

Enhancement of Ferromagnetism in Amine/Organic Acid Capped Au-Nanoparticles by Yttrium-Oxide Inclusion

G. G. Lesseux*, W. Iwamoto*, V. H. Rosas**, C. Vautier-Giongo**,
D. Rettori**, R. R. Urbano*, and C. Rettori*,***

* Instituto de Física “Gleb Wataghin”, UNICAMP, Campinas, SP, Brazil, lesseux@ifi.unicamp.br
** Lab. de Química e Bioquímica de Espécies Altamente Reativas, UNIFESP, Diadema, SP, Brazil
*** Centro de Ciências Naturais e Humanas, UFABC, Santo André, SP, Brazil

ABSTRACT

In this work we report on the enhancement of the ferromagnetism of amine/organic acid capped Au nanoparticles (Au-NPs) by incorporation of yttrium(III) oxide. The magnetization measurements, at 2 K, displayed a ferromagnetic (FM) loop with a coercive field of $H_C \approx 250$ Oe and magnetic saturation moment of $M_{sat} \approx 0.004 \mu_B$ per Au atom on the NP surface. Furthermore, an intense FM resonance (FMR) line was observed from 370 K down to 4.2 K, the field for resonance, H_r , slightly shifts toward lower fields and the normalized integrated intensity remains almost constant in the entire investigated range of temperature. These results are discussed in terms of covalent-like bonds between the NP-capping ligands, Y_2O_3 and the Au atoms, giving rise to an effective hybridization of the 5d-6s electrons at the surface of the AuNPs. This hybridization would be responsible for the Au 5d shell to become magnetic due to uncompensated spins in the 5d orbitals.

Keywords: Au nanoparticles, FMR, Superparamagnetism

1 INTRODUCTION

Gold nanostructures is currently subject of intense scientific investigation due to their wide potential application in catalysis [1], high-density optical data storage [2], sensor devices [3], oncology treatment [4] and other areas of biology and medicine [5]. Furthermore, from the academic point of view, these materials have attracted great attention of the scientific community due to the surprising magnetism found in these materials [6–8], in contrast to the non-magnetic nature of the bulk metal.

In fact, recent experiments have shown that gold nanoparticles (Au-NPs) exhibit an enhanced superparamagnetic behavior. [9] This indicates that individual Au-NPs probably have intrinsic ferromagnetic moments. However, it is still not clear what is the origin of magnetism in this systems because it is possible that some extrinsic magnetic impurities are incorporated during the manufacturing processes. Besides, no theoretical model has been elaborated so far [10].

Presently, it is known that the size of particles, when comparable to the wavelength of an electron at the Fermi level, can change the electronic structure due to the confinement of the electrons. Furthermore, as the particle size decreases the surface effects become more evident because most of the Au atoms will be on the surface of the NPs, becoming responsible for the total energy and stabilization of the system. [11,12] Therefore, the charge distribution on the NPs may be different from that of the bulk due to the electronic quantum confinement. [13,14]

In this paper we report on the ferromagnetism (FM) and the FM Resonance (FMR) of amine/organic acid capped Au-NPs assisted by Y_2O_3 between 2 K and room- T . The results are discussed in terms of the interactions established between the capping ligands and the surface of the Au-NPs.

2 EXPERIMENTAL DETAIL

2.1 Sample preparation

The amine/organic acid capped Au-NPs assisted by Y_2O_3 (Au- Y_2O_3), with diameters ranging between 40 and 70 nm, were prepared by an adapted chemical route taken from the literature. [15–17] The process consists in the preparation of two precursor compounds. Precursor 1 was obtained by dissolving 0.41 mmol of $HAuCl_4 \cdot 3H_2O$ and stoichiometric excess of triphenylphosphine (PPh_3) in 40 mL of acetonitrile. This solution was heated up to 80 °C until the evaporation of the solvent was completed. Needle type crystals of $AuCl(PPh_3)$ were obtained in this stage. Precursor 2 was prepared by heating fine powder of Y_2O_3 (0.02 mmol) and trifluoroacetic acid (6 mL), under argon flow until the evaporation of trifluoroacetic acid was also completed. Then, precursor 1 was dissolved in benzyl ether (20 mL) together with oleylamine (6 mL), oleic acid (6 mL), and precursor 2 was added to this mixture. The complete system was heated up to 100 °C with vigorous stirring under an argon flow for 20 minutes to allow all the water to be evaporated. Thereafter, heating was increased to 200 °C under reflux and 2 mL of a 1 M THF solution of lithium triethylborohydrate reductor was added to the solution. The temperature was then increased to 250 °C for 20 minutes under argon flow. Finally, the solution was cooled down to room- T and centrifuged after

adding excess of ethanol. The nanoparticles can be easily dispersed in nonpolar solvents such as toluene.

