Synthesis and Properties of Bifunctional Fe_3O_4/Ag Nanoparticles

Romina A. Landa[1], Guillermo A. Jorge[2], Fernando V. Molina[1], and P. Soledad Antonel[1]

[1]Instituto de Química Física de Materiales, Ambiente y Energía (INQUIMAE), Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina.
[2]Instituto de Ciencias, Universidad Nacional de General Sarmiento, Los Polvorines, Provincia de Buenos Aires, Argentina.

In this work, a facile synthesis of Fe_3O_4/Ag nanoparticles, with magnetic properties and electrical conductivity, was successfully developed, by reducing Ag(I) ions with D-Glucose, in the presence of a dispersion of superparamagnetic Fe_3O_4 nanoparticles, under ultrasound treatment. Poly(vinylpyrrolidone) (PVP) was used as protecting agent and Ag(I) were incorporated in different molar ratios with respect to Fe_3O_4 nanoparticles. The obtained particles were characterized by XRD studies, SEM and TEM observation, Energy Dispersive X-Ray Spectroscopy (EDS), DC magnetization and conductivity measurements. From TEM and SEM observation it was found that the PVP protection has shown to be partial, as the Fe_3O_4 nanoparticles have a lower diameter after the reduction treatment. Despite this, the particles retain the superparamagnetic behavior and the saturation magnetization decreases as the Ag content increases. From conductivity measurements, a minimum Ag(I)/Fe_3O_4 molar ratio = 1.75 was needed in order to observe electrical conductivity in the metallic regime.

***Index Terms*—conducting materials, magnetic nanoparticles, magnetite, silver**

I. INTRODUCTION

BIFUNCTIONAL nanoparticles of iron oxides and precious metals (such as Ag and Au) have attracted great attention in the last years, due to their potential applications in novel electrical, optical, catalytic, magnetic and sensing technologies [1],[2]. Especially, superparamagnetic Fe_3O_4 nanoparticles have been widely studied for a range of biomedical applications, such as hyperthermia treatment for malignant cells, drug delivery, biosensors, magnetic resonance imaging contrast agents, magnetic separation and cell sorting, owning to their unique magnetic properties and biocompatibility [3]-[6]. In order to think about an application, it is essential to have a colloidal solution of the magnetic nanoparticles; also this dispersion should be stable for a long time. For this purpose, it is necessary to modify the surface of the magnetic nanoparticles, and the coating with gold and/or silver appears as an interesting choice. These shell materials could impose dispersion stability and biocompatibility [7]-[9]. Also, silver-coated magnetic nanoparticles have shown interesting antifungal properties against, for example, *Aspergillus glaucus* [2]. Besides, silver or gold coating gives rise to nanoparticles with also electrical conductivity, allowing to develop new materials with controlled magnetic and electrical properties. For example, Fe_3O_4/SiO_2-Ag nanocomposites have been used recently for the catalytic reduction of 4-nitrophenol [10], finding that the material has a high performance and can be recycled by the application of an external magnetic field. Due to the potential applications, in the last years several works concerning the synthesis and characterization of silver or gold coated magnetite nanoparticles have been published [11],[12]. However, complete characterizations and detailed analysis on the influence of the different synthetic conditions on the final properties of the materials are lacking. All these issues have a great importance in the possible applications of these materials.

In the present work, Fe_3O_4 nanoparticles have been synthesized, by the co-precipitation method. In a second step, an aqueous dispersion of these nanoparticles and poly(vynilpirrolidone) (PVP) has been prepared and through the addition of a Ag(I) solution, D-glucose and NaOH, Fe_3O_4/Ag nanoparticles have been obtained. The molar ratio Ag:Fe_3O_4 has been changed from 0.5 to 5 in order to study the influence of the Ag(I) concentration on the final properties of the Fe_3O_4/Ag nanoparticles. Finally, the materials were characterized by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Energy Dispersive X-Ray Spectroscopy (EDS), DC magnetization and conductivity measurements.

II. MATERIALS AND METHODS

AR grade chemicals and high purity water from a Milli-Q system were employed throughout.

