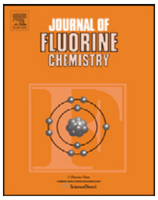
Journal of Fluorine Chemistry 135 (2012) 362–366

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor



Short communication

Fluorination of multiwall carbon nanotubes by a mild fluorinating reagent HPF_6

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ARTICLE INFO

Article history:
Received 6 April 2011
Received in revised form 21 September 2011
Accepted 4 October 2011
Available online 10 October 2011

Keywords:
MWCNT
Fluorine
Functionalization
HPF_6

ABSTRACT

Multiwall carbon nanotubes (MWCNTs) have been fluorinated by using a mild fluorinating agent HPF_6 at different temperatures starting from room temperature to 150 °C to study the effects of reaction temperature on the surface of MWCNTs. The fluorine content increases with increasing reaction temperature. The analysis of Fourier transform infrared (FTIR) and X-ray photo electron spectra (XPS) has pointed out clearly to the formation of chemical bonding between fluorine and carbon atoms on the surface of MWCNTs. Smaller amounts of CF_2 and CF_3 have been bonded primarily at various defect sites of MWCNTs. The XPS result shows that $CF_{0.018}$ stoichiometry composition is attained in this fluorination reaction at 150 °C. The stability of the fluorinated MWCNT has been examined by thermogravimetric analysis. It shows that the largest fluorine loss occurred between 200 °C and 400 °C. TEM image indicates that the raw nanotube structure is preserved after fluorination at temperature 150 °C.

1. Introduction

Fluorination is one of the most effective chemical methods to modify and control physiochemical properties of carbon materials because further substitution can be accomplished [1]. It has been demonstrated that alkyl groups can replace the fluorine atoms using Grignard or organolithium reagents, in addition, several diamines or diol have been reported to react with fluoronanotubes via nucleophilic substitution reactions [2]. The modification of the properties of multiwall carbon nanotube (MWCNT) on fluorination may have rendered the resulting fluorinated MWCNT useful for several potential commercial applications such as: an additive for polymer nano-composites because of greater hydrophobicity, fuel cell (modification of proton exchange membranes, PEM) and heterogeneous catalysis (catalysts and catalyst support) [3,4]. Fluorinated carbons are also commercially used as electrode material for primary lithium batteries, solid lubricants or as reservoir for very active molecular oxidizers such as BrF_3 and ClF_3 [5]. This led to considerable interest to modify surface of carbon nanotubes with fluorine atom. Fluorination of carbon nanotubes has been performed at high temperature and pressure using fluorinating agents like elemental fluorine gas, TbF_4, XeF_2 and CF_4 plasma [6,7]. However, fluorination can be performed by using gaseous BrF_3 at room temperature [8]. Elemental fluorine and many electrophilic fluorinating agents are highly aggressive, unstable and require special equipment and care for safe handling. Moreover, at high temperature fluorination leads to breakage of carbon nanotubes.

In view of that, for large capacities, the fluorination temperature must be optimized to obtain high fluorine content. However, the penetration of fluorine atoms beneath the surface should be limited in order to conserve a conductive nonfluorinated core. Our goal is to produce fluorination reaction at lower temperature and milder condition.

We have reported here the mild fluorinating agent hexafluorophosphoric acid (HPF_6) which can be operated safely and efficiently for MWCNT fluorination. In this communication, we have studied the reaction of HPF_6 with MWCNT at different temperatures ranging from room temperature to 150 °C and confirmed the fluorination on the CNT surface by using FTIR and XPS method. We have also performed the fluorination reaction at 150 °C on acid treated MWCNT using HPF_6 and compared the results with non acid treated MWCNT at 150 °C.

2. Experimental

Hexafluorophosphoric acid (65 wt% solution in water) was purchased from Aldrich Company. Multiwalled CNT was purchased from EM Power Co. Ltd., South Korea. Raw multiwall CNT composition is given in Table 1.