2.2 Experimental Techniques

The size and shape of the sample was analyzed in a HRTEM (JEM 3010, 300 keV microscope) and the structure by X-ray powder diffraction (XRD) using the Cu-K α radiation in a Phillips Diffractometer at room- T . The magnetic properties were characterized by means of magnetization measurements as a function of the magnetic field, H , up to 5 Tesla and temperature, T , between 300 K and 2 K using a superconducting quantum interference device (SQUID) magnetometer MPMS-5 (Quantum Design). For the Ferromagnetic Resonance (FMR) experiments between 4.2 K and 300 K, we used a Bruker ELEXYS-500 X-Band (9.5 GHz) spectrometer with a TE₁₀₂ resonator coupled to a cool helium gas flux cryostat and an Oxford T -controller.

3 EXPERIMENTAL RESULTS

3.1 Structure Characterization

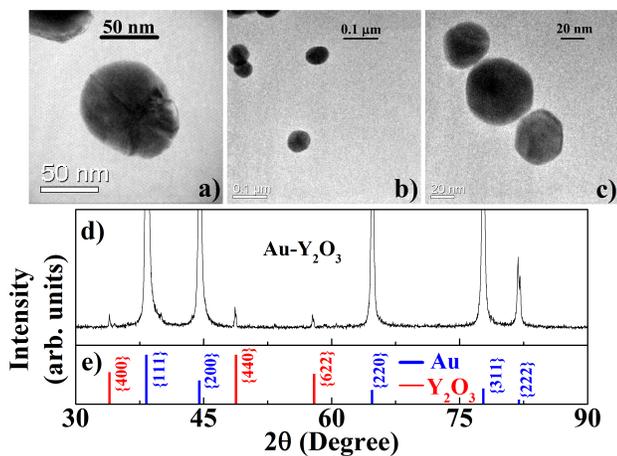


Figure 1: Au-NPs assisted by Y₂O₃ a), b) and c) HRTEM images; d) XRD pattern. In e) the bars and their respective Miller indexes indicate the Au-fcc (blue) [18] and Y₂O₃-bcc (red) [19] peak positions for Cu-K α radiation.

Figures 1 (a-c) present the HRTEM images for Au-Y₂O₃. These images show that the shapes of the NPs are not regular with a rather large size distribution going from 40 nm to 70 nm. Figure 1 (d) presents the XRD pattern for Au-Y₂O₃ which was indexed on the basis of the face-centered-cubic (fcc) Au powder diffraction data (see Figure 1e)). The X-ray pattern also shows the most intense peaks of Y₂O₃ (bcc) in the 2θ investigated region. Using the Scherrer's formula [20] and assuming spherical shapes for the particles the average NPs diam-

eter, $\bar{d} = 67(11)$ nm, was estimated. This estimative is in reasonable agreement with the HRTEM images.

3.2 Magnetization Experiments

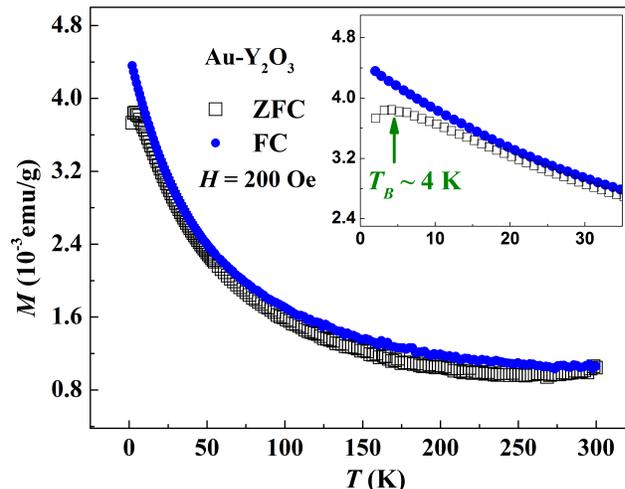


Figure 2: T -dependence of the ZFC (open squares) and FC (blue) magnetization between 2 K and 300 K at $H = 200$ Oe for Au-Y₂O₃. The inset shows the FC-ZFC irreversibility in detail.

