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# **A kinetic, morphological and mechanistic approach of the fluorination of multiwall carbon nanotubes**

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**ABSTRACT:** A comparative study of the fluorination of MWNTs batches of different origin has been performed. Both the addition kinetics and structural organisation of the fluorinated derivatives correlate with the rate of defects initially present in the carbonaceous precursor. These experimental observations lay the foundations for a tentative mechanistic approach of the fluorination process of MWNTs.

## 1. Introduction:

The part of the oxidative chemistry of multiwall carbon nanotubes (MWNTs) that has been discovered hitherto, includes both intercalation [1] and addition compounds [2-8]. Thus, efficient oxidative addition patterns are known with oxygen [2-4] or fluorine [5-8], only. Fluorination is unique in the sense that it represents the only process that can lead to a bulk-addition in the case of MWNTs. Very few attention has been paid to the corresponding fluorinated derivatives, however. So far, it has been shown that the latter mimics to some extent the fluorination chemistry of graphite. Indeed, a covalent  $(CF)_n$  product can be obtained at 500°C [5,6] while, near room temperature and under catalytic conditions,  $CF_x$  intercalation compounds in which the C-F bond possesses a weaker covalent character form, in the vicinity of the outer surface [5,6].

To our knowledge, no comparative study of the fluorinated products derived from MWNTs endowed with different characteristics has been reported. Yet, such information would deserve serious investigation since it may be anticipated that such fluorinated derivatives might be potentially interesting candidates as reinforcing agents of a polymeric matrix, or as lubricants, as recently evidenced [9-11] from their single-walled homologues. In this work, we have observed the fluorination kinetics of MWNTs presenting radically different initial textures, starting from arc-discharge (few surface defects) or CVD-grown (numerous defects) MWNTs batches as model extrema. We then give a morphological description of the subsequent fluorinated products that are obtained at high temperature, according to the initial characteristics of the pristine MWNTs and final fluorine content. In a last step, we have further attempted a mechanistic approach of the fluorination process of MWNTs in order to explain the divergence in the kinetics and final structural arrangements observed.

## **Experimental conditions:**

MWNTs of arc-discharge origin were bought from Aldrich. CVD-grown tubes were catalytically prepared from the disproportionation of carbon monoxide over MgO-supported Co particles at 510 °C, as reported earlier [12]. Each batch was purified according to procedures including heat treatment in air followed by acid bath and already described [13]. Fluorination was carried out at 520 °C, under an elemental fluorine gas flow at 1 Bar, maintained upon cooling of the samples, within a tubular Monel reactor initially drained with nitrogen until the synthesis temperature was reached. The final F/C stoichiometric ratios were determined by weight uptake between the pristine carbon sample and the final fluorinated product, each time.

## **2. Results:**

TEM micrographs in figure 1a clearly display the initial structural differences between the precursor carbonaceous materials used, generated by their respective processing. Not surprisingly, arc-discharge tubes (fig. 1a-2) present a well organised succession of concentric layers containing few defects, while the low temperature CVD process generates a less ordered material in which wall disruptions and waviness are frequent (fig. 1a-1). The interlayer separation is close to 0.34 nm each time. Tubes are open at one end at least.

At 520°C, the amount of fluorine that adds to the carbon matrixes evolves more or less quickly, as shown on figure 2. The initially black colour of the carbon samples progressively turns from brown to cream-white and finally white for moderate fluorine contents, in the vicinity of F/C =1 and for the saturation fluorine level, respectively. It was also checked that

fluorine addition under such conditions goes in parallel with the appearance on IR spectra of the usual strong absorption band at  $1215\text{ cm}^{-1}$ , characterising the stretching vibration of the covalent C-F bond. TEM observations in figure 1 and kinetic curves plotted on figure 2 further show that fluorine addition can readily lead to the complete fluorination of a tubular carbon lattice (fig. 1b), provided sufficient time is let to the reaction to complete to its end. The corresponding duration happens to strongly depend on the MWNTs batch used and therefore correlates with the initial rate of defects within each of the pristine carbonaceous materials. The  $F/C = x$  stoichiometric ratio can even exceed 1, owing to the creation of  $>CF_2$  and  $-CF_3$  groups on edges and at local defect sites, as earlier observed in graphite monofluoride prepared at high temperature. In comparison to single wall carbon nanotubes (SWNTs), for which a maximum fluorination temperature of about  $300\text{ }^\circ\text{C}$  constitutes a critical threshold before degradation starts to occur [14], MWNTs appear much more resistant. This enhanced stability arises from the reduced curvature of the network but also reflects the key role of relaxation effects i.e. ruptures along the sidewall, in diminishing internal strain within the final structure. At the same time, the maximum stoichiometry that is usually reported for fluorinated SWNTs is close to  $F/C = 0.5$  [14-17], whereas fluorination to saturation of the carbon shells can occur here, without degradation of the substrate. This indicates that both sides of the curved sheets must be fluorinated, yielding more or less ordered rolled homologues of poly-monocarbon fluoride  $(CF)_n$ .