2.1. Raw MWCNT for fluorination

Raw MWCNT (0.1 g) without HNO_3 treatment was dispersed in 200 ml mixture of isopropyl alcohol and deionized water (1:1). The suspension was stirred at room temperature for 24 h to increase

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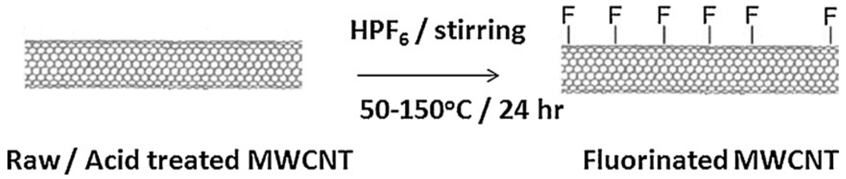
doi:10.1016/j.jfluchem.2011.10.004

Table 1
Raw MWCNT composition.

Component	Length (μm)	Diameter average (nm)	Purity (%)	Impurity (%)	Oxygen content (%)
Raw MWCNT	30–50	15	>95	<5	4.89



Scheme 1. Preparation procedure of fluorinated multiwall carbon nanotubes.

the surface activity of MWCNT. The suspension was then centrifuged and cake was transferred to a Teflon bottle. Hexafluorophosphoric acid (1 ml of 65 wt% solution in water) was added to the slurry. The mixture was stirred using a magnetic stirring bar at four different temperatures (room temperature, 50 °C, 100 °C and 150 °C) for 24 h (Scheme 1).

2.2. Acid treated MWCNT for fluorination

Purification of MWCNT (1 g) was carried out by refluxing the CNT with 200 ml of 60% HNO_3 at 120 °C for 4 h to remove the metal particles. The mixture was diluted, centrifuged and washed with excess DI water. The purified product was dried at 70 °C in vacuum oven for overnight. Purified MWCNT (0.1 g) and hexafluorophosphoric acid (1 ml of 65 wt% solution in water) were taken in a Teflon beaker. The mixture was stirred using a magnetic stirring bar at 150 °C for 24 h (Scheme 1). The mixture was then centrifuged and washed several times with water and acetone. The product was dried at 80 °C in a vacuum oven for overnight.

The formation of C–F bond was confirmed by FTIR spectroscopy using a JASCO FT-IR 300E device. Thermal stability of the material was evaluated by using a thermogravimetric analyzer TA Q50 system TGA. The sample was scanned at a heating rate of 10 °C/min under flow of nitrogen. X-ray photo electron spectroscopy (VG Microtech ESCA 2000) was used to evaluate the material microstructure and chemical composition. Morphology and structure of the materials were examined by transmission electron microscopy (TEM) (Technai G3F30).

3. Results and discussion

The FTIR spectra (Fig. 1) showed the bands located at ca. 1210–1225, 1172 and 1082–1119 cm^{-1}. The bands in the 950–1350 cm^{-1} range are assigned to C–F stretching vibrations [9,10]. The broad band at 1210–1225 cm^{-1} can be assigned to a C–F stretching vibration where covalent bonding predominates [11–13]. There is a broad band at 950–1350 cm^{-1} range in sample fluorinated at room temperature. We do not know the exact reason. Further studies are required to elucidate the precise explanation. The frequency of the C–F stretching vibration is shifted to 1225 cm^{-1} with increasing the reaction temperature. It indicates that covalence increases with increasing fluorination reaction temperature. During fluorination, the C–F bond formation requires the change of the carbon hybridization from sp^2 to sp^3. The curvature prevents the formation of pure sp^3 hybridization for the carbon atom, since it requires an important local strain. The residual sp^2 hybridized orbitals imply a weakening of the overlapping of the hybridized lobes of carbon and the fluorine atomic orbitals. In other terms, this results in a weakening of the C–F bonding covalence [9]. Attachment of fluorine atoms to CNT surface disrupts uniformity of pi-system leading to shortening of the bonds between bare carbon atoms and as could be expected to sharpening of the carbon–carbon stretching [14]. Infrared spectroscopy confirmed the presence of C–F bond in the MWCNT. In addition, the spectra of pristine as well as fluorinated samples exhibited two bands at ca. 1500 and 1650 cm^{-1}, which correspond to the stretching vibration of C–O and C=O bond, respectively.

