Formation of long monatomic carbon linear chains inside multi walled carbon nanotubes.

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1.- Introduction.

In 1978 Whittaker [1] predicted the existence of monatomic carbon linear chains named carbynes. Those structures have a linear sp-hybridation structure, showing an extraordinary mechanical strength. Whittaker also predicted the complete carbon phase diagram where carbyne stability region starts around 2,600 °K, and is extended to around 4,000 °K. Evidently, at room temperature this structure is unstable. For this reason the synthesis of carbynes by chemical routes, although expected on the basis of symmetry considerations [2-4], is difficult and until now has been very elusive [5]. Indeed, up to now, only in few selected experiments it was possible to demonstrate the presence of carbynes in; carbon thin films [6, 7] or on the surface of Aubrite meteorites [5]. In particular, Ravagnan et al. [7] produced it by supersonic cluster beam deposition under ultrahigh vacuum conditions. Moreover, monatomic carbon linear chains as been recently obtained by necking of SWCNT [2, 3, 8-11]. They have the same structure than carbynes, and also outstanding mechanical properties. Indeed, recently Jung [2] and Marquez-Lucero [3] demonstrated, theoretically and experimentally, that those monatomic carbon linear chains have a maximum tensile strength as high as 250 GPa, demonstrating that they are one of the strongest structures known until now. In the present paper, we show the formation of long monatomic carbon linear chains (MCLCs) inside a MWCNT. Those structures probably have been produced by the necking of the internal nanotube walls during their synthesis by spray pyrolysis. The MCLCs observed are stable at room conditions, being preserved by the surrounding MWCNT (this characteristic may permit their eventual characterization, at room conditions, and probable use in nanodevises.)

2.- Experimental.

The synthesis of the MWCNT was carried out by spray pyrolysis in a vycor tubing connected to a pneumatic system employed as solution atomizer. The tubing dimensions were 9.0 mm in diameter and 23.0 cm in length, which was heated by a cylindrical furnace (Thermolyne 1200), with a high precision temperature controller (±1 °C). The solution feed time was kept constant during 15 minutes for all experiments. 25 ml of

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Toluene (Aldrich, 99.8 %) and 1.00 gram ferrocene (Aldrich, 98.00%) were mixed with Argon [99.99 %, Praxair], which was employed as carrier gas. The flow rate was regulated by mass flow controller at 83.33 cm^3/seg. The Argon/toluene/ferrocene mixture was fed into the vycor tubing after furnace temperature was stable at 900°C. As a result a black film of MWCNTs formed at inner surface of vycor tubing, which was removed mechanically and observed by HRTEM. Transmission electron micrographs were obtained in a JEOL 2010F transmission electron microscope (TEM) operating at 200 kV. TEM specimens were prepared by dispersing in acetone and ultrasonic bath for 2 min; a drop of suspension was put onto holey carbon coated Cu grid, and was allowed to dry.

3.- Results

We found that very long carbon chains were formed inside the synthesized MWCNTs, as illustrated in Fig. 1. In this figure, a carbon chain of at least 15 nm long, indicated by an arrow, is present at the interior of a MWCNT. This chain has the same thickness than the adjacent nanotube walls; therefore we can considerer it as a monatomic carbon linear chain (MCLC). It is observed that this chain is attached to the tip of an iron particle located inside the carbon nanotube. Fig. 2 shows a close up of this chain. As previously mentioned, it is important to observe its longitude; which is at least larger than 15 nm. Considering that the diameter of this chain is smaller than 0.35 nm, then its aspect ratio is larger than 40. The only known structure corresponding to this size is the carbyne one, however, at the present time it is not possible to discard the possibility that this chain may have a new structure, different to a carbyne and unknown until now. Evidently, employing EELS or Raman spectroscopy this question may be elucidated, unfortunately the volumetric relation between the monatomic chain and the surrounding MWCNT is too small to use this identification technique successfully.

