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Three different modes of fluorine chemisorption at the surface of single wall carbon nanotubes

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ABSTRACT: Three different modes of fluorine chemisorption at the surface of SWNTs have been unambiguously evidenced and their respective amounts quantified, using selective thermal desorption. The C-F bonds formed in this case seem to correspond to the three kinds of bonds previously identified in the different forms of graphite fluorides. The overall bonding scheme in a fluorotube relates to the fluorination temperature used and always consists of a mixture of several C-F bond types in different proportions, making one essential difference with fluorographites. Metastability or different fluorine locations might be at the origin of the phenomenon.

1. Introduction:

The nature of chemical bonding, within a fluorinated inorganic carbon network containing graphene-like structural units, is well known to be able to evolve from the point of view of its properties [1-5]. Regarding bond strength, it has become customary to characterise the weakening of the C-F bond that sometimes occurs in this case, through a downshift of the corresponding IR stretching vibration band [1,2,4]. The shift of the corresponding F_{1s} XPS signal toward the core level binding energy inherent to anionic fluorine has also proved to be a sensitive probe [2-5] of the phenomenon. Such a behaviour has traditionally been interpreted as arising from a diminution of the covalent character of the bond, and is therefore seen as a manifestation of ionicity. This has led to the so-called covalent, ionic or still ionocovalent bonding modes described over decades for graphite fluorides. Note that the latter denomination is preferred to the usual “semi-ionic”/“semi-covalent” terms, largely used in the past, but whose pertinence is widely open to criticism regarding conventional nomenclature. Yet, recent results by Sato et al. and others [6-8] have made the relevance of a truly ionocovalent nature of this intermediate bonding mode highly questionable.

The natural trend to strength variation of the carbon-fluorine chemical bond seems to be favoured by the re-hybridization of atomic orbitals accompanying an appearance of curvature within a carbon network, as well. Bond weakening has thus also asserted itself among the fluorinated derivatives of the carbonaceous materials endowed with a curved skeleton and could be evidenced in different fluorofullerenes [9,10], for instance, using the above mentioned spectroscopic techniques. It is therefore not surprising that the versatility of the C-F bond has then again been illustrated in some academic studies [11-15] of the reactivity, under an elemental fluorine atmosphere, of single-walled carbon nanotubes (SWNTs). The standard spectroscopic procedures have shown in this case that, depending on the fluorination conditions, bonds qualified by the authors as covalent [11-13] or “semi-covalent” [14,15], on the basis of the old classification used for graphite fluorides, can form and seemingly even coexist [14,15], without further clarification. Similar conclusions, regarding a either covalent or mixed

nature of the chemical bond, were reached in the course of more recent studies on fluorotubes obtained by CF_4 or SF_6 plasma treatment [16-19].

In parallel, theoretical investigations [20-23] have been conducted on fluorotubes. They remain of limited acuteness so far, since beside hazards due to computational methods, calculations are usually performed for a pre-determined F/C stoichiometric ratio, a thermodynamic equilibrium state and given chirality/diameter characteristics. Such conditions can be excessively far from the experimental ones since various F/C compositions can be obtained and bundles of SWNTs are involved in the latter case, i.e. mixtures of chirality/diameter parameters. Therefore, the extrapolation of the results of calculations to the interpretation of experimental results is not always straightforward.

This brief state of the art shows that previous investigations on the subject remain by far incomplete since the reason(s) for the occurrence of different C-F bond types in fluorotubes was never discussed. Furthermore, assigning a different degree of polarity to the different bond types present in fluorinated SWNTs (F-SWNTs) becomes more conventional than really rigorous in the light of Sato and others' results [6-8] on fluorographites. A crucial need of information relative to the true nature of chemical bonding in F-SWNTs emerges and the present work then aims at more clearly specifying this question. Accordingly, we have been able to establish an unequivocal discrimination between three main modes of fluorine chemisorption, instead of the two sometimes reported [14-17], as well as their systematic simultaneous presence within fluorotubes prepared at moderately high temperatures. We have then proceeded, for the first time, with an original quantification of their respective amounts by very simple methods. Tentative interpretations for the existence and nature of a mixed bonding scheme in fluorotubes are initiated in the discussion part.

