

Semi-Ionic Type Bonds in Fluorinated Carbon Compounds

YU.M. NIKOLENKO and A.M. ZIATDINOV

*Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences,
159, Prosp. 100-letiya, 690022 Vladivostok, Russia*

Fluorinated graphite oxides (FGO) and fluorinated lignin (FL) have been investigated by X-ray photoelectron spectroscopy (XPS). In the F1s spectra of both compounds a peak with the energy being intermediate between the value in a typical ionic compound LiF and covalent compounds of type $(CF)_n$ and $-(CF_2-CF_2)_n^-$ was extracted. The substances under study, even at high oxidizer content, contain structure fragments with carbon having sp^2 -hybridized orbitals. The bond formed between fluorine and these fragments is of semi-ionic type. The temperature, which allows the semi-ionic fluorine-carbon bond formation, is found to be between the room temperature and $100^\circ C$. The registration of semi-ionic state of fluorine in the FL allows to assume that the layered structure of initial substance is not necessary for the formation of semi-ionic bond between fluorine and carbon.

Keywords: semi-ionic bonds; fluorinated carbon; XPS

INTRODUCTION

The possibility of practical application and versatility of properties of fluorinated carbon systems maintain interest in their structure and the bond type between a carbon matrix and fluorine. Previous XPS-investigations of fluorinated carbon fibers (FCF)^[1] have shown a possibility of semi-ionic carbon-fluorine bonds. XPS spectra of graphite fluoride C_2F (GF) prepared from graphite- BrF_3 suggest a semi-ionic nature for the C-F bond^[2]. These fluorinated carbon systems were synthesized at temperatures below $100^0 C$ and the initial substances had a layered carbon matrix (matrix fragments) with unsaturated C-C bonds.

This paper presents XPS data on fluorinated carbon compounds synthesized using BrF_3 at temperatures below $100^0 C$. The main objective was to determine the type of carbon-fluorine bond in the final fluorinated products. To estimate the role of unsaturated C-C bond presence in the initial substances

for the formation of the semi-ionic bond between carbon and fluorine, graphite oxides (GO) with different oxygen contents were used to synthesize the FGO. The XPS spectra of fluorinated lignin (FL) allow to estimate the necessity of layered structure of initial substances for receiving the compounds with semi-ionic carbon-fluorine bond.

EXPERIMENTAL

Thirteen GO samples with different oxygen contents (Table I) was used to synthesize the FGO. Fluorination of GO was carried out with BrF_3 at room temperature. The hydrolysis of the fluorinated samples leads to additional oxidation and fluorination of the substances. Thin dispersion and separating of samples under synthesis into the two phases (shares) during hydrolysis took

TABLE I The ratio of carbon to oxygen (C/O) in the GO samples

N (sample)	1	3	4	5	6	7	8	9	10	11	13
C/O	10.2	10.3	10.3	10.0	5.2	4.8	3.4	2.7	2.3	1.5	1.5

place. The hydrophilic phase sinks to the bottom of the solution (bottom phase, "B") but the hydrophobic phase (light, "L") comes to the surface. Details of the synthesis of GO and FGO and chemical analysis data have been presented in previous study^[3]. To synthesize the fluorinated lignin (FL), hydrolyzed lignin was used. Hydrolyzed lignin is a product of polycondensation of the substituted phenolic alcohols; it forms in the process of the vegetable oils hydrolysis. Hydrolyzed lignin is a polymer with branched macromolecules and configurational irregularity. It is amorphous yellow-brown substance which molecular mass varies from 10^2 up to 10^6 . Fluorination of lignin was carried out with BF_3 in hydrogen fluoride atmosphere within the temperature interval 260-270 K. The product obtained was washed with hydrogen fluoride. Excess of hydrogen fluoride was removed in vacuum at 300 K.

