Observation of ferromagnetism in PdCo alloy nanoparticles encapsulated in carbon nanotubes

Daniel Bretas Roa, Ingrid David Barcelos, Abner de Siervo, Kleber Roberto Pirota, Rodrigo Gribel Lacerda, and Rogério Magalhães-Paniago

Citation: Applied Physics Letters **96**, 253114 (2010); doi: 10.1063/1.3454781
View online: http://dx.doi.org/10.1063/1.3454781
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/96/25?ver=pdfcov
Published by the AIP Publishing

Observation of ferromagnetism in PdCo alloy nanoparticles encapsulated in carbon nanotubes

Daniel Bretas Roa,[1] Ingrid David Barcelos,[1] Abner de Siervo,[2,3] Kleber Roberto Pirota,[2] Rodrigo Gribel Lacerda,[1] and Rogério Magalhães-Paniago[1,a)]
[1]*Departamento de Física, Universidade Federal de Minas Gerais, 30123-970 Belo Horizonte, Brazil*
[2]*Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, 13083-970 Campinas, Brazil*
[3]*Laboratório Nacional de Luz Síncrotron, 13084-971 Campinas, Brazil*

(Received 14 April 2010; accepted 24 May 2010; published online 24 June 2010)

Carbon nanotubes terminated by PdCo catalyst nanoparticles were grown by plasma-enhanced chemical vapor deposition. Transmission electron microscopy reveals that these nanoparticles have a droplike shape and are completely encapsulated inside multiwalled nanotubes. Magnetization measurements showed the existence of a permanent magnetization with a small shape anisotropy effect. The magnetization of both cobalt and palladium was confirmed by x-ray magnetic circular dichroism. These results show that nanotubes ended by magnetic PdCo nanoparticles can be grown and could be used in magnetic storage media and electrical spin injection. © *2010 American Institute of Physics*. [doi:10.1063/1.3454781]

The synthesis of carbon nanotubes (CNTs) (Ref. 1) has opened up the possibility of production of several devices taking advantage of the geometry and size of these nanostructures. One of the challenges in their production is the encapsulation of metals inside these nanotubes, which could be used in several applications where a conductive and/or magnetic end is necessary.[2] Usually 3*d* transition metals (e.g., Fe, Ni, and Co) are used as catalysts for the formation of CNTs by plasma-enhanced chemical vapor deposition (PECVD).[2,3] However, the oxidation of these particles or formation of carbides may degrade their properties over time. Therefore, the incorporation of noble metals in these nanoparticles would be very interesting for application purposes. Several groups have already accomplished the growth of CNTs ended by bimetallic nanoparticles (e.g., FePt and PdCo).[3,4]

Bimetalic nanoparticles with palladium are ideal candidates, since Pd is chemically stable and it can become ferromagnetic.[5,9] The introduction of small amounts of 3*d* transition metals such as Fe, Ni, and Co in palladium stabilizes its ferromagnetism.[6] Fujita *et al.*[4] have recently reported the growth of CNTs terminated by PdCo nanocomposites. They have observed, however, a composition separation which resulted in inhomogeneous nanoparticles. In the present work, we have grown CNTs with homogeneous PdCo nanoparticles starting from a Pd(5 nm)/Co(5 nm)/Si film. Transmission electron microscopy (TEM) confirmed the formation of CNTs terminated by drop-shaped nanoparticles, with an aspect ratio of 3:1. Vibrating sample magnetometry (VSM) measurements at room temperature confirmed their ferromagnetism. To prove that an alloy magnetic nanostructure was formed, the separate magnetization of both cobalt and Pd was confirmed by x-ray magnetic circular dichroism (XMCD).

CNTs were grown using a home built PECVD setup with the substrate located on a resistively heated graphite stage. The substrate temperature was measured using a thermocouple attached directly to the upper surface of the stage. Gas flow rates were controlled independently using mass flow controllers and the combined gases were fed into the chamber through a metal pipe which was grounded, acting as an anode for the plasma discharge. The plasma was generated by a dc power supply. The chamber was maintained at vacuum using a rotary pump, with a base pressure of 8×10^{-2} mbar. The substrate was sequentially coated by thermal evaporation of a double layer of metal catalysts [Pd(5 nm)/Co(5 nm)/Si]. Our CNT growth procedure consisted of loading this Pd/Co/Si film onto the graphite stage and heating to 500 °C in NH_3 [200 SCCM (SCCM denotes cubic centimeter per minute at STP) flow rate, achieving a pressure of 2.5 mbar]. At these conditions, the thin film PdCo catalyst agglomerates into nanoparticles suitable for seeding nanotube growth. The dc plasma was then immediately initiated, and C_2H_2 was added into the gas flow as the carbon feedstock for the growth of multiwalled nanotubes.[7] The plasma dc bias was maintained at 600 V, with a current of typically 100 mA. The gas flow rates were 200 SCCM for NH_3 and 60 SCCM for C_2H_2. The heater temperature was regulated to maintain the temperature stably at 600 °C throughout the deposition (~30 min). After this process a forest of vertically aligned nanotubes was formed all over the substrate.

