Synthesis, characterization and magnetic properties of Co@Au core-shell nanoparticles encapsulated by nitrogen-doped multiwall carbon nanotubes

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Abstract

Co/Au bilayer thin films were deposited on Si/SiO_x substrates using the magnetron sputtering method and used as a catalytic support to grow forests of aligned nitrogen-doped multiwalled carbon nanotubes (N-MWCNT) via chemical vapor deposition (CVD) at 850 °C, using benzylamine (C₆H₅CH₂NH₂) as a carbon and nitrogen source. Interestingly, the resulting N-MWCNT contains Co@Au core-shell nanoparticles located at their tips. We

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found that the metal particle cores consist of cobalt coated by an Au shell of few nanometers. Magnetic measurements revealed a ferromagnetic behavior of the system composed of Co@Au nanoparticles encapsulated inside N-MWCNT. The results are compared with pristine N-MWNT containing only Co nanoparticles encapsulated in their cores.

1. Introduction

In recent years, the synthesis and characterization of different types of carbon nanomaterials has drawn wide attention from the scientific community because of their unusual physical and chemical properties [1-6]. One of the most important entities in the controlled production of such materials is the catalyst used during synthesis. For example, it is known that almost any type of metallic nanoparticle can be used as catalyst to produce CNT provided it fulfills certain morphological conditions [7,8]. For example, gold nanoparticles have been used in alumina templates to grow N-MWCNT [9]. In the cited paper, a CNT growth mechanism similar to that accounting for the Fe nanoparticle growth was proposed. The diameter of the gold nanoparticles need to be quite small (< 5 nm) for producing this type of CNTs. Other investigators have grown multiwalled bamboo-like CNTs on bismuth [10]. Some other alloys have been successfully used as catalysts when growing CNTs [11,12]. There are two general routes for using catalyst nanoparticles in CVD: when using a carbon source containing such a nanocatalyst [13] or when using templates incorporating the catalyst [14,15]. Generally, the specific applications determine the material used as the carbon-reacting material in CNT synthesis. In this context, it is also well known that the size and morphology of a catalytic nanoparticle determine its physical and chemical properties [16,17]. For example, due to their applications in biology, catalysis

and nanotechnology, some of the most studied nanomaterials are noble metal nanoparticles [18-20]. In particular, gold (Au) and silver (Ag) nanomaterials have been used in biomedicine [21,22]. However, bimetallic systems are becoming very important [23,24], as the combination of two different materials offers advantages over the use of one single material, from physical and chemical viewpoints. For instance, a gold-silver alloy system has demonstrated enhanced optical applications [25,26]. Several other bimetallic gold and silver systems have been used in a wide range of applications [27,28]. In general, it is possible to classify three types of bimetallic structures: alloys, mixes and core-shell nanoparticles. Due to their importance in a wide spectrum of research fields, we are interested in the third type, but specifically composed of a magnetic core and a noble metal shell [29-33]. This type of shield can prevent the material from oxidizing, thus preserving its magnetic integrity [29]. In addition, the optical properties of noble metals increase the technological value of this hybrid system. In order to fabricate this type of materials, various methods have been used, such as chemical and wet gas-phase/solid-state techniques. The former include arc discharge [34], catalytic methods [35] and sputtering [36,37], whereas the latter involve the chemical reduction of nanostructures [17,21]. The importance of these core-shell nanoparticles has been noted by several authors [38]. For example, Wang *et al.* described the importance of the physical and chemical properties of the surfaces of these types of core-shell nanoparticles, emphasizing that these nanoparticles are crucial in biological and catalytic interfacial reactivity [39]. They can be monodispersed $\text{Fe}_3\text{O}_4\text{@Au}$ core-shell nanoparticles with a 5-15-nm core and a 0.5-2-nm shell. These authors also reported the potential of tailoring the shell thickness by varying some synthesis parameters. It has been demonstrated that the magnetic properties change as the size of the core decreases and the gold shell increases [40].

CNTs have been classified as one of the most important nanomaterials in the last century due to their fascinating properties. This nanomaterial could be considered as a one-dimensional structure with important application in various fields [41,42]. Due to their natural superficial reactivity, nitrogen-doped MWCNT (N-MWCNT) are found to also be very useful in several applications [43,44]. For example, N-MWCNT nanotubes were very recently successfully used for oxygen reduction reaction [38,45-48] and lithium rechargeable battery applications [49]. It is worth mentioning that the synthesis of CNTs can be performed in the absence of catalyst particles [50]. However, the use of catalytic particles of 3d transition metals, such as Fe, Co, Ni or their alloys, increases the CNT quality and quantity [2,51]. Nonetheless, the synthesis of CNTs using noble metals, such as gold or copper, has been reported [1]. Different routes have been implemented to synthesize CNT using Co, Fe, Ni or Co-Fe alloys as catalysts. Typically, the nanoparticles encapsulated in these CNTs exhibit a cylindrical in shape (nanowires) [51]. However, if a catalyst film of Ni, Fe or Co is used to synthesize CNTs, the nanoparticles have a small aspect ratio and occasionally are short (spherical-like), with different diameters and morphologies [52]. Sato *et al.* have used Ti-Co bimetallic nanoparticles to grow CNTs [53]. Depending on the percentage of Ti used, different morphologies were obtained. In that work, the shape of the encapsulated nanoparticles and their chemical composition are unclear. Different morphologies have been observed when gold is used as a catalyst [54-56]. In order to grow CNTs using gold, Ag or Cu nanoparticles as catalysts, Takagi *et al.* subjected the gold nanoparticles to a cleaning process that reduced the size of the Au nanoparticles and produces only single-walled CNTs [56].