2. Experimental section:

Purified, CVD-grown and open-ended SWNTs were used in the present study. The percentage of atomic oxygen, usually present in such samples under the form of residual functional groups, was

estimated by XPS analysis at about 2-3%. TEM observations (fig. 1) showed that tubes have diameters around 1.5 nm and form bundles. Fluorination was carried out at 100 and 300 °C for four hours on 40 mg batches, under elemental fluorine gas flow maintained upon cooling of the samples (about one hour), within a tubular Monel reactor initially purged with nitrogen until the synthesis temperature was reached. No particular precaution in the preparation of the sample was taken for TGA, regarding preliminary air exposure. Anhydrous KBr pellets were used for FTIR analyses.

3. Chemical bonding in fluorotubes:

Qualitative analysis: The fluorination of two identical SWNTs batches was performed at 100 and 300 °C, as described in the experimental part. TEM observations (fig. 1) confirm that no important damages have occurred at the level of the carbon substrate upon fluorination. Even the initial bundle arrangement is globally maintained in the fluorinated products, though some tubes seem to have been cut at high temperature. As usual, IR spectroscopy has enabled a first qualitative insight into the characteristics of the C-F chemical bond created in the tubular CF_x products thus obtained. Both IR spectra presented in figure 2 display large absorption bands covering the 1000-1300 cm^{-1} zone, and undoubtedly reflecting the coexistence of various types of bonds within the F-SWNTs samples. Indeed, and for comparison to standard fluorocarbon references, it may be worth to here recall the usual narrow IR feature observed around 1220 cm^{-1} [2,4] from fluorographite samples synthesised near 300 or 600 °C under the form of addition compounds. The frequency of the homologous C-F stretching vibration becomes then notably shifted to around 1100 cm^{-1} in graphite fluorides catalytically prepared at low temperature [1,2] under the form of intercalation compounds, revealing a weakening of the bond strength in this case.

Therefore, by analogy with the classification previously established over decades for the latter reference compounds, we will then tentatively ascribe the IR features observed from our present fluorotubes samples, over the similar wave number regions, to the presence of bonds labelled as “Type I

and II” in the following. The part of the signal arising in the present case in the lower $\sim 1050\text{ cm}^{-1}$ wave number region must then be assigned to the signature of a third and still weaker carbon-fluorine interaction, labelled as “Type III”. Note that the present convention comes under pure convenience and does not prejudge of any similitude in the nature of the chemical bonds existing in fluorographites and fluorotubes hitherto. As a mnemonic in view of what is following, one may recall that the higher the “Type number”, the weaker the bond.

Quantitative analysis: It has then been assumed that a sequential cleavage of the three different types of C-F bonds, simultaneously present in both fluorotubes samples, could be performed by progressive thermal decomposition. Conventional thermogravimetric analysis under inert atmosphere has then allowed, in the first place, to bracket the temperature intervals permitting the removal of each type of fluorine. Preliminary runs, performed from the former fluorinated SWNTs samples and illustrated on figures 2c-d, indeed exhibit distinct steps of fluorine desorption, tentatively interpreted as the successive rupture of the so-called “Type III, II and I” bonds, over the respective ranges $50^{\circ}\text{C} < T < 150^{\circ}\text{C}$, $150^{\circ}\text{C} < T < 250^{\circ}\text{C}$ and $T > 250^{\circ}\text{C}$, respectively.

It is however obvious that a direct quantification of the different categories of bonds by simple gravimetry is reliable only if complete desorption of each relevant type of fluorine has ended before the temperature reaches the next critical threshold in the order listed above. Therefore, the accuracy and sensitivity of the method turn out to be greatly enhanced when proceeding in stages, carried out at each of the upper critical temperature previously established. Hence, figure 2 shows that at 150°C , a stabilised weight loss can be achieved, providing evidence of the complete removal of the most loosely bound “Type III” F atoms, but about 24h are required to overcome kinetic limitations. A further, again stabilised, weight loss can then be achieved at 250°C , after a similar duration, as the result of the complete removal of the “Type II” bonds. The amount of “Type I” F atoms is then deduced by difference with respect to the total fluorine content of each sample, previously determined by weight uptake after the initial fluorination process. Previous studies dealing with the thermal degradation of F-SWNTs

[14,24] have shown that gaseous fluorocarbons evolve significantly beyond 250 °C only, so that the upper temperature used here guarantees that exclusively fluorine is released. The results of the quantitative analysis thus performed are compiled in table 1. Not surprisingly, the percentage of fluorine atoms involved in the most robust “Type I” bonding mode is found to increase with the synthesis temperature of the fluorinated products, while that of the halogen species possessing a more pronounced labile character is found to decrease in parallel.