Like the addition kinetics, the microstructural morphology within the fluorinated materials is also found to depend on the initial rate of defects. Fibrous imprints still persist after fluorination above  $500^\circ\text{C}$ , but local order varies with the nature of the precursor carbon nanotubes. Thus, in CVD-grown MWNTs, looking at the atomic scale shows that, though poor, some degree of order exists. The presence of lattice fringes following TEM characterisation (fig 1b) reveals a partially ordered stacking of fluorocarbon fragments along

the direction perpendicular to the tube axis. The atomic arrangement consists of the superposition of misoriented small domains, inside which the averaged interlayer distance is 0.65 nm, as revealed by X-ray diffraction. TEM observations also seem to indicate the absence of a hollow core and therefore, the loss of the tubular character. Conversely, in tubes issuing from the arc-discharge process, long fluorinated domains aligned with the tube axis and with a seemingly larger coherence length along the radial direction prevail, as shown on figure 1c. The average interlayer distance is also close to 0.65 nm and the tubular morphology is clearly maintained. More importantly, figure 1c also shows that fluorination can lead to the preservation of a lamellar inner core of pure carbon. Therefore, a partial fluorination rate, i.e.  $x < 1$  in  $CF_x$ , must be interpreted as the superposition of a set of completely fluorinated layers over a set of non-fluorinated carbon layers. This is a strong indication about the way fluorine addition must take place throughout the bulk, as seen in the following.

Consequently, it turns out that a control on both the final degree of order and fluorine content within multiwall fluorotubes can be exerted by proper selection of the carbon precursor and adjustment of reaction times, giving a basis to an engineering process. The latter factors should strongly influence the lubrication or reinforcing properties of such materials, for instance, and intuitively suggest that they may therefore afford some kind of optimisation of the performances in these fields. We shortly emphasise their potential impact throughout the following prospects. Thus, the lubrication durability of single wall fluorotubes was shown [11] to be limited by cracking, owing to the weakening of the frame induced by fluorination. Multiwall fluorotubes might then appear, at first glance, as a possible alternative. Indeed, the partial fragmentation induced by fluorination results in a relaxation of the internal strain which improves flexibility and hence, might help in the preservation, under a mechanical constraint, of tubular-shaped nanoparticles playing the role of nano-bearings. In the second place, one may also try to anticipate to which extent partially fluorinated MWNTs

as those figuring in 1c may efficiently ensure the mechanical reinforcement of composites. Their use would indeed involve a complex combination of effects, i.e. that of a fluorinated outer surface improving dispersion and/or interactions at the fibre-matrix interface and that of a sliding and highly resilient inner carbon core.

### **3. Discussion:**

Basically, the direct penetration of fluorine inside the interlayer space from the tubes edges can be excluded, since otherwise, fluorination would directly occur over the whole thickness of a tube. The opportunity of preservation of an inner carbon core undoubtedly shows that this is not the case. It seems then reasonable to assume that the overall fluorination mechanism of any MWNT follows a scheme allowing progress of a fluorinated front perpendicularly to the tube axis. However, since both the addition kinetics and the intrinsic structural order within the final multiwall fluorotubes strongly depend on the rate of initial defects in the pristine carbon material, this must imply variations in the fluorination mechanism.