In this work, we have produced N-MWCNT containing Co@Au core-shell nanoparticles in their tips. Relative to other similar systems, this structure could be useful in several fields, especially biological [39,57,58], magnetic [59-61] and memory (data storage) [62] applications. To the best of our knowledge, this is the first method developed to fabricate core-shell nanoparticles encapsulated inside CNTs. These particles exhibit a core of cobalt and a shell is a noble metal (gold).

Furthermore, the integration of two nanoscale systems that are relevant in materials science, core-shell nanoparticles and N-MWCNT, will undoubtedly have a positive impact in biomedical applications. Interestingly, the core-shell nanoparticle located at one end of N-MWCNT could be used as a magnetoplasmonic system and the carbon nanotube as drug delivery system taking advantage of its large surface area and biocompatibility [63]

2. Experimental

Co/Au and Co thin films were deposited on Si/SiO₂ substrates. First, the substrates were cleaned ultrasonically for 10 min within a pure acetone solution. This cleaning process was repeated using ethanol, isopropyl alcohol and de-ionized water, and the substrate was then dried with nitrogen gas. To deposit the cobalt and cobalt-gold films, a modified Intercovamex V3 sputtering system was used. This equipment consists of a high vacuum deposition chamber with a loading gate. The cleaned substrates are first placed inside the loading gate/chamber and when the pressure reaches 1.0×10^{-4} Torr, it is then transferred to a rotating holder located in the main deposition chamber. The distance between this holder and the metal targets are 7 cm. The Co and Au targets are circular with 2 and 1 inches in diameter, respectively. In order to drive the magnetrons two different power supplies are

used. For the Co target, a direct current power source MDX-500 is employed. For the Au target a pulsed power supply Pinnacle Advance Plus at zero frequency is operated. The holder rotates at 3 turns per minute and the size of the nominal sputtering area is 2 cm^2 . In all cases, for cobalt and gold, the internal chamber is operated at a pressure of 2×10^{-2} Torr. For the Co(40nm)/Au(2nm) film, we used 30 W to deposit 40 nm of cobalt over 34 min; then 2 nm of gold over 10 s. For the Co 40 nm layer, the same parameters (30 W and 30 min) were used to deposit the films. Other substrates with Co(20 nm) and Co(20nm)/Au(2 nm) were also fabricated and used to grow N-MWCNT. Without any additional processing, the magnetizations of the samples were measured as a function of the magnetic field at several temperatures using a physical properties measurement system (PPMS) with the field applied parallel to the substrates. After this measurement, the samples were then subjected to a typical ultrasonic spray-pyrolysis chemical vapor deposition (CVD) process using benzylamine as the carbon and nitrogen source. In order to grow N-MWCNT containing nanoparticles with a core-shell morphology, a two-furnace setup is necessary, with one furnace operating at $750\text{ }^{\circ}\text{C}$ and the other at $850\text{ }^{\circ}\text{C}$. The samples were located inside a quartz tube and placed in the middle part of the latter furnace. The dimensions of the quartz tube used to grow CNTs are: 114 cm long with an internal diameter of 2.54 cm and outer diameter of 2.794 cm. At around $850\text{ }^{\circ}\text{C}$ and before the temperature conditions are sufficiently high for achieving CNT growth, an argon-hydrogen flow was passed through the quartz tube at a rate of 0.5 l/min for 10 min to prevent the formation of cobalt oxides on the surface of the substrates. After the temperatures in both furnaces were stable, the ultrasonic generator containing benzylamine atomized a solution, and the inert gas flow rate was increased to 2.5 l/min. It is very probable that when the temperature reached $850\text{ }^{\circ}\text{C}$, separate cobalt and gold nanoparticles were formed on the surface of the substrates

[64]; a similar situation could have occurred for pure cobalt. These nanoparticles are randomly distributed, exhibiting diameters ranging between 40 to 120 nm (see below, Figs. 13 and S4). It is possible that the elevated temperature (850 °C) under an Ar-H₂ gas atmosphere led these nanoparticles to slightly segregate and increased their catalytic activity. The complete process is depicted in a hypothetical growth mechanism described below. Next, the system was maintained under these conditions for 30 min. At this point, the sprayer and furnaces were turned off, and the flow rate was set to 0.5 l/m until the furnace reached room temperature. The samples were removed from the quartz tube, and the magnetization was measured using the PPMS system. The samples consisting of forests of aligned N-MWCNT were characterized by scanning electron microscopy (SEM) using an FEI Helios 600 Nanolab apparatus and transmission electron microscopy (TEM) using a 300-kV FEI Tecnai F30 S-TWIN G2 HRTEM. Raman spectroscopy was carried out using a Renishaw micro-Raman spectrometer. The nitrogen and carbon content was obtained with an elemental analyzer COSTECH 4010 in samples obtained by scraping material for the substrates. EDX characterization was also carried out in order to obtain the nitrogen content within samples.

