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Selective substitution of fluorine atoms grafted to the surface of carbon nanotubes and application to an oxyfluorination strategy

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Abstract: Different modes of fluorine chemisorption on the surface of single wall carbon nanotubes (SWCNTs) are shown to result in varied tendencies of the F atoms to behave as leaving groups, in the presence of a nucleophilic reagent. Fluorine species in weak interaction with the carbon matrix can be readily displaced and therefore, exhibit enhanced exchange properties, while those more strongly bound to the sidewall resist substitution. Such a tunable reactivity of the F atoms in a fluorotube has been used to selectively replace some of them by hydroxyl functional groups. The scheme illustrated here represents a first step toward a quantitative functionalisation process of the SWCNT surface by hetero-elements.

1. Introduction

The C-F single bond is listed among the most thermochemically favourable combinations, conferring this moiety a relative chemical stability. It is thus common knowledge that perfluorocarbons are prototypes of chemically inert compounds. However, it has been widely illustrated that the C-F bond strength becomes notably weakened when fluorine is associated with a fullerenic carbon network. This arises essentially from reduction of the carbon and fluorine orbital overlap upon curvature of the pristine carbon framework. From the physicochemical properties standpoint, the “imperfect” C-F covalence realised in curved fluorocarbon lattices does not go without important consequences, related to easy bond cleavage. For instance, fluorine gas is rapidly given off from a sample of fluorinated single wall carbon nanotubes (F-SWCNTs) upon simple prolonged annealing under an inert atmosphere [1-3]. The defluorination of such entities can also simply occur upon gentle chemical reduction [4]. The overall weakening of the C-F interaction makes the former macromolecular clusters sensitive to nucleophilic attack as well, whereas it is widely acknowledged that the fluorine atom is otherwise a very bad leaving group. Originally initiated in the framework of the study of the chemical reactivity of fluorofullerenes [5], investigations on this latter aspect have since been intensively extended to fluorine atoms grafted to the surface of a carbon nanotube and have shown the ability of the latter to be readily displaced. The research group from Rice University had thus initially reported the attachment of alkyl chains [6,7] and various oxygen or nitrogen-based functional groups [8] to the sidewall of a carbon nanotube by starting from a fluorinated precursor.

Beside this overall C-F bond weakening phenomenon, pioneering studies [1-4,9] dedicated to F-SWCNTs also commonly reported that two distinct types of C-F bonds must be distinguished and can seemingly even coexist [3,9] within a sample, depending on the synthesis temperature and precursor SWCNTs used. Similar conclusions, regarding a either uniform or binary nature of the C-F chemical bond, were reached in the course of more recent studies on fluorotubes synthesised by CF_4 or SF_6

plasma treatment [10-13]. Our own contribution to the subject [14] has recently distinguished a third mode of fluorine chemisorption in fluorotubes.

Compiling the two preceding aspects, we have tried in this paper to examine the consequences of a varied C-F bonding scheme on the substitutional properties of fluorotubes. Indeed, a selective reactivity of each C-F bonding mode can be expected, the weakest ones conferring fluorine atoms an enhanced leaving group character and, as a corollary, a greater exchanging power. We have then shown, from the oxyfluorination case, how such differentiated nucleofugal properties can turn out to be a fruitful tool for the subsequent derivatisation of SWCNTs, paving the way toward quantitative methods of synthesis of a hetero-functionalised one-dimensional material.

2. Results

In the following, we present a wet chemistry method to modify the surface of SWCNTs via the co-addition of both fluorinated and oxygenated hetero-functions. The staged pattern developed starts from a sample of fluorotubes, further treated with nitric acid, a common procedure known to yield oxygenated functional groups at the surface of graphitised carbonaceous materials [15-18]. The fluorinated precursor and the final oxyfluoro-compound have then been characterised by x-ray photoelectron spectroscopy (XPS), which allows to establish both the nominal composition and the nature of the functions created for each sample. The successive C_{1s} spectra and elemental contents obtained are presented in figure 1 and table 1, respectively.

