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Synthesis of carbon nanotubes and nano-necklaces by thermal plasma process

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Abstract

High-yield syntheses of peculiar carbon nanotubes and carbon 'necklace'-like morphologies have been obtained using a sophisticated thermal plasma technology. This method is based on a thermal plasma, which vapourizes the carbonaceous precursor in the presence of metal catalyst. Electron microscopy analyses provide evidences for a 'stacked-cup' structure for the carbon nanotubes. Carbon nano-'necklaces' are constituted by the repetition of multi-wall carbon spheres, connected along one direction in a 'bell'-like structure, and containing frequently an encapsulated metal particle. Microscopic growth mechanisms are also proposed to interpret both syntheses. Due to their intriguing topology, these new carbon nanotubes and necklaces may find important applications in nano-technology.

Keywords: A. Carbon nanotubes, Carbon beads; B. Heat treatment, Plasma reactions; C. Electron microscopy

1. Introduction

Carbon nanomaterials reveal a rich polymorphism including multi- and single-wall carbon nanotubes (CNTs) [1], fullerene molecules [2], graphitic onions [3], toroids [4], boxes [5], cones [6], etc. Each step in the discovery of a new carbon material morphology leads to new potential application fields. In particular, it is expected that the original nanometric morphologies of CNTs could have an important potential impact in applicative domains such as molecular electronics or high-strength composite materials [7].

Carbon nanotubes are mainly produced by three conventional techniques: arc discharge [8,9] or laser ablation methods [10], which are two high-temperature processes ($T \sim 4000$ K), and chemical vapour deposition (CVD) methods [11], which operate at medium temperature ($T \sim 1500$ K). In the arc-discharge and laser ablation techniques, the carbon and the catalyst are vapourized simultaneously. In the CVD methods, the carbon source is obtained from the decomposition of a gas phase (CO, methane, ethylene, etc.) in the presence of small metallic particles covering a substrate. In the present letter, a new method, based on a 3-phase alternative current (AC) plasma technology, is used to synthesize carbon nanostructures.

2. Experimental

Our plasma technology, initially designed for the production of carbon black by cracking of liquid or

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gaseous hydrocarbons [12], was adapted in order to treat solid powders at high temperature (carbonaceous and catalytic products) [13,14]. In this process, a carbon aerosol mixed with metal catalysts is injected into the plasma at a predetermined position along the reactor axis, corresponding to precise injection temperature and reactive flow patterns. After a chosen residence time in the plasma zone allowing the total vapourization of the solid powders, the plasma gas, carbon and metal mixture is quenched and extracted from the reactive zone at a so-called extraction position. The main difference with the classical arc and laser processes is the solid carbon flow rate, which is not limited to the electrodes erosion but can be totally controlled independently of plasma gas and metal catalysts flow rates. In addition, a system was specially designed for the sampling of the species inside the reactor, their quenching and their transport up to a filter. This system is mainly composed of a water cooled suction pipe, a set of modular cooling pipes and a filter/exhauster system.

The thermal plasma is produced by an electric arc between three graphite electrodes connected to each phase of a three-phase AC power supply, which allows a maximum power input of 260 kW. In opposition to direct current (DC) torches, which are characterized by a high velocity of the plasma gas, this technology allows low velocities, large high-temperature volumes and long residence times. Carbon black (Ensaco 250G from Erachem), coated with 3% of Ni and 3% of Co as submicronic catalyst, is used as precursor. Among the wide set of parameters that can be evolved in the present technique, the temperature field in the plasma reactor, the carbon concentration, the plasma gas/carbon ratio, the residence time, the quenching rate, the extraction position and the nature of the gas flow are identified to play a key role in the production and the quality of the final product. In the synthesis of the carbon nanostructures presented in the present paper, helium and nitrogen were used as plasma gas. Plasma gas and precursor were injected at atmospheric pressure with flow rates of 2.8×10^{-4} and 13.9×10^{-4} kg s^{-1} for helium and nitrogen, respectively, whereas the solid carbon flow rate was fixed to 2.8×10^{-5} kg s^{-1}. The extraction point was at 0.88 m from the injection position. Once the experiment finished, different samples related to specific process components were collected and analysed. The carbon nanostructures characterized in this paper correspond to samples collected after scraping of the internal wall of the reactor and in the bag filter. In a second step, these carbon nanostructures were characterized using a high-resolution scanning electron microscope (LEO982, SEM-FEG), and a high-resolution transmission electron microscope (LEO922, TEM-200KeV) equipped with electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDXS).