A. *Synthesis of Fe_3O_4 and Fe_3O_4/Ag nanoparticles*

Fe_3O_4 nanoparticles were synthesized by the co-precipitation method [13]-[15]. Briefly, 22.25 mL of a solution containing 0.450 M $FeCl_3.6H_2O$ and 0.225 M $FeCl_2.4H_2O$ (2:1 Fe(III)-Fe(II) molar ratio), in 0.4 M HCl, was added dropwise to 200 mL of 1.5 M NaOH, keeping the pH adjusted at 12, under constant high speed stirring. The synthesis temperature was set at 80º C, using a water-jacketed reaction vessel with a circulating thermostatic bath. Dark brown Fe_3O_4 nanoparticles precipitated immediately after the first drops of the Fe(III)-Fe(II) solution. After the addition of this solution, the reaction media was maintained at 80º C, at high speed stirring, for 2 h. The Fe_3O_4 nanoparticles were separated by centrifugation at 15000 G during 20 minutes at room temperature. The pellet was washed with Milli-Q water, repeating the cycles of washing-centrifugation until neutral pH of the supernatant was reached (about 10 times). Finally, the Fe_3O_4 nanoparticles were dried using a vacuum oven at 40º C during 24 h.

For the preparation of Fe_3O_4/Ag nanoparticles, an aqueous dispersion of Fe_3O_4 nanoparticles and PVP, used as protecting agent, was prepared under ultrasound treatment, in a molar ratio PVP:Fe_3O_4 of 5:1. After 30 min, Ag(I) ions were incorporated into the dispersion, from a 0.5 M $AgNO_3$ solution, in different molar ratios with respect to Fe_3O_4 nanoparticles (0.5, 1, 1.75, 2.5 and 5). The chemical reduction of Ag(I) was performed using D-glucose as an environmentally benign agent [16], in a molar ratio D-glucose:Ag(I) 3:1, and NaOH as a base reaction catalyst, in a molar ratio NaOH:Ag(I) 1:1. In all cases, after 1 h under ultrasound treatment, Fe_3O_4/Ag nanoparticles were separated by centrifugation at 15000 G, and washed with Milli-Q water. After 5 cycles of washing/centrifugation, the materials were dried using a vacuum oven, at 40ºC during 24 h.

B. *Characterization of Fe_3O_4 and Fe_3O_4/Ag nanoparticles*

1) *X-Ray Diffraction (XRD)*

X-Ray powder diffraction analysis of the materials was performed with a Philips X-Pert diffractometer using Cu K_α radiation ($\lambda = 0.154056$ nm).

2) *Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS)*

The particle size and morphology were studied using a Transmission Electron Microscope Philips EM 301. SEM analysis was performed using a Zeiss Supra 40 Gemini microscope, equipped with a EDS detector.

3) *Magnetic properties*

A Lakeshore 7400 Vibrating Sample Magnetometer (VSM) was used for recording magnetization curves at room temperature. The samples were prepared by packing with Teflon tape 10-20 mg of each composite.

4) *Conductivity measurements*

The conductivity of the different samples was measured on pressed circular pellets (1 cm diameter) using a Teq-03 (S. Sobral, Buenos Aires, Argentina) potentiostat under computer control. Following Ohm´s law, a known current (*i*) was applied and the potential difference (*E*) was measured and averaged during 120 s. The resistance was determined for each applied current and potential; the pellet thickness was measured with a caliper.

III. RESULTS AND DISCUSSION

Fig. 1 shows TEM (left) and SEM (right) images of pure Fe_3O_4 and Fe_3O_4/Ag nanoparticles.

FIG. 1 HERE

As it can be seen, the nanoparticles have a nearly spherical shape and from TEM images, the particle diameters could be measured. Over 200 particles were measured, in each case, with the aid of the ImageJ software [17]; the resulting histograms are shown in the inset of Fig. 1, revealing a good monodispersity. The average particle diameters, d_p, are shown in Table I.