2.1 Experimental

A batch of purified SWCNTs, grown from chemical vapour deposition (CVD), was used in the present study. Transmission electron microscopy (TEM) observations showed that the majority of the tubes have diameters between 1 and 2 nm and form bundles. Fluorination was carried out under pure

molecular fluorine (2h, 300°C), within a tubular Monel reactor initially purged with nitrogen until the synthesis temperature was reached. The gas flow was maintained during cooling of the samples. Subsequent oxygenation was performed by reflux in 11 M nitric acid, for 10h at 100 °C, under continuous stirring. The oxyfluorinated compound thus obtained was then filtered, washed with distilled water until complete neutralisation of the filtrate, and dried under vacuum at 60 °C for one night. Anhydrous KBr pellets were used for Fourier transform infrared spectroscopy (FTIR) analysis. Nominal compositions were obtained from XPS analysis, using relative sensitivity factors for fluorine and oxygen, with respect to carbon, adjusted from standards. Charge compensation was ensured via an electron flood gun.

2.2 Characterisation of the precursor fluorotubes

We first proceeded to the fluorination, at 300°C and for two hours, of a CVD-grown batch of SWCNTs, as described in the experimental part. We had previously shown [14] that in such conditions, the chemisorption of fluorine at the surface of such SWCNTs can be classified into three different categories of C-F bonds, differing by their robustness, i.e. by the ease with which fluorine can be released from the carbon substrate.

The C_{1s} XPS spectrum (fig. 1) corresponding to the fluorinated tubes comprises a first feature centred at 284.5 eV, similar to the one present in the C_{1s} spectra of the raw tubes, and therefore related to bare graphitic carbon atoms. It is experimentally well established that the C_{1s} core level energy undergoes substantial primary and secondary shifts in the presence of a strong electron-withdrawing element. Accordingly, the existence of carbon atoms not directly linked to a fluorine atom but having fluorinated nearest neighbours splits the first “graphitic” signal into a second component lying at a higher binding energy, as shown earlier in the case of graphite fluoride $(C_2F)_n$ [19], partially fluorinated

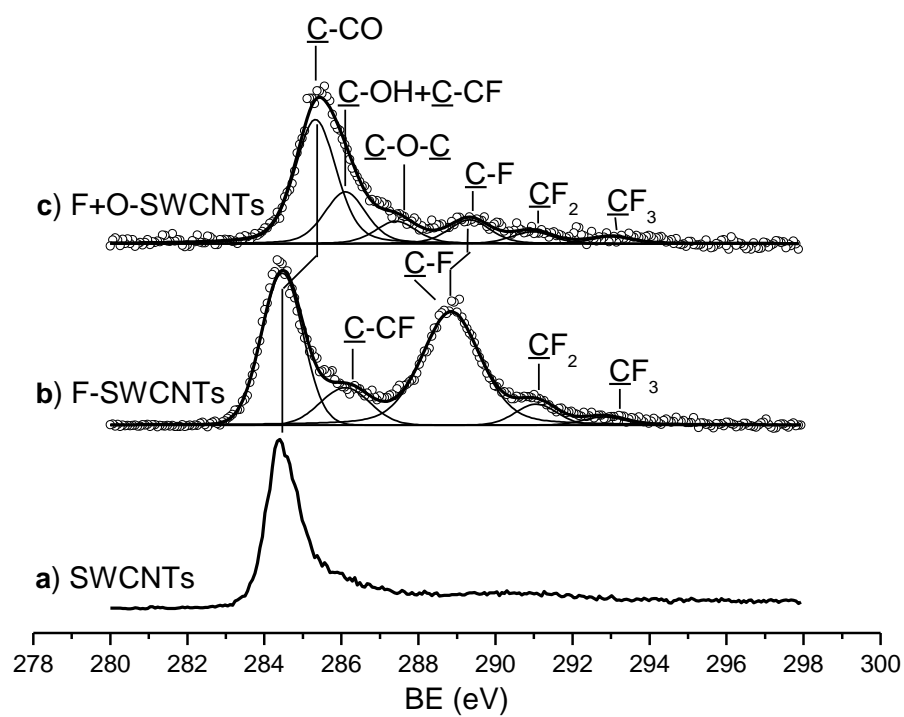


Figure 1. C_{1s} XPS spectra, after background subtraction, of the a) pristine SWCNTs, b) SWCNTs fluorinated for 2h at 300°C, and c) final oxyfluorinated material.

Table 1. Peak analysis arising from the spectral deconvolution of the C_{1s} XPS spectrum of the initial and nitric acid treated fluorinated samples.