3. Results

Scanning electron micrographs (Fig. 1a) reveal large quantities of carbon nanotubes embedded in the carbon black used as the carbon source in the plasma technique. Conical terminations are clearly visible in Fig. 1a, as

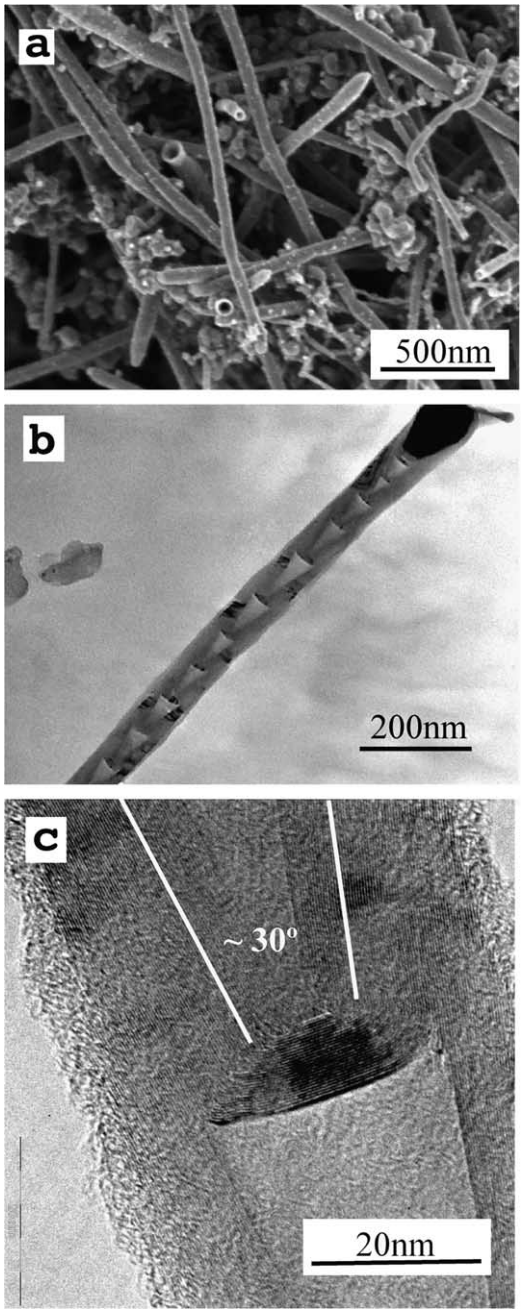

Fig. 1. (a) Scanning electron micrograph of carbon nanotubes embedded into carbon black materials, as synthesized by the plasma technique. (b) Transmission electron micrograph of the 'stacked-cup'-like structure of the carbon nanotubes. The catalytic particle is frequently observed at the end of the nanotube. (c) High-resolution TEM images illustrating the graphene layers in the stacked-cups (white lines are guide for the eyes) and the average conical angle (~30°).

well as opened nanotubes, displaying their cylindrical shape. Although this SEM image shows no visible difference from the conventional CNTs, TEM images reveal a 'stacked-cup' structure consisting of a series of long hollow conical compartments instead of the conventional long cylinders (Fig. 1b). The graphene layers are not oriented parallel to the cylindrical axis (Fig. 1c), but parallel to the surfaces of the catalyst particle. Electron diffraction analyses reveal a conical angle frequently close to 30°, as also observed in Fig. 1c. Such a peculiar structure has already been reported in the literature [15,16], although previously referred to as a 'herring-bone' structure where the graphene sheets do not connect but surround a hollow core. The diameter of the nanotubes ranges from 50 to 100 nm and the length in the order of a few micrometers. As the end of the tubes is often capped by a cone-shaped catalytic particle, a 'tip'-like growth model could be suggested in analogy with carbon fibers and filaments [17,18].

