Synthesis, Characterization and Magnetic Properties of N-doped multiwall carbon nanotubes encapsulated Co@Au core-shell nanoparticles

In recent years, synthesis and characterization of different kind 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 in the synthesis. For example, it is now known that almost any kind of metallic nanoparticle can be used as catalyst to produce carbon nanotubes provided that certain morphology conditions are fulfilled by the catalyst.[7,8] For example, gold nanoparticles have been used in alumina templates to grow nitrogen-doped carbon nanotubes.[9] In that paper a similar CNT growth mechanism than the typical Fe-nanoparticle case was proposed. The diameter of gold nanoparticles must be really small (< 5nm) in this case to fabricate carbon nanotubes. Other investigators have grown multiwall bamboo-like carbon nanotubes on bismuth.[10] Some alloys have successfully used as catalyst too[11,12]. There are two general routes to use the catalyst nanoparticles in the CVD methods by using some substance that contain such nanocatalyst [13] or using templates with the catalyst as thin film[14] or nanoislands.[15] Generally, the specific applications are the input to use determined material as reacting material with carbons in the synthesis of nanotubes. In this context, it is well known that the morphology parameters of a nanoparticle are the main aspect for determining its physical and chemical properties.[16,17] For example, due to their applications in biology, catalysis and nanotechnology, one of the most studied nanomateriales are noble metal nanoparticles. [18-20] In particular, gold and silver nanomaterials have been used to some applications in biomedicine.[21,22] However, because their extended uses bimetallic systems are really taking major importance.[23,24] Since physical or chemical point of view two different materials in one entity could be better than only one separately. For instance, we can found improved optical applications in a gold-silver alloy system. [25,26] Several other bimetallic gold and silver systems have been used in a multitude of applications. [27,28] There are three different most known ways to make these bimetallic structures namely making alloy, mixing or core-shell nanoparticles [references]. For their importance in a wide spectrum of research fields, we are interesting in the third type of bimetallic system composed with magnetic metal core and noble metal shell. [29-33] This type of shield would prevent the material from oxidizing and thus preserves its magnetic properties. [29] In addition the optical properties of noble metal increase the technological value of this hybrid system. In order to fabricate this type of materials different methods have been performed, such as chemical and wet gas-phase/solid-state. The first includes arc discharge,[34] catalytic methods,[35] sputtering.[36,37] The second method involves the chemical reduction of nanostructures[17,21]. In particular, the case of Co as magnetic material is interesting due to their magnetic properties. The significance of protecting the magnetic material with a no-oxidizing shell is because they physical and chemical properties are in general different if a layer of oxide is formed on the surface. The importance of these core-shell nanoparticles have been pointed out by several authors. [38] For example, Wang, *et al.*[39] mentioned the importance of physical and chemical properties of surfaces of these kind of nanoparticles. They emphasize that these nanoparticles will play an important role in biological and catalytic interfacial reactivity. They produced monodisperse Fe_3O_4 at Au core shell nanoparticles of sizes 5-15 nm core and 0.5-2 nm shell. They claimed the possibility of tailoring the thickness of the shell varying some synthesis parameters. It has been demonstrated that the magnetic properties change with reducing the size of the core and the increase of gold shell.[40]

On the order hand, carbon nanotubes have been classified as one of the most important nanomaterials in the last century. This nanomaterial, considered as one dimensional structure and it has had important contributions in varies predicted applications.[41,42] Several modifications have been proposed in the literature. Due to their natural superficial reactivity, between the most turned out modified carbon nanotubes, are nitrogen doped multiwall carbon

($MW-CN_x$) nanotubes. Since the beginning of their fabrication have been utilized in several interesting applications.[43,44] For example, very recently CN_X nanotubes were successfully used for oxygen reduction reaction [45-48] or lithium rechargeable battery applications.[50] It is worth to mention that the synthesis of carbon nanotubes could be carried on in absence of catalyst particles. [51] However, the of use catalytic particles of 3d transition metals such as Fe, Co, Ni or their alloys increases the CNT quality and quantity .[2,52] Nonetheless, it has been else reported the synthesis of carbon nanotubes using noble metals such as gold or copper.[1] Different routes have been implemented to synthesize carbon nanotubes using Co, Fe, Ni or Co-Fe alloys as catalysts. Regularly, in these carbon nanotubes the encapsulated nanoparticles have cylindrical shape or nanowires. [52] However, if a catalyst film of Ni, Fe or Co is used to produce carbon nanotubes, the nanoparticles have a small aspect ratio and sometimes are spherical with different diameters and morphology.[53] Sato *et al.* have used Ti-Co bimetallic nanoparticles as catalyst to grow carbon nanotubes.[54] Depending the percentage of Ti used, different kind of morphologies were obtained in the growth of CNTs. In that work, it is not clear the shape of the encapsulated nanoparticles and their chemical composition. Different morphologies have been found when gold is used as catalyst. [55-57] In order to grow carbon nanotubes using gold, Ag or Cu nanoparticles as catalyst, Takagi et al., carried out a cleaning process to the gold nanoparticles. However, this process reduces the size of Au nanoparticles producing only single wall carbon nanotubes.[57]

Here we have produced nitrogen-doped multiwall carbon nanotubes with internal Co@Au core-shell nanoparticles in their tip part. Comparing with other similar systems, this structure could be useful to several application between the most outstanding we could mention the biological,[58-60] magnetic,[61-62] and data storage,[63] among others. To the best of our knowledge this is the first time a method to fabricate core-shell nanoparticles, where the core is a transition metal nanoparticle (cobalt) and the shell is a noble metal (gold). In addition, a possible mechanism of growth is presented.

In Fig. 1 we show SEM images of carbon nanotubes grown on both a Co-Au bilayer film (Fig. 1a) and pure cobalt film (Fig. 1b). We can appreciate that, in the case of Co-Au layers used as template to grow, the tip of carbon nanotubes have spherical nanoparticles with diameter larger than that of the nanotube. However, the CNTs that grew from the Co film the tips are cylindrical following the structure of typical carbon nanotubes. We can see that the diameter and height are similar but the final parts (the tip) are completely different. The spherical shapes of CNTs catalyzed with Co-Au have diameters between 100 to 200 nm. These spherical parts of carbon nanotubes are formed by carbon layers that are encapsulating a bimetallic core-shell nanoparticle, where the core is cobalt and the shell is gold. This thin layer of gold is around 4 to 8 nm of thickness as will be showed ahead.

Regularly, in carbon nanotubes doped with nitrogen the encapsulated particles have conical form and they have a small aspect ratio (around 3),[64] but when a bilayer Co/Au thin film is used instead, the CNT tip is spherical. This spherical tip morphology can be attributed to the presence of gold (or noble metal, in general) component in the thin film. The explanation of this situation is still unknown, but we are proposing a growth mechanism (see Fig. 7).

To know the chemical composition of the CNTs forests produced by the different catalyst films we used energy dispersive X-ray (EDX) spectroscopy in the scanning electron microscope. In Fig. 2 the relevant results are shown. In Fig. 2a the EDX spectrum of carbon nanotubes grown using Au/Co thin films as catalyst is presented. For these EDX measurements we analyzed only the final part of these carbon nanotubes where Au and Co signal are perfectly observed. Carbon and silicon signal are present due to the carbon nanotubes and the substrate used to grow them. It is important to mention that, in this case, attached nanoparticles to surface of carbon nanotubes were not observed. Fig. 2b shows the

EDX spectrum of carbon nanotubes grown over a pure Co thin film deposited on a silicon substrate. Only cobalt signals are present (silicon signal comes from the substrate). The respective carbon peak is not showed.