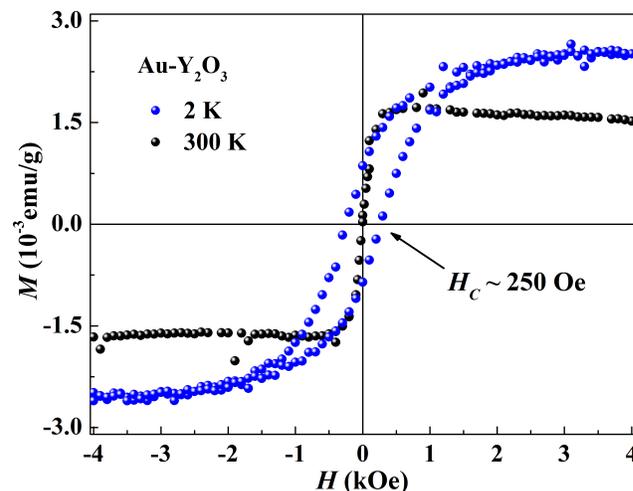


Figure 3: M vs H for Au-Y₂O₃ at $T = 2$ K (blue) and 300 K (black).

The T -dependence of the zero field cooling (ZFC) and field cooling (FC) magnetization (M vs T) at $H = 200$ Oe between 2 K and 300 K for Au-Y₂O₃ sample is shown in Figure 2. The ZFC magnetization has a maximum at ≈ 4 K (inset in Figure 2), it is probably associated with an average Blocking temperature, T_B , of the Au-NPs indicating superparamagnetic behavior of a FM single domain NPs [21]. Above T_B , the ZFC-FC are

not exactly on top of each other, what may be associated with the large size distribution of the NPs [22].

Figure 3 shows the field dependent magnetization measurements (M vs H) at 2 and 300 K for the Au-Y₂O₃ sample. At 2 K a hysteresis loop with coercive field of $H_C \approx 250$ Oe was observed. Above the average T_B , at 300 K, no hysteresis was observed as expected in a superparamagnetic regime [23]. From the saturation magnetization at 2 K and based on the TGA analysis (not shown) we have estimated an effective magnetic moment of $\approx 0.004 \mu_B$ per Au surface atom. The estimation of Au atom on the NP surface was performed assuming spherical shapes and that the number of surface atoms is proportional to the volume of a skin thickness of Au diameter.

3.3 ESR Experiments

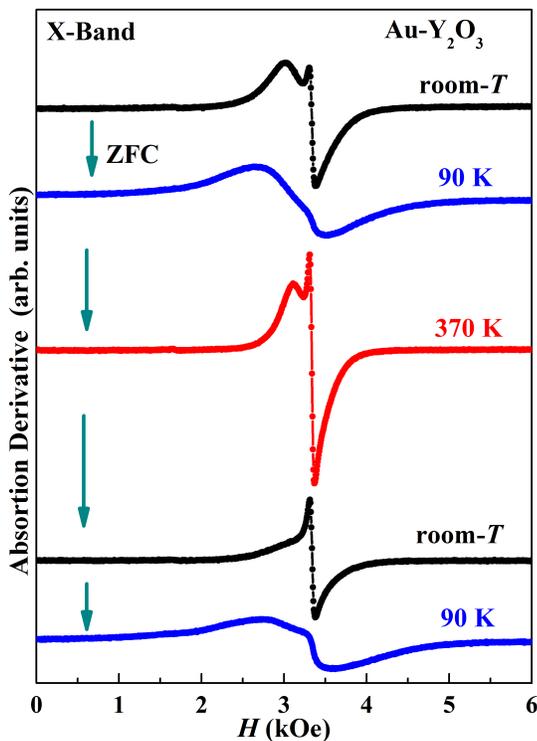


Figure 4: T -dependence of the X-band ESR spectra for Au-Y₂O₃. The arrows indicate the sequence of the thermal cycling.

Figure 4 shows the X-band ESR spectra for Au-Y₂O₃ sample at different temperatures following the in-situ ESR thermal treatment: the "as prepared" sample at room- T (black); then at 90 K (blue), after ZFC cooling; then at 370 K (red), after heating; at room- T again (black), after cooling; and again at 90 K (blue) but, in this case, applying magnetic field to obtain the spectra as a function of temperature. It is clear from these data

that the observed lineshape and structure of the ESR spectra has dramatically changed during this thermal cycling. These observations are associated with demagnetizing NPs shape effects.