TABLE I HERE

It is found that d_p is 8.4 nm for pure Fe_3O_4 nanoparticles and decreases about 2 nm for the lowest Ag proportion used (0.5). Then, when increasing the Ag content (Ag:Fe_3O_4 1:1), d_p decreases about 1 nm and then remains approximately constant. This decrease in the particle diameter could be due to reduction of the magnetite Fe(III) ions by D-glucose, resulting in a partial dissolution of the nanoparticles. Thus, PVP does not result entirely effective as a protecting agent for Fe_3O_4 nanoparticles, at least in the proportion used here. With the purpose of elucidate the effect of D-glucose on nanoparticle stability, a control synthesis (without addition of Ag(I) solution) was performed. In this case, only an orange suspension was obtained (a solid could not be recovered after centrifugation). From TEM (not shown), the particle diameter in the suspension was 4.8 nm. This fact indicates that silver acts as a protecting agent, because in the presence of Ag the obtained nanoparticles are larger and can be separated by the centrifugation process. Also, it can be concluded that D-glucose effectively promotes the dissolution of the Fe_3O_4 nanoparticles. Moreover, from TEM images, it is clear that an increase in Ag content, results in less agglomerated nanoparticles. This can be due to the presence of a thin layer of Ag, covering the surface of Fe_3O_4 nanoparticles, which prevents the nanoparticles agglomeration, and also to the presence of PVP which would give a similar effect. In other words, the better dispersion of Fe_3O_4 nanoparticles suggests that the nanoparticles have been covered, at least in part, with Ag and/or PVP.

From EDS measurements, all the synthesized materials (including the one with a molar ratio Ag:Fe_3O_4 0.5:1) have silver in their composition, thus Ag(I) has been reduced and Fe_3O_4 nanoparticles appear to have been covered by metallic silver, for all the Ag:Fe_3O_4 molar ratios studied. In Table II, the molar ratio Ag:Fe_3O_4 as well as the *w/w* percentage in the materials are presented:

TABLE II HERE

The molar ratio Ag:Fe_3O_4 in the materials results lower than the molar ratio in the feed. That means that probably the reaction time (once the D-glucose is added) was short, then Ag(I) was not completely reduced. In addition, as Ag content in the feed increases, the same happens with the molar ratio Ag:Fe_3O_4 in the materials.

Also, XRD studies have been carried out (fig. not shown). For Fe_3O_4/Ag nanoparticles both phases are present (Fe_3O_4 and metallic silver), confirming the synthesis success.

In Fig. 2, the magnetization loops are presented.

FIG. 2 HERE

Fig. 2(a) shows the magnetization, *M*, expressed in emu/g of material as a function of the applied field, *H*. None of the loops shows hysteresis, thus Fe_3O_4 nanoparticles are superparamagnetic at room temperature. This is in agreement with the fact that the critical size for superparamagnetism in magnetite was reported to be 29 nm [18]. In the case of pure Fe_3O_4 nanoparticles, the saturation magnetization, M_s, is 52 emu/g, in good agreement with earlier works for similar diameters [15]. However, this value is lower than M_s for bulk material (92 emu/g [19]). An explanation given by Lu et al [20] proposes a possible suppression of the magnetization in one or several surfaces layers of the nanomaterial due to a spin disorder structure in its surface. Since the surface/volume ratio increases significantly from bulk (microparticles) to nanoparticles, then the effect of a non-magnetic superficial layer is expected to be larger in the nanoparticles with the consequent relative diminishing of M_s. Continuing with the analysis of Fig. 2(a), for Fe_3O_4/Ag nanoparticles, M_s decreases as the Ag content increases, as it was expected. That is, since metallic silver is a non-magnetic material, an increase in the Ag:Fe_3O_4 ratio produces a decrease in the measured magnetization per gram of material.

Fig. 2(b) shows the magnetization, *M*, normalized by the mass of Fe_3O_4 as a function of the applied field, *H*. To analyze this magnetization, the EDS results were considered (see Table II). Fe_3O_4 is the only magnetic material, so that *M* will be a function of the amount of magnetite present. If the amount of PVP incorporated into the nanoparticles is identical in each case, the magnetization loops should be superimposed. As observed in Fig. 2(b), albeit the loops are not perfectly superimposed, they are fairly close together, considering that the experimental uncertainty in the determination of the averaged % *w/w* Ag:Fe_3O_4 is relatively large (about 5-8 %, depending on the composition). Moreover, as it was commented above, the amount of PVP incorporated in the materials could be different in each case, so this fact also contributes to the observed differences between loops. Taking into account these facts, the magnetization normalization by the mass of Fe_3O_4 (obtained in each case from EDS measurements) results in curves coincident within the experimental uncertainties.

Finally, the conductivities of the different materials were determined, by measuring the potential difference when a current is applied, ranging from 5 x 10^{-9} (Ag:Fe_3O_4 1:1) to 1 x 10^{-2} S/cm (Ag:Fe_3O_4 5:1). Fig. 3 shows the conductivities (in logarithmic scale) as a function of the Ag:Fe_3O_4 ratio.