2. Results

Figure 1 shows SEM images of N-MWCNT grown on both a Co(40nm)/Au(2nm) bilayer film (Fig. 1a) and a pure cobalt (40 nm thickness) film (Fig. 1b). When the Co(40nm)/Au(2nm) film bilayers were used as a catalytic template, the tips of MWCNT exhibited spherical morphologies with a diameter larger than that of the nanotube diameter. However, MWCNT grown on the pure Co film contained uniform and cylindrical tips, typical for CNT. The spherical CNT tip catalyzed using Co(40nm)/Au(2nm) thin films

exhibited diameters around 100 nm (see Fig. 4). These spherical regions of the CNT are caused by the encapsulation of a bimetallic core-shell nanoparticle, in which the core is cobalt and the shell is gold. This thin layer of gold is approximately 4-8-nm thick (see below). With respect to quantity of obtained material, $7.7 \times 10^{-3} \text{ mg/mm}^2$ and $7.4 \times 10^{-3} \text{ mg/mm}^2$ were obtained of N-MWCNT samples grown on Co(40nm)/Au(2nm) and Co(40nm) films, respectively. For N-MWCNT from Co(20nm)/Au(2nm) films the weight of CNT was $1.98 \times 10^{-3} \text{ mg/mm}^2$ and $6.98 \times 10^{-3} \text{ mg/mm}^2$ for nanotubes from Co(20nm) film. The results from elemental analysis indicates that N-MWCNT grown from Co(40nm)/Au(2nm) films contain 99.3% of carbon and 0.7% of nitrogen, whereas nanotubes grown on pure Co(40nm) films contained 99.5 % of carbon and 0.5 % of nitrogen. The reduction of cobalt layer thickness to fabricate N-MWCNT results in different effects depending on the catalytic substrate used to grow them. The nitrogen and carbon content in nanotubes grown on Co(20nm)/Au(2nm) films was 0.57 % and 99.43 % respectively. Using only a pure Co(20nm) film the nitrogen content increased to 1.42%. In order to confirm these results EDX analysis was carried out using the FE-SEM FEI Helios 600 Nanolab. Only in N-MWCNT grown on Co(20nm) and Co(20nm)/Au(2nm) films, a small nitrogen content was observed (see Table S1).

In standard N-MWCNT, the encapsulated metal particles are usually conical with a low aspect ratio (approximately 3) [62]. However, when a Co/Au bilayer thin film is used instead, the N-MWCNT tip exhibits a spherical-like shape depending on size of the catalytic nanoparticles. This spherical tip morphology can be attributed to the presence of a gold component in the thin film. This phenomenon has yet to be explained, but we are proposing a growth mechanism in the following paragraphs.

Fig. 1. SEM images of N-MWCNT grown on two different thin films deposited on Si/SiO₂ substrates: (a) a Co/Au bilayer thin film with a Co thickness of 40 nm and an Au thickness of 2 nm; and (b) a 40-nm-thick Co thin film. Note that in the case (a) some diameters of tips exhibiting spherical-like nanoparticles inside are greater than that of the diameter of CNT body. In case (b), it is not possible to clearly observe the nanoparticles inside of the CNT.

Figure 2 depicts SEM images of N-MWCNT grown on different catalytic thin films; it seems that gold nanolayer aid the growth of nanotubes with uniform dimensions and high degree of crystallinity. Figure 2a depicts SEM images of N-MWCNT grown using pure Co(20nm) films; the height of these nanotubes is around of 12.7 μm. When a Co(20nm)/Au(2nm) thin film is used to grow them (see Fig 2b), the CNT corresponded to 55 μm, which is 4.3 times longer than the tubes grown on pure Co films. The increment of the Co thin film thickness also resulted in longer N-MWCNT. With pure Co(40nm) films, CNTs exhibiting heights of 42.9 μm were recorded; additional gold layers did not result in significant changes in the nanotube length (e.g. 65.5 μm). These results do not agree with those reported by Bower *et al.*, who found that in cobalt films with smaller thicknesses (2

nm) nanotubes grew longer than when using thicker (20nm) films [65]. However, in this case they used a microwave plasma CVD method to grow the nanotubes [65]. Contrarily, Huang et al. found similar results than those presented here [66]. These authors used a plasma-enhanced hot-filament CVD system to fabricate CNTs.

Fig. 2. SEM images of lateral view of N-MWCNT forest grown on Co(20nm) (a); Co(20nm)/Au(2nm) (b); Co(40nm) (c); and Co(40nm)/Au(2nm) films.

Figure 3 exhibits N-MWCNT grown on different thin films, column plots correspond to their respective diameter distribution. N-MWCNT fabricated on pure Co(20nm) substrates

display average diameters ranging from 20 and 70 nm being the most frequently diameters of 40-50 nm. Apparently, the gold thin film slightly affects the average tube diameter by reducing it (see Fig. 3b). N-MWCNT grown on Co(20nm)/Au(2nm) substrates display diameters ranging between 10 and 70 nm with an average of 30-40 nm (Fig 3d). When the pure Co thin film becomes thicker, it is possible to find N-MWCNT with diameters in the range of 10 and 100 nm, but it is also possible to occasionally find CNT with diameters larger than 100 nm (see Fig 3f). Gold thin film deposited on pure Co(40nm) films (substrate Co(40nm)/Au(2nm)) promote N-MWCNTs with diameters of 20 to 80 nm, although CNT with diameter less than 10 nm and larger than 80 could also be found (see Fig. 3h). Similar results were found in the case of N-MWCNT grown on other Co(40nm)/Au(2nm) substrates (see Fig. S2). Interestingly, Bower and collaborators reported a complex distribution of nanotube diameters obtained using their method [65]. For example, diameters ranging from 20 nm to more than 300 nm were reported by these authors.