Fig. 3 shows another interesting formation. This structure is a carbon ripple of decreasing thickness attached to the walls of another nanotube. The ripple thickness continuously decreases until becoming a MCLC at its tip (as it is indicated by an arrow). This photograph gives us a very important hint about the formation mechanism of these MCLCs. Indeed, similar ripples are observed when a MCLC, formed from the necking of a SWCNT, is broken under tension [3, 8].

Finally, Fig. 4 shows another remarkable structure where six internal walls are attached to the tip of an iron particle. It is interesting to note the twisting of these walls at their middle. This denotes that those walls are longer than the external ones, because they need more room to fit in there. The difference in longitude is probably due to a plastic deformation. Also, it is possible to observe an incipient necking in the same place. It is important to note that the onset of this type of neck is an indication of the beginning of a CNT plastic instability that led to the formation of a monatomic carbon linear chain as is indicated by Jeng [2].

4.- Discussion.

On the basis of the previous observations, is probable that the MCLC observed has been formed by the necking of a number of internal walls initially attached to an iron particle, according to the following mechanism:

Fig. 5.a schematizes the first growing stages of a MWCNT (after its initial nucleating process.) As indicated by Vaezzadeh [8], the interaction between CNT and its catalyst is

provided by van der Waals forces. When those forces are surpassed, a new carbon atom may be placed between the catalyst and the tube. The probability than this event occurs depends on carbon concentration and temperature. Considering that carbon atoms are coming from the toluene decomposition, its concentration should diminish at the center of the catalyst, where is thicker, because it is required a longer time to diffuse until there. In consequence, a gradient concentration of carbon should be developed inside the nanotube, as is illustrated in Fig. 5.b. This gradient should lead to a differential in the growth speed of nanotube walls; the external walls must grow quicker than inner ones. Considering that the friction among walls is very large, the external walls should drag along the internal ones. Subsequently, the internal walls should pull up the area of catalyst to which they are entangled inside the MWCNT. The literal suction of the catalyst to the interior of a nanotube may be due to the compression of the surrounding walls around the catalyst particle; and the pull force of the internal walls anchored to it (see Fig. 4). Fig. 6 exemplifies this last case, which is may be the mechanism responsible for the formation of the MCLC observed in the previous figures.

a) Fig. 6.a schematized the geometry of the MWCNT in the first stages of the nanotube growth, where due to the smaller growing rate of the central walls, the external fast-growing walls hauled them, in a similar way as a telescopic hydraulic jack works. At the same time the central walls drag an iron particle, at which they are entangled, pulling it inside the nanotube. This operation demands of a considerable mechanical effort, which may produce a plastic deformation of the central walls. Indeed, in Fig. 4 the central walls attached to the iron particle seem longer than the external ones, this evidences that the first ones suffered a plastic deformation that generates a neck.
b) In Figure 6.b is described how this neck is developed until the walls collapse in a single monatomic carbon lineal chain. The necking process of SWCNT is very well described from a theoretical point of view for Jeng [2]. The plastic deformation of those nanotubes is possible after a Stone-Wales transformation where a number of defects are produced. In particular the Stone-Wales transformation, in a graphitic network, changes four hexagons into two pentagons and two heptagons, which form a sort of dislocation that facilitates the plastic deformation. This transformation is promoted by the temperature and the presence of a catalyst; both conditions are present during the present synthesis of a MWCNT.
c) Finally, Fig. 7.c describes the moment where this chain breaks leaving aside an extremity stuck to a iron particle, like it is appreciated in the Figs. 1 and 2. On the other hand, another extremity is entangled to the internal layers, as it is observed in Fig. 3.

Evidently, a deeper study is necessary to demonstrate the previous model, also is necessary to study the thermodynamical phase conditions inside of the MWCNT to determinate the conditions of grown of a MCLC, however, it gives us a first light to understand these interesting phenomena.

Finally, it is important to remark that this observation may lead to develop a method capable to provide long MCLC, in a significant amount and easy way, permitting to characterize their properties. Also, considering that those species are one of the strongest

structures which are known until now, they can be employed in a number of commercial nanodevices.

5.- Conclusion.

