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Fluorine addition to single-wall carbon nanotubes revisited

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ABSTRACT: Contrarily to the widely-held opinion, the addition pattern issuing from the high temperature fluorination of single wall carbon nanotubes does not consist of a distribution of *exo*-addends on the outer surface of a tube. Instead, fluorotubes possess a varied bonding scheme consisting of graphite fluoride-like, fluorofullerene-like and internally “addended” sections.

1. Introduction:

The set idea of an *exo*-addition pattern, following fluorine addition to a single-walled carbon nanotube (SWNT), has intuitively prevailed hitherto [1-6], guided by the initial view using scanning tunneling microscopy (STM) [1] on the outer profile of a fluorotube (F-SWNT) and probably also influenced by antecedent findings about the parent, *exo*-functionalised, fluorofullerene molecules [7-11]. Yet, attention should be drawn on the facts that STM does not allow observation of inner regions, which might well bias our empirical apprehension of such systems, and that fullerene molecules are closed cages which only permit external “addending”, while this is usually not the case for tubes, open at tips most of the time. Consequently, a more rigorous state of mind on the question is necessary and in parallel, seems also dictated by the most recent experimental characterisations performed on F-SWNTs. Hence, the existence within such entities of a mixture of up to three different C-F bond types, differing by their respective strength, has been mentioned by several authors [12-16] but without reliable explanation regarding their origin up to now. Though it has sometimes been argued [12-14] that the former differentiation between the fluorine chemisorption modes present in single-walled fluorotubes has to be related to the emergence of an enhanced partial ionic character at the level of some bonds, the irrelevance of such a bonding concept for fluorocarbons is now established both experimentally and theoretically [17-20].

The present brief overview brings to light that, contrarily to a widespread opinion, F-SWNTs exhibit too important disparities, of unknown origin, in their bonding properties for a selectively *exo*- decoration of their surface with fluorine addends to be inferred. Therein, a new model of organisation is proposed.

2. Results:

A sample of bundled SWNTs has been fluorinated at 300 °C for two hours, up to the final nominal composition C_2F , following a procedure already described [16]. After fluorination, the TEM micrograph on figure 1a seemingly shows local swelling in the sidewall of the scarce individualised tubes observable, that may witness the already depicted [1] sequenced character of fluorine addition along the main axis. Yet, no advanced conclusion regarding the atomic scale architecture can be drawn from such a direct observation. The corresponding F_{1s} XPS spectrum is made of an apparently single symmetric feature centred on 687.5 eV, not excluding the presence of unresolved components, however. On the other hand, the IR spectrum (fig. 1b) spreads over a wide wave number range and is therefore consistent with the presence of several C-F bond types, which *a priori* contrasts with the conceptual view of a simply *exo*- spatial distribution of fluorine.

Accordingly, the less sophisticated way to tentatively account for an again evidenced divergence in the fluorine chemisorption modes present in fluorotubes consists in anticipating a multiple location of the fluorine addends. Given that grafting to a tubular sidewall can be made following two distinct ways only, i.e. either from the inner or from the outer side, the simple mixed bonding scheme illustrated on figure 2 forces then itself upon us and would well account for up to three energetically different categories of C-F bonds, in compliance with earlier experimental statements [12-16]. Indeed, from the energetic standpoint, one can intuitively postulate stability in the respective order: group I > II > III, so that II and III appear as metastable subsystems that may be at the origin of progressively softened covalent bonds. As a matter of fact, fluorine atoms of group I abide by the well-known architecture [17] of the highly stable $(CF)_n$ compound (poly-monocarbon fluoride), while fluorofullerene-like motives of group II are destabilised by local strain at the level of the carbon frame plus probable steric

hindrance between nearest neighbours in eclipsed position, if 1-2 addition is respected. The group III *endo*-addends possess a still more reduced stability, owing to the concave deformation that they should generate at the convex carbon surface and also to their probable mutual steric repulsion.