Fig. 3. SEM images of N-MWCNT grown in different substrates: (a) Co(20nm); (c) Co(20nm)/Au(2nm); (e) Co(40nm) and (g) Co(40nm)/Au(2nm). Column plots are diameter distribution corresponding to each kind of CNT.

In order to determine the chemical composition of the CNT forests grown using different catalyst films, we used energy dispersive X-ray (EDX) spectroscopy using a scanning electron microscope. **Figure 4** depicts an EDX spectrum of CNTs grown using Co(40nm)/Au(2nm) thin films as a catalytic support. We analyzed the ends of these CNT, where the Au and Co signals were clearly observed. Aluminum, copper and silicon signals come from the grids where the N-MWCNT were placed for TEM characterization. It is important to mention that, in this case, nanoparticles anchored to CNTs were not observed.

Fig. 4. SEM images of N-MWCNT containing Co@Au core-shell nanoparticles inside their tips. Red plots correspond to EDX spectra of CNT grown using Co(40 nm)/Au(20 nm) thin

film as catalysts. This figure clearly shows that gold is located at the ends of N-MWCNTs.

The O, Al, Si and Cu signal come from the TEM-grids used to deposited the samples.

To elucidate the origin of the Au signal in the EDX spectrum, samples were also analyzed by TEM. Figure 5 shows TEM images of two representatives N-MWCNT fabricated using a Co(40nm)/Au(2nm) bilayer thin film. The grown CNTs exhibit a bamboo-like morphology with large cavities. The nanoparticles are almost spherical, and exhibit diameters of *ca.* 100 nm. The CNT are approximately 80 nm in diameter, and the wall is *ca.* 24 nm thick. For the CNTs shown in Fig. 5a, it seems that the spherically shaped tip is not connected to the hollow interior of the CNT and that no other metallic particle is close to the tip. However, in the case of Fig. 5b, the spherical-like tip is connected to the hollow interior of the CNT, and the compartments are easily observed. In this particular case, a small thin wire is close to the tip. In this image, we can observe a CNT with compartmentalized morphology and with smaller dimensions than the CNT containing the a big “spherical” tip.

Fig. 5. Transmission electron microscopy (TEM) images of N-MWCNT with a spherical tip morphology grown over a Co(40 nm)/Au(20nm) thin film deposited on a Si/SiO₂

substrate. Fig. 5a depicts a 70-nm-diameter CNT with a spherical tip that seems not to be well connected to the core hole. The encapsulated 100-nm-diameter Co@Au spherical nanoparticle is located inside of the surrounding carbon spherical structure. Fig. 5b is another CNT (83.7 diameter) with a spherical tip exhibiting a better connection with the core hole of the CNT. In addition, its bamboo shape is clearly seen, and a small thin wire (80 nm long and 10 nm in diameter) is observed. Note that although both samples have bamboo-like structures, the CNT in Fig. 5a has a longer compartment than that in Fig. 5b.

Figure 6 shows TEM images of other N-MWCNT with nanoparticles exhibiting a core-shell morphology fabricated using Co(40nm)/Au(2nm) bilayer thin films. In Fig. 6a, N-MWCNT of 90 nm outer diameter (OD) and 35.8 internal diameter (ID) is shown. Notice that the bamboo-like compartments are not well defined in this particular case. The nanoparticle possess an oval shape of 57 nm in length and 39.5 nm width. Figure 6b exhibits another spherical-like nanoparticle; in this case there is a short nanowire very close to the nanoparticle of 126 nm in diameter, and the CNT diameters correspond to 28.6 nm (ID) and 84.5 nm (OD). Figure 6c shows a N-MWCNT tip encapsulating a nanoparticle with a pear-like shape, in which the bamboo-like morphology is clearly observed and the particle dimensions are 13.95 nm width and 21.56 nm length whereas the tube shows diameters of 101 nm (OD) and 31.7 nm (ID). Finally, Fig. 6d exhibits a high-resolution TEM image showing both carbon layers (52) and the encapsulated nanoparticle crystal planes.

Fig. 6. TEM bright field images showing CNT tips encapsulating Au@Co core-shell nanoparticles: (a) nanoparticle with approximately oval shape; (b) short nanowire that is touching to a spherical nanoparticle, the bamboo shape in CNT is not well noticeable; (c) nanoparticle with a pear-shape; here the bamboo-shape morphology is clearly appreciated; (d) high resolution TEM exhibiting the crystallinity of nanowire and the carbon layers. In this CNT were grown on Co(40nm)/Au(2nm) thin film bilayer.