In order to elucidate the origin of the Au signal in the EDX spectrum, we analyzed our samples with a high resolution transmission microscopy (HRTEM). Fig. 3 shows HRTEM images of two representative carbon nanotubes fabricated using a bilayer thin film of Au/Co. The carbon nanotubes show bamboo shape morphology with large cavities. The nanoparticles are almost spherical with diameters of 100 nm. The diameter of carbon nanotubes are around 80 nm the respective wall has 24 nm of thickness. In the case of nanotube of Fig. 3a, it seems that the spherical tip is not connected with the hollow interior of the CNT and no other metallic particle is near to the tip. However in the case of Fig. 3b the spherical tip is connected with the hollow interior of the CNT and the compartments are easily perceptible. In this case a thin small wire is close to the tip. In this image we can observe carbon nanotubes with bamboo shape structure which have smaller dimensions than the carbon nanotube with spherical tip.

Concerning the chemical composition of the carbon nanotube encapsulated nanoparticles, an elemental mapping analysis was performed on the carbon nanotube and it is presented in Fig. 4. A super-imposed elemental mapping of that carbon nanotube provide important information about the chemical composition of materials, different colors can be associated to different materials. Fig. 4a shows a mapping image of the carbon nanotube of Fig. 3a. In this case green correspond to carbon, blue to cobalt and red to gold. It is clear that gold and cobalt is distributed in the nanoparticles, although the cobalt nanoparticle is not completely covered by gold since it is possible to see a blue color inferior part of the spherical nanoparticles wish corresponding to cobalt metal. In Fig. 4b we show an EDX global spectrum line where it is possible to note the Co and Au signals. In Fig. 4c we show the TEM-EDX concentration profile along the same line which crosses the nanoparticle encapsulated inside the carbon nanotube tip. Red line correspond to the gold profile and blue one to cobalt. The carbon is plotted using a black line. The intensity of both blue and red are observed in the Fig. 4c. Note that in the left border the intensity of gold is not similar than the right border. This situation can be due to the cobalt core is not completely encapsulated by the gold- shell.

In favor of answering the question if the crystalline structure of our carbon nanotube samples is affected by the presence of gold we performed a Raman spectroscopy study (see Fig. 5). For that proposes we use a Micro-Raman spectrometer RENISHAW with an excitation energy of 2.4 eV (λ = 514 nm). It was observed that in the case of carbon nanotubes with spherical Au-Co core-shell nanoparticles inside the tip, the ratio between the intensities of D and G bands is smaller than the case when only a Co thin film is used to grow the carbon nanotubes. These results could be due to the presence of gold over the thin film of cobalt. In this case, the effect of nitrogen atoms to close the compartments is diminished because the catalytic action of thin gold nanoshell which is formed above the cobalt nanoparticles. This could be the reason that the compartments are larger than the carbon nanotubes grown with cobalt only. In that situation could be less sp^3 bonds causing that the ratio I_D/I_G be smaller than the respective case when gold is not participating as catalyst.

Measurements of magnetic properties were made using PPMS Evercool equipment. Three systems were studied a) cobalt films, b) cobalt film coated with a gold film and c) the systems of carbon nanotubes encapsulating nanoparticles core- shell. For all three cases we observed the typical behavior of ferromagnetic materials (see Fig. 6). Measurements showed that the coercive field was larger in the a) case. In the other two cases the coercive field is basically the same. The differences are about the shape of the hysteretic loop. Regularly, the ferromagnetic nanoparticles inside of N doped carbon nanotubes produced with benzylamine and ferrocene have conical shape.[64] Due such situation carpets of N-doped carbon nanotubes present different shapes of their hysteretic loops depending of the direction of applied magnetic field. The same situation is happening with the thin films of cobalt or bilayer cobalt-gold. The structure of this bilayer thin film is constituted by islands joined together. The size of that nanoparticles are around 10-20 nm. Although they still present a magnetic anisotropic behavior the necessary field to reverse the magnetic moments is smaller because the effects of Au layer. Another situation is happening with the core shell magnetic-noble metal system encapsulated in the carbon nanotubes. In this case the magnetic anisotropic is not present and the total magnetic moment is diminished as the field is decreasing. That situation it is very common in superparamagnetic systems, which it is corresponding with our spherical core-shell nanoparticles. Obviously, there are cobalt on the Si/SiO_2 substrate interacting with gold material and cylindrical ferromagnetic nanoparticles in the total system that is the reason that the hysteresis loop shape is still ferromagnetic-type with coercive field different to zero. Several routes have been used to control the magnetic properties of ferromagnetic nanoparticles inside or attached to carbon nanotubes.[65-68] However, here it is the first time that core-shell inside carbon nanotubes have been produced.

Considering all our results, in Fig. 7 we are showing the tip-growth mechanism (see Fig. 7a-g). The catalyst consists of a Co film covered with a a ultra-thin Au on top, this heterostructured film has a surface morphology with different sizes of nanoparticles (Fig. 7a). During the CVD process the nanoparticles are separating forming nanoparticles as those shown in Fig. 7c. A simplified schematic of the hypothetic process is presented in Fig 7b for a single nanoparticle; it is possible that the actual mechanism is more complicated than that. The nanoparticle formed during the CVD is formed with a thin film layer covering the cobalt nanoparticle (Fig. 7c); the inferior part of this nanoparticle should be uncovered to react with the carbon resulting in the crystallization of carbon layers than adopt the nanoparticle shape (Fig. 7d); it is possibly that due to the gold thin layer this last process is partially inhibited at least at the beginning and only few carbon layers are covering the bimetallic nanoparticle (Fig. 7e). However, the catalytic process continues and the carbon nanotube is forming and at the surface cobalt is uncovered and a normal process of growing is carried out (Fig. 7f); in sometime, due to the uncovered part of the surface, a cobalt nanoparticle is pushed to the tip following the tubular structure and forming small cylindrical nanoparticles. In addition, due to nitrogen atoms the bamboo shape is also conformed (Fig. 7g). In some part of the process the carbon nanotube cannot follow the vertical growing possibly due to the weight of the big nanoparticle in the top and start to blend forming the structures seen in the TEM images (see Fig. 3).

Conclusion

In conclusion, we have reported a novel method to synthesize Co@Au core-shell nanoparticles inside carbon nanotubes doped with nitrogen. It was observed that the presence of very thin film of gold favors the growth of more crystalline carbon nanotubes comparing with the case where only a thin film of cobalt is used as catalyst. In both cases the mechanism of growth is tip-type, but with cobalt-gold as substrate the carbon nanotubes present larger diameters. The ferromagnetic-type combined with a superparamagnetic behavior of the core shell nanoparticles presented by this system making them a promissory material to be applied in nanomedicine to cancer target or to destroy cancer cells. We are studying other similar systems to see the effect of the combinations of two noble metals (gold and silver due to their no toxic properties) in the magnetic and morphological properties of doped carbon nanotubes.