XPS spectra of GO, FL and both phases of FGO have been measured using a standard XPS spectrometer ES 2401 with AlK_α radiation. The resolution at the Au $4f_{7/2}$ peak was 1.5 eV. During the measurements, the vacuum in the analyzer chamber was maintained at 6×10^{-8} mm Hg. The calibration of the spectrometer energy scale was conducted according to the C1s peak of carbon contaminations (285.0 eV). The correlation function that takes into account the different spectral yields of the C1s and F1s photoelectrons was found experimentally for the reference compounds $(\text{CF})_n$ and $-(\text{CF}_2-\text{CF}_2)_n-$. The relative concentrations of the other elements were determined using the photoionization cross-section values borrowed from^[4].

RESULTS AND DISCUSSION

For the first six GO samples, the main components of C1s photoelectron spectra have asymmetric shape of lines that is typical for conductive materials. This means that carbon atoms of the matrix keep the sp^2 -hybridization of the valent electron orbitals and these compounds may be defined as graphite hydroxide hydrates. For the GO samples with $N>6$, the matrix spectra lines become symmetrical. It means that the type of hybridization of the matrix valent orbitals changes from sp^2 to sp^3 .

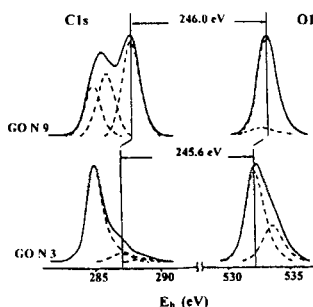


FIGURE 1 The examples of C1s and O1s spectra of graphite oxides (GO).

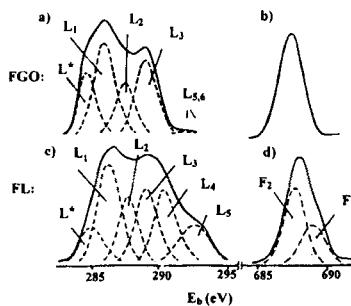


FIGURE 2 C1s ('a' and 'c') and F1s ('b' and 'd') XPS spectra of the fluorinated graphite oxide (FGO) and the fluorinated lignin (FL).

The peak of C1s-electrons attributed to C-OH is present in all spectra but begins to increase apparently from the GO sample N 6. For the GO samples with $N<7$ the difference between core electron binding energy (ΔE_b) of the carbon bound with oxygen and oxygen core electron is 245.6 ± 0.1 eV while for the other samples this value is 246.0 ± 0.1 eV (Fig. 1). One can suggest that in the GO samples with $N<7$ oxygen is bound with carbon atoms on the edges of basal planes of the matrix. In the GO samples with $N>6$ the oxygen-containing fragments are bound with sp^3 -hybridized carbon atoms of the matrix distorted planes.

The measured C1s spectra of the FGO samples of both phases consist of some basic lines. As example, the FGO N 8 "B" C1s spectrum after the treatment by computer is presented in Fig. 2. The main steps of the spectrum treatment by computer are presented in Fig. 3. The method of treatment uses the procedures from^[5-7] and consists of two stages: 1) statistical noise reducing (Fig. 3b), the background subtraction, subtraction of satellite structure that results from non-monochromaticity of the X-ray source (Fig. 3c), and 2) correction of the instrumental broadening with the aims to estimate the number

of the lines in the complex spectra and their positions (Fig. 3d). Next, FGO and FL spectra after the first stage of treatment were simulated with components, which have a Gaussian line shapes (Fig. 3f).

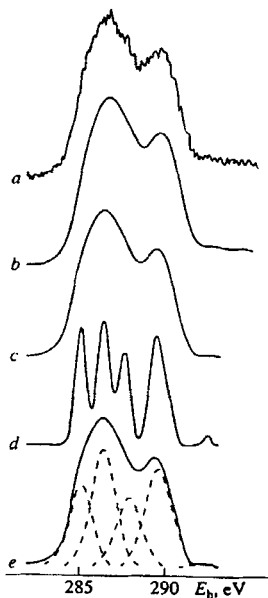


FIGURE 3. The example of treatment of the experimental XPS spectrum by computer: C1s spectrum of the FGO N 8 "B". a) Actual spectrum, b-d) stages of computer processing (see text), f) results of computer simulation.