Figure 7 shows bright field HRTEM images displaying other N-MWCNT encapsulating Au@Co core-shell nanoparticles. In this case the thin film used to grow CNTs was Co(20nm)/(2nm). **Figure 7a** exhibits an oval-shaped nanoparticle (23.9 nm and 17.47 nm). This CNT has an OD of 17.63 and an ID of 6.67 nm. Note that few carbon layers (2.36 nm thickness) are isolating the nanoparticle from the CNT body. **Figure 7b** shows a small nanowire with an aspect ratio of 1.33. It is noticeable that one side of this nanowire does

not have carbon coating whereas the other side has. [Figure 7c](#) exhibits a N-MWCNT tip encapsulating an oval nanoparticle similar to that showed in [Fig. 7a](#), but in this case the nanoparticle is accompanied by a conical wire of 123 nm long. Note that these nanoparticles are very small when compared to those grown when using Co(40nm)/Au(2nm) thin films as a substrate. A nearly spherical nanoparticle is presented in [Fig. 7d](#). This nanoparticle is completely covered by 18 carbon layers (approximately 5.85 nm) and has a diameter of 12.33 nm. The inset shows the fast Fourier transform (FFT) obtained from this image exhibiting the planes corresponding to the Co hexagonal crystal structure (i = $\square 1010$; ii= $\square 1100$; iii= $01\square 10$); the zone axis is [0001]. [Figure 7e](#) exhibits another N-MWCNT with two kinds of encapsulated nanoparticles, one at the tip and the other inside the CNT core. [Figures 7f](#) and [7g](#) correspond to HRTEM images showing the FFT and their associated crystallographic planes (insets). The zone axis in [Fig. 7f](#) is also [0001].

Fig. 7. TEM bright field images showing CNTs filled with Au@Co core-shell nanoparticles: (a) nanoparticle with oval shape completely covered by carbon layers, a

large part of its surface is protected by only few carbon layers; (b) nanowire with a very small aspect ratio, note the differences between the compartments placed to each side of the nanowire; (c) another oval nanoparticle with bigger dimensions than the case (a), here it seems that a conical nanowire is attached to the oval nanoparticle; (d) high resolution TEM image of a spherical nanoparticle; the inset is the fast Fourier transform (FFT) exhibiting the planes from this nanoparticle (i = $\square 1010$; ii= $\square 1100$; iii= $01\square 10$). The sample correspond to N-MWCNT grown on Co(20nm)/Au(2nm) substrates; (e) is another N-MWCNT which present two kind of nanoparticles one in the body and the other in the tip; (f) and (g) are the HRTEM images of the tip and body nanoparticles, respectively. The inset are showing the FFT.

Figure 8 shows bright field TEM images of N-MWCNT grown on pure Co(20nm) films. Figure 8a exhibits a N-MWCNT with diameter of 29.6 nm. Note that the bamboo-like morphology is very well defined in this nanotube. In Fig. 8b, two kinds of N-MWCNT are shown: one with a well-defined compartmentalized morphology (vertical nanotube) of 32.1 nm in diameter, and other two N-MWCNT (horizontal not showing a homogeneous bamboo-like shape morphology. Figs. 8c and d depict Co nanoparticles with a typical conical morphology. The nanotubes shown in Figs. 8c and 8d possess diameters of 25.7 nm and 56.2 nm, respectively. It is also noteworthy that regularly Co nanoparticles do not promote the formation of spherical-like nanoparticles when benzylamine is used as carbon and nitrogen source during the growth of N-MWCNT by CVD, but conical shapes are usually observed (see Figs. 8c and d).

Fig. 8. TEM bright field images showing N-MWCNT grown on pure Co(20nm) thin films: (a) shows a nanotube with a bamboo-like morphology; (b) nanotubes with inhomogeneous bamboo-like compartments were also found; (c) encapsulated conical Co nanoparticle typically found in these N-MWCNT; (d) another Co nanoparticle with a conical shape. Notice that in these last two cases the tip nanoparticles are covered on their top part by only a few carbon layers.

Concerning the chemical composition of the carbon-nanotube-encapsulated nanoparticles, elemental mapping analysis was performed on N-MWCNT grown on Co(40nm)/Au(2nm) and it is shown in Fig. 9. A super-imposed elemental mapping provides important information about the chemical composition of the particle; different colors indicate different materials. Figure 9a shows a mapping image of the CNT with a metal particle at its tip; green corresponds to carbon, blue to cobalt and red to gold. It is clear that gold and cobalt are distributed over the nanoparticles, although the cobalt nanoparticle is not completely covered by gold, as revealed by the blue color at the bottom of the nanoparticle. In Fig. 9b, the EDX global spectrum of the particle is shown; Co and Au are clearly present. In Fig. 9c, we an EDX concentration line profile along across the nanoparticle is depicted. The red line corresponds to the gold profile and the blue line to cobalt. The carbon is plotted using a black line. It is clear that the intensity of gold differs between the left and right borders of the particle, which suggests that the cobalt core is not perfectly encapsulated by the gold shell.

Fig 9. Chemical analysis of a N-MWCNT grown on a Co(40nm)/Co(2nm) thin film; a) superimposed elemental mapping of the CNT shown in Fig. 3a, the combination of red (Au) and blue (Co) produces the purple tone in the center of the nanoparticles; the spherical

nanoparticles seem to be incompletely covered by gold, as some blue is observed at the bottom of this area; **b**) corresponding EDX global spectrum for the nanoparticle diameter; **c**) concentration of Au (red), Co (blue) and C (black) derived from the EDX spectrum. Note the $\text{Fe}_{\text{K}\alpha}$ line (not indexed) is possibly present because some contamination in the deposition or CVD processes.