Experimental section

Co/Au and Co thin films were deposited on Si/SiO_2 substrates. Previously, the substrates were ultrasonic cleaned during ten minutes within a pure acetone solution. This cleaning process was repeated using ethanol, isopropyl alcohol, and de-ionized water solutions, and then the substrate was dried with nitrogen gas. In order to deposit the cobalt and cobalt-gold films a modified sputtering system INTERCOVAMEX V3 was used. In all cases cobalt and gold, the internal chamber works at a pressure of $2x10^{-2}$ Torr. In the case of Co-Au film, we used a power of 30 W 40 nm to deposit cobalt first and then 2 nm of gold during 34 minutes and 10 seconds, respectively. In the case of Co layer, the same parameters (30 W and 30 minutes) were used to obtain the sample. Without any additional procedure, the magnetizations versus magnetic field of the samples were measured using a physical properties measurement system (PPMS) with the field parallel to the substrates and at several temperatures. After this measurement, the samples were subjected to a typical ultrasonic spray-pyrolysis chemical vapor deposition (CVD) process using benzylamine as carbon and nitrogen source. In order to grow carbon nanotubes with core-shell characteristics a set up of two furnaces is necessary. The temperature in the first furnace must be at 750 °C and the second at 850 °C. The samples were collocated inside of a quartz tube and inside of the furnace in the middle part of second furnace. Previous to the adequate conditions for growing were reached, an argon-hydrogen flow was passed through the quartz tube in the CVD arrangement at 0.5 l/m during 10 minutes to remove the possibly formed cobalt oxides at the surface of substrates. After the temperatures in both furnaces were stable the generator benzylamine atomized solution was turned on and the inert gas flow rate was increased to 2.5 l/min. It is very probably that at the moment when the temperature reached 850 °C separated cobalt and gold nanoparticles were formed at the surface of substrates [69] (similar situation it could have happened in the case of cobalt). These nanoparticles are randomly distributed with diameters between 20 to 50 nm. It is possible that with the raise of temperature (850 °C) under an Ar-H_2 gas atmosphere these nanoparticles are slightly separated and their catalytic activity is increased. The total process could be seen in the hypothetical mechanism drawn in Fig. 11. At this stage, the experiment is maintained in these conditions 30 minutes. At the end the sprayer and furnaces are turned off, the flow is put set at 0.3 l/m during the whole time that the furnace reached room temperature. The sample was removed from the quartz tube and the magnetization is measured in a PPMS system. An additional 40 nm cobalt sample was fabricated and characterized. The samples with nitrogen doped carbon nanotubes (CNx) were characterized by scanning electron microscopy (SEM) using a FEI Helios 600 Nanolab and by transmission electron microscopy (TEM) using a HRTEM 300 kV FEI TECNAI F30 STWIN G2. The Raman spectroscopy was carried out using a Micro-Raman spectrometer RENISHAW.

References

[1] J. Hu, T. W. Odom, C. M. Lieber. *Acc. Chem. Res*. **1999,** 32, 435-445.

[2] W. Yang, K. R. Ratinac, S. P. Ringer, P. Thordarson, J. J. Gooding, and F. Braet. *Angew. Chem. Int. Ed.* **2010**, 49, 2114 – 2138.

[3] J.-P. Salvetat, J.-M. Bonard, N. H. Thomson, A.J. Kulik, L. Forro, W. Benoit, L. Zuppiroli. *Appl. Phys. A-Mater. Sci. Process.* **1999**, 69, 255–260.

[4] S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo. *Nature* **2001**, 412 169-172.

[5] N. W. S. Kam, M. O'Connell, J. A. Wisdom, H. J. Dai. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, 102, 11600-11605.

[6] C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, A. Govindaraj. *Angew. Chem. Int. Edit.* **2009**, 48, 7752-7777.

[7] I. Ibrahim, A. Bachmatiuk, J. H. Warner, B. Büchner, G. Cuniberti, and M. H. Rümmeli.

Small.l **2012**, 8, 1973–1992.

[8] D. Takagi, Y. Homma, H. Hibino, S. Suzuki, and Y. Kobayashi. *Nano Letters* **2006**, 6, 2642-2645.

[9] G. N. Ilinich, B. L. Moroz, N. A. Rudina, I. P. Prosvirin, V. I. Bukhtiyarov. 2012. *Carbon* 50, 1186-1196.

[10] Sahoo, RK (Sahoo, R. K.)1; Daramalla, V (Daramalla, V.)1; C. Jacob. *Mater. Sci. Eng. B-Adv. Funct. Solid-State Mater* **2012**, 177, 79-85.

[11] W. H. Chiang, R. M. Sankaran, *Carbon* **2012**, 50, 1044-1050.

[12] A. L. Elías, J. A. Rodríguez-Manzo, M. R. McCartney, D. Golberg, A. Zamudio, S. E. Baltazar, F. López-Urías, E. Muñoz-Sandoval, L. Gu, C. C. Tang, D. J. Smith, Y. Bando, H. Terrones, M. Terrones. **2005** *Nano Letters* 5, 467-472.

[13] E. N. Nxumalo, V. O. Nyamori, N. J. Coville, J. Organomet. Chem., **2008**, 693, 2942-2948.

[14] Y. Y. Wei, Gyula Eres, V. I. Merkulov, and D. H. Lowndes, *App. Phys. Lett*. 2001, 1394-1396.

[15] T. Yamada, T. Namai, K. Hata, D. N. Futaba, K. Mizuno, J. Fan, M. Yudasaka, M. Yumura, S. Iijima, *Nature Nanotechnol*., 2000, 1, 131-136.

[16] C. Burda, X. Chen, R. Narayanan,M. A: El-Sayed *Chem. Rev*. **2005**,105, 1025-1102.

[17] K. L. Kelly, E. Coronado, L. L. Zhao , G. C. Schatz, *J. Phys. Chem. B*, **2003**,107, 668-677.

[18] M.-C. Daniel, D. Astruc, *Chem. Rev*. **2004**,104, 293-346.

[19] Y. Sun, Y. Xia, *Science* **2002**, 298, 2176-2179.

[20] B. Nikoobakht, M. A. El-Sayed, *Chem. Mater*. **2003**,15, 1957-1962.

[21] X. Huang, I.H. El-Sayed, W. Qian, M. A. El-Sayed, *J. Am. Chem. Soc*. **2006**, 128, 2115-2120.

[22] P. Alivisatos, *Nature Biotechnology* **2004,** 22, 47-52.

[23] N. Toshima, T. Yonezawa, *New J. Chem*. **1998**, 22, 1179-1201**.**

[24] R. Ferrando, J .Jellinek , R. L. Johnston, *Chem. Rev*. **2008,** 108, 845-910.

[25] L. M. Liz-Marzan, *Langmuir* **2006,** 22, 32-41.

[26] S. Link, Z. L. Wang, M.A. El-Saye, *J. Phys. Chem. B* **1999**, 103 3529-3533.

[27] R. L. Johnston, *Dalton Trans*. **2003**, 22, 4193-4207.

[28] A. Rapallo, G. Rossi, R. Ferrando, A. Fortunelli, B. C. Curley, L. D. Lloyd, G. M. Tarbuck, R. L. Johnston, *J. Chem. Phys*. **2005**,122, 194308.

[29] Y. Qiang, J. Antony, A. Sharma, J. Nutting, D. Sikes, D. Meyer, *J. Nanopart. Res*. **2006**, 8, 489–496.

[30] J. Hormes, H. Modrow, H. Bönnemann, C. S. S. R. Kumar, *J. Appl. Phys*. **2005**, 97, 10R102.

[31] T. Bala, S. D. Bhame, P. A. Joy, B. L. V. Prasad, M. Sastry, J. Mater. Chem. **2004**, 14, 2941-2945.

[32] M. Mandal,S. Kundu, S. K. Ghosh, S. Panigrahi, T. K. Sau, S. M. Yusuf, T. Pal, J. Colloid Interface Sci. **2005**, 286,187-194.

[33] W. L. Zhou,E. E. Carpenter, J. Lin, A. Kumbhar, J. Sims, C. J. O'Connor, Eur. Phys. J. D. **2001**, 16, 289-292.

[34] C. Hao, F. Xia, Z. Cui, J. Nanopart. Res. **2008**, 10, 47–51.

[35] B.H. Liu, J. Ding, Z. Y. Zhong, Z .L. Dong, T. White, J. Y. Lin, Chem. Phys. Lett. **2002**, 358, 96–102.

[36] H. W. Kim, H. S. Kim, C. Lee, M. A. Kebede, K. -H. Yoo, D. Y. Kim, J. Korean Phys. Soc. , **2009**, 55,1887-1891.

[37] X. N. Guo, P. Brault, G. J. Zhi, A. Caillard, C. Q. Jin, X. Y. Guo, *J. Phys. Chem* C 2011, 115 24164-24171

[38] J. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, *Science* **2009**, 323, 760-764.