In conclusion, we found that at the interior of a MWCNT an extraordinary long monatomic carbon linear chain was formed. This structure, which is stable at room conditions while it is preserved inside the nanotube, has at least a longitude of 15 nm and an aspect ratio of 40. It is the longest MCLC ever photographed. This chain has been probably developed by the necking process of a number of internal walls that deformed until becoming an atomic linear chain. It is very probable that this chain is actually a carbyne because it has the same geometry; however we are presently unable to demonstrate its sp-hybridization.

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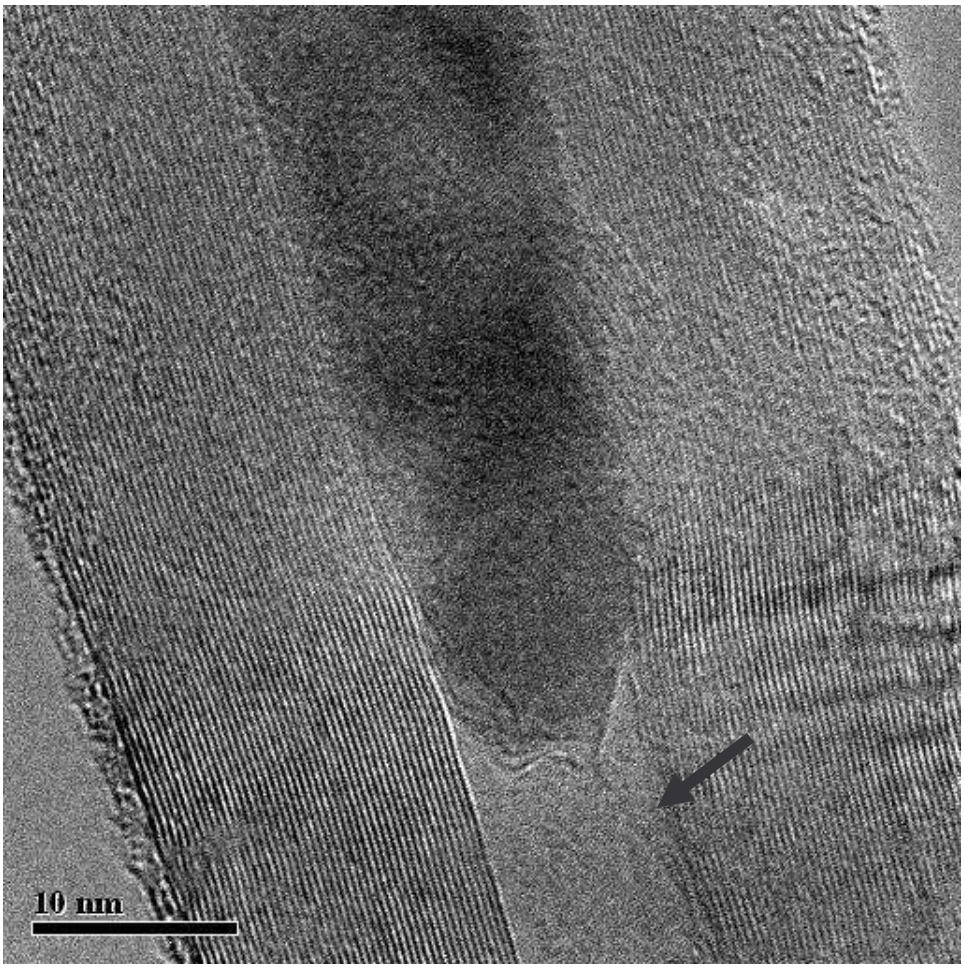

Figure 1. Tip of a monatomic carbon linear chain attached to an iron particle, inside a MWCNT.