When Co(40nm)/Au(2nm) was used as a catalytic substrate to grow CNTs, EDX also revealed the presence of Co and Au in all analyzed samples (see [Fig. 10](#)). In particular, we studied three spherical-like nanoparticles located in the tip of CNTs ([Fig. 10 a, g and j](#)), and one nanowire encapsulated inside a N-MWCNT (see [Fig. 10d](#)). In all cases, a Fe contamination was also found (see [Figs. 10c, f, i and l](#)), possibly due to the presence of Fe impurities within the ultrasonic sprayer. Generally, we noted that the amount of gold and cobalt does not dramatically along the line scan within the nanoparticle (see [Figs. 10b, h and k](#)). In the case of the small nanowire ([Fig. 10e](#)) the concentration profile does not change. It is also important to note that the Cu signal arises from the TEM grid used for the characterization.

Fig. 10. Elemental line profiles of core-shell nanoparticles encapsulated inside N-MWCNT grown on Co(40nm)/Au(2nm) thin films. Figs 10a, d, g and j are dark-field TEM images showing several nanoparticles which are encapsulated in N-MWCNT. The figures (b), (h) and (k) are concentration profiles of cobalt and gold across the particles, derived from EDS spectrum obtained by Z-contrast technique (HAADF); (k) concentration profile from a

small nanowire located inside the CNT body; (c), (f), (i) and (l) are the corresponding EDS global spectra for the corresponding nanoparticle or nanowire studied.

Similar experiments were carried out when growing N-MWCNT on pure Co(20nm) (see Fig. 11a) and Co(20nm)/Au(2nm) thin films (see Fig. 11 d and g). According to these results, the nanoparticle shown in Fig 11a shows a non-uniform concentration profile because the nanoparticle possess a conical-like morphology (see Fig. 11c). However, when the nanoparticle has a spherical-like morphology Co and also Au present a nearly uniform concentration profile (see Fig. 11f). However, for the nanowire inside a N-MWCNT (Fig. 11g), the concentration profile for gold exhibited a decrease concentration towards the middle section (see second part of gold profile exhibited in Fig. 11i). The EDS overall area spectrum for each nanoparticle studied is presented in Figs. 11b, e and h; notice that the Fe contamination is also detected in all the cases, possibly due to residues present in the ultrasonic sprayer.

Fig. 11. Dark field TEM images of various N-MWCNT filled with Co (a) or Co@Au core-shell nanoparticles, (d) and (g) images. The N-MWCNT were grown on pure Co(20nm) (a) or Co(20nm)/Au(2nm) (d) and (g) thin films. Fig. 11c corresponds to the concentration profile of Co derived from EDS spectrum. Figures 11(f) and (i) show concentration profile of Co and Au across the nanoparticles. Figures 11b, (e), and (h) correspond to the overall EDS spectra for each nanoparticle studied.

In order to determine whether the crystalline structure of our N-MWCNT samples is affected by the presence of gold, we performed a Raman spectroscopy study (see Fig. 12) using a Renishaw micro-Raman spectrometer with an excitation energies of 1.96 and 2.41

eV ($\lambda = 633$ nm and $\lambda = 514$ nm). For N-MWCNT encapsulating spherical Co@Au core-shell nanoparticles inside their tips grown using Co(40nm)/Au(2nm) thin films, the ratio between the intensities of the D- and G- bands is lower than for CNTs grown on a pure Co(40nm) thin film. These results could be due to the presence of gold over the thin film of cobalt. Possibly the tendency of nitrogen atoms to create compartments within tubes decreases because of the catalytic action of the thin gold nanoshell. In addition, the lower number of sp^3 hybridized carbon bonds could lead to low values of I_D/I_G relative to the case without using gold as a catalyst. Raman spectra of N-MWCNT using Co(40nm)/Au(2nm) or Co(40nm) thin films also present this behavior. The I_D/I_G ratio for Co(40nm) and Co(40nm)/Au(2nm) correspond to 0.692 and 0.532, respectively (see Fig. S3). The lower the value of I_D/I_G , the more crystalline the sample becomes (e.g. less defects, amorphous carbon and/or dopants). In this case the excitation energy of 2.4 eV ($\lambda = 514$ nm) was used for recording the Raman spectra. In this context, it is also important to note that the value of I_D/I_G is dependent on the laser excitation energy; the lower energy the higher the value of I_D/I_G [67]. Therefore, one has to compare these values with other reports using the same laser excitations. In this work, when comparing N-MWCNT samples grown using Co(40nm)/Au(2nm)S1 and Co(40nm) (Fig. S4) with Co(40nm)/Au(2nm)S2 and sample Co(40nm) (see Fig. 12), I_D/I_G ratios of 0.8779, 1.032, 0.539 and 0.673 were found for Co(40nm)/Au(2nm)S2, Co(40nm), Co(40nm)/Au(2nm)S1, and Co(40nm) substrates, respectively. Thus, N-MWCNT grown on Co/Au thin film exhibit less degree of crystallinity when compared to nanotubes grown on Co film (see Fig. 12), and a competition between the Co and gold films appears to determine the crystallinity of the carbon nanotubes; further detailed studies should be carried out along this direction.

