MULTISHELL NANOTUBE STRUCTURES

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Introduction

Multishell nanotubes [1] can be produced in controlled quantities [2] and have interlayer spacings bigger than graphite. Measurements of nanotube interlayer d spacings yielded values between $.340\ nm$ [3] and $.344\ nm$ [4].

Graphitic sheets comprise hexagons that are formed by sp^2 hybrid carbon atoms connected to three neighbors by σ bonds. Nanotube structures of different radius can be formed by rolling graphitic sheets [5]. The perfect closing of a graphitic sheet over itself allows only particular values of tubes radius. Topology calculations are performed through the analysis of these steric constraints and a structure proposal for annealed multishell carbon nanotubes is tested with Rietveld refinement of X-ray diffraction (XRD) spectra.

Structure Calculations

If a graphitic sheet is characterized by the position of the center of hexagons in a coordinate system by vectors $a\,.\,j$ and $a\,.\,k$ with an angle of $\pi/3$, where $a = .2461\ nm$ and j, k are integer numbers, the distance from the origin to any hexagon will be $a\sqrt{(j^2 + j\,.\,k + k^2)}$. The ordered pair (j, k) defines the helicity of the tube [5]. If polyhedrical faces of the tubes are approximated by cylindrical surfaces, they will have the following circumferences with radii r such that:

$$2\pi r = a\sqrt{M}\ ;\quad M = j^2 + j.k + k^2 \qquad (1)$$

In the case of high temperature annealed multishell nanotubes it can be considered that interlayer d spacings are constant. The difference of the integer variable M between two tubes with a d spacing will be $\Delta M = M' - M$ ($M' = [2\pi(r + d)/a]^2$). Using Eq. (1) this difference can be expressed as:

$$\Delta M = M_o\left(1 + 2\sqrt{\frac{M}{M_o}}\right);\quad M_o = \left(\frac{2\pi d}{a}\right)^2 \qquad (2)$$

Since M and ΔM are integers, we first consider those solutions of Eq. (2) in which M_o are the possible integers that can adopt M values from Eq. (1). In these cases, general solutions of Eq. (2) will be obtained when $M = (q/2)^2 M_0$, where $q = 0, 1, 2, 3, \ldots$. For a given value of M_0, each of these general solutions of M can be used as the first shell value M_1 of different multishell structures. To obtain the complete sequence M_i for each structure ($i = 1, 2, 3, \ldots\ldots$ is the number of shell) Eq. (2) can be used in a recursive form. Once we know the first value $M(q) = M_1$ we can obtain $M_2 = M_1 + \Delta_1 M$, $M_3 = M_2 + \Delta_2 M$, etc, where $\Delta_1 M$ is the value obtained from Eq. (2) when $M = M_1$. From the $q + 1$ multishell structures that can be obtained, one or a few possible sequences of shells can be identified. Others will only be different in the starting inner shell. Particular solutions of Eq. (2) for M_0 non-integer or different than the values that M can adopt are discarded because they do not generate integer sequences for the next shells.

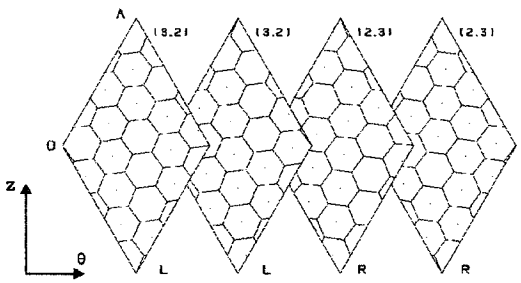

Figure 1. Unit cell (152 atoms) representation of multishell nanotubes. The four layered structure correspond to two pairs of graphitic stacking rotated between them $13.17°$. The tube axis is in the z direction.