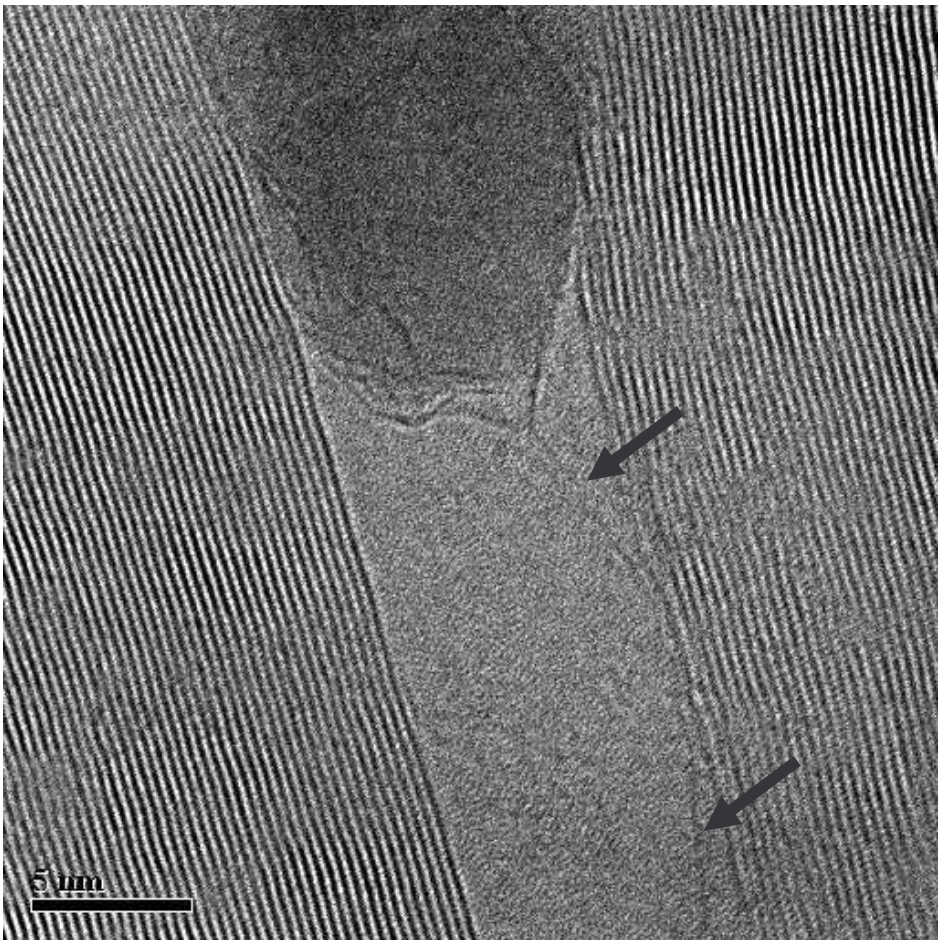

Figure 2. Close up of the monatomic carbon linear chain.