Sample	Binding energy (eV)	Carbon environment	Relative intensity
Fluorinated precursor	284.5	C-C-C ^(a)	37.0 %
	286.1	C-CF	10.8 %
	288.8	C-F	45.1 %
	291.1	CF ₂	5.1 %
	292.8	CF ₃	2.0 %
			Composition
From assignment of C _{1s} peaks			CF _{0.61}
From peak area ratio			CO _{0.02} F _{0.52}
Acid treated material	285.3	C-CO] 72.9 %
	286.1	C-OH + C-CF	
	287.4	C-OC or C=O ^(b)	9.3 %
	289.3	CF or O=C-OH ^(b)	9.9 %
	291.0	CF ₂	5.0 %
	293.0	CF ₃	2.9 %
			Composition
From assignment of C _{1s} peaks			CO _y F _{0.29}
From peak area ratio			CO _{0.47} F _{0.29}

^a C indicates the atom responsible for the photoemission signal, each time.

^b The contribution of carbonyl and carboxyl groups to the corresponding XPS signal can be safely neglected according to the IR data analysis.

carbon fibres [20], or fluorofullerenes [21], and here present at 286.1 eV. To further proceed with the analysis of the spectrum, one may recall that the C_{1s} signal related to carbon atoms attached to one fluorine atom usually appears in the 287-289 eV region [19-22]. A corresponding feature is observed here, with a large width reflecting multiple contributions that therefore confirms the presence of several C-F bonding modes in the fluorotubes sample. The latter signal has been treated as a unique envelope, adjusted in width and position. Finally, weak shoulders at 291.1 and 292.8 eV have been attributed to some $>CF_2$ and $-CF_3$ groups appearing on edges or at local defect sites. The fluorine content (table 1) calculated from the relative intensities thus assigned corresponds to $CF_{0.61}$, not in contradiction with the nominal composition $CF_{0.52}$ determined from the XPS F_{1s}/C_{1s} area ratio, taking into account the respective elemental sensitivity factors. 5 and 2 % of atomic oxygen with respect to carbon have also been detected in the pristine carbon material and after its fluorination, respectively. At last, one may note that though a similar peak assignment was already made in earlier XPS studies of F-SWCNTs [2,12,23,24], it seems to never have been noted that the formerly described splitting of the photoelectron peak related with bare carbon atoms must also reflect the texture of the compound at the nanometre scale. Indeed, a uniform halogenation pattern with an F/C ratio close to $\frac{1}{2}$ would constrain each carbon atom to have at least one fluorinated neighbour in its immediate surrounding, suppressing the component assigned to purely graphitic carbon. The persistence of the latter then necessarily implies a non homogeneous distribution of fluorine atoms along the longitudinal axis of a tube, and the presence of fluorine depleted zones alternating with fluorinated sections. A compelling evidence of the phenomenon was given earlier by Kelly et al. [25], through direct observation by scanning tunnelling microscopy of the SWCNT addition pattern.

The F_{1s} spectrum (Fig. 2) of the fluorocarbon matrix presents an apparently single peak, centred at 687.6 eV. Such a symmetrical line shape may contrast with the previously inferred existence of distinct