FIG. 3 HERE

The sample Ag:Fe_3O_4 1:1 shows a very low conductivity. That is, the amount of metallic silver is too low and the sample has a high resistance. When the ratio Ag:Fe_3O_4 is 1.75:1 the conductivity increases about 6 orders of magnitude and then it remains approximately constant with an increase in the silver content. Even though the maximum conductivity obtained (about 10^{-2} S/cm) is much lower than the conductivity of bulk silver (about 10^4 S/cm) [21], the materials with Ag:Fe_3O_4 ratio $\geq$ 1.75 have acceptable values of electrical conductivity. This increase in the electrical conductivity with the silver content was also observed by Sun et al [12], who attributes this behavior to the covering of Fe_3O_4 nanoparticles by a thin layer of metallic silver.

IV. CONCLUSIONS

Fe_3O_4:Ag nanoparticles synthesized in this work show both good magnetic properties and electrical conductivity. The dispersion of the particles was improved by a thin layer of metallic silver deposited on magnetite nanoparticles, as it was observed in TEM images. From the magnetization and conductivity measurements we conclude that bifunctional materials, both paramagnetic and conductive, have been successfully synthesized and characterized.

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REFERENCES

[1] K. Kimishiva, W. Yamada, M. Uehara, T. Asaka, K. Kimoto, and Y. Matsui, “Study on anomalous magnetoresistance in nano-Fe_3O_4/Ag granular System,” *Mater. Sci. Eng. B*, vol. 138, pp. 69-73, 2007.

[2] B. Chudasama, A. K. Vala, N. Andhariya, R. V. Upadhyay, and R. V. Mehta, “Antifungal activity of multifunctional Fe_3O_4-Ag nanocolloids,” *J. Mag. Mag. Mat.*, vol. 232, pp. 1233-1237, 2011.

[3] L. Babes, B. Denizot, G. Tanguy, J. J. Le Jeune, and P. Jallet, “Synthesis of iron oxide nanoparticles used as MRI contrast agents: a parametric study,” *J. Colloids and Interface Sci.*, vol. 212, pp. 474-482, 1999.

[4] M. Kubovcáková, M. Koneracká, V. Závisová, M. Múcková, M. Timko, L. Schmidtová, P. Bartos, and P. Kopcansky, “Biodistribution and *in vivo* anticancer effects of taxol loaded magnetic nanospheres,” *IEEE Trans. Magn.*, vol. 49, no. 1, pp. 353-358, 2013.

[5] J. Wang, Y. Sun, L. Y. Wang, X. N. Zhu, H. Q. Zhang, and D. Q. Song, “Surface Plasmon resonance biosensor based on Fe_3O_4/Au nanocomposites,” *Colloids Surf. B: Biointerfaces*, vol. 81, pp. 600-606, 2010.

[6] E. Pollert, P. Kaspar, K. Záveta, V. Herynek, M. Burian, and P. Jerdelová, “Magnetic nanoparticles for therapy and diagnosis,” *IEEE Transactions on Magnetics*, vol. 49, no. 1, pp. 7-10, 2013.

[7] M. Garza-Navarro, A. Torres-Castro, V. González, U. Ortiz, and E. De la Rosa, “Magnetite and magnetite/silver core/shell nanoparticles with diluted magnetic-like behavior,” *J. Solid. State Chem.*, vol. 183, pp. 99-104, 2010.

[8] K. S. Shin, J.-Y. Choi, C. S. Park, H. J. Jang, and K. Kim, “Facile synthesis and catalytic application of silver-deposited magnetic nanoparticles,” *Catal. Lett.*, vol. 133, pp. 1-7, 2009.

[9] E. Iglesias-Silva, J. Rivas, L. M. León Isidro, and M. A. López-Quintela, “Synthesis of silver-coated magnetic nanoparticles,” J. Non-Cryst. Solids, vol. 353, pp. 829-831, 2007.

[10] Y. Chi, Q. Yuan, Y. Li, J. Tu, L. Zhao, N. Li, and X. Li, “Synthesis of Fe_3O_4@SiO_2-Ag magnetic nanocomposite based on small-sized and highly dispersed silver nanoparticles for catalytic reduction of 4-nitrophenol,” *J. Colloid. Interf. Sci.*, vol. 383, pp. 96-102, 2012.

[11] Z. Zhang, W. Jiang, X. Gong, and Z. Zhang, “Sonochemical synthesis and characterization of magnetic separable Fe_3O_4/Ag composites and its catalytic properties,” *J. Alloys and Compounds*, vol. 508, pp. 400-405, 2010.