4. Discussion:

The coexistence of mixed bonding properties has remained scarcely evoked within the framework of fluorine addition to SWNTs, and had never really been properly characterised so far, while it is clear from the present work that a gradual classification does exist. It is highly likely that a continuum in the bonding strength even exists inside each of the three categories of C-F bonds here defined, giving the conventional thermograms previously presented their smooth aspect, instead of displaying abrupt transitions. The persistence of a non-homogeneous C-F bonding character, even at 300 °C, i.e. close to the ultimate fluorination temperature before degradation of the tubes starts to occur [11], suggests that the same still holds true in most samples previously reported in the literature and synthesised above 100 °C. The related spectroscopic signatures recorded and previously published have then to be understood in terms of average envelopes reflecting only the predominant type(s) of bond(s).

The first question that naturally arises concerns the origin of such a mixed bonding scheme in fluorotubes, which sharply contrasts with the bond uniformity encountered within other fluorocarbon materials and somewhat, with the results of the theoretical calculations which predict the formation of one single bond type at equilibrium. The first explanation might be that the C-F bond dissociation energy in F-SWNTs strongly correlates to the diameter and/or helicity of a tube. Since bundles of SWNTs consist of mixtures of individual entities with different intrinsic characteristics, fluorination

would then be expected to lead to varied bond strengths. However, one may note that according to some computational investigations [21,22], variation in the tube diameter seems to be the parameter having the greatest influence on bond strength. The diameter distribution in our pristine SWNTs sample being rather narrow, the present hypothesis constitutes at best a partial explanation of the phenomenon here observed. It is more certainly consistent with the idea of a probable continuum in the bonding strength inside a same category of bond, evoked at the beginning of the previous paragraph.

We may then examine, as a second hypothesis, the case of metastability. Isomeric configurations usually exhibit very small energy differences, according to theoretical calculations [20], and can not account for so large variations in the C-F binding energies. Instead, it is highly likely that owing to a high activation energy and/or difficulty in getting ordered at the surface of a tube, some fluorine atoms can be trapped into local energy minima. Such an out of equilibrium C/F subsystem may more surely participate in a satisfying explanation of the non-homogeneous bonding scheme observed in the fluorocarbon networks under study. The increased rate of the most stable bonding mode following the increase of the synthesis temperature seems to confirm the influence of kinetic factors.

At last, one may also infer the existence of secondary binding sites, that can account for further fluorine storage once the most accessible sites saturated. The consideration of such sites is dictated by the topology of the carbon substrate itself. Thus, beside the outer surface of a tube, different regions may contribute to fluorine fixation. The latter include both the interstitial channels between contiguous tubes belonging to a same bundle and the inner hollow core of a tube. Consequently, potential multiple locations of the fluorine atoms within a bundle may also involve notably different bond strengths.

Given the already existing background in fluorocarbon materials science, shortly depicted in the introductory part, the second point to be addressed should logically concern the nature of the C/F association here formed. In other words: if the so important variations in bond strength found in fluorotubes arise as a direct consequence of the scenarios mentioned in the previous paragraph, are they also accompanied by a change in the polarity of the C-F chemical bond ? Though a definitive answer to

the present question requires intensive complementary characterisations and is beyond the scope of this article, we may here try to provide preliminary clues. Thus, an assimilation of the presently revealed three different categories of C-F bonds to the three bond-types depicted over decades in the different forms of graphite fluorides would be highly tantalising, though not straightforward. Nevertheless, such a comparison seems dictated by the similarity in the IR band shifts, which recalls that encountered between the latter CF_x forms.

Hence, the strongest “Type I” interaction that prevails at 300 °C in F-SWNTs can then reasonably be assigned a similar covalent character as that present in the $(C_2F)_n$ addition derivative of graphite, since the latter forms around the same temperature (or still in $(CF_1)_n$ that forms at higher temperature).

The weakest “Type III” interaction, responsible for a high fluorine lability, might compare to the weak ionic bonding mode identified into the $CF_{x-0.1}$ intercalation compounds of graphite, which kind of similarly allows an easy mobility of the fluorine species in the interlayer space [7]. One may then legitimately wonder if such an ionic bond is possible from a SWNT. The answer seems to be clearly yes in the light of numerous works previously devoted to the p-type doping of nanotubes [25], and reporting the formation of charge transfer complexes. In this sense, we may also prudently suggest that the ill-defined IR spectrum, corresponding to the fluorination process carried out at 100°C, has to be related to a high electrical conductivity, in spite of an already appreciable fluorine content (table 1). This could represent an indirect evidence that covalence is insufficiently developed to trap the most part of the charge carriers from the π network and that some C-F bonds might really have a true ionic character.