From Eq. (2) it is seen that measured values of d correspond to $M_o = 76$. For this value of M_0, the minimum values of M_1 with physical sense that are solutions of Eq. (2) are 76 or 171 ($q = 2$ and $q = 3$ respectively), generating two possible sequences corresponding to M_i values of: $76, 304, 684, 1216$ ..... and $171, 475, 931, 1539$ ..... Since the general solution of Eq. (2) for $M_0 = 76$ can be expressed as $M = 19\,q^2$, from the M expression of Eq. (1) it is

seen that the graphitic sheets can only have equal pitch helixes multiples of *(3 , 2)* and *(2 , 3)*, corresponding to left and right turn with an angle between them of *13.17°*. The possible stacking of layers that conform the shells can be of four types with equal probability: *left-left*, *right-right*, *left-right* and *right-left*. An average stacking can be represented with only four layers ordered as *left-left-right-right*, where each of the individual equal probabilities of stacking of two subsequent shells are present. A unit cell of this four layered structure can be represented with *152* atoms. Fig. 1 shows the atom positions in each of the layers.

Experimental and Structure Refinement

For testing the validity of this structure we synthesized carbon nanotubes in an arc reactor chamber [6] using known procedures. Special precautions -attained with heat shielding of the arc zone- were taken into account for the extraction of well annealed samples [7]. Rietveld refinement method was carried out using the proposed structure as a triclinic unit cell. The stacking of atoms produced by curvature was simulated by the displacement of layers introduced by the inclination of the unit cell ***C*** axis (perpendicular to the tube axis) in a transverse to the tube plane (angles α and β where defined equal and refined simultaneously).

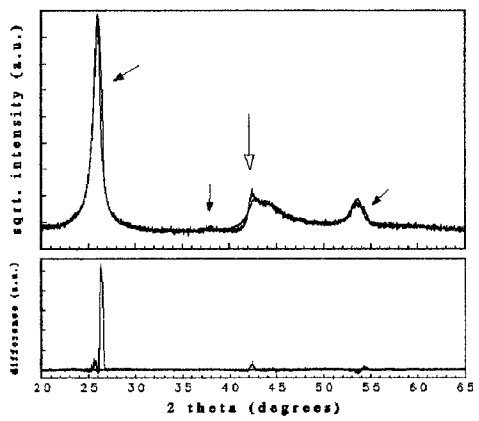

Figure 2. XRD and Rietveld refinement of annealed nanotubes. Differences between experimental and calculated diagrams correspond to the presence of stable onions (solid arrows) and to the not exact simulation of the curvature stacking (empty arrow).

The results of this refinement process (Fig.2) where: $A = B = 1.072 \pm .002$ nm, $C = 1.3670 \pm .0005$ nm, $\alpha = \beta = 88.41°$, $\gamma = 120.07°$, corresponding to $a = .2460 \pm .0002$ nm and $d = .3412 \pm .0002$ nm, with $(2\pi d/a)^2 = 75.9 \pm .3$.

Discussion

There is a small broad peak at $2\theta = 38°$ *(2.37 nm)* and shoulders in the right side of the maximum peak at interplane distance $.3369 \pm .0002$ *nm* and another one at half this distance. These features shown in Fig. 2 by solid arrows indicate the presence of a structure of smaller ***d*** with extremely deformed hexagons *(~ 4 %)* that breaks symmetry showing a forbidden structure factor peak. We consider that this strained structure of deformed hexagons correspond to stable onions.

Although with some other values of rotated layers qualitative approaches can also be obtained, the relative peak intensities of the four proposed superposed sheets as an average simulation of the structure are unique. No good agreements were found for $M_0 = 75$ where $(j, k) = (5, 5)$ or other cases of $(j, 0)$ or (j, j) helixes where there are no relative rotations between shells. It cannot be discarded the presence of isolated shells with other helixes that will not be detected by XRD studies.

Conclusions

Experimental observations and topological considerations has allowed us to propose and resolve the average structure of annealed multishell nanotubes. We were able to differentiate the global structural features satisfying closing up boundary conditions from particular defects generally present in not homogeneisized samples [8]. Resolution of interlayer spacings dependence of graphitic sheets with rotations [9] and more knowledge in formation and annealing kinetics are needed for a total understanding of closed carbon structures.

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