

In situ X-ray diffraction observation of two-step fullerene coalescence in carbon peapods

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Abstract – We report an *in situ* X-ray diffraction study of the high-temperature coalescence of C₆₀ and C₇₀ peapods. The monitoring of the structural evolution with time at two successive temperatures (1000 °C and 1200 °C) allows highlighting the occurrence of a two-step process for both peapods samples. The first step of the process, slower for C₇₀ peapods than for C₆₀ ones, is attributed to the transformation of individual molecules into corrugated tubules recalling the fullerenes one-dimensional periodicity. Even after long annealing time at 1000 °C this transformation is found to stagnate, until the temperature is set higher than 1050 °C, where the corrugated tubules evolve into well-formed inner nanotubes.

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Introduction. – Besides chemical vapor deposition [1], one way to synthesize double-walled carbon nanotubes (DWNT) is to use single-walled nanotubes (SWNT) containing fullerenes, or “peapods”, as a starting material [2,3]. The coalescence at high temperature of fullerene molecules into an inner nanotube paves the way towards DWNT diameter selective large scale synthesis. Indeed, former X-ray diffraction (XRD) [4,5] and Raman [6] studies have shown that the inner tube diameter depends on both the outer tube diameter and the synthesis temperature.

It has been shown that fullerene coalescence inside nanotubes starts above $\sim 800^\circ\text{C}$ [3] and that the kinetics of the transformation depends on the atmospheric environment [7]. Raman and diffraction studies [8] have moreover shown that the transformation process goes through an intermediary state with corrugated tubules in which the fullerene periodicity remains. However, previous experimental studies of fullerene coalescence in peapods were performed *ex situ* [3–9], and despite theoretical studies [10–14], the formation of DWNTs from fullerenes peapods is not yet fully understood. Computational simulations have suggested that, for C₆₀ peapods, the coalescence process occurs through Stone-Wales rotations,

after (2+2) cycloaddition polymerization, occurring for facing double bonds between neighboring molecules [12]. In the case of C₇₀ peapods, depending on the tube diameter, the C₇₀ molecules are found either in a lying or a standing configuration at room temperature, in which their long axis is, respectively, parallel or orthogonal to the tube axis [15–17]. Due to geometrical constraints, lying molecules cannot rotate at high temperature [5] and a molecule coalescence mechanism involving (2+2) cycloaddition appears unlikely. Yet, C₇₀ coalescence is observed in the same conditions as C₆₀ [5], which questions the validity of the simple cycloaddition process as a first step for the coalescence. Some authors have suggested that the coalescence process may involve the migration of free-standing atomic carbon atoms [6,9].

In order to bring new experimental insight on DWNT formation from peapods, the next step is to perform *in situ* measurements and to study the kinetics of the transformation at various temperatures. In this letter, we report the first *in situ* XRD study of C₆₀ and C₇₀ peapods coalescence. Monitoring of the structural evolution with time at two successive temperatures (1000 °C and 1200 °C) allows us to demonstrate the occurrence of a two-step process for both C₆₀ and C₇₀ peapods samples.

Experiment. — We have prepared C_{60} and C_{70} peapods samples in the form of buckypapers, as described in refs. [18,19]. The peapods synthesis procedure consists essentially in heating opened nanotubes (in the form of buckypapers) together with a fullerene powder at 500 °C in vacuum, so that the powder sublimates and the fullerenes adsorb inside the nanotubes. The samples were further pressed into pellets in order to increase their density.

XRD measurements were performed on the beamline DIFFABS at synchrotron SOLEIL, using a Buehler oven with beryllium windows, under 10^{-6} mbar dynamic vacuum. X-rays incoming wave length was 1.409 Å. The temperature ramps we used are plotted in fig. 3: temperature increase rate during the ramps was of 15 °C/min. Due to time constraints during the experiment, the 1200 °C plateau for the C_{70} peapods sample was limited to 55 minutes. Images taken during 1 minute were collected continuously using an XPAD3.1 hybrid pixel detector [20,21]. The detector is made of several inclined tiles (chips) surrounded by a guarding ring, resulting in the “holes” visible in the diffraction diagrams in figs. 1 and 2. The obtained diffraction diagrams have been normalized to monitor and subtracted of the measured background due to sample environment.