[39] L. Wang, J. Luo, Q. Fan, M. Suzuki, I. S. Suzuki, M. H. Engelhard, Y. Lin, N. Kim, J. Q. Wang, C.-J Zhong, *J. Phys. Chem. B* **2005,**109, 21593-21601.

[40] S. Mandal, K. M. Krishnan, *J. Mater. Chem.* **2007**, 17, 372-376.

[41] Y. Xia, P. Yang,Y. Sun, Y. Wu, B. Mayers, B- Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mat.* **2003**,15, 353-389.

[42] R. H. Baughman, A. A. Zakhidov, W. A. de Heer, *Science* **2002**, 297, 787-792.

[43] O. Stephan, P. M. Ajayan, C. Colliex, Ph. Redlich, J. M. Lambert, P. Bernier, P. Lefin, *Science* **1994**, 266, 1683-1685.

[44] M. Terrones, P. Redlich, N. Grobert, S. Trasobares,W.-K. Hsu, H. Terrones, Y.-Q. Zhu, J. P. Hare, C. L. Reeves, A. K. Cheetham, M. Rühle, H. W. Kroto, D. R. M. Walton, *Adv. Mat.* **1999**, 11, 655-658.

[45] K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, *Science* **2009,** 323, 760-764.

[46] J. Vazquez-Arenas, D. Higgins, Z. Chen, M. Fowler, Z. Chen, *J. Power Sources* **2012**, 205, 215-221.

[47] X. Lepro, R. Ovalle-Robles, M. D. Lima, A. L. Elías, M. Terrones, R. H. Baughman, *Adv. Func. Mater.* **2012**, 22, 1069-1075.

[48] C. V. Rao, Y. Ishikawa, *J. Phys. Chem*. C **2012**,116, 4340-4346.

[49] M. Kaukonen, R. Kujala, E. Kauppinen, *J. Phys. Chem*. C **2012,** 116, 632-636.

[50] X. Li, J. Liu, Y. Zhang, Y. Li, H. Liu, X. Meng, J. Yang, D. Geng, D. Wang, R. Li, X. Sun, *J. Power Sources* **2012**, 197, 238-245.

[51] S. Iijima, *Nature* **1991**, 354, 56–58.

[52] A. L. Elías, J. A. Rodríguez-Manzo, M. R. McCartney, D. Golberg, A. Zamudio, S. E. Baltazar, F. López-Urías, E. Muñoz-Sandoval, L. Gu, C. C. Tang, D. J. Smith, Y. Bando, H. Terrones, M. Terrones, *Nano Lett*., **2005,** 5, 467-472.

[53] Z.P. Huang, D.Z. Wang, J.G. Wen, M. Sennett, H. Gibson, Z.F. Ren, *Appl. Phys. A* **2002**, 74, 387–391.

[54] S. Sato, A. Kawabata, D. Kondo, M. Nihei, Y. Awano, Chem. Phys. Lett. **2005**, 402, 149-154.

[55] S.-Y. Lee, M. Yamada, M. Miyake, Carbon **2005**, 43, 2654–2663

[56] S. Bhaviripudi, E. Mile, S. A. Steiner III, A. T. Zare, M. S. Dresselhaus, A. M. Belcher, and J. Kong, J. Am. Chem. Soc. 2007, 129, 1516-1517. [CVD Synthesis of Single-Walled Carbon Nanotubes from Gold Nanoparticle Catalysts]

[57] D. Takagi, Y. Homma, H. Hibino, S. Suzuki, Y. Kobayashi, *Nano Lett.*, **2006**, 6, 2642-2645.

[58] M. Prato, K. Kostarelos, A. Bianco, *Acc. Chem. Res*. **2008,** 41, 60-68.

[59] L. Wang, L. Wang, J. Luo, Q. Fan, M. Suzuki, I. S. Suzuki, M. H. Engelhard, Y. Lin, N. Kim, J. Q. Wang, C. -J Zhong. *J. Phys. Chem. B* **2005**, 109, 21593-21601.

[60] V. Salgueirino-Maceira, M. A. Correa-Duarte, *Adv. Mat*. **2007**, 19, 4131-4144.

[61]A.-H. Lu, E. L. Salabas, F. Schüth. *Angew. Chem. Int. Ed. Engl*. **2007**, 46, 1222–1244.

[62] H. Zeng, J. Li, Z. L. Wang,J. P. Liu, S Sun, *Nano. Lett*. **2004,** 4,187-190.

[63] S. Sun, *Adv. Mat.* **2006**, 18, 393-403.

[64] F. Lopez-Urias, E. Muñoz-Sandoval, M. Reyes-Reyes, A.H. Romero, M. Terrones, and J.L. Morán-López, Phys. Rev. Lett. **2005**, 94, 216102-4.

[65] D. Meneses-Rodríguez, E. Muñoz-Sandoval, G. Ramirez-Manzanarez, D. Ramirez-Gonzalez, S. Diaz-Castañon, J.C. Faloh-Gandarilla, A. Morelos-Gómez, F. Lopez-Urias, and M. Terrones. J. of Nanoscience and Nanotech. **2010**, 10, 5576-5582.

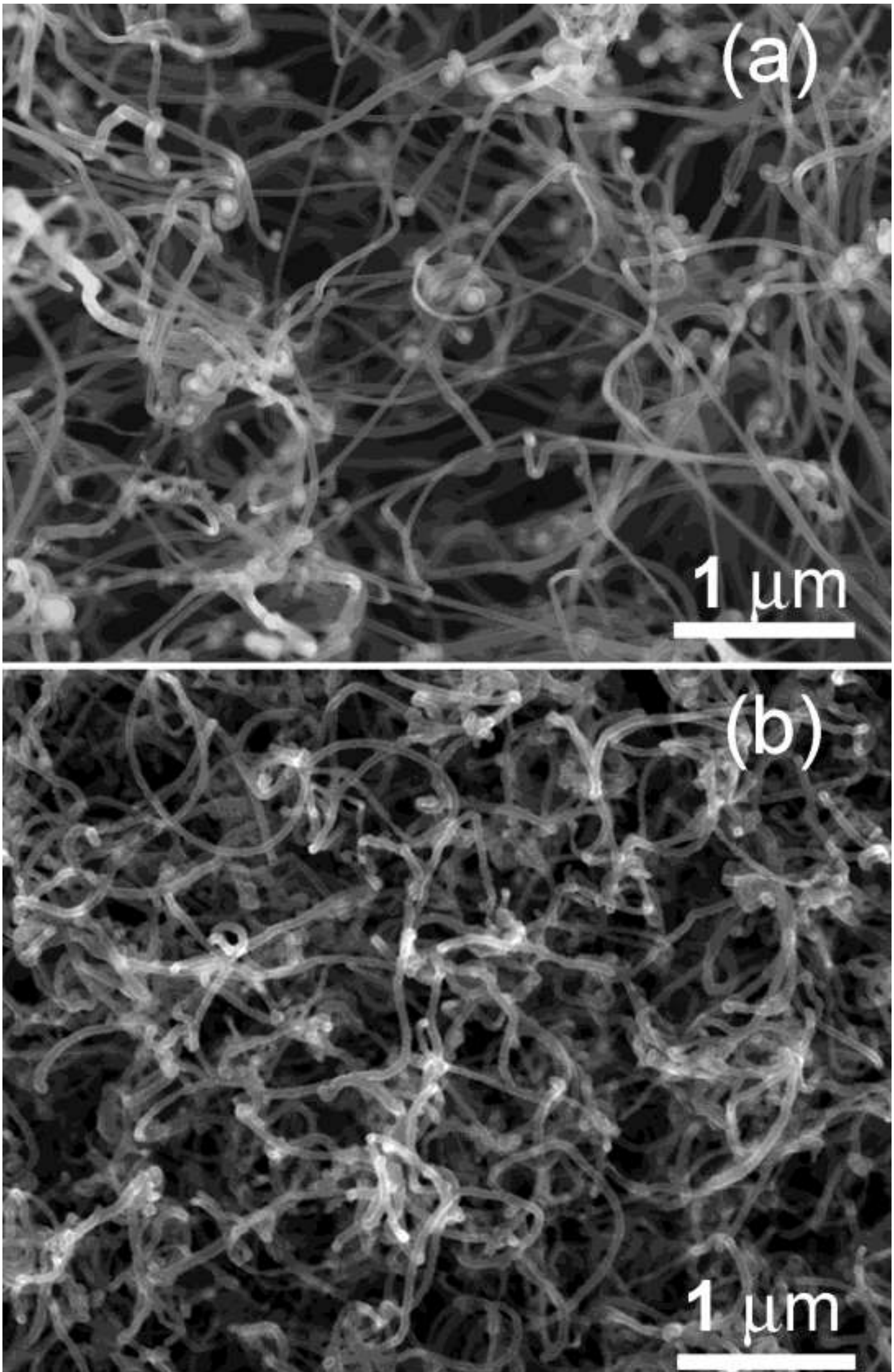
[66] A. Morelos-Gomez, Aaron, F. Lopez-Urias, E. Munoz-Sandoval, C. L. Dennis, R. D. Shull, H. Terrones, M. Terrones, J. Mater. Chem. **2010**, 20, 5906-5914.