Large scale synthesis of 'necklace'-like carbon nanostructures is also revealed by SEM micrographs (Fig. 2a). These nano-necklaces are up to several μm long with outer diameters in the range 50–100 nm. Carbon spheres are found to be regularly spaced along the filament. Unlike the straight nanotubes (Fig. 1), carbon nano-necklaces usually curve smoothly and entangle together (Fig. 2a). The necklace can include more than 50 bell-like units linked from the end of the bell to its head. In order to analyse their nano-structure, these carbon necklaces are also characterized by TEM, illustrating the repetition of an elementary unit looking like a nano-bell, sometimes filled by catalytic particles. The segments, which are completely filled with the Ni–Co catalyst used during the synthesis, are observed as segments with dark core in Fig. 2b. The joined segments in the carbon nano-necklaces are actually short variable-diameter compartments with one end sealed and the other one open. The number of graphene layers can vary between the top of the nano-bell and its end (see Fig. 2b, inset).

Understanding the connection between the successive nano-bells is not an easy task. Fig. 3a shows this connection for a nano-necklace, constituted by joined spherical segments, nearly parallel to the electron beam of the microscope. The connections seem to be performed by the open part of the nano-bell. High-resolution TEM characterization (HRTEM) shows that these segments of the carbon necklaces are composed of graphitic shells (Fig. 3b). The separation between these planes is estimated around 3.4 Å, and is clearly visible in Fig. 3c–d. The connection between the nano-bells is illustrated in Fig. 3d, where all the graphitic sheets of the previous unit (six graphitic sheets remaining at the open region) are surrounding the graphene-based shells of the next one. The interaction between the two segments is thus probably strong. Similar structures have been previously reported for CN_x [19,20] and BN [21] systems. In Ref. [22], highly deformed carbon structures looking like 'necklaces' have been reported in a very low yield and at very high pressure.

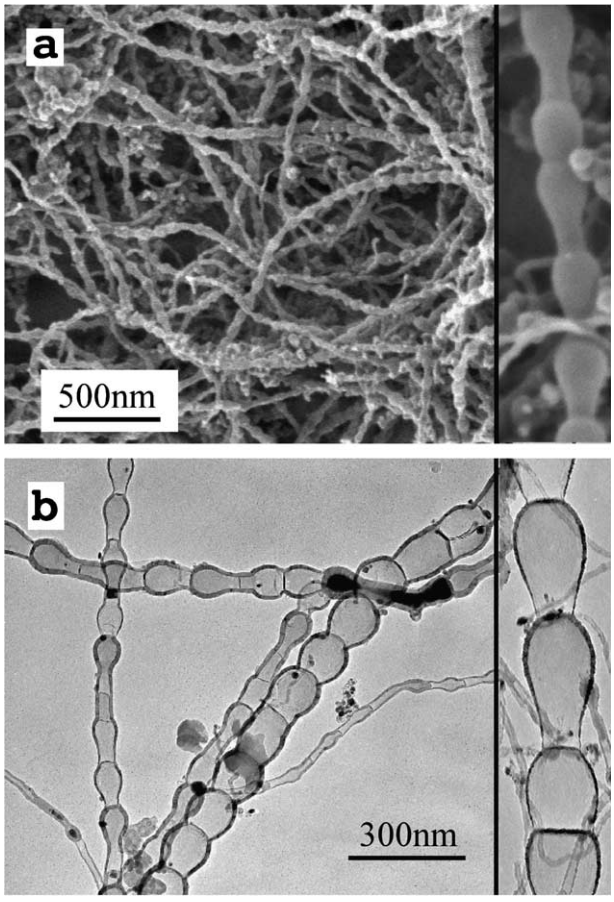

Fig. 2. (a) Scanning electron micrographs of carbon necklaces embedded into carbon black materials, used as carbon source in the plasma technique. These nano-necklaces are made of carbon spheres regularly spaced along the filament. (b) Transmission electron micrographs of carbon necklaces presenting the repetition of an elementary unit looking like a nano-bell, sometimes empty or filled with a metal particle. Both insets (on the right) are magnification of an isolated nano-necklace in SEM (a) and TEM (b), respectively.