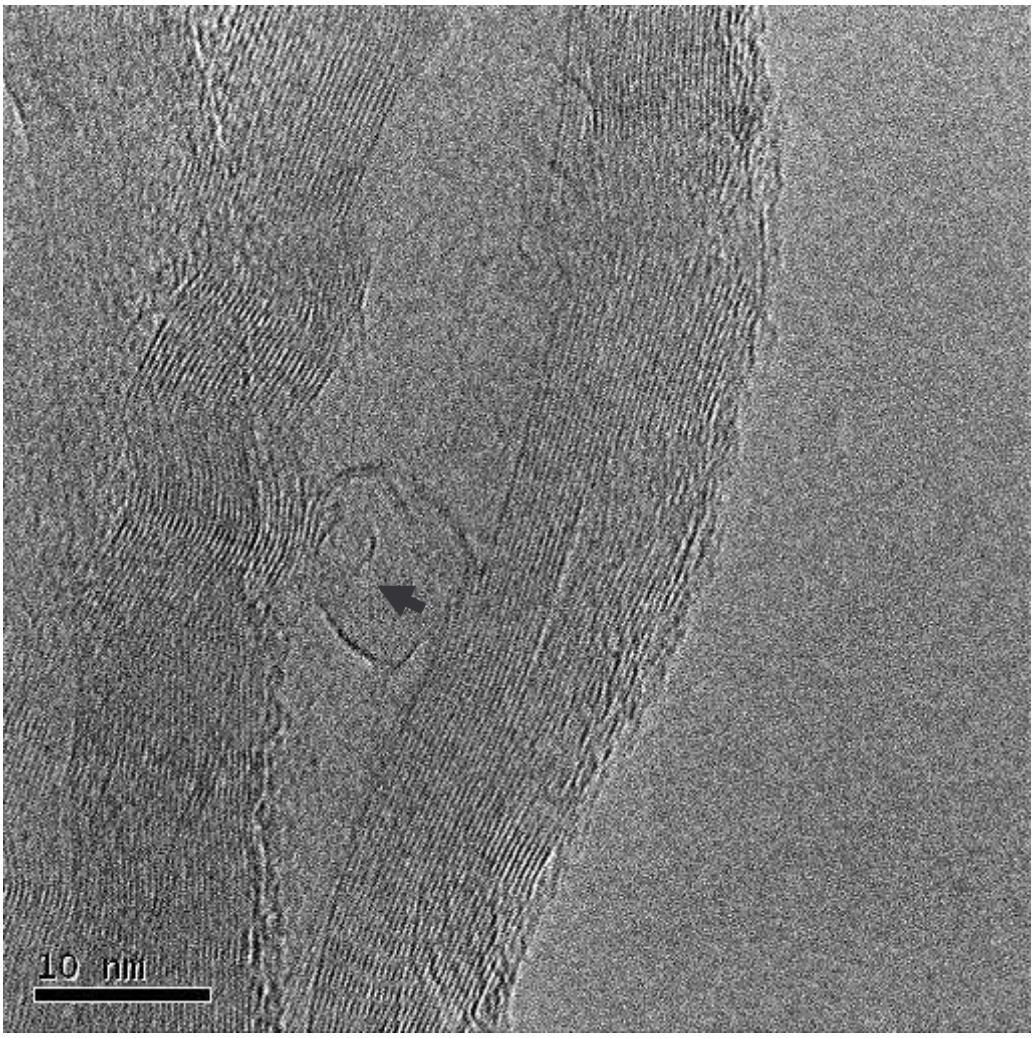

Figure 3. Carbon ripple of decreasing thickness attached to the walls of a MWCNT.