[67] F. Zhao, H. Y. Duan, W. G. Weigao, J. Wang, Physica B, **2012**, 407, 2495-2499.

[68] Y. Li, C. Zhu, Ch. Wang, J. of Phys. D-Appl. Phys. **2008**, 41, 125303.

[69] Y. J. Yoon, J. C. Bae, H. K. Baik, S. Cho, S.-J. Lee, K. M. Song, N. S. Myung, Chem. Phys. Lett. **2002**, 366 109, 114.

Figures and Figure Captions


(a)
1 μm
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1 μm

Fig. 1. SEM images of nitrogen doped carbon nanotubes grown on two kind of thin films deposited in Si/SiO2 substrates: (a) The thin film is a Au/Co bilayer with Co thickness of 40 nm and Au thickness of 2 nm; (b) in this case the thin film is only a Co layer of 40 nm thickness (see supplementary information). Note that most of nanoparticles in the case (a) are spherical and with diameters bigger than the diameter of the carbon nanotube. In case (b) it is not possible to note clearly the nanoparticles inside of the carbon nanotubes.

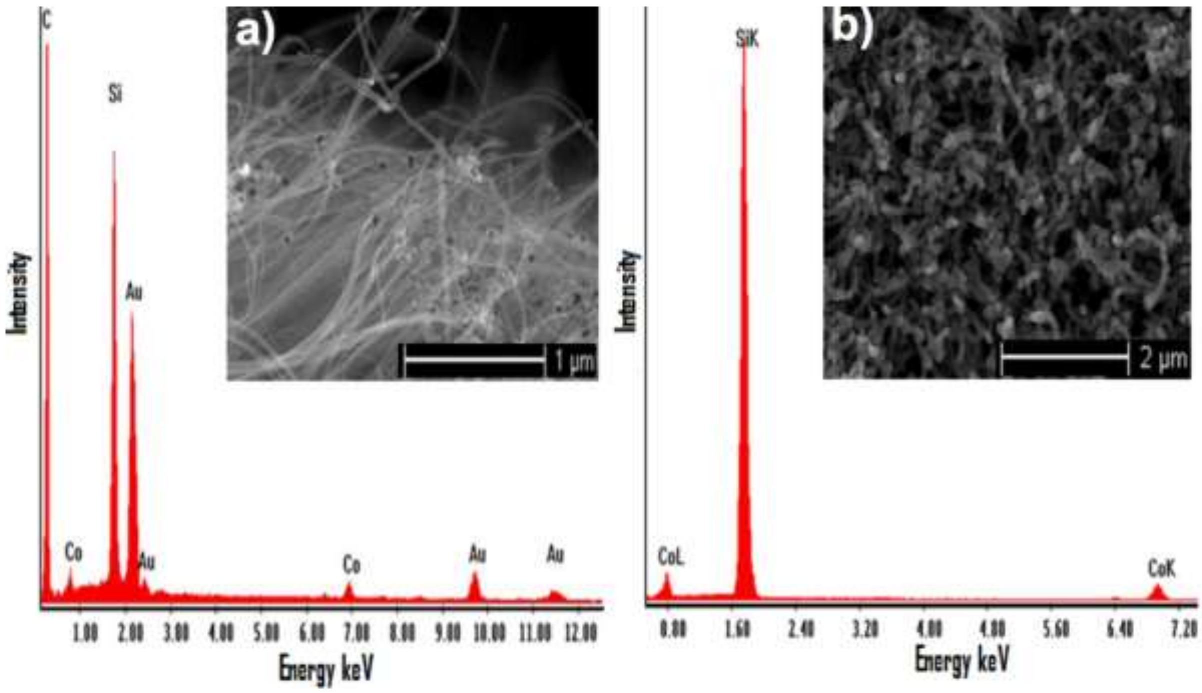

Fig. 2**.** EDX spectrum of a part of carbon nanotubes grown using different catalyst. In Fig. 2a an Au/Co bilayer thin film was used in the CVD experiment. From this figure is clear that gold is distributed in the final part of carbon nanotubes (C and Si signals come from carbon nanotubes and substrate, respectively). However, it is not conclusive that Au is in the encapsulated nanoparticles. In Fig. 2b carbon nanotubes were grown using a Co thin film as catalyst. The signal of Co is clearly observed, there is not additional signal of another material in the spectrum (the Si peak is because the substrate).

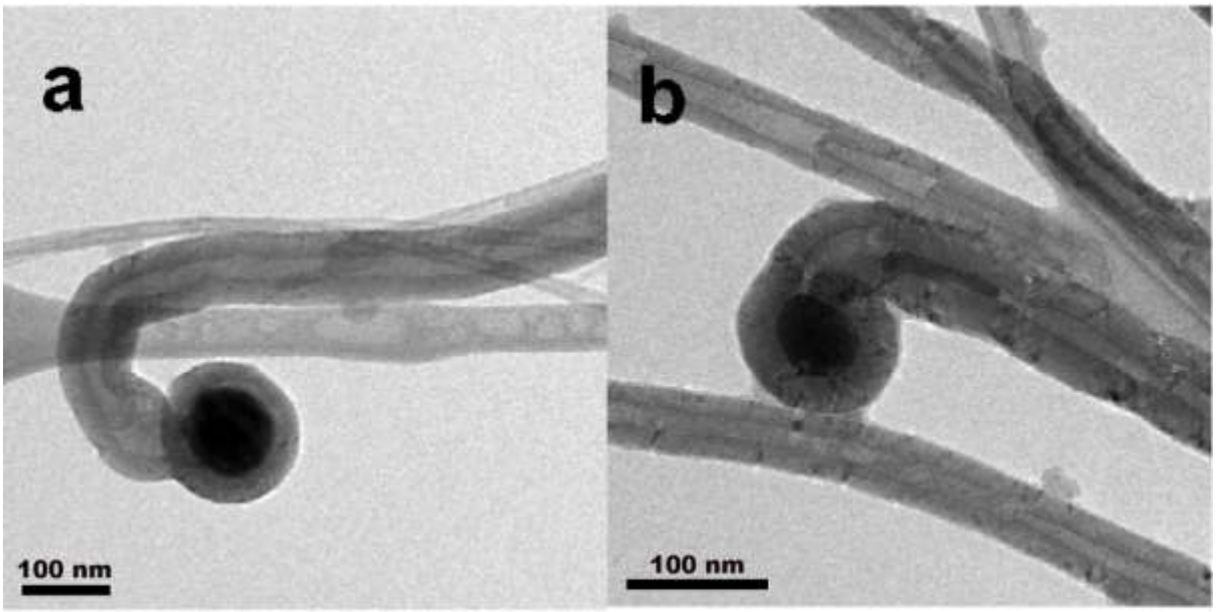

Fig. 3. Images of transmission electron microscopy (HRTEM) of carbon nanotubes with spherical tip morphology grown over Co/Au thin film deposited on silicon substrates. Fig. 3a corresponds to a carbon nanotube with 70 nm of diameter with a spherical tip apparently with a not clear connection with their core hole. The encapsulated Co@Au spherical nanoparticle has 100 nm of diameter and it is inside of a carbon spherical structure surrounded it. Fig. 3b is another carbon nanotube with spherical tip showing a better connection with the core hole of carbon nanotube. In addition their bamboo shape is clearly seen and a thin small wire (80 nm long and 10 nm of diameter) is observed. Although in both cases they have bamboo-like structures along its structure, the carbon nanotube of Fig. 3a show a longer compartment than the case showed in Fig. 3b.