The nanoparticles were analyzed with a 300 kV JEM transmission electron microscope. In Fig. 1(a) one can see several nanotubes distributed over a transmission grating with a Lacey-type carbon film deposited on top. The size distribution of both nanotubes and nanoparticles is quite uniform and the average diameter of the nanoparticles was determined to be (79 ± 30) nm. The length and density of our CNTs are (3.1 ± 0.7) μm and $(6.9\pm0.9)\times10^9$ cm^{-2}, respectively. It should be noted that all nanotubes are perfectly terminated by homogeneous droplike PdCo nanoparticles, which explains the response to magnetic fields applied parallel and perpendicular to them. In Fig. 1(b) a TEM micrograph of an isolated PdCo nanoparticle is shown, where one can see that the nanoparticles are completely encapsulated inside the CNTs. The image was taken with the particle center oriented along the [001] zone axis. No fringes due to

a)Electronic mail: rogerio@fisica.ufmg.br.

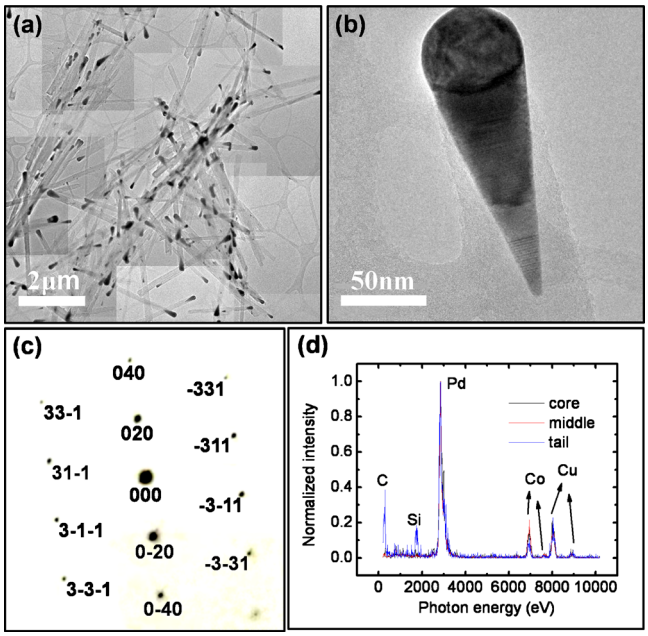

FIG. 1. (Color online) (a) Composition of 16 TEM micrographs of approximately 3×3 μm^2 producing an overview of the distribution of several CNTs, which all have encapsulated PdCo nanoparticles. (b) High resolution TEM of a single drop-shaped PdCo nanoparticle. The nanoparticles are composed of a spherical core followed by a conical tail. (c) Electron diffraction pattern (taken at the center of the particle) aligned along the [301] zone axis identifying a structure close to palladium fcc. (d) EDS spectrum of three different regions of the particle, showing the signal from Pd and Co. The signal for Cu and C is from the transmission grating.

oriented planes can be seen due to the thickness of the nanoparticle of approximately 60 nm. All particles have the same 3:1 aspect ratio and exhibit a spherical core and a conical (crystalline) tail, where several stacking faults are visible.[8,9] There is probably a defined crystallographic orientation between the core and the conical extension, since once we orient the core along one zone axis several fringes due to oriented planes are visible. Selected area electron diffraction [Fig. 1(c)] showed that the structure of the particle core is the same of the tail [close to pure palladium, face-centered cubic (fcc) with a=0.389 nm], with the possible presence of stacking faults in between them. Analysis by energy dispersive spectroscopy [EDS, Fig. 1(d)] of three different regions of the particle indicated that the concentration of Pd and Co is nearly constant. No residual content of oxygen and nitrogen was observed.