The peapods are preferentially aligned within the pellet plane, with in-plane isotropy. The beam was set perpendicular to the pellet plane in order to observe homogeneous diffraction rings on the detector (two perpendicular scattering directions would stand out in the case of a beam parallel to the sample plane [17,22–24]). In the chosen experimental geometry, the signal arising from the one-dimensional (1D) fullerene chains is thus increased compared to the powder case, which allows a fine monitoring of the inter- C_{60} distance.

Results and discussion. — We first discuss initial and final states, before and after the heating procedure. Typical XRD diagrams measured at room temperature are shown in fig. 1(b). Peapods diffraction diagrams feature peaks characteristic of the organization of the peapods in hexagonal bundles. These bundle peaks are indexed with their Miller indices (hk) in the reciprocal hexagonal lattice. In addition, the C_{60} peapods diagram features a sawtooth peak at $\sim 0.64 \text{ Å}^{-1}$ (marked with an asterisk) that is characteristic of the 1D ordering of the fullerenes inside the tubes [25–27]. One can show that it is not the maximum of the sawtooth peak but its inflection point position (Q_1) on the small Q side that is related to the average inter-fullerene distance within the chains by $Q_1 = 2\pi/L$ [27,28]. Moreover, in the case of C_{70} peapods, the ovoid fullerene molecules can adopt two configurations, namely “lying” (L) or “standing” (S), in which the C_{70} long axis is, respectively, parallel or orthogonal to the nanotube axis. These two configurations result in two different inter- C_{70} distances and thus in two peaks in the diffraction diagram [26].