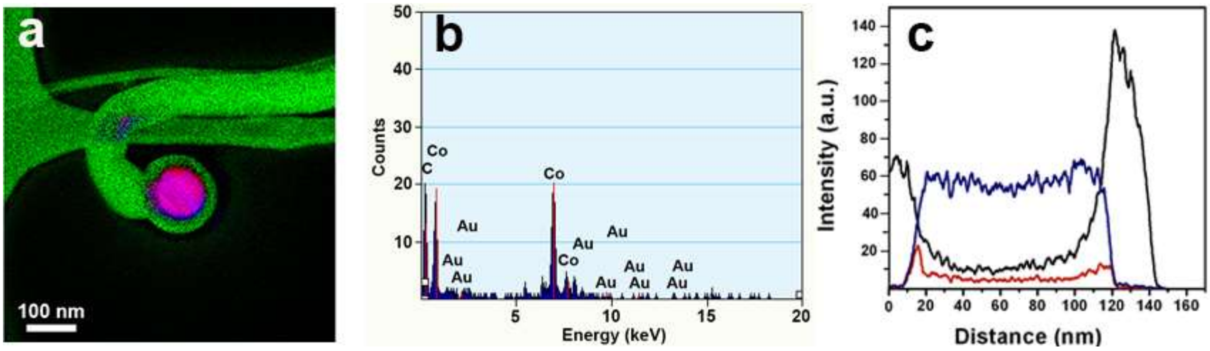

Fig 4. Images showing the chemical analysis over carbon nanotubes produced on Au/Co thin film: **a**) superimpose elemental mapping of carbon nanotube showed in Fig. 3a, the combination of red and blue give the purple tone in the center of the nanoparticles. It seem that the spherical nanoparticles in not totally covered by gold since a blue color is observed at the bottom of it; **b)** corresponding EDX global spectrum line taken on the diameter of the nanoparticle; **c)** concentration of Au, Co and C derived from EDX spectrum line.

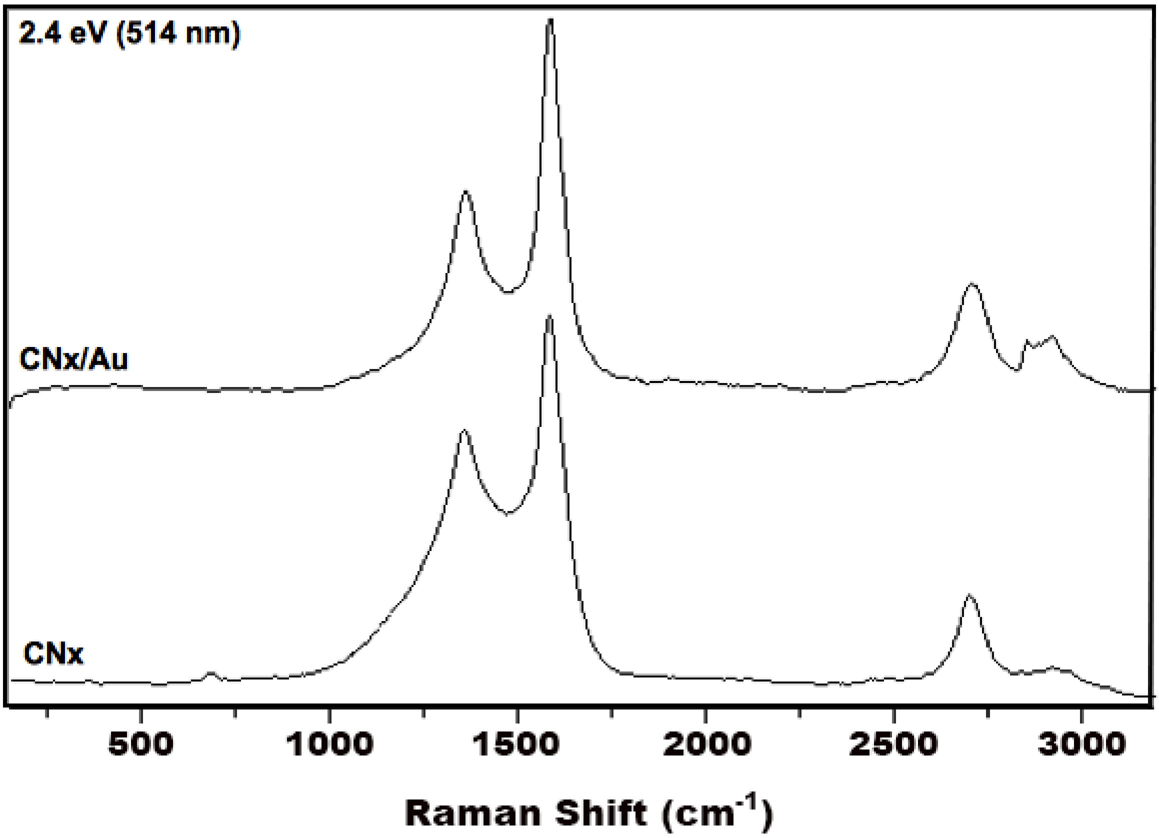

Fig. 5. Raman spectroscopy plots performed in carbon nanotubes grown using a bimetallic Au/Co thin film as catalyst (CNX/Au superior curve) and only a thin film of cobalt (inferior curve). The ratio between the intensities of D and G band is bigger in the case of CNx/Au than the case of CNx. It seems that the thin film layer of gold helps to produce more crystalline carbon nanotubes. (Falta indexer los espectros)

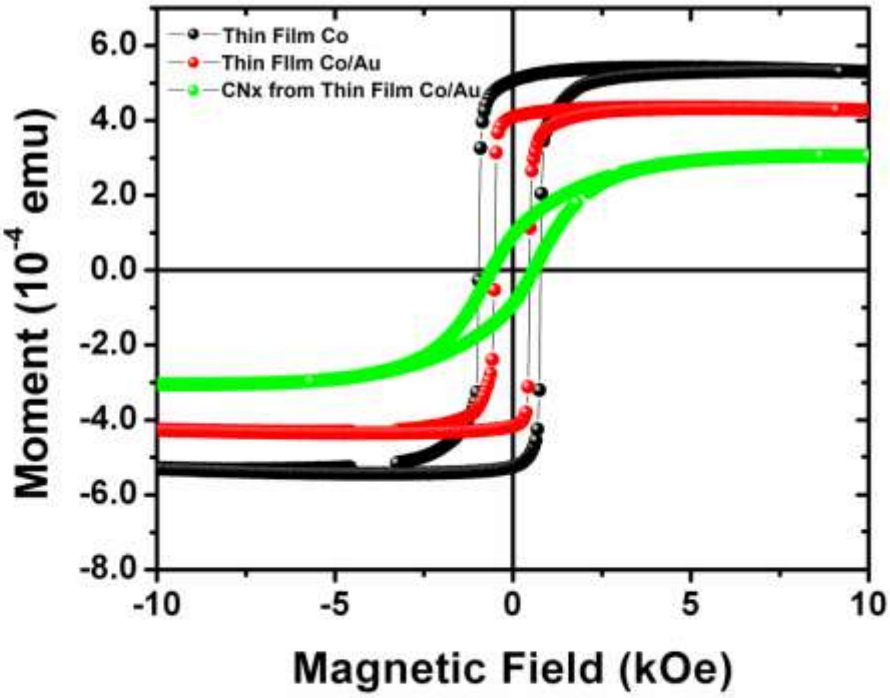

Fig. 6. Plots of hysteretic loops taken on thin film of cobalt (black); thin film of cobalt-gold bilayer (red); and a carpet of N-doped carbon nanotubes (green). The measurement was realized at 2 K with a maximum magnetic field of 1 Tesla. The red and black curves present a typical ferromagnetic behavior and with a very similar shape. However, the green one has a superparamagnetic-like behavior. Note the reduction of the saturated magnetic moment in the two last cases.