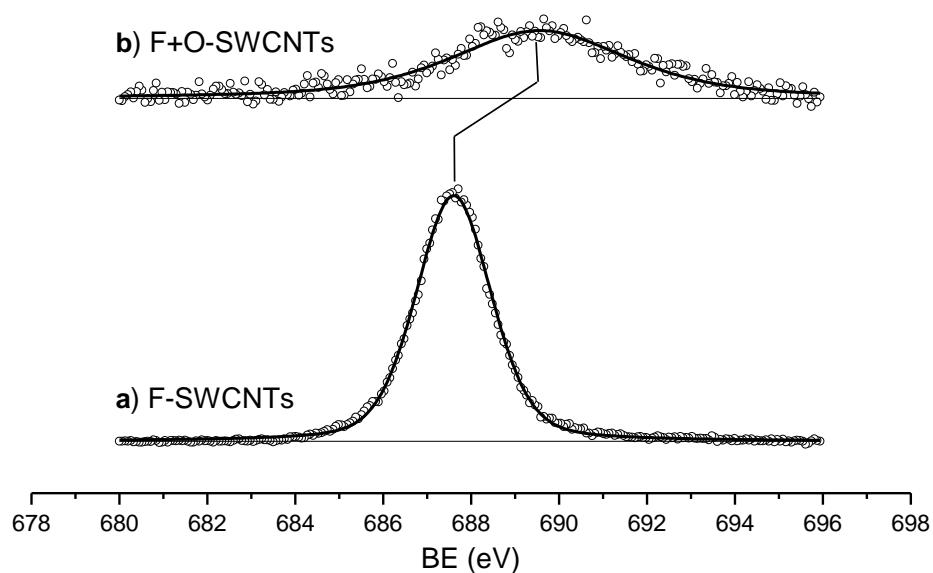


Figure 2. F_{1s} XPS spectra, after background subtraction, of the a) SWCNTs fluorinated for 2h at 300 °C, and b) final oxyfluorinated material.

Comment: The large peak width in b) arises from the overlapping contributions of the different covalent CF_n groups subsisting, since CF, CF₂ and CF₃ moieties in the nearly 1:1:1 ratio with respect to atomic fluorine were detected in the course of the C_{1s} spectrum analysis. Their separation has here not been attempted, given its highly uncertain character.

C-F bonding modes in the sample, but resolution of signal overlap at the F_{1s} level remains limited owing to the restricted energy splitting range and larger peak width characterising the latter (even the minor $>CF_2$ and $-CF_3$ groups present appear as part of the line foot and can not be distinguished).

At last, the IR spectral data presented in figure 3 display large unresolved bands covering the 1000-1250 cm^{-1} zone, unambiguously revealing that the strength of the C-F bonds formed covers a significant amplitude interval. In contrast, IR spectra of conventional fluorocarbons always exhibit narrow bands over a usual 1100-1250 cm^{-1} wave number range. The continuous variation in bond energy here established is consistent with the conclusions drawn from the XPS analysis regarding the presence of different chemisorption modes of fluorine within the present fluorotubes.

2.3 Characterisation of the final oxyfluorotubes

The precursor fluorinated sample obtained has then been further treated with nitric acid (see experimental section). Once the whole functionalisation process was completed, subsequent TEM observations showed individualised tubular entities (Fig. 4). Though some fragmentation could be evidenced, it seems that F-SWCNTs offer much better resistance to destruction than raw tubes, probably because the hydrophobic CF groups present on their outer surface initially make them slowly wet by the aqueous medium, so that it takes time before the well-known etching effect of nitric acid on tubes can manifest.

The elemental stoichiometry of the sample issued from the complete chemical treatment, as determined by XPS, was $CO_{0.47}F_{0.29}$, giving evidence of a mixed final functionalisation state and of a significant increase in the global addition level. No other element has been revealed by the survey spectrum. The shift toward higher binding energies of the peak arising from the non-directly “addended” carbon atoms is noticeable on the C_{1s} spectrum displayed on figure 1. This drastic change

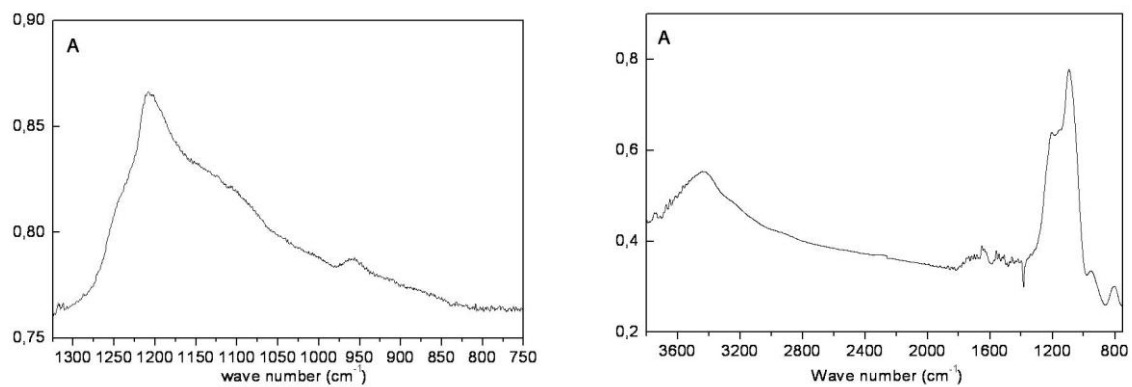


Figure 3. FTIR spectrum of the precursor fluorotubes (left) and final oxyfluoro-compound obtained (right).