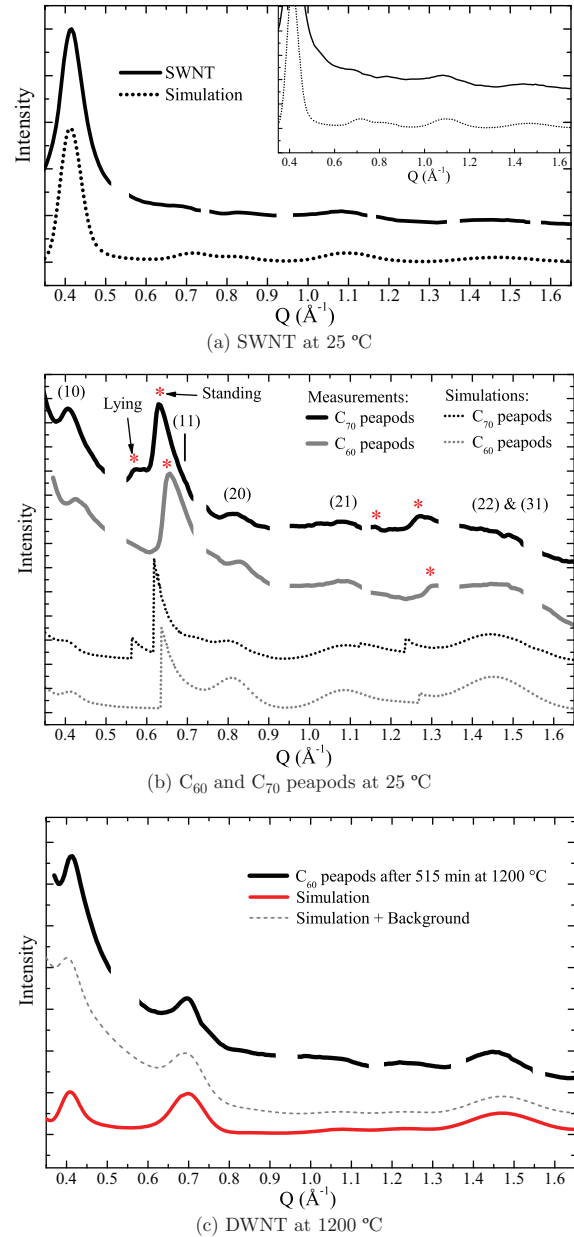


Fig. 1: (Colour on-line) Experimental and simulated XRD diagrams of empty nanotubes (a), C_{60} and C_{70} peapods (b), and of C_{60} peapods fully transformed into DWNT (c). In (b), a Gaussian background centered in $Q = 0$ is added to the calculated diagram in order to account for sample porosity effects, etc.

We have simulated the diffraction diagrams of the samples in their initial and final states using an improved version of the model described in refs. [25,26]. This version takes into account the anisotropy of the pellet samples with a Gaussian off-plane misalignment of $\pm 30^\circ$ [24], which results in modifications of the relative intensities of the peaks characteristic of 1D fullerene periods and

of the (hk) peaks, compared to the powder case [24]. Figure 1 shows that all experimental diagrams are well reproduced using the following parameters: a Gaussian outer-tubes diameter distribution centered at 14.2 \AA with Full Width at Half-Maximum $\text{FWHM} = 2.0 \text{ \AA}$; inter-tube distance in triangular lattice: 3.2 \AA (SWNT and peapods at room temperature) or 3.4 \AA (DWNT at 1200°C); bundle mean size: 85 tubes; inter-wall distance inside DWNT: 3.6 \AA ; inter-fullerene distance: 9.9 \AA (C_{60}), 10.2 \AA (standing C_{70}) and 11.2 \AA (lying C_{70}); nanotubes initial filling ratio by fullerene molecules: 97% (for both peapods, as determined for the C_{60} sample in a previous study [27]); lying/standing (L/S) switching diameter: 13.6 \AA . It corresponds to a population of 76% of standing molecules. One shall emphasize that the simulation of the final product in fig. 1(c) is based on the same fullerene filling ratio as the one of the initial state¹. Therefore, we conclude that no fullerene has been ejected from the tubes during the heating ramp, as will also be discussed below.

Figure 2(a) shows the evolution of experimental XRD diagrams of C_{60} peapods with time and temperature. The asterisks indicate the first- and second-order peaks of the periodic C_{60} chains. Below 800°C , evolutions of the positions of the sawtooth peaks are reversible and correspond to the evolution in temperature of the mean inter-fullerene distance [19,27]. The (10) peak intensity, which is closely related to the amount of fullerenes inside the nanotubes [25], does not change in a noticeable way. It shows that no fullerenes are expelled from the tubes upon heating, in agreement with the result from our simulations of the final DWNT structure. An opposite result was reported by Pfeiffer *et al.* [8] in their *ex situ* study.

Above 800°C , the evolution of the chain peak is irreversible as the C_{60} start to coalesce (slow process compared to our heating ramp [6]). Upon reaching 1000°C , the C_{60} peak has lost its asymmetric shape and its intensity has dropped. The evolution continues with increasing annealing time at constant temperature. After 675 minutes, the intensity drop has slowed down and almost no evolution of the diffraction diagram is observed a hundred minutes later. The reaction seems stopped. Nevertheless, the coalescence into DWNT is not complete at this point, as the diffraction diagram is not yet that of a DWNT (fig. 1(c)). After 785 minutes at 1000°C , the C_{60} peapods have therefore transformed into a state intermediary between peapods and DWNT. The full description of this intermediary state, using XRD alone, is a difficult task. Molecular dynamics (MD) simulations of fullerene coalescence have shown that the full transformation goes through a phase where the monomer C_{60} chain has turned into a corrugated tubule [11] in which the

¹The ratio between inner and outer tube lengths in DWNT is equal to $\frac{60p}{\pi\sigma(D-2d)L}$, where p is the C_{60} filling rate in the initial state ($p = 0.97$), $\sigma = 0.37 \text{ atom/\AA}^2$ is the nanotube atomic surface density, D is the outer tube diameter, d is the distance between inner and outer tube ($d = 3.6 \text{ \AA}$) and L is the fullerene periodicity in the initial state ($L = 9.9 \text{ \AA}$). For $D = 14.2 \text{ \AA}$, this ratio is equal to 72%.