A confocal laser Raman spectrometer (Labram) has also been used to characterize the carbon necklaces. The measurements were performed using a 10 mW power beam (632.8 nm excitation wavelength) with a spot of about 1 μm in diameter. The Raman spectrum of the necklaces (Fig. 4) shows the typical signature of a well-graphitised material. The spectrum displays the typical peak at 1580 cm^{-1} associated to the G-band mode of graphite compounds. As the necklace structure is spherical, it certainly contains several topological defects such as pentagons in the hexagonal network in order to curve the graphite sheets (spherical shape, connection between segments, etc.). The peak around 1330 cm^{-1} is attributed to disorder, inducing Raman scattering (D-band mode). In the region of higher-order

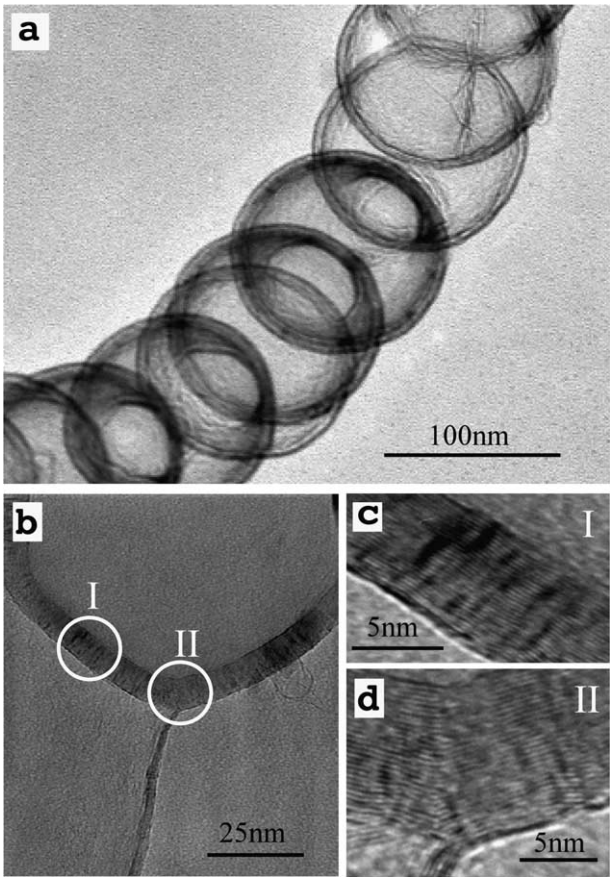

Fig. 3. High-resolution transmission electron microscopy (HRTEM) of carbon necklaces. The images present the connection between the successive elementary units (a), called nano-bells. The nano-necklace is nearly parallel to the electron beam of the microscope. This nano-bell consists of graphene-based shells (b). HRTEM images (c and d) respectively detail region I and region II of the necklace illustrated in (b).

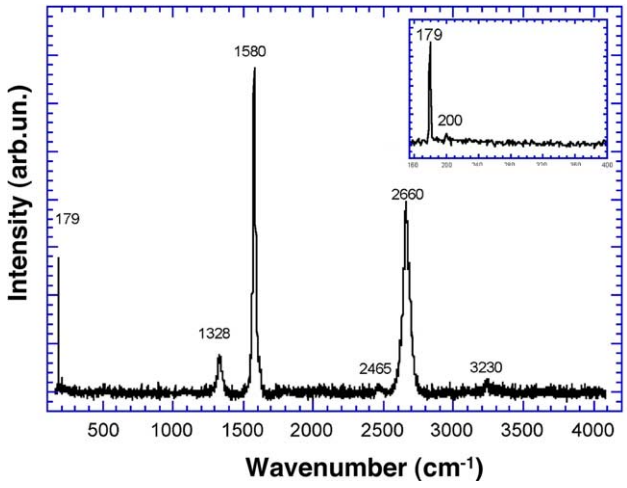

Fig. 4. First and second-order Raman spectrum of carbon necklaces obtained using a laser excitation wavelength of 632.8 nm.