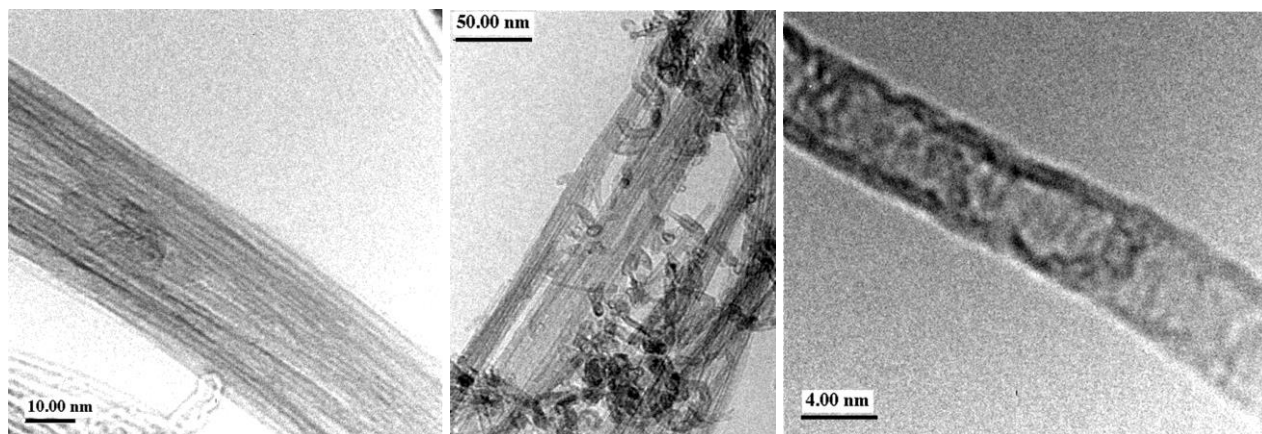


Figure 4. From left to right: TEM micrographs obtained from the pristine (bundle), fluorinated (bundle), and oxyfluorinated (individual tube) SWCNT samples, respectively.

finds its origin in the fact that bare carbon atoms now systematically have at least one immediate carbon neighbour attached to a strongly electronegative element (F or O), in compliance with the increase of the global addition rate. This leads to a general core level secondary shift and to the extinction of the previously observed purely “graphite-like” photoemission line. The remaining part of the spectrum can be deconvoluted with the help of five additional components at higher energies, assigned to carbon atoms bonded either to oxygen under the form of ether and hydroxyl groups or to fluorine, according to standard chemical shift tables [26]. The attributions thus performed are listed in table 1 and are consistent with published data dealing with the identification, by means of core level photoelectron spectroscopy, of oxygenated functional groups grafted to the surface of carbon fibres [15,16] or carbon nanotubes [17,18]. Because of excessive peak overlap at low energy, reliable relative intensities in this region can not be confidently extracted, but taking the global oxygen content and the sufficiently resolved ether signal as references, the following approximate quantitation $C_{\approx 0.30}(CF)_{0.10}(CF_2)_{0.05}(CF_3)_{0.03}(C_2O)_{\approx 0.05}(COH)_{\approx 0.42}$ has been obtained, i.e. more than 50% of the carbon atoms seem functionalised.

The corresponding IR spectrum is shown in figure 3. The distinct absorption bands can be easily identified and fully confirm the conclusions drawn from the XPS study, regarding the nature of the functions created. One may therefore successively identify the signature of hydroxyl groups (3100-3600 cm^{-1}), covalent C-F moieties (1205 cm^{-1}) and C-O (alcohol and ether) bonds (1090 cm^{-1}). Another noticeable fact is that only very few carbonyl functions from ketones and carboxylic acids are present.

