FLUORINATION OF GRAPHITE AT HIGH TEMPERATURES

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Dedicated to the memory of Professor Miloš Hudlický.

Graphite powder (57–74 μm) was fluorinated at 380 °C for 1 h–2 weeks. The composition of the products ranged from $CF_{0.055}$ to $CF_{0.659}$. X-Ray diffractometry showed the formation of graphite fluoride, $(C_2F)_n$ with a trace of C_xF phase with planar layers in addition to unreacted graphite which finally disappeared. Raman spectroscopy clearly revealed the existence of a fluorinated phase with planar layers with sp^2 structure.

Keywords: Fluorine; Fluorination process; Graphite; Graphite fluoride; Raman spectra.

Graphite reacts with elemental fluorine in a wide range of temperatures, yielding several different types of carbon-fluorine compounds[1–3]. Fluorine-graphite intercalation compound, C_xF with ionic or semi-ionic C–F bond is obtained at temperatures below *ca* 100 °C. This type of compound keeps planar graphene layers, *i.e.* the sp^2 character after fluorine intercalation and is a good electric conductor of black color. The fluorination rate of graphite is slow between 100 and 350 °C, only the surface region of graphite being fluorinated. However, graphite fluorides, $(C_2F)_n$ and $(CF)_n$, with covalent C–F bond are obtained between 350 and 600 °C. The two types of carbon-fluorine compounds are quite different in structures, C–F bonding and electric properties from the C_xF prepared at low temperatures. They have puckered graphene layers, *i.e.* the sp^3 character and are therefore electric insulators. The color is changing from black to white through gray with fluorination temperature increasing from 350 °C to 600 °C. The $(C_2F)_n$ is obtained between 350 and 400 °C, and $(CF)_n$ at around 600 °C. Between 400 and 600 °C, mixtures of $(C_2F)_n$ and $(CF)_n$ are obtained. When graphite is fluorinated at a low temperature, for example, at room temperature, fluorine adsorbed on the surface of graphite makes a charge transfer complex

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and diffuses inside graphene layers. On the other hand, when graphite is allowed to react with elemental fluorine at high temperatures, graphene layers are changed to the puckered sp^3 structure by the formation of covalent C–F bonds. However, the details of the formation of graphite fluorides with puckered graphene layers are still unknown. In a previous paper[4], the structure, composition and reaction course of graphite fluorinated with elemental fluorine at 515 °C were investigated and compared with those of graphite highly fluorinated with elemental fluorine and a high oxidation state fluoride complex in anhydrous HF under pressure. The fluorination rate of fine natural graphite powder with average diameter of 7 μm was very high at 515°C. In the present study, fluorination of graphite has been made at 380 °C, using graphite powder with a larger particle size than 7 μm to clarify the process at high temperatures by X-ray diffractometry and Raman spectroscopy.

EXPERIMENTAL

The starting material is a natural graphite powder (Madagaskar, 57–74 μm) with purity of 99.4%. It was fluorinated at 380 °C with elemental fluorine (99.4–99.7%, supplied by Daikin Industry Ltd.) of $1.0 \cdot 10^5$ Pa by varying the fluorination time from 1 h to 2 weeks. The composition of fluorinated graphite was determined by elemental analysis of C and F at the Elemental Analysis Center of the Faculty of Pharmaceutical Science of the Kyoto University. The fluorination was investigated by X-ray diffractometry (Shimadzu XD-610 with CuKα radiation) and Raman spectroscopy (Jobin–Yvon T-64000 with Ar ion laser of 514.5 nm).

RESULTS AND DISCUSSION

The composition of fluorinated graphite is given in Table I. The fluorine content increased with increasing fluorination time, reaching the usual composition of the $(C_2F)_n$ type of graphite fluoride in 5 days. As mentioned in the introduction, two types of graphite fluorides, $(CF)_n$ and $(C_2F)_n$ are known[1]. They have puckered graphene layers to which fluorine atoms above and below the layers are covalently bonded. $(CF)_n$ is the stage-1-type structure and $(C_2F)_n$ is the stage-2-type[5]. The ideal composition of $(C_2F)_n$ is $CF_{0.5}$. However, $(C_2F)_n$ usually has a slightly larger fluorine content than $CF_{0.5}$ since $(CF)_n$ is formed around the surface region of graphite particles. The surface region is somewhat disordered even in natural graphites with high crystallinity as shown by Raman spectrum[4]. In the surface region, $(CF)_n$ is formed of *ca* 350–400 °C where $(C_2F)_n$ is obtained in the graphite bulk. When graphite powder is fluorinated between 350 and 400 °C, the composition of products in containing mainly $(C_2F)_n$ ranges between $CF_{0.6}$

and $CF_{0.7}$ [1,6]. The composition of the samples fluorinated for 5 days–2 weeks is within the range as shown in Table I.

