# Air-stable Fe@Au Nanoparticles Synthesized by the Microemulsion's Methods

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Magnetic particles covered by gold are very important in many biological applications. However, there are not simple methods to produce small (< 5-10 nm) nanoparticles. One of the main reasons for that is the general use of iron oxides as magnetic cores, which have a large crystalline mismatch with gold. The use of Fe would be more appropriate, but its high tendency to oxidation has largely precluded it from being used as a core. Here, we will show that using a simple "one-pot" successive reaction method in microemulsions, can avoid such problems and is able to produce very stable core-shell Fe@Au nanoparticles. With this procedure, nanoparticles of  $\sim 6$  nm with a Fe core of 3 nm can easily be obtained. These Fe@Au nanoparticles, with a saturation magnetization of 1.13 emu/g, are very stable even in air after magnetic separation from the solution, which shows the good covering of the Fe core by the Au shell. In this contribution we will report the key parameters, which have to be taken into account, to prepare such stable Fe@Au dispersions and analyze their optical and magnetic properties, as well as their possible applications as biosensors, targeted magnetic separation, *etc.* 

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## I. INTRODUCTION

The interest in core-shell nanoparticles (NP) is driven by the fact that substantially different functionalities arising from the core and shell can be joined to obtain in a single nano-device a complete set of physical potentialities [1].

Gold reassembles a set qualities, such as it is nontoxic and biocompatible, it is chemically easy to engineer due to its ability for surface functionalization (via thiol groups bonding) and it has remarkable optical properties with its surface plasmonic response that can be tuned from the visible to the near IR, making it the best choice as coating material for contrast agent in X-Ray tomography, drug nanocarriers, enhanced imaging of cells, bio-sensing, among others [2].

Iron presents a very large magnetic response arriving to a saturation magnetization  $M_s = 215$  emu/g at room temperature, more than twice that of magnetite, which is the biocompatible magnetic material most used in bioapplications. In this sense, the use of iron as magnetic core would allow to highly reduce the size of the nanodevice or the external exciting magnetic source and in that, still being of magnetic interest.

However, iron is non biocompatible and, from the chemical point of view, largely reactive on air conditions, therefore a protective coating has to be performed to assure stability against oxidation and assure non toxicity for bio-applications. Conveniently coated, magnetic NPs are used as contrast agents for MRI, magnetic heaters combined with therapeutic agents in magnetic hyperthermia, magnetic driving agents for collecting target

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species in nanosensing, etc. [3,4].

Gold coated iron NPs combine biocompatibility and large magneto-plasmonic response, and additionally due to the structural similarities of both materials (bulk Fe is Body Centred Cubic (BCC) lattice and Au is Face Centred Cubic (FCC) with similar interplanar distances), crystal mismatches on the core-shell interface are minimized.

In the last years, research on iron NPs has experienced a surge in interest due to the availability of new synthetic techniques that have allowed circumventing the problem of its huge reactivity in water or air. From the early mercury based methods [5] to nowadays, many attempts are being used to obtain core-shell Fe@Au NPs comprising wet chemistry, high energy milling or laser ablation that result in products with different degrees of polidispersity, shape and magnetic qualities [6].

In this work we present a very simple successive onepot wet procedure based on a microemulsion method, which we have successfully applied in the past to obtain Co@Ag and maghemite NPs [7,8], to obtain ultra-small core-shell Fe@Au NPs. Purified and magnetically separated samples have been characterized by XRD, TEM, and HRTEM, EDXS, UV-Vis absorption and magnetic measurements showing to be very monodisperse with very good morphological and structural properties as well as interesting optical and magnetic properties, reassembling multifunctional abilities.

## **II. SYNTHESIS AND INSTRUMENTATION**

A simple "one-pot" successive reaction method based on microemulsions, has been used to produce stable coreshell Fe@Au nanoparticles. The reverse micelle reaction was carried in water-in-oil microemulsions formed by CTAB (cetyltrimethylammonium bromide) as surfactant, octane as the organic phase and water as aqueous reactant. The water droplet size and, therefore, the entrapped nanoparticle size, can be controlled by adjusting the ratio w between water and surfactant,  $w = [H_2O]/[CTAB]$ . Mixing with an additional amount of buthanol as cosurfactant, allows the stability of the droplets to be increased by increasing the non-polar chain volume head, and this in turn allows to have a larger amount of water available for carrying on the reaction.

The reaction is completed following three consecutive steps. First, two microemulsions are prepared with a ratio w = 8, one with ferrous sulphate (FeSO<sub>4</sub>) 0.1 M and the other with sodium borohydride (NaBH<sub>4</sub>) 0.6 M. Both solutions are degassed and mixed up with gently stirring under argon atmosphere. After a few minutes, iron nanoparticles are formed completing the first stage of reaction. Next stage is achieved by enlarging the size of droplets by adding sodium borohydride to provide for enough space to allocate the Au shell around the Fe NPs. Last stage of reaction is made by adding immediately a microemulsion w = 10 of 0.1 M of HAuCl<sub>4</sub>, for 5 hours under argon atmosphere and magnetic agitation.

Finally the micelles are disrupted with the addition of acetone and NPs are washed several times with a (1/1) chloroform/methanol mixture to remove the surfactant.