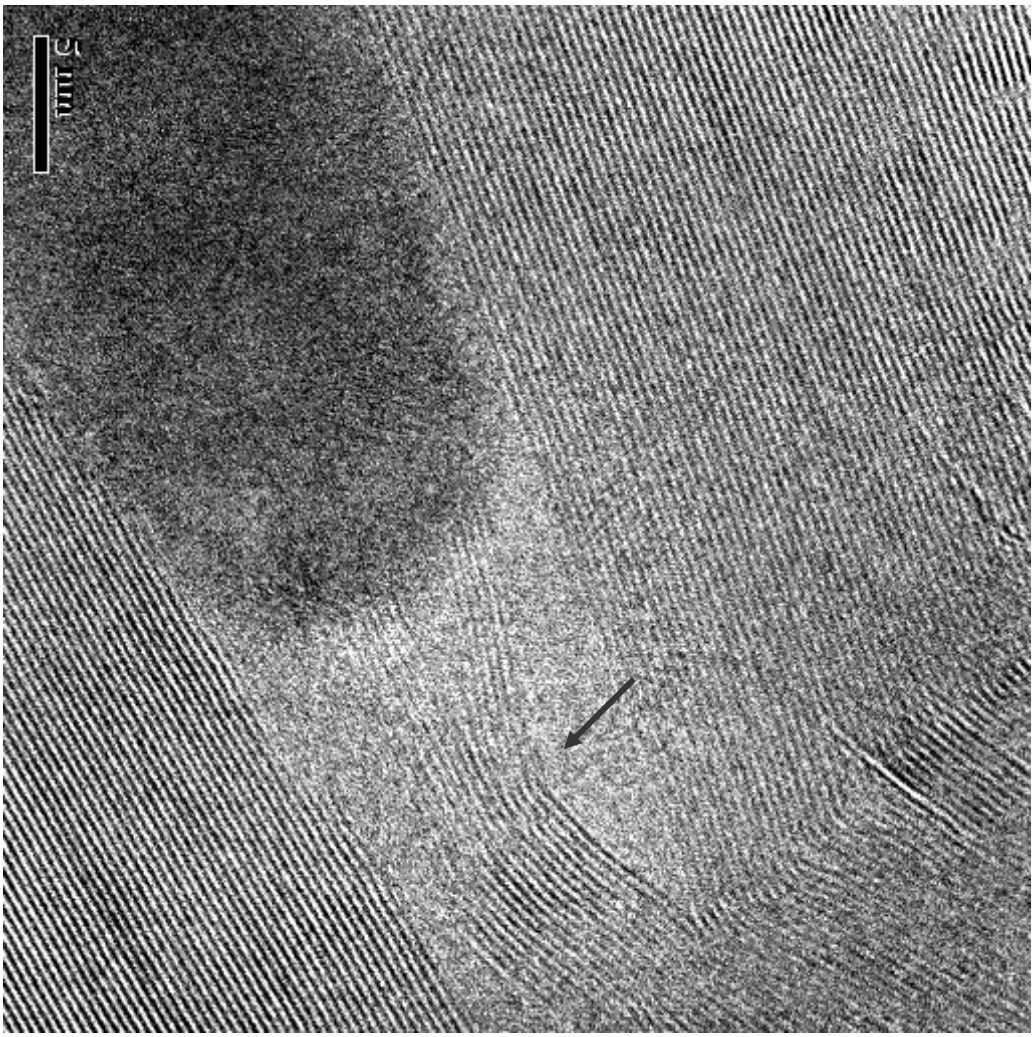

Figure 4. Internal walls attached to the tip of an iron particle.