Fig. 12. Raman spectra for nitrogen-doped MWCNT grown using a bimetallic Co/Au thin films as a catalyst (red and blue curves) and only a thin film of pure cobalt (green and black). The ratio of the intensities of D and G bands are 1.032, 0.8779, 0.9263, 0.9504 for N-MWCNT grew on Co(40nm), Co(40nm)/Au(2nm)S2, Co(20nm) and Co(20nm)/Au(2nm), respectively. According these results the quality of N-MWCNT grown on Co(40 nm)/Au(2 nm)S2 thin films more crystalline than the others. It seem that when Co is thicker the gold thin film improves the crystalline quality of CNTs. However, if Co is very thin the situation is inverse. In this case, the degree of crystallinity of CNTs when Co/Au is used, is not as good as the respective CNTs used with a Co film. The excitation wavelength used in this case was 633 nm.

In order to understand the growth mechanism of N-MWCNT, SEM characterization was performed on substrates at different stages of the deposition/growth processes. Figure 13

shows images for films of Co(40nm) films (Fig. 13a, e and i), and Co(40nm)/Au(2nm)S2 (Fig. 13c, g and k). In particular, Figs. 13a and 13c correspond to SEM images of as-deposited thin films. Figures 13e and 13g show the same substrates but exposed to an Ar-H₂ flow from room temperature to 850 °C. Figures 13i and 13k are SEM images of annealed substrates for 10 minutes at 850 °C under Ar-H₂ gas. As deposited thin films exhibit a “flat” morphology with nanoparticle sizes ranging between 7-12 nm and 6-14 nm in diameter for the Co (40nm) and Co(40nm)/Au(2nm)S2 films, respectively. However, Fig. 13e shows only nanoparticles exhibiting spherical shapes, but plenty of Co islands showed complex structures that were also formed, the diameters of the spherical nanoparticles were more or less uniform. Diameters ranging from 40 to 120 nm diameter are more frequently found in this case. For nanoparticles containing Au (Fig. 13g), most of the nanoparticles reveal spherical shape and diameters of 40-160 nm. A bimodal distribution of nanoparticle diameters is forming with a second maximum centered at 200 nm. In the EDX spectrum shown in Fig. 13e (inset), it is evident that only cobalt nanoparticles are involved. However, in Fig. 13g (inset) Au is present and the nanoparticles are composed of Co and Au. Fig. 13 i and k reveal the changes observed in the nanoparticles of Co and Co-Au when heated under Ar/H₂ at 850 prior to start the nanotube growth. In this case, we observed nanoparticles with diameters ranging between 20 and 180 nm. Big Co nanoparticles with diameter as large as 440 nm can also found. For Co-Au nanoparticles, a bimodal distribution is evident; nanoparticles with diameters of 40 nm and 100 nm and nanoparticles with diameters around 200 nm can be also observed. It is believed that larger nanoparticles do not catalyze the growth of N-MWCNT, and only nanoparticles with diameters < 100 nm are the responsible for growing nanotubes with Co or Co@Au core-shell nanoparticles inside the tips. Figure S4 in supplementary

information shows a similar study performed in N-MWCNT fabricated on Co(20nm) and Co(20nm)/Au(2nm) thin films.

Fig. 13. SEM images showing the catalytic substrates consisting of pure Co(40nm) (a, e and i), and Co(40nm)/Au(20nm)S2 (c, g, k) thin films: (a) and (c) are as-grown samples. (e) and (g) are SEM images of the same substrates heated from room temperature to 850 °C for the second furnace; (i) and (k) are SEM images of samples heated after 10 minutes at 850 °C under a flow of Ar-H₂ at 0.5 l/m. The column plots (b, f, j are the Co(40nm) thin film and d, h, l are Co(40nm)/Au(2nm)S2 thin film) are the corresponding diameter distribution of nanoparticles forming the respective thin film. The plots (insets in Figs. 13e, i, g and k) correspond to EDX spectra for different nanoparticles. For insets shown in (i) and (g) only Co, C and Fe are present, for insets (g) and (k) Co, C, Fe and Au are present. These results

indicate that Co and Au are present within the catalytic nanoparticles used to grow N-MWCNT containing the Co@Au core-shell nanoparticles inside the nanotube tip.