X-Ray diffraction patterns of 8 samples are shown in Fig. 1, which indicates the formation course of graphite fluoride $(C_2F)_n$. The fluorination rate of graphite is slower under the present conditions than in fluorination of

TABLE I
Composition of graphite fluorinated at 380 °C

Sample	Fluorination time	Composition
1	1 h	$CF_{0.055}$
2	2 h	$CF_{0.059}$
3	14 h	$CF_{0.344}$
4	1 day	$CF_{0.446}$
5	4 days	$CF_{0.550}$
6	5 days	$CF_{0.639}$
7	1 week	$CF_{0.634}$
8	2 weeks	$CF_{0.659}$

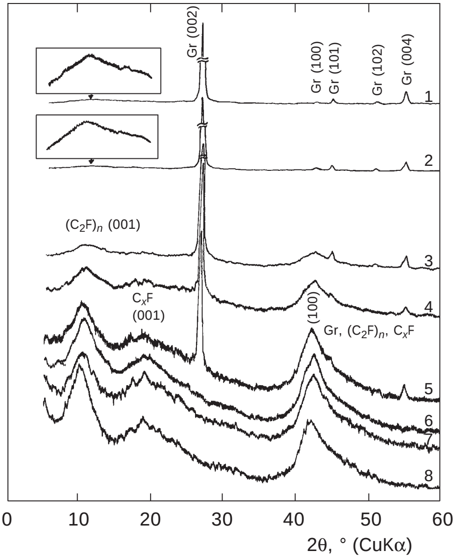

FIG. 1
X-Ray diffraction patterns of graphite fluorinated at 380 °C as a function of fluorination time. Sample numbers are the same as given in Table I

graphite powder (≈7 μm) at 515 °C [4]. The strong (002) diffraction line and very weak (004) line of graphite itself were observed on fluorination for 1 h–4 days. Very weak (101) and (102) diffraction lines indicating graphitic stacking of graphene layers were also detected in samples 1–4 and 1–3, respectively.

Very broad and weak diffraction lines suggesting the (001) line of $(C_2F)_n$ appeared at 2θ 11.70° (*d* value: 0.756 nm) and 11.20° (*d* value: 0.789 nm) for samples 1 and 2, respectively. The intensity of this peak increased with increasing fluorination time and the *d* value approached 0.85–0.87 nm corresponding to the (001) diffraction line of $(C_2F)_n$ [5,6]. The (001) lines of $(C_2F)_n$ were strong for samples 5–8 fluorinated for 4 days–2 weeks. Nevertheless, weak diffraction lines indicating the (001) line of stage-1 C_xF with planar graphene layers were observed in these samples, of which no graphitic phase was detected for samples 6–8. The weak (001) diffraction line for C_xF was observed even for sample 8 fluorinated at 380 °C for 2 weeks. The existence of the C_xF phase indicates that a trace of graphitic phase with the sp^2 character still exists after two weeks fluorination at 380 °C. This could be the reason why $(C_2F)_n$ is always black. When $(C_2F)_n$ prepared between 350 and 400 °C is treated with fluorine at a high temperature between 500 and 600 °C, the color of $(C_2F)_n$ changes from black to almost white[1,6]. This means that C_xF with planar graphene layers has changed to graphite fluoride with puckered graphene layers.

The (100) diffraction line was very weak in samples 1–3 which were only partly fluorinated. However, it was strong in samples 5–8 which were highly fluorinated though sample 5 still contained the graphitic phase. The disappearance of (101) and (102) diffraction lines and increase in the intensity of the (100) line show that the high structural order of graphite along the *a* and *c* axes is lost by fluorination.

The lattice parameters along the *a* axis, calculated from *d* values of (100) line, are in the range of 0.2469–0.2478 nm larger than that of graphite, *i.e.* 0.2461 nm. The *a* value increased with increasing fluorination time. This shows that the C–C bond length increases by the formation of covalent C–F bond.