To analyze the global magnetic properties and possible magnetization reversal mechanisms, VSM measurements were done at room temperature for magnetic fields applied parallel and perpendicular to the CNTs axis. As seen in Fig. 2, the PdCo nanoparticles exhibit a typical ferromagnetic hysteresis curve, at room temperature, with a saturation net magnetic moment of 3.5×10^{-4} emu and a coercive field of about 100 Oe for both orientations. A slight difference in shape can be seen for fields applied parallel and perpendicular to the tubes axes, which can be ascribed to a uniaxial magnetic anisotropy, desired for magnetic storage media, with contributions from crystalline and shape anisotropy of the PdCo nanoparticles. For a better determination of the saturation field, the second derivative (d^2m/dH^2) of the magnetization (inset of Fig. 2) shows that for fields above 1500 Oe no change in curvature is seen, which reveals that the

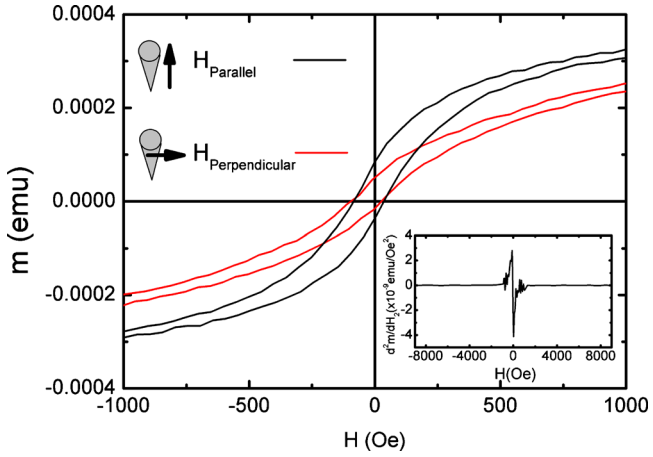

FIG. 2. (Color online) Magnetization as a function of magnetic field for PdCo nanoparticles is noticeable as the slight difference in lineshape for fields applied perpendicular and parallel to the CNT axis. A small hysteresis of ≈100 Oe is also observed. The inset shows the second derivative of the parallel magnetization, from which a saturation field of ≈1500 Oe was inferred.

additional magnetic response above this field is due to residual paramagnetic material. It should be also pointed out that in remanence the nanoparticles retain only about 25% of the total magnetization in both directions, not expected for a single domain nanoparticle with perfect uniaxial anisotropy. This fact could have origin in a magnetic domain structure favored by the nanoparticles size (~100 nm) or in magnetic dipolar interactions (not considered in this work).

Simple magnetization measurements always give us the global behavior of the sample. In order to confirm the contributions of both cobalt and palladium to the total magnetization, we have XMCD measurements of this sample. The XMCD experiments were done at beamlines SGM (near the cobalt L2 and L3 edges) and SXS (Pd L2 and L3 edges) at the Brazilian synchrotron light source (Campinas, SP) in total electron yield mode. Measurements were performed with fixed circular polarization and alternating the magnetic field of 8000 Oe for each x-ray photon energy measure.[10] Circular polarization was obtained by collecting the synchrotron light below the electron orbit planet, obtaining thereby a beam with 65% of circular polarization.

In Figs. 3(a) and 3(b) both the absorption spectra as well as the XMCD difference are shown for both atomic L edges.

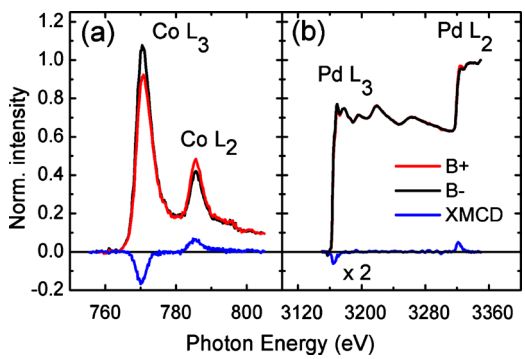

FIG. 3. (Color online) Normalized x-ray absorption spectra at the $L_{2,3}$ edges of cobalt (a) and palladium (b) of PdCo nanoparticles in CNTs. In all spectra a linear background was subtracted. At the bottom the difference curves normalized by the degree of circular polarization are shown, from which the magnetization of both atoms was determined.

The separate magnetization state of cobalt and palladium can be determined following the XMCD sum rules,[11,12] which allow us to infer directly the orbital and spin momentum of the atoms. According to these rules for $L_{2,3}$ edges,[11] the orbital and spin momentum can be obtained from $m_{orb}=-4q(10-n)/3r$ and $m_{spin}=-(6p-4q)(10-n)/r$, where q is the integrated area of the XMCD signal over the two (L_3 and L_2) edges, p the integrated area of the XMCD signal over the L_3 edge, and r the sum of the integrated areas of the absorption spectrum for positive and negative magnetic fields. n is the occupation number in the $3d$ band for cobalt and the $4d$ band for palladium.