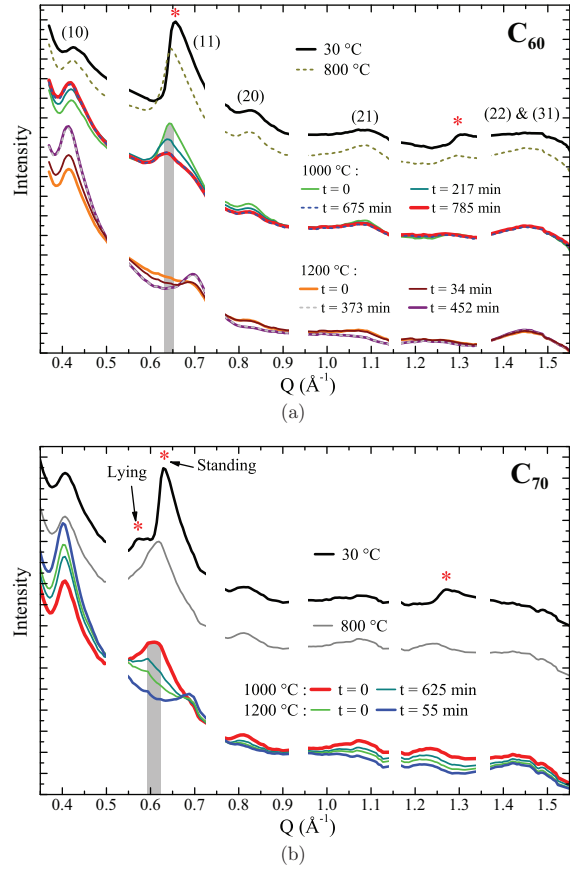


Fig. 2: (Colour on-line) Time evolution of the (a) C_{60} and (b) C_{70} peapods diffraction diagrams at 1000°C and 1200°C . The first measurement at 1200°C is performed after the plateau at 1000°C (plus the time to reach 1200°C , see fig. 3). Data are normalized to an I_0 monitor and vertically shifted for clarity. Peapods are organized in bundles on a 2-dimensional hexagonal lattice, leading to Miller indices (hk) in reciprocal space. The asterisks indicate the fullerene correlation peaks, and the shaded area the range over which the intensity of the fullerenes peak is integrated in order to monitor the coalescence reported in fig. 3.

C_{60} intermolecular distance is still underlying. The persistence of a (broad) peak around $Q = 0.64 \text{ \AA}^{-1}$ at the end of the 1000°C plateau is in agreement with such an image of corrugated tubules, as this peak indicates the correlations with the same spatial period as the one in monomer peapods. This observation is in agreement with the *ex situ* XRD measurements of Pfeiffer *et al.* [8], where the authors studied the progressive disappearance of the C_{60} correlation peak after various exposure time at 1250°C .

Upon increasing the temperature to 1200°C , a strong diminution of the peak at 0.64 \AA^{-1} is observed (fig. 2(a)). Approximately 70 minutes after reaching 1200°C , no more evolution of the diffraction diagram is observed, and the final diagram is characteristic of a DWNT sample. The

increase of the (10) peak intensity visible in the diagrams at 1200 °C is thus due to a form factor effect, *i.e.* due to the formation of a well-formed inner nanotube. We shall remind here that the intensity of the (10) peak is strongly affected by the filling of the nanotubes by fullerenes, the stronger the filling the weaker the (10) peak intensity [25]. Nevertheless, as shown in fig. 1(c), the (10) peak intensity is also increased in the DWNT case compared to the peapod one. As a consequence, looking at the (10) peak only, one could interpret an increase of the intensity of this peak either by a decrease of the fullerene filling ratio or by the coalescence of the fullerenes. Discrimination between the two cases can be made by looking at the shape and intensity of the fullerene chain peak. More precisely, the intensity at 0.64 \AA^{-1} (for C_{60} peapods) is a local minimum in the DWNT diffraction diagram whereas it is a local maximum in the peapods ones (at high temperature, see fig. 2). Monitoring of the intensity of the fullerene peak will thus allow evaluating the advancement of the transformation.