Figure 5 presents the T -dependence of the ESR parameters extracted from the observed spectra of Au-Y₂O₃. These data show that resonance field, H_r , is shifted towards low field at $T < 120$ K due to the presence of an internal magnetic field. The relative intensity, $I(T)/I(118 \text{ K})$, does not follow a Curie-Weiss behavior at low- T . These features are signatures of a FM resonance (FMR). [24] Therefore, we argue that the amine/organic acid capped Au-NPs assisted by Y₂O₃ is a new and promising route for the production of magnetic Au-NPs.

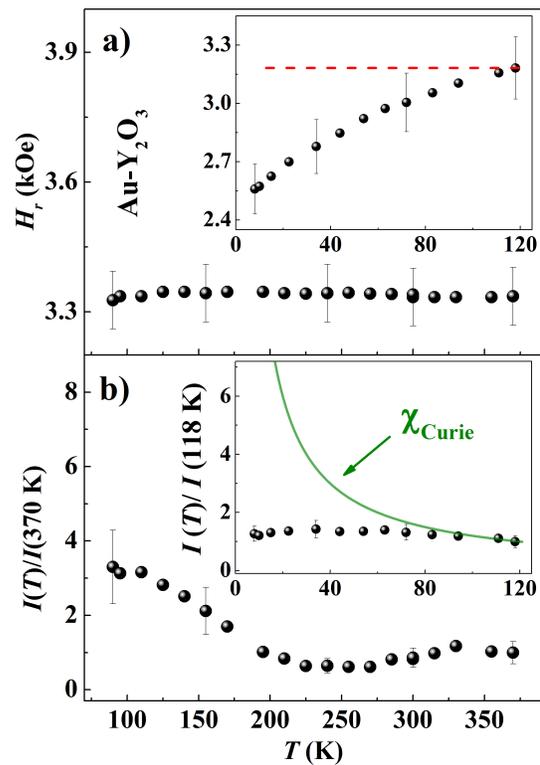


Figure 5: T -dependence of the X-band ESR parameters extracted from the observed spectra for Au-Y₂O₃: a) resonance field, H_r , and b) normalized integrated intensity, $I(T)/I(370 \text{ K})$, for Au-Y₂O₃. The insets in and indicate the behavior of a) H_r and b) $I(T)/I(118 \text{ K})$ at $T \leq 118 \text{ K}$.

4 ANALYSIS AND DISCUSSION

Nowadays there are some speculations regarding the origin of magnetism in Au-NPs. Our results are in good agreement with the so-called "ligand effect" scenario, where 5d localized holes are generated by the Au-X bonds on the surface of the NPs. X is a highly ox-

idative element like S, [25] P and Cl. [26] These holes may give rise to localized magnetic moments with high spin-orbit coupling (1.5 eV) for Au in a local low symmetry due to the Au-Au and Au-X bonding. [27] Although the "size effect" tends to decrease the number of holes, [28] it has been argued that the "ligand effect" may counter balance the "size effect" and thus the capped Au-NPs may exhibit an observable magnetism. [13] The assisted amine/organic acid capped Au-NPs assisted by Y_2O_3 studied in this work present a saturated magnetization and a FMR between room- T and 2 K, indicating the existence of a magnetic collective state for the coupled magnetic moments. The origin of this collective state is probably caused by the exchange coupling between the spins of the localized Au-5d holes which are responsible for the FM in these Au-NPs. In summary, our work in Y_2O_3 assisted amine/organic acid capped Au-NPs has demonstrated that: i) the magnetic properties of these Au-NPs can be observed via a FMR experiments; ii) via the FMR it is possible to show the existence of demagnetizing shape effects of the magnetic Au-NPs; and iii) the chemical route of amine/organic acid capped Au-NPs assisted by Y_2O_3 is an alternative method very efficient for the producing an enhanced magnetism in capped Au-NPs via, presumably, additional surface Au-O bonds.

ACKNOWLEDGMENT

The authors thank Prof. O. L. Alves for the TGA experiments performed at the LQES-IQ (UNICAMP-BRAZIL). The TEM data was acquired at the HRTEM-LME/LNNano at the Brazilian Synchrotron Light Laboratory (LNLS). This work was supported by FAPESP, CAPES and CNPQ (BRAZIL).