[12] Y. Sun, Y. Tian, M. He, Q. Zhao, C. Chen, C. Hu, and Y. Liu, “Controlled Synthesis of Fe_3O_4/Ag core-shell composite nanoparticles with high electrical conductivity,” *J. Electron. Mater.*, vol. 41, pp. 519-523, 2012.

[13] Y. I. Kim, D. Kim, and C. S. Lee, “Synthesis and characterization of $CoFe_2O_4$ magnetic nanoparticles prepared by temperature-controlled coprecipitation method,” *Physica B: Cond. Matter*, vol. 337, pp. 42-51, 2003.

[14] P. Soledad Antonel, G. Jorge, O. E. Perez, A. Butera, A. Gabriela Leyva, and R. M. Negri, “Magnetic and elastic properties of $CoFe_2O_4$-polydimethylsiloxane magnetically oriented elastomer nanocomposites”, *J. App. Phys.*, vol. 110, pp. 043920(8), 2011.

[15] J. L. Mietta, M. M. Ruiz, P. Soledad Antonel, O. E. Perez, A. Butera, G. Jorge, and R. M. Negri, “Anisotropic magnetoresistance and piezoresistivity in structured Fe_3O_4-silver particles in PDMS elastomers at room temperature,” *Langmuir*, vol. 28, pp. 6985-6996, 2012.

[16] P. Vasileva, B. Donkova, I. Karadjova, and C. Dushkin, “Synthesis of starch-stabilized silver nanoparticles and their application as a surface plasmon resonance-based sensor of hydrogen peroxide,” *Colloids and Surfaces A: Physicochem. Eng. Aspects*, vol. 382, pp. 203-210, 2011.

[17] W. Rasband, 2012, *ImageJ* (Bethesda, Maryland, USA: National Institute of Health, Research Services Branch).

[18] A. Angermann, and J. Töpfer, “Synthesis of magnetite nanoparticles by thermal decomposition of ferrous oxalate dihydrate,” *J. Mater. Sci.*, vol. 43, pp. 5123-5130, 2008.

[19] D. H. Han, J. P. Wang, and H. L. Luo, “Crystallite size effect on saturation magnetization of fine ferromagnetic particles,” *J. Mag. Mag. Mat.*, vol. 136, pp. 176-182, 1994.

[20] H. M. Lu, W. T. Zheng, and Q. Jiang, “Saturation magnetization of ferromagnetic and ferromagnetic nanocrystals at room temperature,” *J. Phys. D: Appl. Phys.*, vol. 40, pp. 320-325, 2007.

[21] Y.- C. Hsu, and D. D. L. Chung, “Silver particle carbon-matrix composites as thick films for electrical applications,” *J. Electron. Mater.*, vol. 36, pp. 1188-1192, 2007.

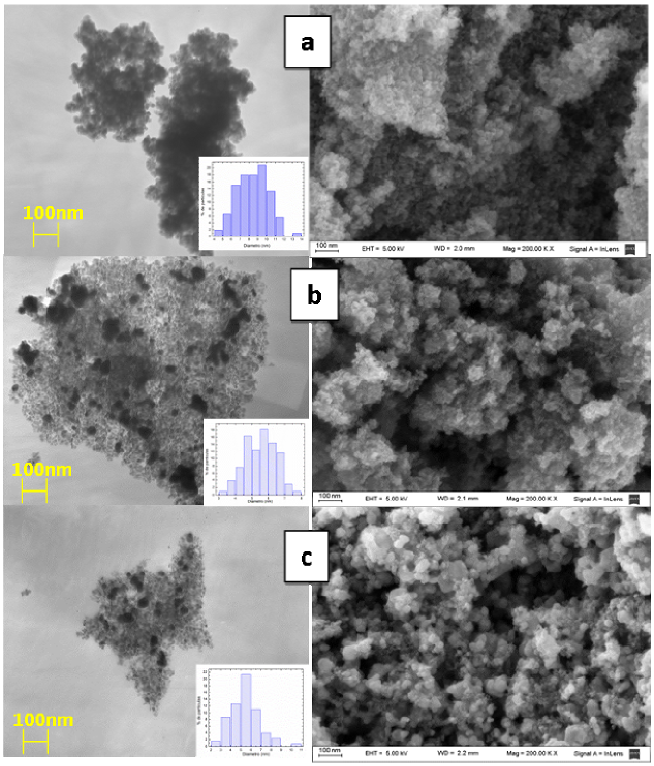

Fig. 1. TEM (left) and SEM (right) images of some of the materials synthesized. (a) pure Fe_3O_4 nanoparticles; (b) Ag:Fe_3O_4 1:1; (c) Ag:Fe_3O_4 2.5:1. Inset: particle size histograms.