Finally, given the similarity in their C-F stretching frequencies, one may further assign the remaining “Type II” chemisorption mode to the intermediate bonding mode present in some fluorine graphite intercalation compounds, and previously believed as ionocovalent. Shifts in the position of the main IR absorption band of CF_x compounds toward low wave numbers have usually been correlated with an increase in the polarity of the C-F bond, until recent convincing evidence for a groundless interpretation was given [6-8]. Consequently, it turns out that the IR downshift from “Type I” to “Type II” C-F bonds in our F-SWNTs samples can not be reasonably retained as an evidence of a change in bond polarity.

The same holds true regarding conclusions drawn in earlier papers [14-17] and mentioning the presence of covalent plus “semi-covalent” bonds in F-SWNTs. Following Sato et al. [6] we may then also here retain the hypothesis of a covalent bond, weakened by hyperconjugation with the subsisting π scheme of a tube to interpret the nature of the “Type II”.

A fluorocarbon sample gathering the three independent kinds of C-F bonds separately identified in the different categories of graphite fluorides is an appealing picture, though still somewhat speculative at this stage. In order to emphasise the need of further investigations in this field, we may alternatively refer to a computational study [22] predicting a metastable Van der Waals interaction between an F atom and the surface of a nanotube to account for the weakest “Type III” fluorine sorption mode.

5. Summary and concluding remarks:

It has been shown that the carbon-fluorine interactions within fluorinated SWNTs samples can be classified into three different categories, recalling those commonly associated to the three known classes of graphite fluorides. Nevertheless, whereas the nature of chemical bonding within one of the latter graphite fluoride forms is usually uniform, all three types of C-F bonds are simultaneously present in a fluorotube. The respective amounts of each can be quantified using sequenced thermal desorption procedures, showing that the relative proportions of each type of C-F bond can be modulated according to the synthesis temperature of the CF_x products. We infer that metastable states or different locations of the fluorine atoms are the most probable factors responsible for the variations observed in bond strength.

An extension of the present preliminary approach is in progress in order to try to determine the consequences of such a varied bonding scheme on the chemical properties of fluorotubes. Indeed, a selective reactivity of each C-F bonding mode is expected, the weakest ones conferring the F atoms enhanced nucleofugal properties and hence, a greater exchanging power. The differentiated atomic labilities that result may then pave the way toward innovative methods of derivatization of SWNTs materials.

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Table and figure caption

Table 1. Relative amounts of the different C-F bonding modes according to the synthesis conditions.

Figure 1. TEM observations of the pristine SWNTs (left) and F-SWNTs obtained at 300 °C (right).

Figure 2. FTIR spectra (absorbance) and thermogravimetric analysis of the SWNTs samples fluorinated for 4h at 100 °C (a, c and e) and 300 °C (b, d and f).