Qualitatively, similar evolution is observed for C_{70} peapods (fig. 2(b)) compared to the C_{60} ones. One shall note that at 800 °C, the C_{70} molecules have not yet started to coalesce, but that the two fullerene correlation peaks (L and S molecules) are strongly affected and mixed in one single central peak. Indeed, at high temperature, the standing molecules undergo isotropic rotations and the lying molecules undergo truncated isotropic rotations, as reported in ref. [5]. These rotations result in a mean inter- C_{70} distance intermediate between the two low-temperature configurations (*i.e.* $\sim 10.3 \text{ \AA}$).

In fig. 3, we have reported the time evolution of the temperature and the time evolution of the intensity of the XRD diagrams within the shaded areas drawn in fig. 2. The intensity of the first point measured at 1000 °C is arbitrarily set to 1 and the intensity after full transformation to zero². We emphasize here that this representation does not allow a completely quantitative measurement of the coalescence's kinetics, as the observed intensity is not directly proportional to the percentage of remaining fullerene molecules. For a quantitative measurement, one would have to know the actual structure of all the intermediary states and to simulate all the diffraction diagrams. However, this simple representation allows a good qualitative description of the coalescence's kinetics.

For both samples and during both temperature plateaux, the time evolution of the intensities are well reproduced by exponential decay functions $I(t) = I_0 + I_1 e^{-t/\tau}$. The fitted values of I_0 and of time τ are listed in table 1 (only for the 1000 °C plateau, the 1200 °C one having too few points to obtain an accurate fit of τ). It appears from fig. 3 and table 1 that, at 1000 °C, the complete coalescence into well-formed DWNT cannot be

²Note that the transformation of C_{70} peapods is not fully accomplished after 55 minutes at 1200 °C. The intensity in fig. 3 (bottom) has been rescaled after extrapolation of the intensity evolution by an exponential decay law.

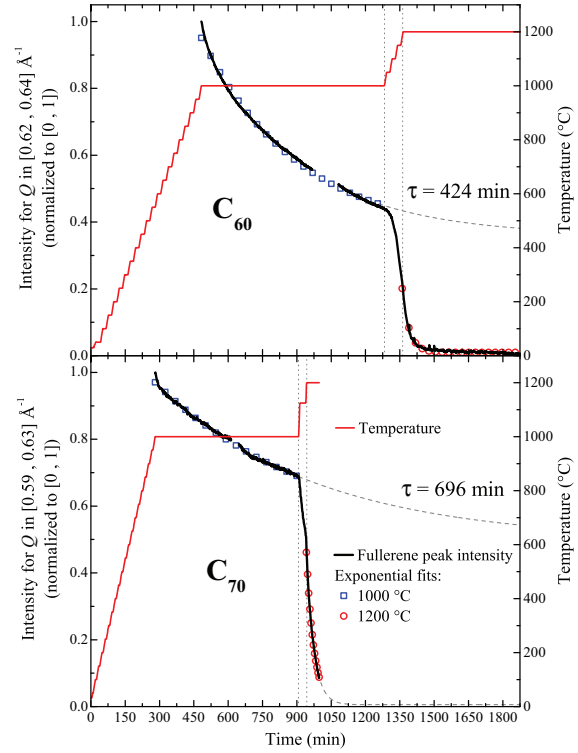


Fig. 3: (Colour on-line) Time evolution of the temperature (right axis) and of the fullerenes peak intensity (left axis) for C_{60} (top) and C_{70} peapods (bottom). Intensities are normalized to the $[0, 1]$ interval (see the text). For each temperature plateau (1000 °C and 1200 °C), the time evolution of the intensities is fitted with an exponential decay.