Raman spectrum, the three peaks at 2465, 2660 cm^{-1} (2D), and 3230 cm^{-1} (2D′) are also observed in pristine highly oriented pyrolitic graphite [23]. However, the peak at 179 cm^{-1} cannot be easily explained for graphitic systems, although for single-wall carbon nanotubes, it is attributed to the radial breathing mode of the tube in the region (180, 200 cm^{-1}) [24]. In our case, such

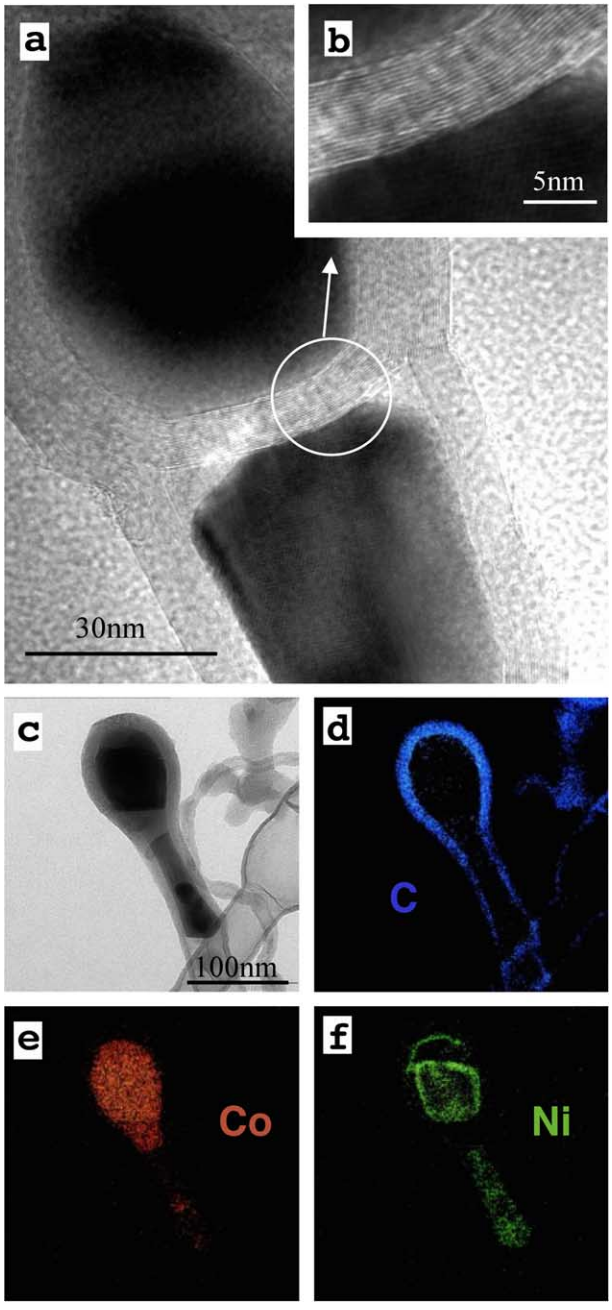

Fig. 5. HRTEM images of necklaces filled with metal (a). The crystalline nature of the catalyst is observed in (b). Low resolution TEM image of the end of a nano-necklace (c). Electron energy loss spectroscopy (d) carbon mapping (blue), (e) cobalt mapping (red), and (f) nickel mapping (green) of the image shown in (c). The nano-necklace contains non-uniform concentration of catalyst (Co and Ni) inside the nano-bell only constituted of carbon.

a peak could be attributed to the presence of metallic particles, enhancing inelastic Raman scattering at the interface between metal and graphite due to electronic effects such as charge transfer.