3. Discussion

3.1 O/F substitution

The experimental statement of the decrease in the elemental F/C ratio and concomitant increase in the O/C one, after acid treatment, is noteworthy. A straightforward interpretation would be that some

fluorine atoms are consumed during the grafting of the oxygenated functionalities to the carbon lattice, implying therefore a fluorine-mediated reaction mechanism. Such an assumption is supported by the fact that the oxygen-containing functional groups here obtained are clearly different from those formed via the direct action of nitric acid on a non-fluorinated carbon network. Numerous studies [15-18] have indeed shown that the functionalisation by nitric acid of carbon fibres or nanotubes results in the formation of $>C=O$ terminations in significant amounts, whereas these are almost absent here. Further support is gained through the high oxygenation level here obtained, which is quite well above the around 10% functionalisation rate usually resulting from the previous process.

In the second place, one may have a closer look at the nature of the subsisting C-F groups in the oxyfluorinated product. The F_{1s} spectrum of the latter remains characteristic of fluorine atoms attached to carbon, as shown by a corresponding broad hump centred around 689.7 eV (figure 2). However, this apparent average position is upshifted by +2.1 eV, with respect to its value before acid treatment, and is therefore indicative of stronger C-F interactions. One may also note a similar shift in the same direction (see table 1 and figure 1), though of lower amplitude, between the positions of the respective \underline{C} -F signals on the C_{1s} spectra of the CF_x and CO_yF_z products, confirming the stronger nature of the residual carbon-fluorine bonds after oxygen fixation. This can only be explained by the vanishing of the weakest C-F bonds initially present in the precursor material, while the strongest ones have been preserved.

Confronting the two former aspects, a tantalising conclusion is that a selective displacement of fluorine by oxygen can take place. Recent work by Plank et al. [27] has also supported such an hypothesis, following reaction of plasma-prepared F-SWCNTs with 1,2-diaminoethane. However, the extremely low residual fluorine contents obtained after amino-functionalisation reflected a very poor variation in reactivity between the different C-F bond types that the authors identified in their precursor fluorotube samples. Owing to the lower nucleophilicity of the O atom with respect to that of the N atom, selectivity is greatly enhanced in the present study and the evolution in the nucleofugal properties of fluorine atoms grafted to a SWCNT is then given here a solid quantitative basis.

3.2 Primary and secondary mechanisms

Though a formal and detailed mechanistic approach of the O/F exchange process lies beyond the scope of this work, one may invoke a path similar to the one initially inferred to account for the nucleophilic substitution of fluorofullerenes [28], and whose relevance has since been confirmed [29], to presently explain the formation of the –OH groups. The fluorine departure may then take place through the S_N2' mechanism, since a tubular topology prevents the occurrence of a direct backside attack. As conjectured earlier [29,30] in the homologous case of the hydroxylated derivatives of fluorofullerenes, a secondary reaction between hydroxyl and fluorine linked to contiguous carbons can also result in cyclisation. Therefore, it is likely that at least part of the C-O-C functions identified in our oxy-fluorinated SWCNT samples exists under the form of epoxides, which can not be distinguished from alkoxides in the light of the spectroscopic techniques employed in this work.

Yet, it should be noted that according to the former substitution pattern anticipated, an exact balance between the levels of oxygen and fluorine should result, a condition which is not verified in the present case, since the final number of oxygen atoms significantly exceeds that of the missing fluorine species. This unbalance highly likely results from an independent side-reaction involving the direct oxidation by nitric acid of the carbon-carbon π bonds [15-18] which subsist in the precursor fluorotubes. This secondary reaction should therefore be at the origin of the creation of further –OH and C-O-C functions and of the very few $>C=O$ ones detected by IR. It can be hold responsible for the fragmentation observed at the level of the oxyfluorinated carbon frame, meaning marked edge effects on the final O/C stoichiometry determined.

4. Summary and conclusion

Partial fluorination is an efficient way to stimulate the subsequent fixation of organic terminations at the surface of SWCNTs. In order to emphasise the consequences, from a reactivity standpoint, of the

existence of carbon-fluorine interactions of different strength within the overall C-F bonding scheme of an F-SWCNT, we have illustrated the opportunity of a selective O/F exchange. The related mechanism involves the substitution of fluorine by oxygen and the selectivity encountered lies on the enhanced nucleofugacity of those fluorine atoms involved in the weakest C-F bonds present at the surface of a fluorotube. In the short term, one may imagine that the relative proportions of each C-F bond type may be modulated according to the preparation conditions of the initial CF_x precursor, and that so may be the displacement of fluorine by oxygen and the consequent final O/F/C stoichiometric ratio.

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