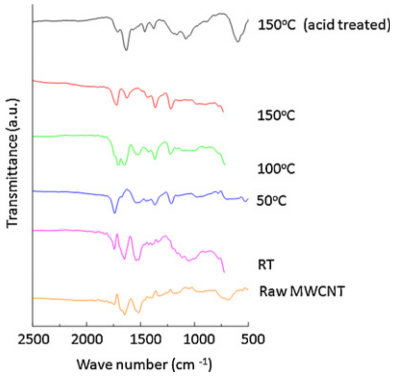


Fig. 1. FTIR spectra of fluorinated multiwall carbon nanotubes.

Fig. 2 shows a TEM image of fluorinated MWCNT at 150 °C. TEM investigation clearly confirms that effective covalent fluorination by using HPF_6 after 150 °C reaction temperatures does not disturb the MWCNT morphology. Mickelson et al. have reported that SWCNT structure fluorinated at 500 °C does not survive [15]. As in our case, the fluorination reaction temperature is low and there is no destruction of MWCNTs structure.

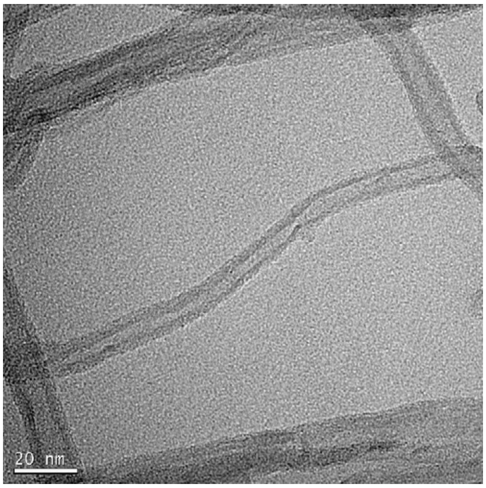


Fig. 2. TEM image of fluorinated MWCNT at 150 °C.

Table 2

Relative atomic concentration (%) for main elements and total composition in MWCNT sample, fluorinated by different temperature, evaluated by XPS.

Reaction temperature (°C)	Carbon	Fluorine	Oxygen	Total composition
Room temperature	96	0	4	–
50	95.669	0.619	3.711	$CF_{0.006}$
100	96.225	0.629	3.145	$CF_{0.006}$
150	93.978	1.749	4.28	$CF_{0.018}$
150 (with acid treated MWCNT)	82.96	0.96	16.08	$CF_{0.011}$

In XPS, the binding energies of the fluorinated samples were corrected for charging effect by calibration on the CNT C 1s peak at 284.6 eV. All spectra were normalized on the intensity of the principal peak. The overall XPS show signal of carbon, fluorine and oxygen. The oxygen group in MWCNT may result from the storage of the CNTs in laboratory air as well as from the acid treatment. Relative atomic concentration for main elements in fluorinated MWCNT is presented in Table 2. The curve fitting was accomplished with Gaussian–Lorentzian mixing ratio. Deconvoluted C 1s and F 1s peaks are presented in Figs. 3 and 4 respectively. Components of C 1s and F 1s along with binding energies and assignments of the chemical bonds are given in Table 3. The C 1s curve fitting spectra of the fluorinated MWCNT exhibit four main features corresponding to different chemical states of carbon atoms. The intense peak at 284.6 eV is assigned to the non-grafted carbon, the peak around 288.8 eV is attributed to the carbon atoms covalently bonded to the fluorine atoms (C–F), and the shoulder at 285.6 eV corresponds to the carbon atoms positioned near the CF-groups (C–CF) [14,16]. The peak is noticed at 287.1 eV corresponding to C=O group [17]. The binding energy of carbon atom covalently bonded to the fluorine atoms jumps from 288.8 to 289.1 eV in case of acid treated MWCNTs fluorinated at 150 °C. Also oxygen containing group contribution peak at 286.2 eV is found on acid treated MWCNTs fluorinated at 150 °C. The peaks at 290–292 eV corresponding to the binding energy of C 1s electrons in the perfluorinated C–F (CF_2 and CF_3) are observed for the studied fluorinated samples. These species are assumed to be bonded primarily at the edges such as open tube ends and their low content in the fluorinated samples evidences the high aspect ratio