The magnetic properties were measured using PPMS Evercool equipment. For N-MWCNT grown on Co(40nm)/Au(20nm)S1 film, three systems were studied: (i) the cobalt films; (ii) the cobalt films coated with a gold film and (iii) the nitrogen-doped CNT encapsulating the core-shell nanoparticles. For all three cases, we observed a typical behavior of ferromagnetic materials (see Fig. S5). Measurements showed that the coercive field was stronger in case (i). In the other two cases, the coercive field is basically the same. The differences are a result of differences in the shapes of the hysteretic loops. The ferromagnetic nanoparticles inside of N-doped CNT produced with benzylamine and ferrocene are conical [62]. For this reason, carpets of N-doped CNT present differently shaped hysteresis loops depending of the direction of the applied magnetic field. The same phenomenon occurs for pure Co or Co/Au bilayer thin films (see Fig. S5). The structure of this bilayer thin film is constituted by small nanoparticles interacting between them [68]. The nanoparticles are approximately 6-14 nm in size (see Fig. 13). For the core-shell magnetic-noble metal system encapsulated in the CNT, the magnetic anisotropy is absent, and the total magnetic moment decreases as the field weakens. This behavior is very common in superparamagnetic systems, thus suggesting that our spherical core-shell nanoparticles can be classified as such. Several routes have been used to control the magnetic properties of ferromagnetic nanoparticles encapsulated inside or deposited outside CNTs [69-71]. However, we report the first study on core-shell nanoparticles encapsulated inside CNTs. Figure 14 depicts the hysteresis loops of N-MWCNT grown on Co(20nm), Co(20nm)/Au(2nm)S2, Co(40nm) and Co(40nm)/Au(2nm)S2 thin films. The effect of the Au thin film when the thickness of Co is small results in an increase in the coercive field of N-MWCNT forests. However, there is a decrease of

saturation magnetization for Co/Au films when compared to the Co thin film. This phenomenon could be related to the morphological characteristics and the number of catalytic ferromagnetic nanoparticles which are responsible for the CNT growth. For example, we found a larger number of Co(20nm)/Au(2nm) (Fig. 13g) small nanoparticles formed when compared to Co(20nm) (see Fig. 13e). Contrary, for N-MWCNT synthesized on Co(40nm) and Co(40nm)/Au(2nm)S2, the coercive field for nanotubes grown on Co(40nm) is larger than the coercive field of nanotubes synthesized on Co(40nm)/Au(2nm)S2 films. According to Figs. 13i and 13k, the number of big nanoparticles in the Co(40nm)/Au(2nm) case is larger when compared to Co(40nm) films.

Fig. 14. Hysteresis loops for forests consisting of aligned N-MWCNT grown on pure Co thin films (black) and Co/Au bilayer thin films (red). The measurement was carried out at 2 K and a maximum magnetic field of 1 T. Both the red and black curves exhibit typical ferromagnetic behavior and a very similar shape. The reduction of the saturated magnetic moment for the Co/Au case is evident in both situations presented, namely (a) Co(20nm)/Au(2nm) and (b) Co(40nm)/Au(2nm).

Figure 15 depicts the tip-growth mechanism proposed based on our results (see Fig. 15a-g). The catalyst consists of a Co film covered with an ultra-thin Au layer on top. The surface morphology of this heterostructured film features nanoparticles of different sizes (Fig. 15a). During CVD, the nanoparticles separate, thus forming the nanoparticles shown in Fig. 15c. A simplified schematic of the hypothetical process is presented in Fig. 15b for a single nanoparticle. It is possible that the actual mechanism is more complex. The cobalt of the CVD-formed nanoparticle is covered with a thin film layer (Fig. 15c). The inner part of this nanoparticle should be uncovered to react with the carbon, resulting in the crystallization of carbon layers that adopt the nanoparticle shape (Fig. 15d). The gold thin layer might somewhat inhibit this process, at least at the beginning, and only a few carbon layers cover the bimetallic nanoparticle (Fig. 15e). However, the catalytic process continues, and the CNT keeps growing. At the surface, cobalt is uncovered, and a normal growth process occurs (Fig. 15f). At some point, as a result of the uncovered portion of the surface, a cobalt nanoparticle is pushed to the tip of the tubular structure and forms small cylindrical nanoparticles. In addition, due to the presence of nitrogen atoms, a bamboo-like morphology is found (Fig. 15g). At some point in the process, the CNT cannot continue to grow vertically, possibly due to the weight of the large nanoparticle on the top, and starts to bend, thus forming the structures observed by TEM (see Fig. 5).

Fig. 15. Schematic diagram of N-MWCNT growth during the CVD process. (a) a structured Co/Au thin film is formed after the sputtering process; (b) the Co-Au system is well formed during the 10-min annealing process of the previous CVD experiment; (c) magnification of the small nanoparticle shown in (b); (d) because the cobalt is not completely covered by gold, the catalytic process begins; (e) the gold layer prevents the tip growth process, and the growing root is removed; (f) the cobalt film is uncovered, and some small cylindrical nanoparticles are formed and pushed to the top; (g) at some point in the growth process, the nanotube tip covering the Co@Au nanoparticle is bent, possibly because of the weight of the tip.

3. Conclusions

We have reported a novel method to synthesize Co@Au core-shell nanoparticles inside N-MWCNT. When the thickness of Co is 40 nm, the presence of very thin film of gold favors the growth of highly crystalline CNTs. In both cases, the growth mechanism is tip-growth, but the CNTs exhibit larger diameters when a cobalt-gold thin film is used as the catalytic substrate. For pure Co films of 20 nm thickness the situation is inverse. For example, a 2 nm-gold thin film improves the degree of crystallinity of N-MWCNT by reducing its I_D/I_G ratio obtained from Raman spectroscopy. The combination of ferromagnetic and superparamagnetic behaviors of the core-shell nanoparticles presented in this work make them attractive for applications in nanomedicine, in which they can be used to target or destroy cancer cells. We are currently studying other similar systems in order to determine the effect of the combination of two noble metals (gold and silver due to their non-toxic properties) on the magnetic and morphological properties of nitrogen-doped MWCNT (see [Fig. S6](#)).

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