In order to accurately check the chemical composition of the carbon necklaces, the EDX technique has been used for their chemical characterization. Fig. 5a shows two compartments containing metal catalysts, connected by several graphene-based shells. The metal is found not to fill completely the empty space. The interface between the graphene-based shells and the catalyst is illustrated in Fig. 5b which also shows the crystalline nature of the catalyst after solidification. Empty and filled nano-bells can be easily distinguished using the EDXS technique. When the nano-bell is empty, the spectrum presents only the carbon peak. On the other hand, in the presence of a catalytic particle, a small peak, compared to the dominant carbon peak, is detected and attributed to Ni and Co. These EDXS results are corroborated by electron energy loss spectroscopy (EELS) measurements which have also been performed in order to investigate the chemical composition of the nano-necklaces. From the elemental chemical mapping (Fig. 5c–f), it is clear that the nano-bell is only constituted of carbon (Fig. 5d). However, the metal composition of the catalytic particles encapsulated in these carbon structures is not always homogeneous. In the present example, the cobalt is homogeneously distributed in the empty space (Fig. 5e), while the nickel is more localized at the surface of the metal particle (Fig. 5f). Such situation cannot be generalized, and is found to be varying from case to case. As only a threshold value of carbon can be detected by the EELS technique, the absence of the carbon which forms the top and the bottom of the cavity in Fig. 5d is an artefact. Consequently, the chemical mappings of Fig. 5e and f does not allow us to state the absence of a small quantity of carbon inside the catalytic particle.

4. Discussion

Within this original thermal plasma technique, the synthesis of these two nano-structures can be easily triggered by modifying the nature of the plasma gas in the reactor. The nature of the plasma gas has a strong influence on the arc voltage of the plasma generator and hence strongly modifies the power input and therefore temperature prevailing in the system. When helium is used as plasma gas, the temperature of the reactor walls is medium (1000–1300 °C) and mainly carbon nanotubes are produced. On the other hand, carbon necklaces are favoured when the temperature of the reactor walls is higher (1700–2400 °C), and the plasma gas used is nitrogen. Consequently, the temperature distribution inside the plasma reactor is thus an important factor to explain the growth of these carbon nanostructures.

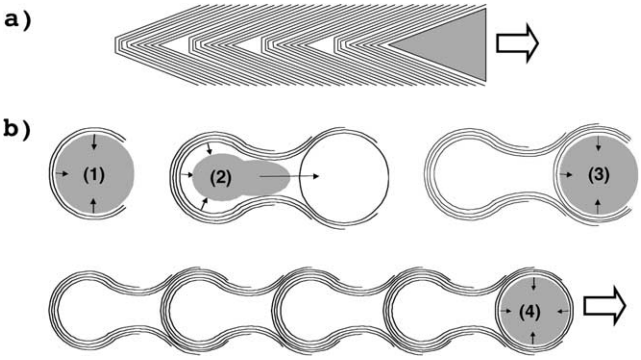

Fig. 6. Schematic representations of proposed growth mechanisms for carbon nanotubes (a) and nano-necklaces (b). The black lines and curves represent graphene layers. The catalytic particle is illustrated in light grey. The small black arrows represent the pressure on the catalytic particle, while the big arrows show the direction of the motion of the catalytic particle during the growth process.

At medium temperature (1000–1300 °C), the catalytic particles are still solid, although very close to the melting point (i.e. the melting temperature of the Ni–C eutectic is 1311 °C). The carbon nanotubes are suggested to form through diffusion of carbon at the particle heated surface, which promotes its precipitation into graphene sheets (Fig. 6a). As the carbon nanotube grows further, the metal particle is pushed upward, forming a metal cap which stabilizes the dangling bond at the edge of the tube by saturating them. The growth of the nanotube is stopped when the catalytic particle is completely solidified and encapsulated by graphene layers (Fig. 1b). This growth mechanism, adapted from the process proposed previously for the CVD-grown carbon filaments [17,18], easily explains the stacking of graphene-based cones observed along one peculiar surface direction of the catalytic particle and the presence of the latter at the end of the structure.