The pertinence of this model finds a proper justification throughout different experimental and theoretical facts. First, the structure of fluorinated multiwall carbon nanotubes was claimed to be made of a stacking of rolled (CF)_n-like sheets [21,22], in which addends regularly alternate on both sides of a corrugated carbon sheet, so that at least partial filiation is highly likely to occur when dealing with single-walled homologues. In parallel, the scarce computational investigations [5,6], which considered such an *a priori* exotic succession of *exo/endo*- fluorine addends on the sidewall of an F-SWNT, concluded in the enhanced or competing thermodynamic stability of this latter functionalisation pattern with respect to its equivalent but purely *exo* counterpart. More importantly, the ¹⁹F NMR spectrum of F-SWNTs synthesised at high temperature was described [23] as being made of a broad hump centred on -175 ppm, which is very close to the -180 ppm chemical shift recorded for the (CF)_n compound [17]. All these points suggests almost unambiguously that (CF)_n-like sections should constitute a notable, if not dominant, part of the fluorine addition pattern within F-SWNTs, contrarily to the more intuitive than really rigorous former interpretations made. Moreover, the present IR spectroscopy data strictly confirm this latter assumption. Indeed, the spectrum displayed on figure 1 distinctly shows a major absorption band at 1205 cm⁻¹, approaching the well-known feature at 1215-1220 cm⁻¹ that characterises the C-F stretching vibration in the (CF)_n compound. The small frequency downshift simply occurs as a manifestation of the curvature effect on bond strength.

In the second place, IR spectroscopy also fully confirms the parallel existence of fluorine atoms belonging to the second group here envisaged. Indeed, a broad but distinct

absorption feature is clearly apparent over the 1100-1170 cm^{-1} zone, which is the typical main absorption range of the *exo*- C-F moieties present in the structurally parent fluorofullerene molecules [7-11], taken as reference. Note also the presence of a significant shoulder near 1250 cm^{-1} which perfectly matches to the lateral bands of the global fluorofullerenes' signature in the IR region [7-11]. The coexistence of a fluorofullerene-like subsystem in the overall addition pattern of F-SWNTs is therefore highly likely, as well. In this framework, the earlier interpretation of fluorine addition to SWNTs appears partly correct but with the present essential differences that *exo*-addition is definitely not the unique grafting mode occurring, is not necessarily dominant quantitatively speaking, and is certainly not the thermodynamically stable addition scheme.

Finally, the existence of the third category of fluorine addends seems in turn not contradicted by a weak absorption tail around the 1050 cm^{-1} region and below*, but happens to be more difficult to strictly establish since no homologous reference compound is known. However, some authors reported [24] that, at constant final F/C ratio, the comparative fluorination at high temperature of open versus closed-end SWNTs generates a lesser intertubular expansion if tubes are open. This is an indirect experimental evidence that fluorine atoms are able to graft to the inner side of a tube according to mode III. In parallel, the opportunity of formation of *endo*-“addended” fluorotubes has also been well established by theory [3,25], though less energetic than the former *exo*- or *endo/exo*- fluorinations.

* It might be prudently inferred that the tooth at 960 cm^{-1} might also witness the formation of addends of the third group, but we have also observed [21] such a feature in the IR spectrum of fluorinated multiwall carbon nanotubes endowed with the $(\text{CF})_n$ structure, so that this minor peak can arise from addends of the first group too.

3. Discussion:

Alternatively, it might be argued that bond mixing in F-SWNTs could also be the result of the formation of a mixture of distinct solid phases. Fluorotubes are indeed known to be fragile macromolecular edifices, rather easily turning to multishell carbon phases [13,26,27]. The re-fluorination of such degradation products in the course of the synthesis process could then well produce the (CF)_n-like C-F bonds identified, for instance. However, such an eventual mechanism should be limited by the short exposure time used here and above all, we have observed only very scarce multishell particles during our TEM observations, showing that a potential post-conversion to a (CF)_n-like phase can not be held responsible for the strong signature at 1205 cm⁻¹ and that the corresponding bonding scheme is therefore intrinsic to a fluorotube.