In the case of arc-discharge tubes, the rather well organised final material observed suggests the occurrence of concerted successive steps. Accordingly, we propose a “zipper” model, in which attack by fluorine starts by the outermost sidewall. Once the latter is fluorinated, the corresponding shell radius is notably expanded, upon changing the associated carbon-carbon bond order from double to simple, and so is the interplanar distance with the immediately underlying wall. The separation is now large enough to allow diffusion, from the edge, of fluorine molecules between the first and second outer walls, involving fluorination of the latest, on the border region first logically. A local radial inflation follows, due to the lengthening of carbon-carbon bonds and a mechanical strain is then exerted on the previously

fluorinated adjacent envelope. This induces tearing on the border of the latter (fig. 3a bottom), in order to maintain a physically reasonable local Van der Waals gap between the two superimposed fluorinated zones. The diffusion and subsequent fixation of fluorine molecules can then rapidly progress along the longitudinal axis of the tube, within the area comprised between the first two outer shells (fig. 3a, bottom). The ripping of the upper one is thus propagated concomitantly, recalling the opening of a zipper. In the meanwhile, the diffusion of fluorine molecules in the interlayer space comprised between the second and third outer walls becomes possible according to the same scheme, and so on... We believe that such a speculative fluorination//rupture sequence may efficiently contribute to the preservation of some kind of order within the lamellar organisation of the final fluorinated material (fig. 3a, upper right).

In the case of tubes catalytically prepared at low temperature, in spite of a seemingly identical overall mechanism, the initial presence of numerous ruptures along the sidewalls involves as many independent multi-site attacks. Indeed, once the outermost shell fragments fluorinated, the diffusion of fluorine toward the inner core, according to the scheme previously depicted, is made possible at the level of each pre-existing discontinuity (fig. 3b, left). Owing to the independent character of each local attack, the progression of the fluorinated front is not constant, depending on the easiness with which the radial diffusion of fluorine can take place across each zone, i.e. on the local density of pre-existing defects encountered level by level. Non correlated regimes over different regions should induce loss of coherence (fig. 3b right) between the atomic rearrangements that follow fluorine fixation, resulting in rather randomly spaced layers. Hence, such a multi-site pattern is at the origin of a much faster overall fluorination regime and turns out to be less propitious to the preservation of a regular final lamellar organisation.



#### **4. Summary and conclusions:**

The addition kinetics and morphological profiles issuing from the fluorination of MWNTs strongly correlate with the presence of structural defects in the precursor carbon material: the higher the initial rate of defects, the faster the addition regime. The presence of numerous pre-existent defects seems to hinder preservation of ordered layers in the final fluorinated material, as well. Based on such experimental observations, the different steps involved in a fluorination mechanism have been tentatively assessed. The different characteristics here evidenced provide strong suspicion that a tuning effect on some properties of multiwall fluorotubes materials can result, likely to stimulate further development in the corresponding field.

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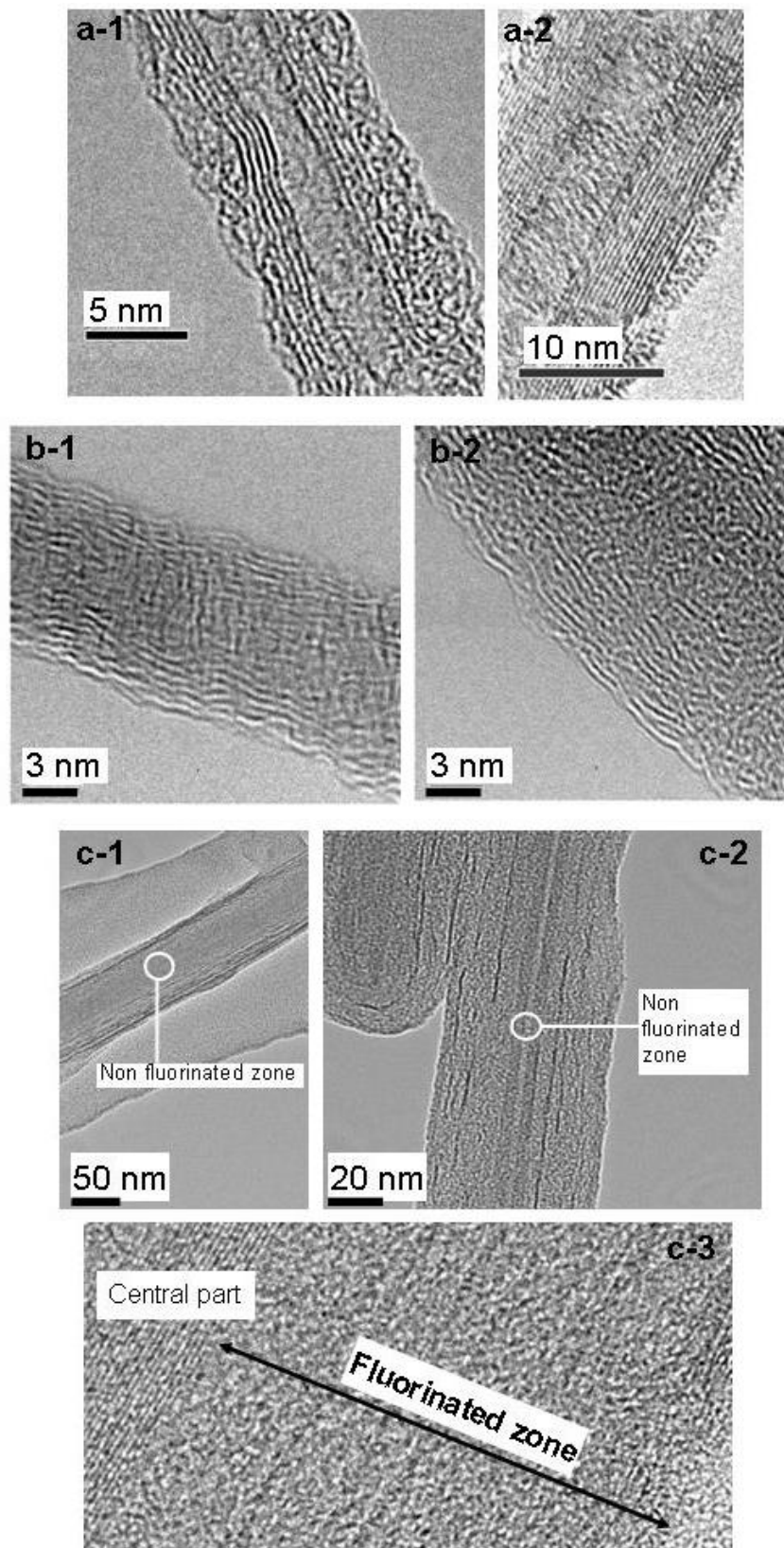
## Figure caption