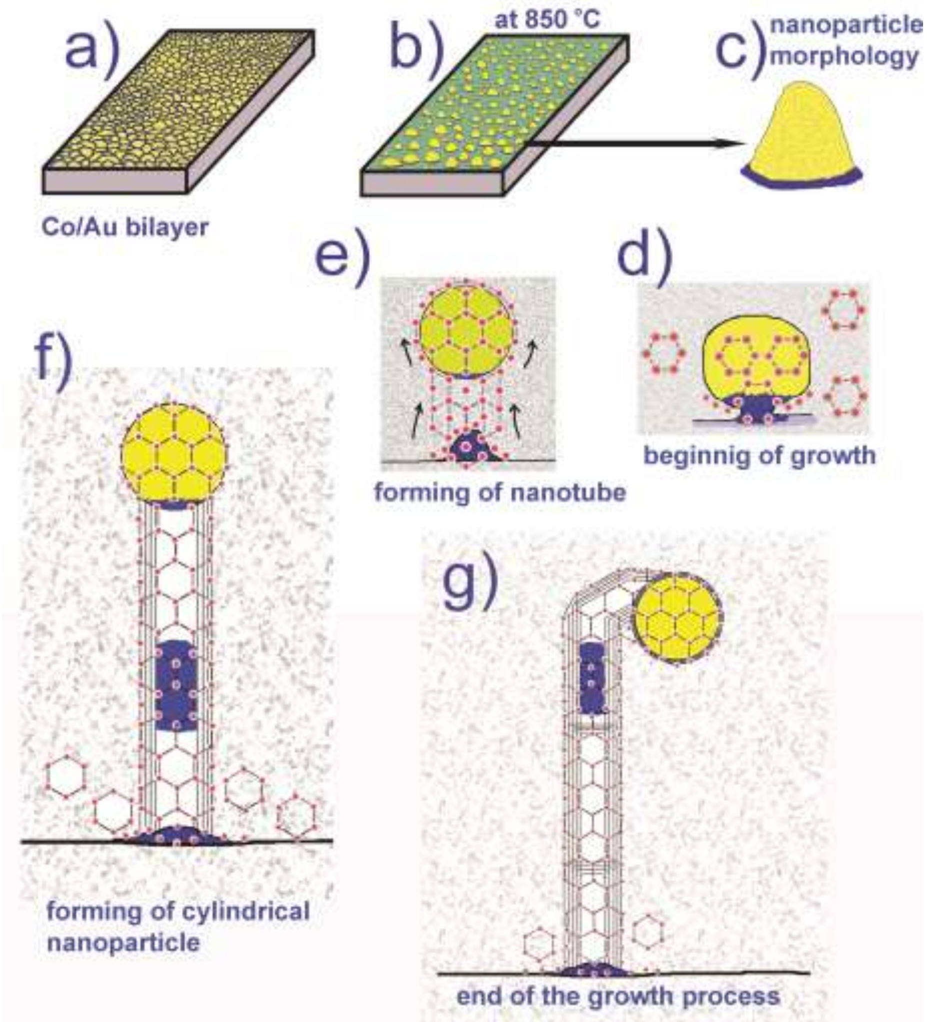

Fig. 7 Schematic diagram accounting for the carbon nanotube growth during the CVD process: (e) structured thin film Co/Au formed after sputtering process; b) Co-Au system are well conformed during the 10 minutes annealing process previous CVD experiment; c) a magnification of a small nanoparticle showed in b); d) Due to cobalt is not completely covered by gold the particular catalytic process starts ; e) gold layer avoid the tip growth process and the root growing is taken out; f) cobalt film is uncovered now and some small cylindrical nanoparticles are formed and pushed to up; g) in some time of the growth processes the nanotube tip covering the Co@Au nanoparticle is blend possibly because the weight of the tip.

Supporting Information should be included here (for submission only; for **publication**, please provide Supporting Information as a separate PDF file).