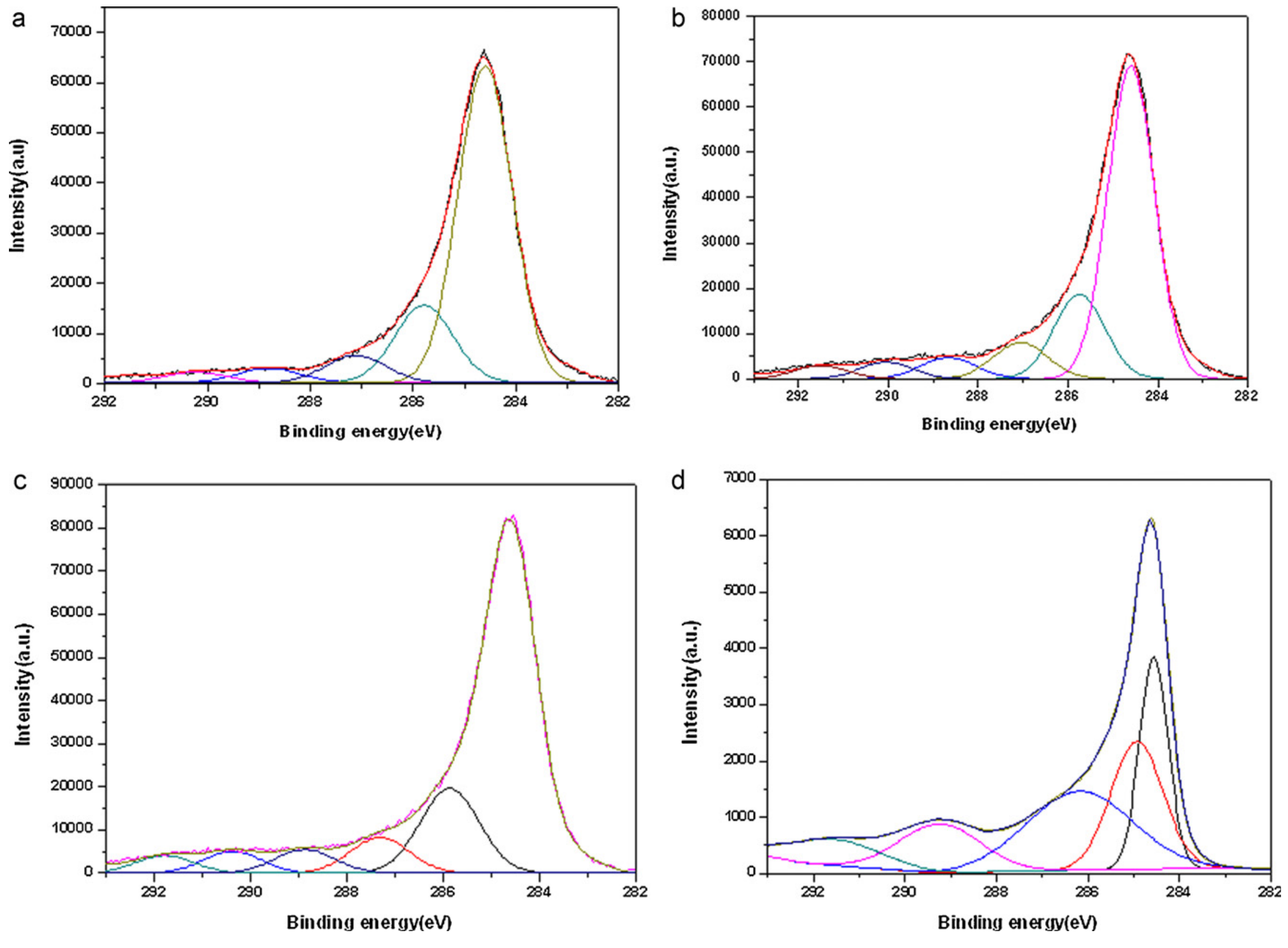


Fig. 3. C 1s deconvolution of fluorinated MWCNT: (a) 50 °C, (b) 100 °C, (c) 150 °C, and (d) 150 °C (acid treated).

Table 3

Assignments of different binding energies of C 1s and F 1s components in XPS.