TABLE I

PARTICLE DIAMETERS, OBTAINED FROM TEM IMAGES, FOR PURE FE_3O_4 AND FE_3O_4/AG NANOPARTICLES

Ag:Fe_3O_4 ratio	Particle diameter (nm)
0:1	8.4
0.5:1	6.4
1:1	5.5
1.75:1	5.4
2.5:1	5.4
5:1	5.4

TABLE II

AG:FE_3O_4 MOLAR RATIO AND %*W/W* AG:FE_3O_4 IN SYNTHESIZED PARTICLES, OBTAINED FROM EDS MEASUREMENTS

Ag:Fe_3O_4 ratio (feed)	Ag:Fe_3O_4 ratio (particles, EDS)	% *w/w* Ag:Fe_3O_4 (particles, EDS)
0.5:1	0.21	0.30
1:1	0.31	0.43
1.75:1	0.45	0.63
2.5:1	0.71	0.99
5:1	1.12	1.56

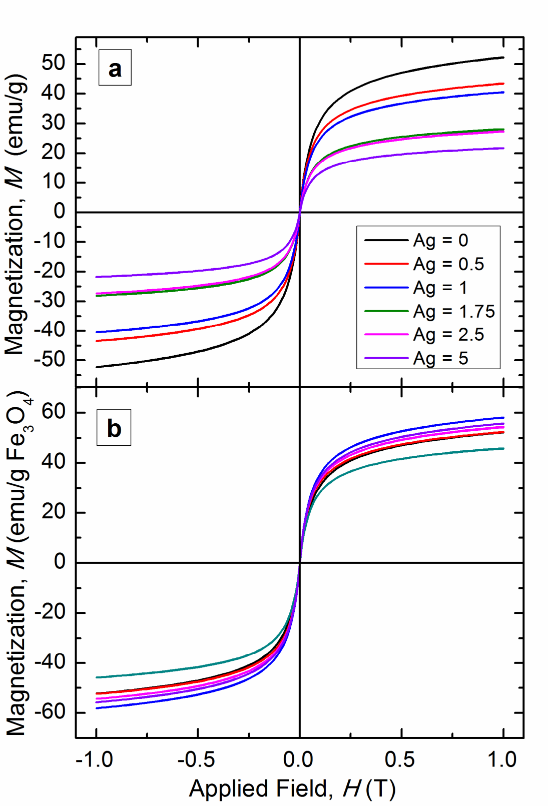

Fig. 2. Magnetization, *M*, as a function of the applied field, *H*, for pure Fe_3O_4 and Fe_3O_4/Ag nanoparticles. (a) *M* expressed per gram of material; (b) *M* expressed per gram of Fe_3O_4.

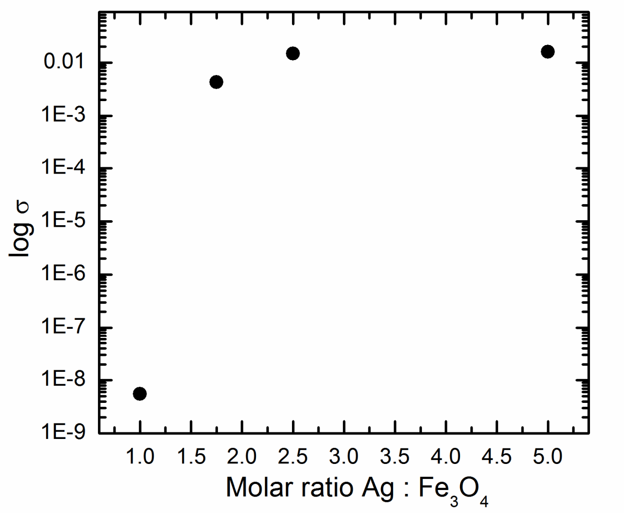

Fig. 3. Conductivity (in logarithmic scale) as a function of the molar ratio Ag:Fe_3O_4 in the feed.