compounds $(CF)_n$ and $-(CF_2-CF_2)_n$. The C1s peaks which may be attributed to the groups $>CF_2$ and $-CF_3$ (L_5 , L_6) (in accordance with their binding energies) are presented in some FGO, but their intensities are too little. In Fig. 2 the XPS-spectra of the fluorinated lignin are also presented. The treatment of the spectra by computer was carried out as was used for the FGO samples. The similar structures of the peaks forming the C1s spectra have been determined. Here the C1s peak of the FL, which may be attributed to the bonds $>CF$ (L_4) and $>CF_2$ (L_5) according to their E_b , (290.5 ± 0.2 eV and 292.5 ± 0.2 eV,

The first line (L^*) in the spectrum (Fig. 2) has been attributed to the surface carbon contaminations. Next line (L_1) is attributed to the carbon atoms, which are bound with neither oxygen nor fluorine. Binding energy of the line L_2 is close to E_b of the line of carbon bound with the oxygen-containing fragments in the samples of GO with $N > 6$. The difference between E_b of L_2 and O1s in the FGO is of 246.0 ± 0.1 eV. It enables to attribute the line L_2 to the carbon bound with oxygen covalently. As it is shown in ^[3,8], the carbon-oxygen bonds (oxygen presence) are stable during the fluorination process.

In the compounds under investigation the line L_3 appears after the treatment of samples with BrF_3 . Consequently, this peak may be attributed to the carbon bound with fluorine. But we should point out that the E_b of F1s-electrons in FGO (687.6 ± 0.5 eV) is less than the energies usually observed in covalent carbon materials (the most often observed values of the E_b are in the range 689.6 ± 0.5 eV both for aliphatic and cyclic forms^[9]). Simultaneously, taking into account the values of L_3 in the FGO (289.3 ± 0.3 eV) one may conclude that the interaction between fluorine and carbon atoms, which give the signal L_3 in the FGO, differs from that in typical covalent

respectively), has far greater intensities than those in the FGO. The line shape of this spectrum is asymmetric and shows that F1s line is multicomponent. The computer processing of F1s spectrum of the FL gives two main components (Fig. 1). The peak with E_b being equal to 688.9 ± 0.2 eV (F_1) may be attributed to the fluorine of $>CF$ and $>CF_2$ bonds, while the other with $E_b = 687.8 \pm 0.2$ eV (F_2) to the carbon-fluorine bond observed in the FGO (corresponding C1s peak of the FL has the E_b being equal to 289.2 ± 0.2 eV).

The quantitative and qualitative characteristics obtained from the data of XPS study are related to the surfaces and nearby layers (50 ± 100 Å) of compounds under investigation. According to the XPS data, the ratio of the total quantities of matrix carbon and oxygen (C/O) in the GO series is less than that obtained from chemical analysis data^[10]. This results from the fact that we deal with the spectra of the sample surfaces which are more influenced by the oxidizing reagents. However, during the hydrolysis of the fluorinated compounds, a thinner dispersion of the samples takes place. As a result, domains of compounds, which were inside the samples before, get to surfaces. The C/O ratio determined from XPS spectra of C1s- and O1s-electrons of the surfaces of thin dispersed FGO compounds becomes closer to the chemical analysis data^[10]. Besides, the ratio of the total quantities of matrix carbon to fluorine (C/F) determined from the XPS spectra is also less than follows from the chemical analysis data^[10]. The above fact may be explained, if we bear in mind two circumstances: 1) BrF_3 interacts with carbon of certain fragments of the structure of initial GO matrix which are present in all GO samples, and 2) the dispersion of the samples during the hydrolysis process occurs with these fragments resulting in the increased (as compared with the bulk of substance) fluorine and fluorine-containing admixtures concentration on the thin dispersed FGO sample surfaces.