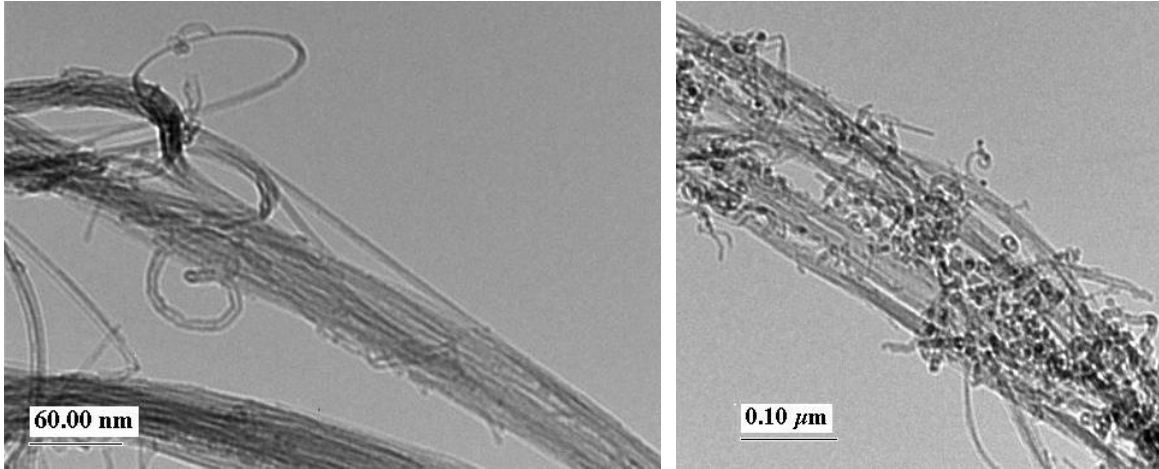


Figure 1

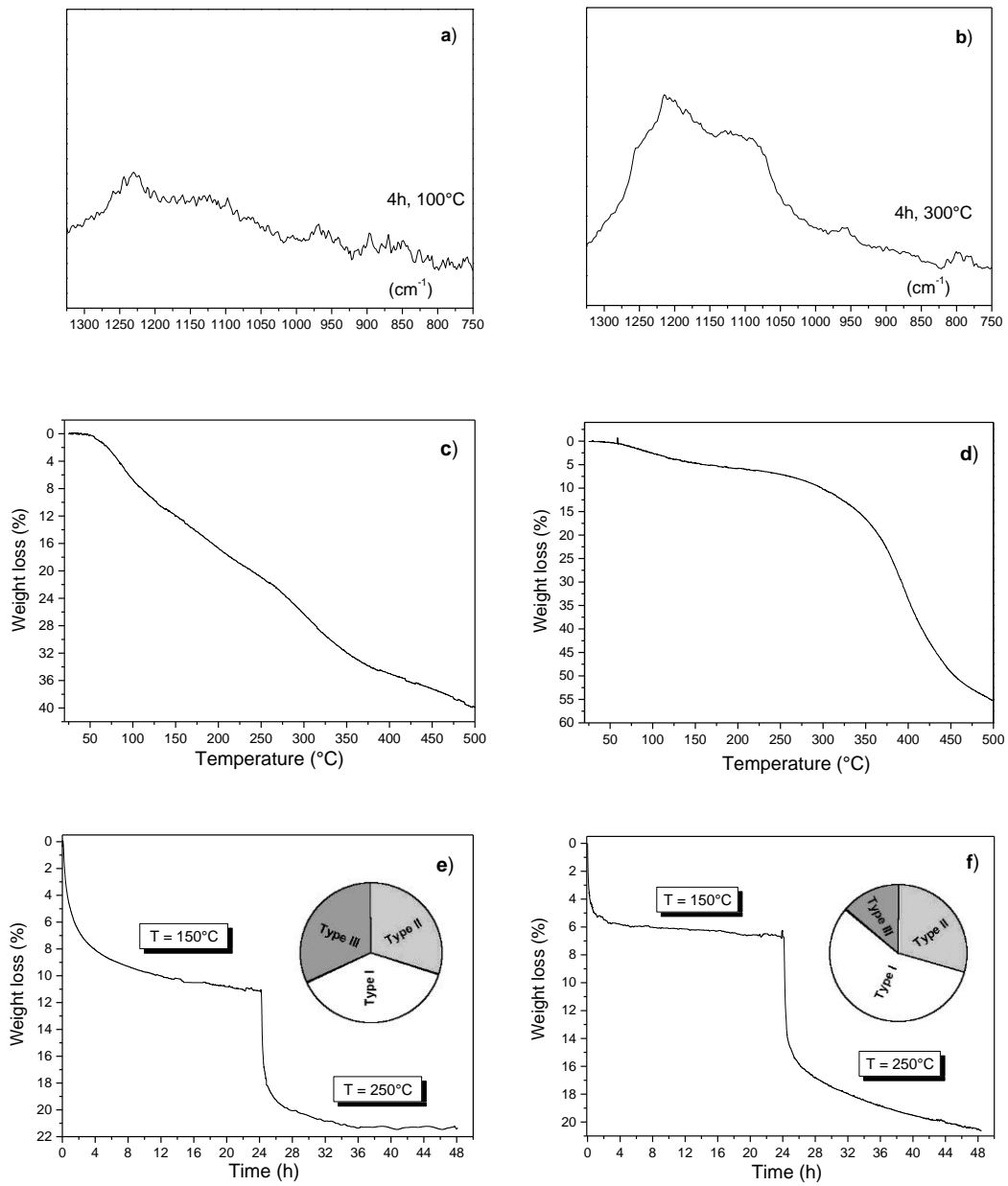


Figure 2

Fluorination temperature

C-F bonding	100 °C		300 °C	
	% atomic F involved	F/C ratio	% atomic F involved	F/C ratio
Type III	31.8 %	CF _{0.11}	14.0 %	CF _{0.08}
Type II	30.0 %	CF _{0.10}	29.3 %	CF _{0.16}
Type I	38.2 %	CF _{0.13}	56.7 %	CF _{0.32}
Total ⁽¹⁾	100 %	CF _{0.34}	100 %	CF _{0.57}

(1) Determined by weight uptake after fluorination.

Table 1