Reaction temperature (°C)	Binding energy (eV)							
	Non grafted carbon	C–CF	C–O	C=O	Covalent C–F	Perfluorinated C–F bond	Covalent C–F	Perfluorinated C–F bond
50	284.6	285.7	–	287.1	288.8	290.2 and 291.7	687.3	689.3
100	284.6	285.7	–	287	288.6	290 and 291.5	687.1	689.5
150	284.6	285.8	–	287.3	288.8	290.3 and 291.7	686.6	688.4 and 690.2
150 (acid treated)	284.6	285.2	286.2	–	289.1	291.6	–	689.3

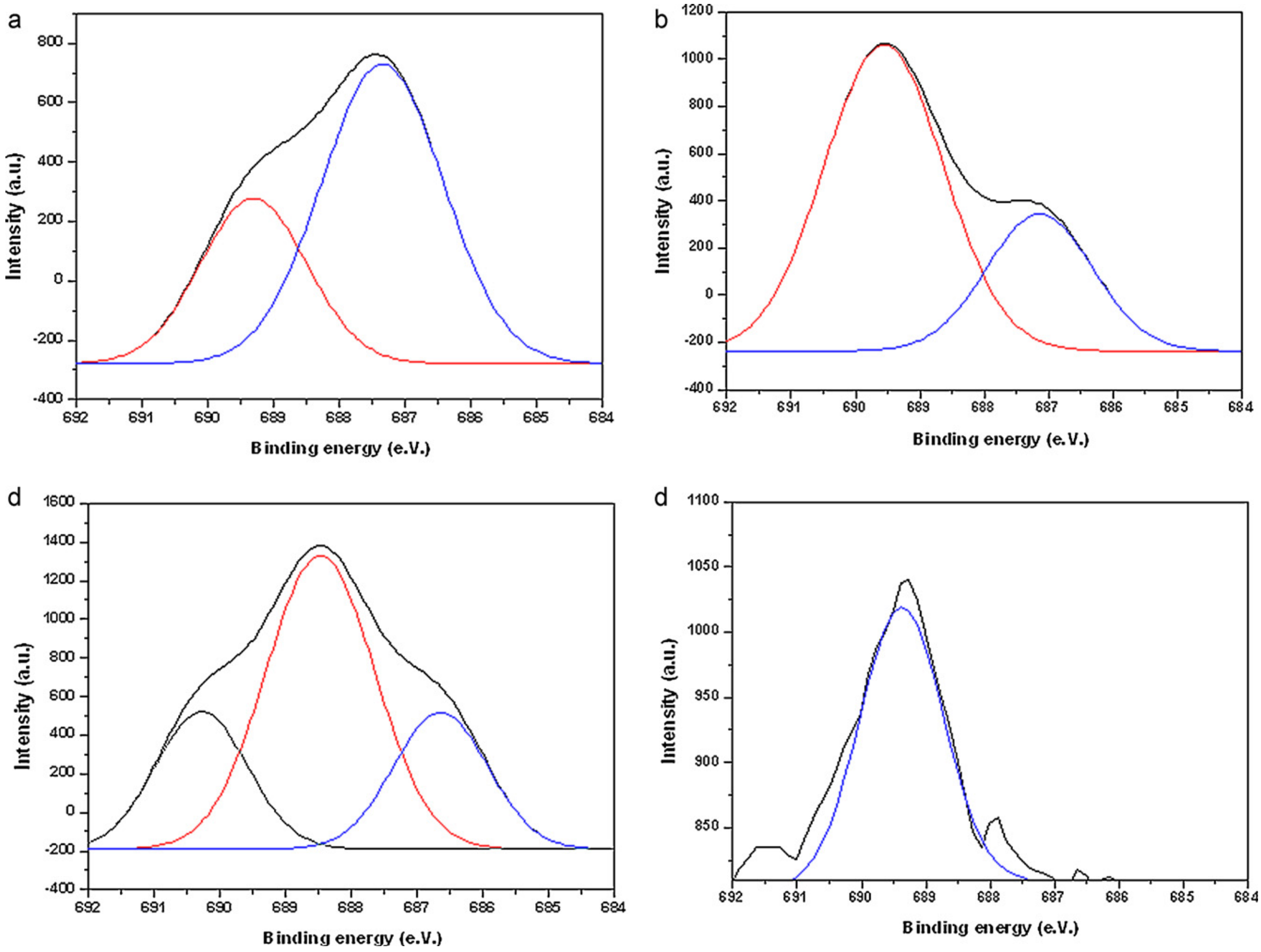


Fig. 4. F 1s deconvolution of fluorinated MWCNT: (a) 50 °C, (b) 100 °C, (c) 150 °C, and (d) 150 °C (acid treated).