Interestingly, the present multisite model for the fluorine arrangement on the surface of a SWNT allows to *a posteriori* justify the varying IR characteristics of fluorotubes depicted throughout different works [12,14-16], by simply considering that the different C-F groups form in different proportions according to the synthesis conditions (see below). The reason why the characterisation of F-SWNTs has often led to varied core level spectroscopic signatures throughout the literature (either multicomponent F_{1s} XPS spectra [13,14] or falsely single F_{1s} profiles as obtained here and elsewhere [20,23,24] or still in many other works) can now be foreseen and also simply depends on the more or less pronounced prevalence of one bonding mode within each sample under study. Indeed, upon implicit but reasonable acknowledgement that changes occurring at the core level also mirror those occurring at the valence level on going from group I to group III C-F bonds, the latter spectroscopy will happen to be highly sensitive to the individual C-F bond energies, i.e. to the individual bond types. Evolution in the binding energies of F_{1s} peaks can then be simply accounted for from

charge-independent changes in the C-F bond energy diagram, avoiding recourse to the now obsolete ionocovalent model for fluorocarbons.

The forthcoming paragraphs will deal with the reasons why synthesis conditions should undoubtedly exert a strong influence on the final quantitative constitution of the mixed bonding scheme, giving birth to the above mentioned apparent discrepancies in the characterisation from sample to sample. Some experimental observations [13,16] have already indicated that the synthesis temperature is a key parameter affecting the respective proportions of the so far unidentified various bond types within a fluorotubes sample, but the fluorination method retained (gaseous fluorine vs fluorinating agents, plasma techniques...), the reaction time (see [15]) and some morphological characteristics at the level of the precursor SWNTs batch (average tube diameter, bundled or individual tubes...) may also more or less significantly influence the way the final global fluorine arrangement will look like. It turns then out that the maintenance of the surface motives characterising groups II and III, with respect to the more energetically favourable disposition of group I, must arise from kinetic limitations that are progressively overcome upon increasing the synthesis temperature and/or reaction time, allowing the whole set of addends to evolve toward the most stable of the three subsystems. In this context, the most reliable addition pathway toward the formation of fluorine addends of the first group is a “backside completion” of the groups II and III motives, which additionally implies potential rearrangement if 1-2 addition initially prevails. Indeed, in terms of probability, the direct creation of group I motives seems difficult, because simultaneous attack on opposite sides by two fluorine molecules is required. Therefore, the stepwise creation of addends of the first category should slow down their apparition, so that a high temperature and a significant reaction time will be required to observe their proliferation over the surface.

At last, some complementary mechanistic grounds responsible for a facile development of *endo*-fluorination can be reasonably anticipated, as well. Indeed, a bundled arrangement of tubes often prevails within SWNTs samples. Owing to the compactness of such nanosized ropes, the diffusion of fluorine molecules into the bulk of the carbon lattice is hindered from the lateral sides. Fluorine admission must then rather occur from the bundles tips, where different apertures pre-exist. Consequently, fluorine species will diffuse into the compact network either via migration in the intertubular channels or directly through the hollow core of a tube. The cross section of a tube being about ten times that of an interstitial channel, the contact of fluorine molecules with the inner side of a tube rather than with the outer side is clearly favoured, facilitating *endo*-addition. In such conditions, a high temperature route is necessary to initially provide sufficient kinetic energy to the fluorine molecules and carbon lattice, so that to force “de-cohesion” within the ropes and to allow the parallel formation of the other addition modes.

4. Summary and conclusion:

We have pointed out that the *exo*-fluorination of SWNTs has so far been established more empirically than rigorously. Furthermore, experimental and theoretical results [17-20] have shown that the ionocovalent model that has asserted itself over decades to describe chemical bonding in some graphite fluorides was largely erroneous. The extrapolation of such a model to interpret the results of SWNTs fluorination becomes then highly criticisable. Consequently, all previous experimental observations made on single-walled fluorotubes can rather be accounted for by assuming a mixed bonding scheme that includes graphite fluoride-like, fluorofullerene-like and internally “addended” cylindrical sections.