In accordance with the E_b of C1s and F1s, the type of the bonds formed between fluorine and carbon in the above mentioned fragments may be attributed to the so-called semi-ionic type of the bond. The formation of semi-ionic bond is connected with the presence of carbon atoms bound with each other by unsaturated bond in the initial matrix. The reason for existence of these structure fragments with unsaturated C-C bonds in FGO may be the fact that in the GO synthesis used the phase of graphite hydroxide hydrate remains in the samples with maximum oxidation degree as well. In this case, this phase may be considered as a residual admixture phase and its presence is revealed only during fluorination followed by hydrolysis of the substance. However, the matrix regions of sp^2 -hybridized carbon may also be the characteristic of the oxidized graphite itself.

The characteristics of XPS-spectra (such as E_b of components of the C1s-spectra as well as F1s binding energy) of FL are similar to those of FGO. The structure of initial lignin includes benzoic rings. The method of fluorination is similar to that used in FGO synthesis. These facts suggest that in FL samples there is observed a bond between fluorine and carbon similar to that found in FGO.

CONCLUSION

In this paper it was determined by the X-ray photoelectron spectroscopy that there is a peak in the F1s spectra of FGO and FL which E_b are intermediate between this value in a typical ionic compound LiF and covalent compounds of type $(CF)_n$ and $-(CF_2-CF_2)_n-$. The substances under study, even at high oxidizer content at all synthesis stages contain structure fragments with carbon having sp^2 -hybridized orbitals of the valent electrons. The bond formed between fluorine and these fragments is of semi-ionic type at the method of fluorination used followed by hydrolysis. The temperature, which allows the semi-ionic fluorine-carbon bond formation, is found to be between the room temperature and 100°C . The registration of semi-ionic state of fluorine in the FL allows to assume that the layered structure of initial substance is not necessary for the forming of semi-ionic bond between fluorine and carbon.

Acknowledgments

The authors are thankful to Drs. A.K. Tsvetnikov, T.Yu. Nazarenko and L.A. Matveenko for the synthesis of the samples investigated. This work was supported by the grant from the Russian Foundation for Basic Research (№ 97-03-33346).

References

- [1] N. Watanabe, T. Nakajima, H. Touhara, *Graphite Fluorides* (Elsevier, Amsterdam, 1988), Chap. 2, p. 80.
- [2] A.S. Nazarov, V.G. Makotchenko and V.V. Lisitsa, *Material Science Forum ISIC-6*, **91-92**, 10(1992).
- [3] A.K. Tsvetnikov, T.Yu. Nazarenko, L.A. Matveenko and Yu.M. Nikolenko, *Material Science Forum ISIC-6*, **91-92**, 201(1992).
- [4] J.H. Scofield, *J. Electron Spectrosc. Relat. Phenom.*, **49**, 129(1976).
- [5] D.V. Yudin and V.V. Gorchakov, *Zhurnal Prikladnoy Spektroskopii (Russia)*, **49**, 462(1988).
- [6] D.V. Yudin and Yu.V. Zelensky, *Zhurnal Prikladnoy Spektroskopii (Russia)*, **52**, 445(1990).
- [7] Yu.V. Zelensky and D.V. Yudin, *Zhurnal Prikladnoy Spektroskopii (Russia)*, **54**, 40(1991).
- [8] A. Hamwi, I.Al. Saleh, D. Djurado, J.C. Cousseins, *Material Science Forum ISIC-6*, **91-92**, 245 (1992).
- [9] V.I. Nefedov, *X-ray Photoelectron Spectroscopy of Chemical Compounds* (Chemistry, Moscow, 1984), 256P.
- [10] Yu.M. Nikolenko, A.K. Tsvetnikov, T.Yu. Nazarenko, A.M. Ziatdinov, *Zhurnal Neorganicheskoi Khimii (Russia)*, **41**, 747(1996); *Russian Journal of Inorganic Chemistry*, **41**, 721(1996).