of CNTs [16]. The F 1s spectra of our samples showed the binding energy at 686.6–687.9 and 689.3–690.2 eV. It is reported that the peak at 687.7 ± 0.3 eV has been observed for fluorine covalently bonded to the carbon nanotubes [16]. It is seen one additional large peak at 688.4 eV in case of MWCNTs fluorinated at 150 °C which is about to be a strong covalent-bonding nature. Fig. 4 demonstrated that with increasing the reaction temperature, intensity of the 687 eV peak decreases and at the same time intensity of the 689 eV peak increases. In case of acid treated MWCNTs fluorinated at 150 °C, the peak at 689.3 eV (high binding side) indicates the preponderate nature of perfluorinated C–F bond which is good agreement with C 1s curve fitting spectra. This observation clearly pointed out that a rise in temperature not only increases the fluorine content but also resulting in shift of the F 1s peak to the higher binding side which illustrate the predomination of the perfluorinated C–F bond. In XPS, it is clearly observed that the fluorination reaction does not take place at room temperature. The stoichiometric composition (CF_x) of MWCNT from XPS is calculated by taking into account the atomic concentration of carbon and fluorine and the obtained value is in between 0.006 and 0.018 (Table 2). The maximum $CF_{0.018}$ composition is attained in this fluorination reaction at 150 °C. The result shows that fluorine content increases with increasing reaction temperature. The fluorine content in non acid treated MWCNT is higher than acid treated MWCNT at 150 °C. It is observed that acid treatment retards the surface functionalization of nanotubes for fluorination. It was reported that CF_x composition with $x > 0.5$ is prohibited in the side wall fluorination due to electrostatic repulsion between fluorine atoms [18]. The fluorinating capacity by HPF_6 on the MWCNT surface is quite impressive not only CF_x composition point of view but also safe handling and mild reaction condition compared to different fluorination techniques like F_2 at elevated temperature, gaseous BrF_3 at room temperature and using a treatment with CF_4 plasma.

A typical TGA plot represents the percent mass remaining and change in mass with change in temperature. The TGA results in Fig. 5 illustrate the decomposition behavior of the fluorine functionalized MWCNTs. The percentage weight loss curve

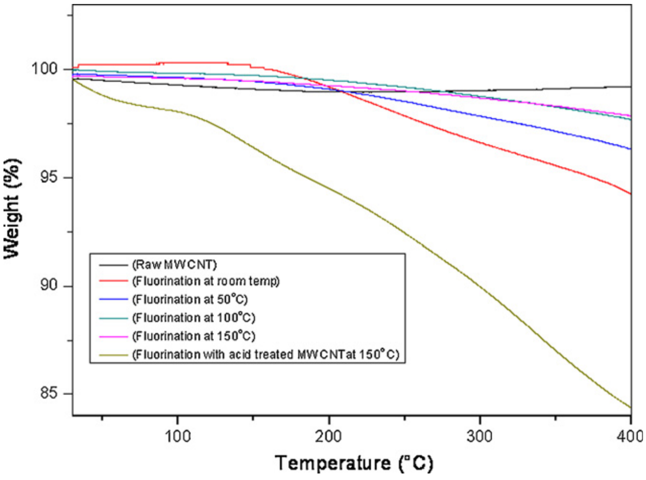


Fig. 5. TGA plots of fluorinated multiwall carbon nanotubes (F-MWCNTs).