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Figure caption

Figure 1. (a) TEM observation and (b) IR spectrum of the C₂F F-SWNTs sample.

Figure 2. Schematic representation of the overall fluorine addition pattern to SWNTs.

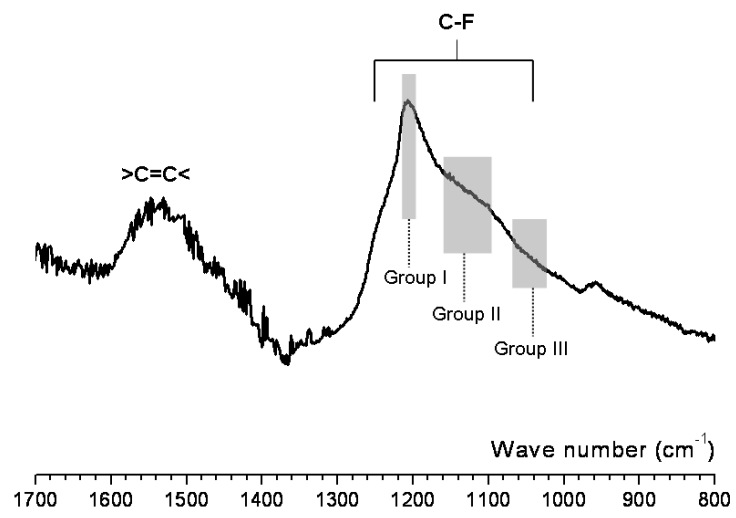
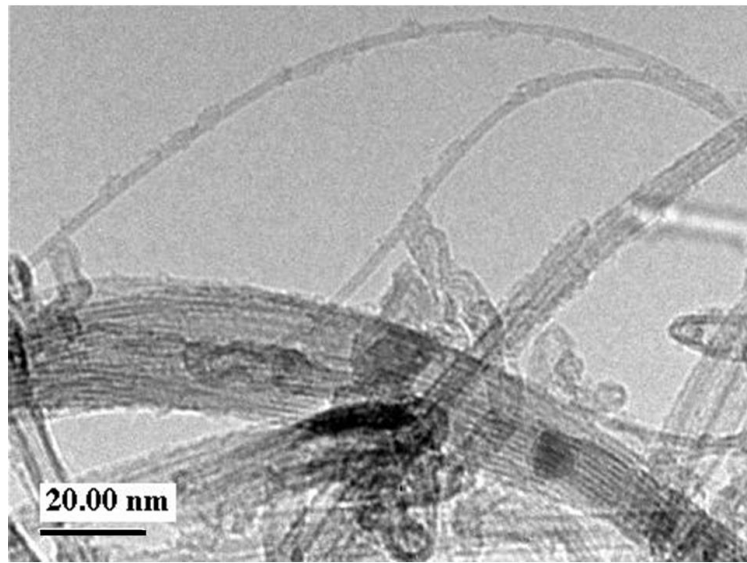


Figure 1

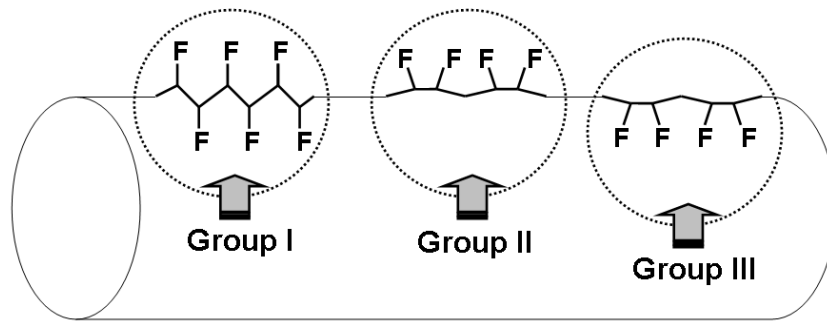


Figure 2