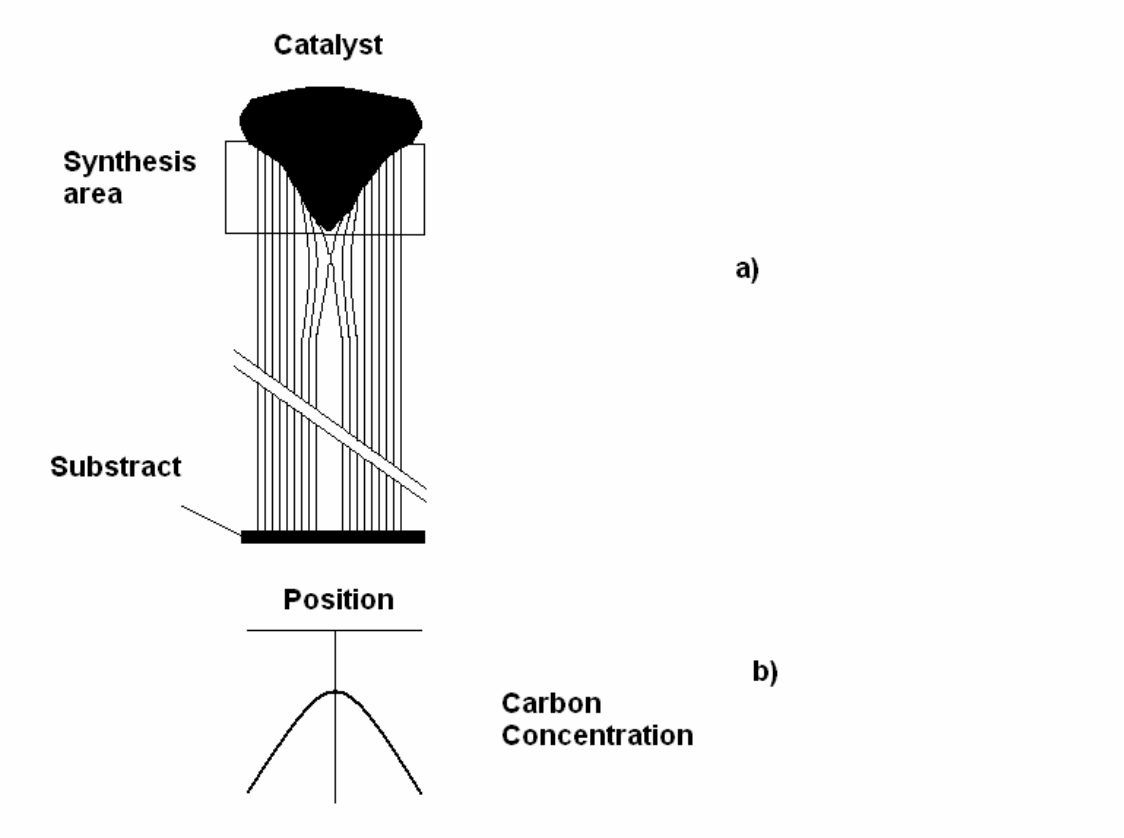

Figure 5. First stages of the growth of a MWCNT. a] After its initial nucleating process. b] Carbon concentration gradient due to the diffusion time needed for the C atoms to reach the center of the tube during growing.

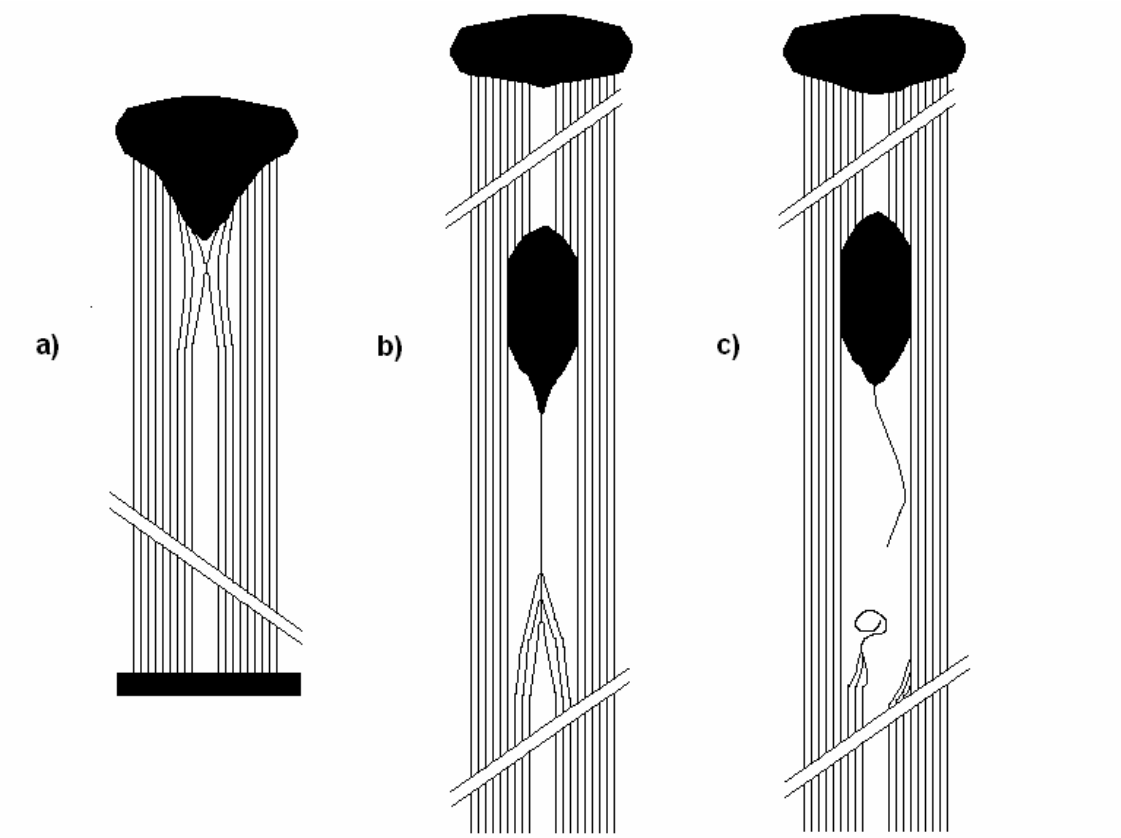

Figure 6. Model of the MCLC formation. a] Onset of the necking of MWCNT internal walls. b] Walls collapse into a monatomic carbon lineal chain. c] Chain break.