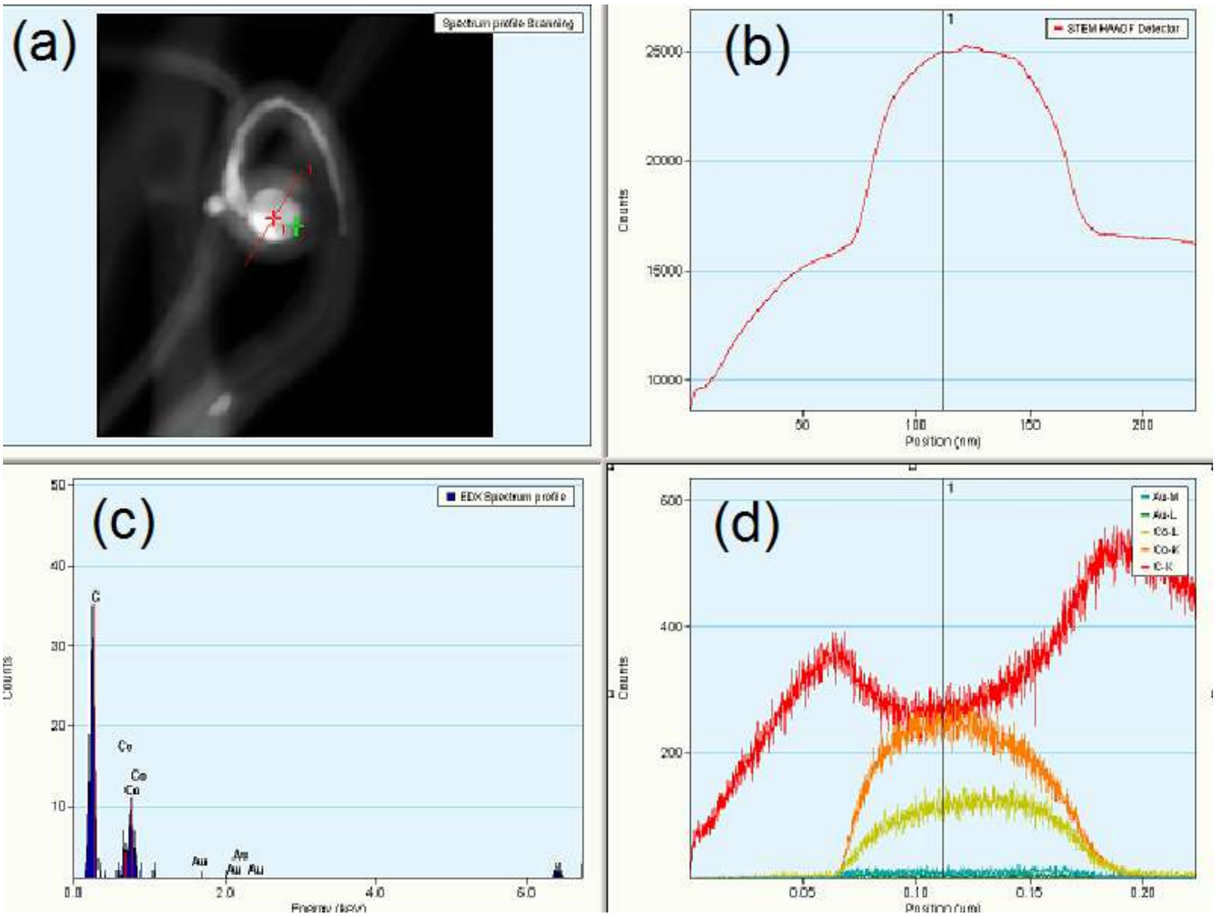

Fig. S1. Chemical analysis of Co@Au core-shell nanoparticles encapsulated in nitrogen carbon nanotubes: (a) Spectrum profile scanning image of core-shell nanoparticle; (b) STEM HAADF detector image; (c) corresponding EDX global spectrum line taken on the diameter of the nanoparticle; (d) concentration of Au, Co and C derived from EDX spectrum line.

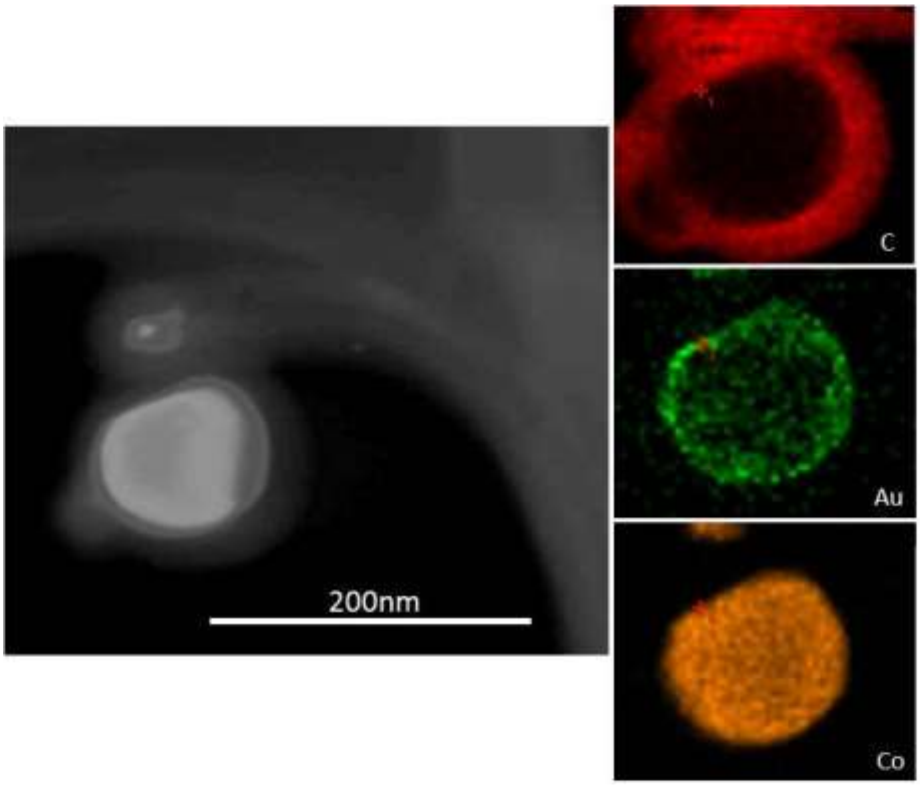

Fig. S2. Elemental mapping of Co@Au core-shell nanoparticles encapsulated in nitrogen carbon nanotubes; the right images are showing their chemical composition.

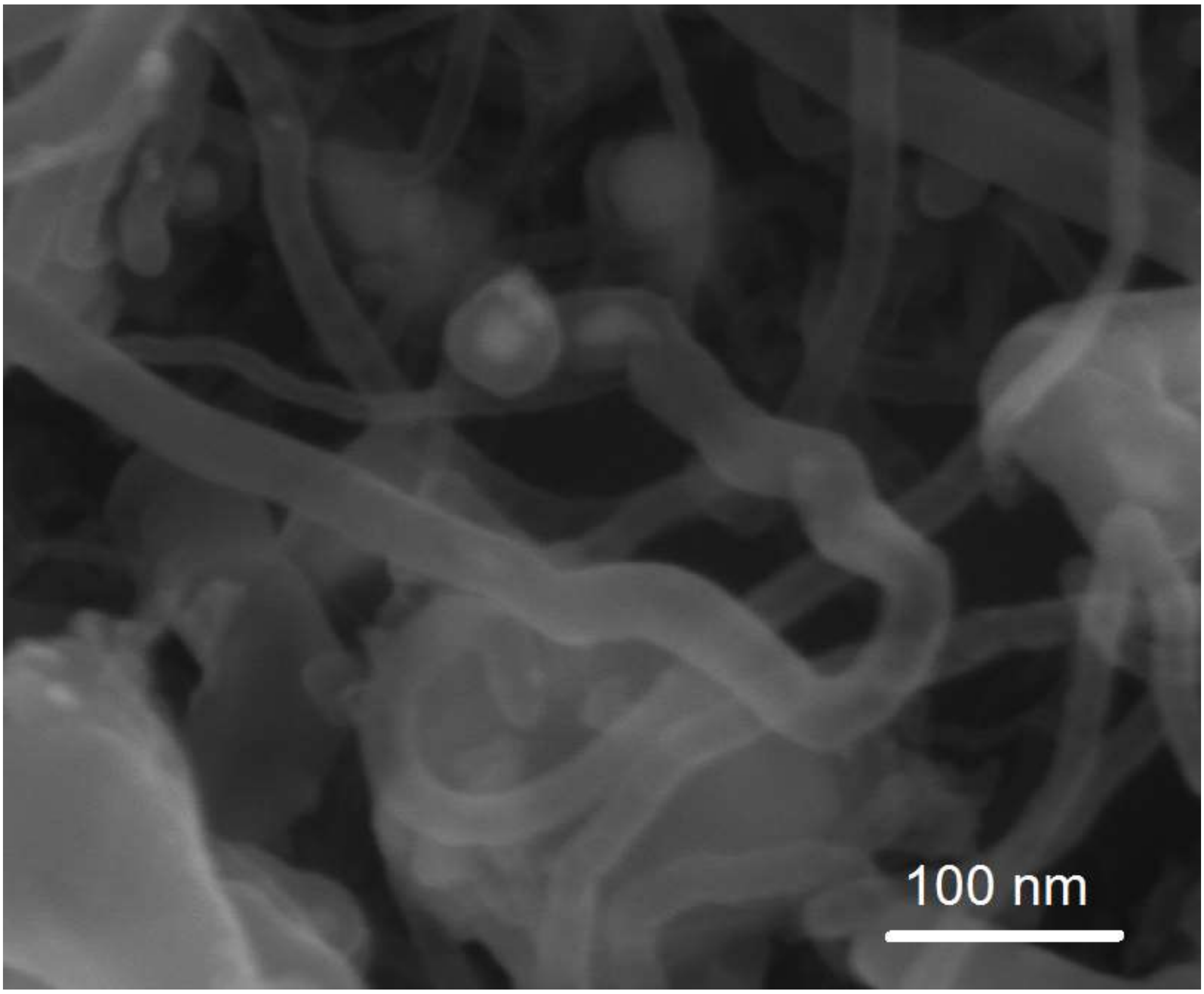

Fig. S3. Preliminary results of Ag(2 nm)/Co (20 nm) thin film deposited on Si/SiO2 substrate and synthesis by CVD method of nitrogen doped carbon nanotubes on it. The structure is similar, but a deeper characterization is needed.