

# Functionalization of graphene oxide by fluorination and its characteristics



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## ABSTRACT

We report on the gas fluorination of graphene oxide (GO) to control functionality. GO is fluorinated at room temperature using fluorine–nitrogen mixed gas in different ratios. X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FT-IR) are used to characterize the surface functional groups on the fluorinated GO. The oxygen functional groups in GO are getting decreased according to an increase of fluorine gas ratio. The proportion of semi-covalent C–F bond is increased with increasing the fluorine gas ratio. The structural properties of the fluorinated GO are investigated by X-ray diffraction (XRD) and Raman spectroscopy. The d-spacing and crystallite size of fluorinated GO are decreased to 0.771 and 2.125 nm, respectively. The thermal and morphological characteristics are also investigated. The results suggest that gas fluorination of GO enables to control the functionality and crystallite size of GO.

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## 1. Introduction

Fluorination is one of the most powerful methods of modifying the physical and chemical properties of carbonaceous materials to broaden their range of application [1]. Fluorinated carbon materials have been incorporated into numerous materials, including electric double layer capacitor (EDLC) electrodes [2,3], carbon molecular sieves (CMSs) [4], fillers in composites, solid lubricants [5], and as reservoirs for very strong molecular oxidizers such as BrF<sub>3</sub> and ClF<sub>3</sub> [6]. In all of these applications, the chemical, electrochemical, and tribological properties of the fluorinated carbon materials depend strongly on of their C–F bonding. Additionally, fluorination can be used to control the surface area and pore volume of porous materials [4,7].

Graphene oxide (GO), which is graphite with an enlarged interplanar distance due to the repulsion of introduced oxygen groups, has been investigated for the mass production of graphene in the liquid phase. Recently, GO itself has attracted attention because of its interesting properties, such as its diverse oxygen functional groups and multiform defects [8,9]. Because of the reactivity of oxygen, specific hetero-atoms, especially fluorine or nitrogen, can be introduced at oxygen-group sites. This possibility makes GO applicable to various industrial uses, such as in various composites, sensors, and catalysts [10]. In addition, GO exhibits

high reactivity as an oxidizing agent and catalyst. Therefore, the control of oxygen functional groups and structural defects in GO is a promising area of research. However, there are few methods for control of oxygen functional groups and the methods are limited. A general reducing agent (hydrazine) removes all oxygen functional groups [11,12]. Heat-treatment leads to restacking and defect in carbon skeleton, which can fall electrical and mechanical properties of graphene oxide. On the other hand, fluorination is time- and process-efficient method to control of oxygen functional group [13–15]. Because fluorine atom having electron lone pair is useful to react with nucleophilic substitution for carbon–oxygen bond.

In this work, the potential of fluorination was explored to control and functionalize GO surface using gas fluorination with fluorine–nitrogen mixed gases. Changes of chemical composition, structural, and thermal properties of GO were confirmed by X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) techniques, X-ray diffraction (XRD) analysis, Raman spectroscopy, and thermogravimetric analysis (TGA).

## 2. Results and discussions

### 2.1. Surface chemical composition

The obtained samples were analyzed by XPS. The XPS survey spectra in Fig. 1 and the elemental compositions in Table 1 indicate that, the oxygen coverage decreased from 39.55% in GO to 11.67% in

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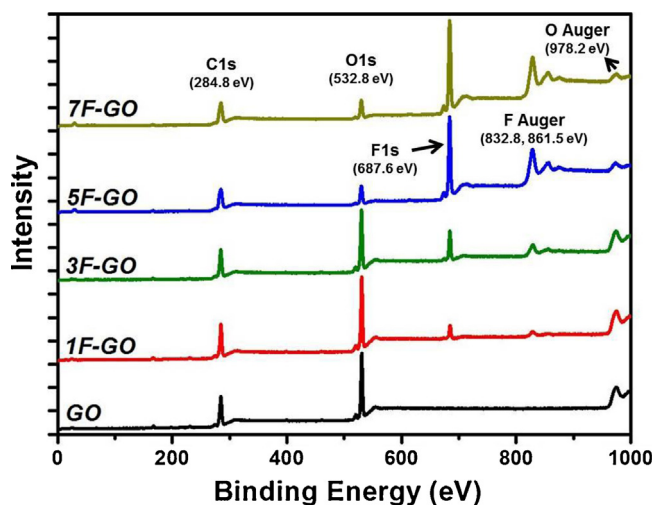


Fig. 1. XPS survey spectra of GO and fluorinated GO.

7F-GO as the ratio of fluorine gas increased. New peaks corresponding to 684.14, 832.8, and 861.5 eV appeared in the spectrum of 1F-GO. These peaks were indexed as F1s of the C–F bond (684.14 eV) and F Auger (832.8, 861.5 eV), respectively [16]. The fluorine atomic percentage reached a maximum of 37%, which is higher than that of reported other fluorinated carbon materials [2,4]. This result is attributed that fluorine is easy to burrow down between GO sheets compared to graphite sheets because of the extension of the plane spacing. The F1s peak of fluorinated GO was located at 687.6 eV, which indicates that covalent C–F bonds were successfully introduced on GO surface. After fluorination with a fluorine–nitrogen mixed gas of 5:5, the functional groups related to fluorine and oxygen definitely differed.