Table 1: Fitted values of I_0 and of exponential decay time τ at 1000 °C, for C_{60} and C_{70} peapods samples.

	C_{60}	C_{70}
I_0	0.36 ± 0.01	0.49 ± 0.01
τ (min)	424 ± 4	696 ± 15

achieved. Indeed, at infinite time, $I(t)$ tends towards I_0 that is not equal to zero. For both C_{60} and C_{70} peapods, the coalescence process therefore occurs in two steps, that correspond to two different energy barriers. At 1000 °C, the coalescence of single fullerenes inside nanotubes only leads to an intermediary state, with underlying fullerene periodicity (corrugated tubules). As soon as the temperature of $\sim 1050 \text{ °C}$ is reached, the evolution of the fullerene intensity starts again until complete transformation into a well-formed nanotube, which means that, in first approximation, the second energy barrier is of the order of $\sim 1050 \text{ °C}$.

The decay time τ at 1000 °C is significantly larger for C_{70} peapods than for C_{60} peapods, so the energy barrier to the first step of the DWNT formation, that is,

the transformation from individual fullerenes into corrugated tubules, appears higher for the C₇₀ peapods than for the C₆₀ ones. For C₆₀ peapods, the commonly accepted coalescence mechanism starts with (2+2) cycloaddition between adjacent molecules, followed by Stone-Wales rotations [11–13]. At high temperature, in the larger nanotubes, the standing C₇₀ molecules (76% of C₇₀ population) rotate in an isotropic way (fig. 2(b) and ref. [5]). Due to the anisotropic shape of C₇₀ molecules, the mean distance between facing double bonds is larger than in the case of C₆₀ molecules which may explain the observed difference in reaction time, the probability of having two facing double bonds sufficiently close being lower for isotropically rotating C₇₀ molecules than for rotating C₆₀ ones. In the case of the lying C₇₀ molecules in small-diameter nanotubes (24% of the C₇₀ molecules in our samples), adjacent molecules face through pentagonal rings. A possible mechanism for coalescence of lying C₇₀ could involve head-to-head coalescence as described in ref. [10] for facing (5,5) nanotubes—which are geometrically analogous to facing C₇₀ molecules in lying orientation. However, the energy cost of this process should be higher than for (2+2) cycloaddition between facing double bonds, since head-to-head coalescence does not occur in the case of C₆₀ molecules [29]. Thermal fluctuations around the C₇₀ mean orientation and positions may also allow for dimer formation implying active double bonds close to the molecules tips [5]. The reaction time required for this process should however be higher than in the case of the rotating C₆₀ molecules since the probability to get facing and sufficiently close double bonds is obviously smaller. In short, one may reasonably hypothesize that the reaction times required for the formation of the corrugated tubules is higher for C₇₀ molecules (in both small- and large-diameter nanotubes) than for C₆₀, which is in agreement with experimental observations.

Conclusion. — We have performed an *in situ* XRD study of the coalescence of C₆₀ and C₇₀ peapods, under vacuum, at 1000 °C, followed by further heating at 1200 °C. We have shown that, for both samples, the coalescence is a two-step process. The first step, slower for the C₇₀ peapods than for the C₆₀ ones, is the formation of an intermediary product, most likely corrugated tubules, in which the fullerene periodicity is still visible. Once the tubules are formed, at 1000 °C, further energy input is needed. Upon setting the temperature at ~ 1050 °C, the transformation process can continue rapidly until the formation of smooth internal nanotubes. Moreover, no fullerene expulsion is observed during the heating step, all fullerenes contributing thus to the tube formation. These new results should allow one to get a deeper understanding of the transformation mechanism from peapods to double-wall nanotubes.

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