**Figure 1.** TEM micrographs reflecting the structural order present within the (a) pristine CVD-grown (a-1) and arc-discharge grown (a-2) MWNTs (b) catalytic tubes fluorinated up to saturation (c) arc-discharge tubes partially fluorinated during 6h.

**Figure 2.** Composition vs reaction time, at 520 °C.

**Figure 3.** Schematic illustration of the (a) well-sequenced pattern presumably accounting for an ordered arrangement of fluorocarbon shells (b) effect on stacking of a random fluorine addition, initiated by differentiated diffusion paths (Arrows indicate the directions of propagation of fluorine).

**Figure 1**



**Figure 2**

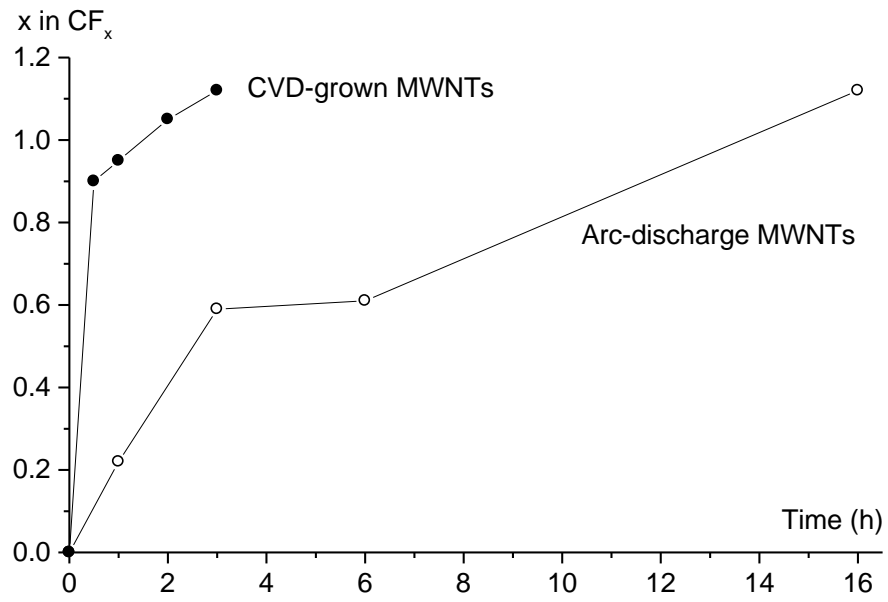


Figure 3

