F(6)	-	Covalent CF_x (type I structure)
F(7)	1.2	Covalent CF, CF_2 (type I structure, shifted by charging)
F(8)	2.0	Perfluorinated CF bonding (type structure)
F(9)	3.5	Perfluorinated CF bonding (type structure, shifted by charging)

component ratios of carbon-fluorine covalent bonding are 10% (OF10-MWCNTs), 18.2% (OF20-MWCNTs) and 27.1% (OF30-MWCNTs), respectively. The carbon-fluorine covalent bonding concentration increased as increment of fluorine mixing ratio. The four components between C(1) and C(6) are attributed to carbon atoms which is located at β-position of fluorine atoms. The difference between binding energy of C(1) and binding energies of other components is fluorination degree. The detail results of each carbon component are listed in Table 3.

The F1s core level spectra of oxyfluorinated MWCNTs show in Fig. 4. The F1s main component of all samples is F(5) located around 686.73. This peak is attributes to semi-ionic bound fluorine which is intercalated sp^2 carbons [21]. Component F(4) is corresponding to adsorbed or entrapped fluorine. As Table 4, F(4) concentrations decreased as increment fluorine mixing ratio. Covalently bonded fluorine atoms are attributed to F(6) to F(10). Among these components, F(6) and F(7) are Type I structure. Especially, F(6) located around 687.7 eV, is corresponding to C(6). The difference between F(6) and F(7) is about 0.9 eV. This phenomenon is results from charging effect of fluorine atoms. Perfluorinated carbon-fluorine bonding, Type II structures are located around 689.5 eV and 691.0 eV corresponding to F(8) and F(9), respectively. The assignments of each component are listed in Table 5 [12, 15, 18, 19]. According to Table 4, among the samples, OF30-MWCNTs have most carbon-fluorine covalent bonding component ratio. It suggests that high fluorine mixing ratio leads to many carbon-fluorine covalent bonding. Similar results were observed in C1s peak as shown in Table 3.

Fig. 5 shows O1s core level spectra of as-received MWCNTs and oxyfluorinated MWCNTs, peak parameters

Table 6. Assignments of the different component of O1s spectra

Component	Assignment
O(1)	Carbon Oxygen double bond
O(2)	Carbon Oxygen single bond
O(3)	Oxygen bonded at fluorinated carbon
O(4)	Oxygen bonded at perfluorinated carbon
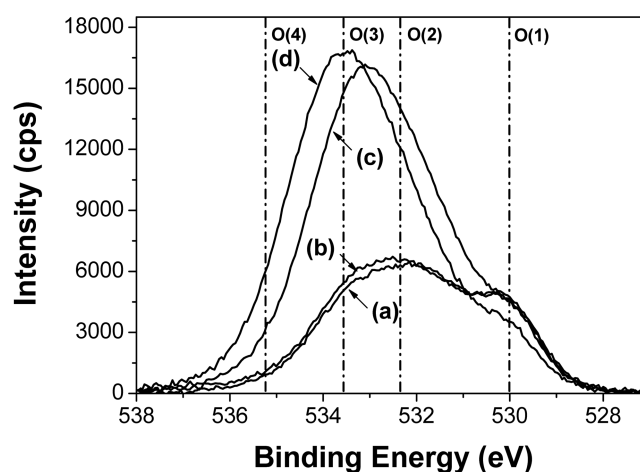
Fig. 6. Core level O1s spectra of as-received MWCNTs (a);OF10-MWCNTs (b); OF20-MWCNTs (c); OF30-MWCNTs (d).

and components assignments obtained by deconvolution with several Pseudo-Voigt functions are listed in Table 6 and Table 7, respectively [14, 22]. In the deconvolution of Fig. 5, OF10-MWCNTs were deconvoluted by only 2 components as same as as-received MWNT while OF20-MWCNTs and OF30-MWCNTs were deconvoluted by 4 components. This induced an important concolusion that low concentration of

Table 7. O1s peak parameters of as-received and oxyfluorinated MWCNTs

Component	As-received MWCNTs			OF10-MWCNTs			OF20-MWCNTS			OF30-MWCNTs		
	Peak Position (eV)	FWHM (eV)	Concentration (%)	Peak Position (eV)	FWHM (eV)	Concentration (%)	Peak Position (eV)	FWHM (eV)	Concentration (%)	Peak Position (eV)	FWHM (eV)	Concentration (%)
O(1)	529.99	1.55	17.7	530.04	1.64	16.7	529.96	1.64	9.7	529.98	1.64	6.6
O(2)	532.43	3.45	82.3	532.48	3.45	83.3	532.23	2.49	51.6	532.13	2.62	33.1
O(3)							533.63	1.89	34.0	533.69	2.15	50.8
O(4)							535.21	1.65	4.7	535.16	2.18	9.5

fluorine gas of fluorine-oxygen mixed gas couldn't form carbon-oxygen bonding on MWCNTs used in this study. Whereas, as shown in Table 1, oxygen atomic ratio of OF20-MWCNTs and OF30-MWCNTs increased around 22% and 47%, respectively. In addition, we can observe two new peaks assigned to O(3), oxygen bonded at fluorinated carbons and O(4), oxygen bonded at perfluorinated carbons. The concentrations of O(3) and O(4) onto OF20-MWCNTs are 34.0% and 4.7%, and concentrations in OF30-MWCNTs are 50.8% and 9.5%, respectively.

Fig. 6 shows that the influence of fluorine-oxygen mixing ratio in oxyfluorination on MWCNTs. Dot lines represent to the binding energy of oxygen components. The shape and intensity of OF10-MWCNTs are similar with those of as-received MWCNTs. However, the intensity and binding energies of main peak position of OF20-MWCNTs and OF30-MWCNTs were dramatically increased by oxyfluorination. In the case of OF30-MWCNTs as compared with OF20-MWCNTs, the amount of O(1) component assigned to oxygen-carbon double bonding was decreased, that of O(4) component was increased. This phenomenon suggests that oxygen component can be controlled by using different fluorine-oxygen mixing ratio. In this study, we confirmed that the types of functional groups on MWCNTs can be different, and oxygen group significantly increased from 20% of fluorine mixing ratio. In addition, oxygen-carbon double bond stat to be destroyed up to 30% of fluorine mixing ratio under used conditions.

4. Conclusions

The surface characteristics of as-received MWCNTs and oxyfluorinated MWCNTs were investigated using XPS. According to C1s core level spectra, the component ratios of carbon-fluorine covalent bonding are 10% (OF10-MWCNTs), 18.2% (OF20-MWCNTs) and 27.1% (OF30-MWCNTs), respectively. Peak shapes and component ratio of as-received MWCNTs and OF10-MWCNTs are almost same, whereas oxygen atomic ratios of OF20-MWCNTs and OF30-MWCNTs increased around 22% and 47%, respectively. It suggests that high fluorine mixing ratio leads to many carbon-fluorine covalent bonding. The types of functional group on MWCNTs can be different, and oxygen group significantly increased from 20% of fluorine mixing ratio. In addition, oxygen-carbon double bonds stat to be destroyed up to 30% of fluorine mixing ratio under used conditions.

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