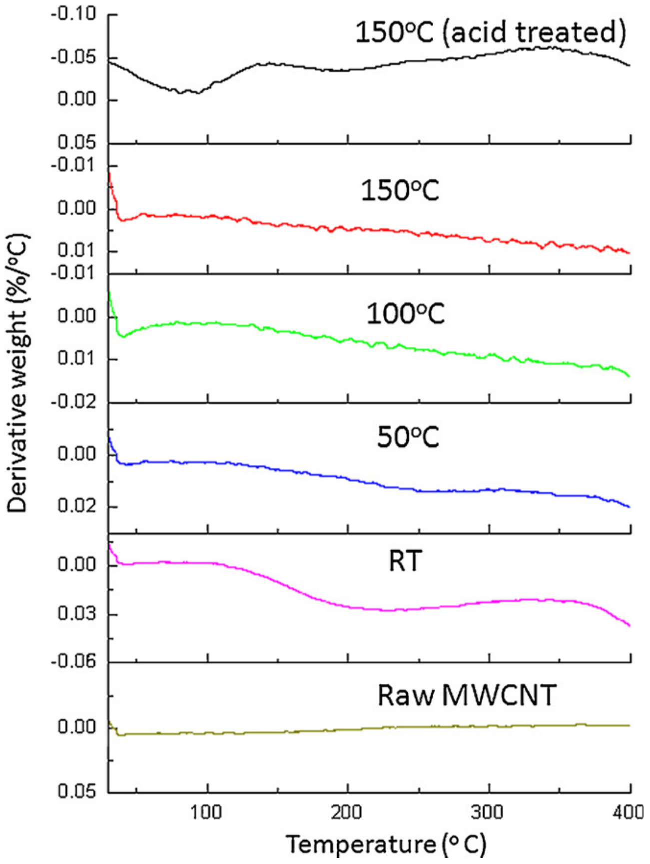


Fig. 6. Derivative of TGA plots of fluorinated multiwall carbon nanotubes (F-MWCNTs).

Table 4
Weight loss at 200–400 °C for fluorinated MWCNT.

Reaction temperature for fluorinated MWCNT (°C)	Weight loss at 200–400 °C (%)
Room temperature	5
50	4.5
100	1.83
150	1.41
150 (acid treated MWCNT)	11

indicates that the weight loss occurred between 200 °C and 400 °C showing defluorination of the MWCNT. It was reported that upon heating, the largest fluorine loss occurred between 200 °C and 300 °C, and defluorination was virtually complete at 400 °C [16]. The derivative of TGA (DTGA) curves shows that main weight loss is observed in the 200–400 °C temperature range for fluorinated MWCNT at different reaction temperatures (Fig. 6). However supplement weight loss is also observed in the 50–150 °C temperature range for acid treated MWCNT. The weight losses at 200–400 °C are 4.5, 1.83 and 1.41% for MWCNTs treated at 50 °C, 100 °C and 150 °C respectively whereas it is 11% for acid treated MWCNTs fluorinated at 150 °C (Table 4). The thermogravimetric investigation of the sample at different temperatures reveals that weight loss decreases with increasing the fluorination temperature except for acid treated MWCNT. At room temperature fluorination reaction, weight loss is higher compared to other non acid treated MWCNT. Although it is evident in FTIR and XPS analysis that there is no C–F bond formation taking place at room temperature reaction condition. This may be attributed that at lower reaction temperature the intercalated species PF_6^- molecules trapped in the intertube space and removal of trapping molecule goes on with increasing the fluorination temperature. Interestingly, acid treated MWCNT for fluorination at 150 °C shows highest weight loss. This may be due to the fact that acid treatment generates the acid functionality on the MWCNT surface and decomposition of this acid functionality may be one of the reasons for highest weight loss. Because fluorine atoms are removed as COF_2 and CF_4 species, additional oxygen atoms, which are needed to provide weight balance, can originate from molecules adsorbed on the MWCNT surface [19]. During the thermal defluorination, CF_2 and C_2F_4 are emitted and that it changes to various gaseous products by secondary reactions [20,21]. However, further study is required to ascertain the actual mechanism of this type of fluorination reaction.

4. Conclusion

We conclude that the applied fluorination technique gives a controlled and mild functionalization on the MWCNT surface. The process is simple and efficient comparing with other fluorinating reagent condition. The fluorination of MWCNT starts from 50 °C and has been found to result in low fluorination level varying from 0.006 to 0.018 with increasing the reaction temperature. Most of the F is covalently bonded to a single carbon atom with smaller amounts of CF_2 and CF_3 without destroying the tubes structure.

Acknowledgements

This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0093823) and was financially supported by a grant to MEMS Research Center for National defense funded by Defense Acquisition Program. This work was supported (in part) by the Yonsei University Research Fund of 2010. We are also thankful to Defense Nano Technology (Center) for supporting this research.

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