Considering that it was extremely difficult to measure r reliably, we could only determine the ratio $m_{orb}/m_{spin}=2q/(9p-6q)$, which can be inferred directly from p and q. We found $m_{orb}/m_{spin}=(0.12\pm0.05)$ for cobalt and (0.07 ± 0.05) for palladium. These values should be compared with 0.099 for bulk cobalt[12] and up to 0.09 for palladium films,[13] which indicates that magnetic nanoparticles with properties close to bulk PdCo were formed. Future studies will focus on minimizing the Co content of these nanoparticles (to control the chemical reactivity) and changing its shape anisotropy, while maintaining the magnetic properties.

One can argue about possible applications of nanotubes terminated by magnetic PdCo nanoparticles. As already suggested in previous works,[3,4] oriented and regularly spaced nanotubes ended by magnetic nanoparticles could be used in magnetic storage media, where the shape anisotropy would also be very important to retain the magnetic information. These nanotubes could also be used for electrical injection, where the magnetization of nanoparticles is essential to polarize the electron spins before injection.[14]

This work was financed by Instituto Nacional de Ciência e Tecnologia (INCT—NanoCarbono). The technical assistance of F. Vicentim (beamline SGM), and P. de Tarso (SXS) and the staff of the Microscopy Center (LME) of LNLS is gratefully acknowledged. The authors also gratefully acknowledge the financial support from CNPq, FAPESP, and FAPEMIG.

[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] See, e.g., T. Fujita, Y. Hayashi, T. Tokunaga, and K. Yamamoto, Appl. Phys. Lett. **88**, 243118 (2006).
[3] F. Schäffel, C. Täschner, M. H. Rümmeli, V. Neu, U. Wolff, U. Queitsch, D. Pohl, R. Kaltofen, A. Leonhardt, B. Rellinghaus, B. Büchner, and L. Schultz, Appl. Phys. Lett. **94**, 193107 (2009).
[4] T. Fujita, Y. Hayashi, T. Tokunaga, T. Butler, N. L. Rupesinghe, K. B. K. Teo, and G. A. J. Amaratunga, Appl. Phys. Lett. **90**, 133116 (2007).
[5] See, e.g., T. Taniyama, E. Ohta, and T. Sato, Europhys. Lett. **38**, 195 (1997); T. Shinohara, T. Sato, and T. Taniyama, Phys. Rev. Lett. **91**, 197201 (2003).
[6] J. Crangle and W. R. Scott, J. Appl. Phys. **36**, 921 (1965); G. J. Nieuwenhuys, Adv. Phys. **24**, 515 (1975).
[7] M. S. Bell, R. G. Lacerda, K. B. K. Teo, N. L. Rupesinghe, G. A. J. Amaratunga, W. I. Milne, and M. Chhowalla, Appl. Phys. Lett. **85**, 1137 (2004).
[8] Although the magnetism in Pd was previously ascribed to the presence of stacking faults, (Ref. 9) the alloying with Co is clearly the most important factor for the magnetization of Pd (see, e.g., Ref. 6).
[9] B. Sampedro, P. Crespo, A. Hernando, R. Litrán, J. C. Sánchez López, C. López Cartes, A. Fernandez, J. Ramírez, J. González Calbet, and M. Vallet, Phys. Rev. Lett. **91**, 237203 (2003).
[10] J. J. S. Figueiredo, R. Basílio, R. Landers, F. Garcia, and A. de Siervo, J. Synchrotron Radiat. **16**, 346 (2009).
[11] P. Carra, B. T. Thole, M. Altarelli, and X. Wang, Phys. Rev. Lett. **70**, 694 (1993); B. T. Thole, P. Carra, F. Sette, and G. van der Laan, *ibid.* **68**, 1943 (1992).
[12] C. T. Chen, Y. U. Idzerda, H.-J. Lin, N. V. Smith, G. Meigs, E. Chaban, G. H. Ho, E. Pellegrin, and F. Sette, Phys. Rev. Lett. **75**, 152 (1995).
[13] J. Vogel, A. Fontaine, V. Cros, F. Petroff, J.-P. Kappler, G. Krill, A. Rogalev, and J. Goulon, Phys. Rev. B **55**, 3663 (1997).
[14] S. Sahoo, T. Kontos, C. Schönenberger, and C. Sürgers, Appl. Phys. Lett. **86**, 112109 (2005).