At higher temperature (1700–2400 °C), the catalytic particles are in a liquid state. The formation of carbon necklaces proceeds via solvation of carbon vapour into metal particles, diffusion through the bulk, followed by the precipitation of carbon in excess at the surface of the particles. This scenario is based on the vapour–liquid–solid (VLS) model proposed long ago to explain the synthesis of silicon whiskers [25]. When the catalytic particle is formed by condensation of metal plasma/vapour in the reactor, carbonaceous structures are preferentially adsorbed at its surface and dissolved into the liquid metal phase, leading to a supersaturation of carbon. During the synthesis, the catalytic particle is able to incorporate a large amount of carbon (30–50 at.%) depending on the local temperature and on its size. Upon cooling, the solubility limit of carbon decreases and carbon starts to segregate. This effect increases as the temperature decreases and the segregation force is

maximum close to the solidification point. Below the solidification temperature (which value depends on the composition of the particle), there is at equilibrium a complete segregation between metal and carbon. The occurrence of such a segregation process is supported by the absence of carbon inside the catalytic particles after complete solidification (Fig. 5d). Once expulsed, carbon crystallizes at the surface of the particles and forms graphene sheets around the droplet. The formations of the first polyaromatic layer defines a volume for the particle. After the formation of several graphene-based layers, the catalytic particle is trapped inside a smaller volume. As the confinement increases, the particle elongates, allowing the formation of longer graphene-based layer. This explains the thinning down observed at the open part of the nano-bell (Fig. 2b inset and Fig. 3b). When the compression is too intense, the nano-particle is expulsed from the bell-like graphene-based structure and restarts the process. This growth scenario is illustrated in Fig. 6b. Sometimes, the catalytic particle is not entirely expulsed, which explains the presence of catalyst trapped in several cavities of the necklaces. The structure observed in Fig. 3d confirms the internal growth scenario. This figure shows that the internal graphene-based sheets of the previous nano-bell are linked by the end to the head of the next one and are surrounding the shells of the following bell, as schematically illustrated in Fig. 6b. A similar mechanism, based on a sequential growth has recently been proposed for nanofilaments made of repeated units of multi-wall carbon nanotubes with a metal particle encapsulated at one end. These morphologies were synthesized by thermal chemical vapor deposition (CVD) of methane on Ni–Fe catalysts [26].

At last, a structural model based on the Haeckelite approach [27], has been proposed to explain the structure of the necklaces, which is assumed to be composed by the regular occurrence of non-hexagonal rings at the atomic level, instead of regular graphene layers [28].

5. Conclusion

We report on the characterization of carbon nanotubes and nano-necklaces synthesized by thermal plasma process. Both carbon nanostructures have been linked to specific operative conditions and more particularly to the nature of the plasma gas used and by consequence, to the temperature field in the reactor. To resume, the 'stacked-cup'-like structure is the result of the growth of carbon nanotubes at a temperature where the metal catalyst is at a solid state whereas the 'necklace'-like structure has grown at a temperature where the metal catalyst is liquid.

This technique could be easily scaled up to obtain even large amount of these new compounds. Both nanostructures could be designed for many potential applications based on their respective morphologies. The stacked-cup carbon nanotubes exhibit a surface structure with a very high density of open ends of graphene-based layers, which could serve as emitting centres for field emission applications. This structure also exhibits a large amount of opened graphene-based layers which could be advantageous for gas storage. The nano-necklaces, which are composed of varying numbers of connected nano-bells may also have interesting electrical properties. Due to their morphology, they could certainly be used in composite materials with an intrinsically strong interaction with the host matrix. The presence of topological defects at the surface of these nanostructures can also be useful for functionalisation.

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