Raman spectroscopy gives two important Raman shifts at 1 580 and 1 360 cm^{-1} for carbon materials. The Raman shift observed at 1 580 cm^{-1} is due to the E_{2g} vibration mode originating from graphitic structure (G band), and that observed at 1 360 cm^{-1} is ascribed to the A_{1g} symmetric vibration mode in disordered structure and/or the edge of graphite powder (D band)[7,8]. The Raman shift at 1 580 cm^{-1} moves to 1 615 cm^{-1} by the formation of C_xF at room temperature, and this shifted peak gradually moves to the lower wavenumber with increasing intercalated fluorine[4,9–11]. The explanation is based on the change of the C–C bond length in the graphene layer due to fluorine intercalation[11]. During the formation of stage-2 or higher-stage C_xF, the nature of C–F bond is ionic or almost ionic. At these stages, the C–C bond length is shortened by electron transfer from graphite to intercalated fluorine[2,4,12–15], *i.e.*, the vibration energy of graphene layer increases. However, the C–C bond length in the graphene layer increases due to the formation of stage-1 C_xF with semi-ionic C–F bond and with increasing fluorine content in stage-1 C_xF from C_4F to $C_{1.3}F$ [2,4,12–15], *i.e.*, the vibration energy of the graphene layer decreases with increasing fluorine content at stage-1. The upshifted peak moves back to the original position of 1 580 cm^{-1} in C_2F [4,9]. When graphite fluoride with puckered graphene layers is formed, Raman shifts in the region of 1 200–1 800 cm^{-1} disappear.

Figure 2 shows Raman spectra obtained in the present study. The profile of the spectra is similar to those for highly fluorinated C_xF samples and graphite powder (≈7 μm) fluorinated at 515 °C for 1–3 min [4]. Raman spectra 1–5 clearly show that fluorinated parts of these samples still maintain the

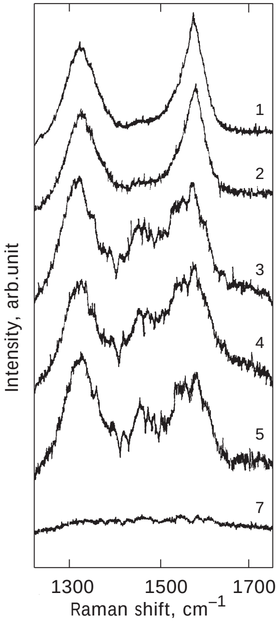

FIG. 2

Raman spectra of graphite fluorinated at 380 °C as a function of fluorination time. Sample numbers are the same as given in Table I planarity of graphene layers, *i.e.* sp^2 character after fluorination along with the unreacted graphitic phase because no Raman shift is observed in the same region in graphite fluoride with puckered graphene layers[4]. Raman spectra of the samples fluorinated for 1 and 2 h (Fig. 2, 1 and 2) show a strong G band at 1 580 cm^{-1} and D band at 1 333 cm^{-1}. The G band is mainly due to unreacted graphite and the D band shifted to 1 333 cm^{-1} could arise from the fluorinated surface area with high disorder. The shift of D band from 1 360 to 1 333 cm^{-1} can be explained by an increase in the C–C bond length due to the formation of covalent C–F bond as already mentioned. Samples 3, 4 and 5 fluorinated for 14 h–4 days show a higher disorder in the spectral profile. The intensity of the G band, derived from mainly unreacted graphite, decreased with increasing fluorination time. According to the decrease in the G band intensity, the relative intensity of the D band increased. In addition, several shifted bands appeared in samples 3, 4 and 5. A shoulder observed at 1 600 cm^{-1} is attributed to the G band upshifted due to fluorination[4,9–11]. The other shoulder observed at 1 545 cm^{-1} could be due to the highly fluorinated C_xF phase with higher fluorine content than C_2F [4]. The fluorinated phase having composition of C_2F may overlap with the G band indicating the graphitic phase[9]. The spectrum 7 in Fig. 2 was obtained for graphite fluorinated for 1 week, which gave no Raman shifts because the sample was graphite fluoride, $(C_2F)_n$ with a trace of the C_xF phase. The samples fluorinated for 5 days or 2 weeks showed almost the same Raman spectra as that of sample 7 (Fig. 2, 7).

As shown in Fig. 2, various Raman shifts were observed for samples fluorinated for 1 h–4 days. This indicates that the fluorinated phase keeping the planarity of graphene layers with the sp^2 character coexists with the phase already converted to $(C_2F)_n$ with puckered graphene layers in the course of fluorination because graphite fluoride $(C_2F)_n$ gives no Raman shifts in the region of 1 200–1 800 cm^{-1}. The results show that the fluorination of graphite at a high temperature proceeds with formation of the C_xF phase having planar graphene layers in the intermediate state and the C_xF phase is then converted to graphite fluoride with puckered graphene layers.

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