The composition of the chemical bonds of the samples was investigated in detail by deconvolution of the XPS spectra in Fig. 2. In the case of GO, the C1s peaks were deconvoluted into five peaks at 284.5, 285.2, 286.5, 287.4, and 288.4 eV, which correspond to C=C, C–C, C–O, C=O, and O=C–O, respectively [17]. After fluorination, new three peaks appeared at 288.9, 290.3, and 291.2 eV. These peaks are assigned to semi-ionic C–F, covalent C–F, and C–F<sub>2</sub> bonds, respectively. Meanwhile, oxygen reduction was also clearly observed during the process [16,18].

The oxygen and fluorine functional groups of the fluorinated GO samples were adjusted by varying the ratio of fluorine gas. A detailed analysis of the chemical composition is given in Table 2. Small and large increases were observed in the fluorine coverage as the fluorine–nitrogen gas ratio was varied from 1:9 to 7:3. An oxygen coverage decreased dramatically showing color change of the GO from yellow to brown. Meanwhile, most of the injected fluorine gas attacked oxygen functional groups. Other paper supported this result considering the reduction of oxygen content rather than carbon content in graphene [19]. The attack of oxygen functional groups might stem from the fact that the fluorine radical favors oxygen at room temperature because the C–O binding energy (351 kJ/mol) is lower than the C–C binding energy (368 kJ/mol). The fluorine radical induces decomposition of C–O and C=O on the surface of GO [20–22], thereby contributing to the restoration of sp<sup>2</sup> carbon on graphene. A semi-covalent C–F bonding was greatly increased at a fluorine–nitrogen gas ratio of 5:5, in particular, because fluorination progressed at room temperature [23]. Additionally, the formation of covalent C–F bonds appeared to show a preponderance at room temperature, as indicated by the concentration of covalent C–F<sub>2</sub> being somewhat increased compared to the concentrations of covalent C–F and C–F<sub>2</sub> under fluorine gas ratios of 5:5 and 7:3.

Table 1  
XPS surface elemental analysis parameters of the GO and fluorinated GO.

Component	Elemental content (at%)			O/C(%)	F/C(%)	F/O(%)
	C1s	O1s	F1s			
Raw GO	60.45	39.55	–	65.43	–	–
1F-GO	56.79	38.27	4.94	67.39	8.70	12.91
3F-GO	53.47	35.22	11.3	65.87	21.13	32.08
5F-GO	53.55	12.09	34.36	22.58	64.16	284.20
7F-GO	51.32	11.67	37.01	22.74	72.12	317.14

The FT-IR results supplemented XPS analysis describing the functional groups. The characteristic FT-IR spectra of GO and fluorinated GO are shown in Fig. 3. The main absorption band at approximately 3400 cm<sup>-1</sup> is assigned to the O–H group stretching vibrations. The absorption peak at approximately 1740–1750 cm<sup>-1</sup> is assigned to C=O stretching of the carboxylic functional group. This C=O group in GO would facilitate attachment to other materials through covalent coupling or electrostatic interaction [24,25]. The absorption peak at 1047 cm<sup>-1</sup> in GO is attributed C–O group stretching vibrations. However, these peaks were shifted to approximately 1100 cm<sup>-1</sup> in the spectra of fluorinated GO and increased in intensity as the fluorination gas content was increased. This result indicates that C–F bonds were formed. The absorption peaks at 1600 cm<sup>-1</sup> and 1475 cm<sup>-1</sup> are attributed to C=C bonds in an aromatic compound. The intensity of the peak at 1475 cm<sup>-1</sup> decreased as the fluorine gas ratio was increased; this change is attributed to C–F bond formation through the attack of fluorine radical on a carbon atom in C=C [26,27]. The more interesting result is that an adsorption peak at 2341 cm<sup>-1</sup> appeared in the spectra of 1F-GO, 3F-GO, and 5F-GO. This peak is typically associated with C≡C, ketene (X=C=Y), and nitriles (C≡N). Apparently, X=C=Y were formed via the removal of oxygen by fluorine radical, alternatively, the introduction of the fluorine functional groups have similarly affected as CF<sub>2</sub> group as mentioned above. Therefore, the extent to which fluorine is introduced can be controlled through gas fluorination and the simultaneous fluorination of oxygen is achieved.

## 2.2. Structural properties

XRD analysis was conducted to investigate the crystallinity of GO and fluorinated GO according to gas fluorination. After gas fluorination, fluorinated GO sheets can be prevented from stacking or aggregating, as confirmed by the XRD pattern shown in Fig. 4. The peak of the (101) and (001) plane at 2θ=42° and 10.4°, respectively, were still existed in the 1F-GO and 3F-GO, compared to non-treated GO. In the case of 5F-GO and 7F-GO fluorinated under higher fluorine gas ratio, the peak of the (001) plane was hardly observed. The decrease of the peak intensity at 10.4° indicated that crystallites arranged with (001) orientation were disordered by fluorination under an excess of fluorine gas. This phenomenon is caused by an explosive reaction between GO and a strong dose of fluorine. In addition, it seems to be hard to be ordered by a diminished crystallites (see Table 3).

The detailed XRD parameters are listed in Table 3. The crystallite length  $L_a$  and d-spacing were calculated using the equations

$$L_a = K\lambda / (\beta \cos\theta) \quad (1)$$

$$d_{002} = \lambda / (2\sin\theta) \quad (2)$$

where  $K$  is a shape factor (1.84 here),  $\lambda$  is the wavelength of X-rays used,  $\beta$  is the half width of the (001) peaks, and  $\theta$  is the

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