REFERENCES

- [1] G. J. Hutchings and J. K. Edwards, *Frontiers of Nanoscience*, 3, 249-293, 2012.
- [2] J. W. M. Chon, C. Bullen, P. Zijlstra, and M. Gu, *Advanced Functional Materials*, 17, 875880, 2007.
- [3] Y. Ofir, B. Samanta and V. M. Rotello, *Chemical Society Reviews*, 37, 1814-1825, 2008.
- [4] C. Alric et al., *J. Am. Chem. Soc.* 130, 5908-5915, 2008.
- [5] R. Shukla, V. Bansal, M. Chaudhary, A. Basu, R. R. Bhonde, and M. Sastry, *Langmuir*, Vol. 21, 10644-10654, 2005.
- [6] H. Hori, Y. Yamamoto, T. Iwamoto, T. Miura, T. Teranishi, and M. Miyake, *Physical Review B* 69, 174411, 2004.
- [7] S. J. Cho, B. R. Jarrett, A. Y. Louie and S. M. Kauzlarich, *Nanotechnology*, 17, 640644, 2006.
- [8] J. S. Garitaonandia, M. Insausti, E. Goikolea, M. Suzuki, J. D. Cashion, N. Kawamura, H. Ohsawa, *Nanoletters*, 8, 661-667, 2008.
- [9] H. Hori et al, *Phys. Lett. A* 263, 406, 1999.
- [10] S. Trudel, *Gold. Bull.*, 3, 44, 2011.
- [11] K. Nobusada, *J. Phys. Chem. B*, 108, 11904, 2004.
- [12] H. Liu, B. S. Mun, G. Thomson, S. R. Isaacs, Y. S. Shon, D. F. Ogletree, and M. Salmeron, *Phys. Rev. B*, 72, 155430, 2005.
- [13] P. Zhang, T. K. Sham, *Phys. Rev. Lett.*, 90, 245502, 2003.
- [14] C. Lopez-Cartes, T. C. Rojas, R. Litran, D. Martinez-Martinez, J. M. de la Fuente, S. Penades, and A. Fernandez, *J. Phys. Chem. B*, 109, 8761, 2005.
- [15] J. M. Vargas, W. Iwamoto, L. M. Holanda, S. B. Oseroff, P. G. Pagliuso and C. Rettori, *J. Nanosci. Nanotechnol.* 11, 2126, 2011.
- [16] Y. Tang and M. Ouyang, *Nature Materials*, 6, 754, 2007.
- [17] G. Schmid and B. Corain, *Eur. J. Inorg. Chem*, 17, 3081, 2003.
- [18] E. Owen and E. Yates, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 15, 472-488, 1933.
- [19] A. Fert, *Bulletin de la Societe Francaise de Mineralogie et de Cristallographie.* 85, 267-270, 1962.
- [20] B. D. Cullity and S. R. Stock, *Elements of X-Ray Diffraction*, Third edition, 170, 2001.
- [21] Stephen Blundell, *Magnetism in Condensed Matter*, 170, 2001.
- [22] B. Sohn, R. Cohen and G. Papaefthymiou, *Journal of Magnetism and Magnetic Materials*, 182, 216-224, 1998.
- [23] F. C. Fonseca, G. F. Goya, R. F. Jardim, R. Mucillo, N. L. V. Carreno, E. Longo and E. R. Leite, *Phys. Rev. B*, 66, 104406, 2002.
- [24] G. Lopes, J. M. Vargas, S. K. Sharma, F. Beron, K. R. Pirota, M. Knobel, C. Rettori and R. D. Zysler, *J. Phys. Chem. C*, 114, 10148, 2010.
- [25] J. de la Venta, A. Pucci, E. F. Pinel, M. A. Garca, C. J. Fernandez, P. Crespo, P. Mazzoldi, G. Ruggeri, and A. Hernando, *Adv. Mater.* 19, 875, 2007; P. Dutta, S. Pal, and M. S. Seehraa, M. Anand, and C. B. Roberts, *Appl. Phys. Lett.*, 90, 213102, 2007.
- [26] M. A. Munoz-Marquez, E. Guerrero, A. Fernandez, P. Crespo, A. Hernando, R. Lucena, and J. C. Conesa, *J. Nanopart. Res.* 12, 1307, 2010.
- [27] P. Crespo, R. Litran, T. C. Rojas, M. Multigner, J. M. de la Fuente, J. C. Sanchez-Lopez, M. A. Garcia, A. Hernando, S. Penades, and A. Fernandez, *Phys. Rev. Lett.* 93, 087204, 2004
- [28] I. Coulthard, I. S. Degen, Y. Zhu, and T. K. Sham, *Can. J. Chem.* 76, 1707, 1998.