Magnetic separation of the washed NPs with a strong magnet has been performed in order to assure that the samples analyzed further bear iron and gold phases simultaneously.

Ultraviolet-visible (UV-Vis) spectra were performed by using a Hewlett Packard 8452A Diode Array Spectrophotometer working under wavelengths from 190 to 820 nm. Usually samples with a volume of 3 mL were placed in a 10 mm quartz cuvette. A "blank spectra" was performed to the solvent prior to the measurements in order to check their purity. Transmission electron microscopy (TEM) images were obtained using a Philips CM-12 microscope (100 kV). NP's samples were prepared by dropping the dispersion onto Formvar-coated or a Carbon coated copper grid. Additional High Resolution Transmission electron microscopy (HRTEM) images were made with a JEOL JEM-2010 FEG (200 kV) microscope. Energy Dispersed X-Ray Spectroscopy (EDXS) characterization was performed with an Oxford Inca Energy 200 accessory incorporated to this equipment, allowing to perform qualitative analysis of the sample chemical composition.

X-ray diffraction **(XRD)** patterns of powdered samples were obtained by using a Philips PW1710 type Diffractometer working with Cu K $\alpha$  radiation ( $\lambda_{Cu} = 1.54186$  Å). Measurements were collected between 10° <  $\theta < 80^{\circ}$  with steps of 0.02° and 10 s/step.

Magnetic studies were carried out on dried powder after evaporating the solvents of the magnetic fluids Zerofield-cooling and Field- cooling characterizations were performed with a Superconducting Quantum Interference Device (SQUID), Quantum Design, under a maximum applied magnetic field of 2 T at temperatures from 5 to 300 (K). Magnetization versus field characterizations were obtained with a physical property measurement system (**PPMS**) working with fields between [-2,2] (T) at fixed temperatures in the range T = [5,100] (K).

#### III. RESULTS

#### 1. Structural and Morphological Properties

Representative powder XRD patterns of Fe@Au samples synthesized by microemulsion synthesis are presented in Fig. 1 compared to patterns of -Fe body centred cubic (BCC) and Au face centred cubic (FCC) crystal structures and the inverted spinel crystal structure of a typical crystalline iron oxide phase (Fe<sub>3</sub>O<sub>4</sub>). It can be seen in the Fig. that cubic Fe pattern is hidden under the Au cubic pattern due to the overlap of their main



Fig. 1. (Color online) X-Ray Diffraction pattern of Fe@Au MNPs, Au (FCC),  $\alpha$ -Fe (BCC) and magnetite (Fe<sub>3</sub>O<sub>4</sub>).

reflection peaks onto the same locations,  $2\theta_{Au(220)} = 2\theta_{Fe(110)} = 44.8^{\circ}$  and  $2\theta_{Au(220)} = 2\theta_{Fe(200)} = 65.3^{\circ}$ .

The reflections of the diffraction pattern of the Fe@Au NPs are located precisely on the overlapping gold and iron patterns revealing the cubic crystalline structure of our NPs. Moreover, it is important to remark that the absence of extra reflections the Fe@Au pattern indicates that no iron oxides as secondary phases are present in the samples, as it can be seen by comparison to the magnetite pattern spectra presented in Fig. 1. In this way, it can be assured that gold has successfully passivated the iron core preventing its oxidation on air conditions, which is one of the main issues in stabilizing iron NPs.

The additional small peaks that can be observed in the small angle region have been assigned to  $Na_2SO_4$ , which is a reaction product of ferrous sulphate (FeSO<sub>4</sub>) and sodium borohidride (NaBH<sub>4</sub>) during the synthesis procedure.

The crystallite size,  $d_{hkl}$ , was calculated from the broadening of the (220) peak of gold and iron located on  $2\theta_{Au(220)||Fe(220)} = 65.3^{\circ}$  following the Debye-Scherrer [9] equation:

$$d_{hkl} = \frac{K \cdot \lambda(\mathring{A})}{\beta(2\theta) \cdot \sin \theta_0} \tag{1}$$

where  $\beta(2\theta)$  is the full width of the half maximum (FWHM) of the peak centered at  $2\theta_0$ ,  $\lambda$  is the wavelength of the X-Ray source ( $\lambda$ (CuK $\alpha_1$ ) =1.54186 Å) and the Scherrer constant for spherical NPS with cubic symmetry K = 0.9 [10]. After performing a fitting of the data we have obtained a crystallite size  $d_{220} \approx 7.7$  nm.

Morphology and crystal structure of gold-coated iron nanoparticles were characterized by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) techniques, respectively. Figure 2 shows the uniform quasi-spherical shape of non aggregated and well dispersed individual iron@gold magnetic NPs (MNPs) along the grid. The great contrast

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Fig. 2. (Color online) TEM image of Fe@Au samples and size histogram of the samples on the left inset.



Fig. 3. HRTEM image of individual Fe@Au NPs with different fringes from diffraction of Fe and Au crystalline planes.

variations can be ascribed to different orientations of the crystallites on the grid.

The average particle size and distribution is presented in the corresponding histogram on the left of the image. The synthesized NPs have an averaged diameter of  $d_{TEM} = 6.5 \pm 1.5$  nm, which is comparable with the crystallite size obtained by XRD  $d_{220} = 7.7 \pm 1.5$  nm. Both values are well below the critical single domain size  $d_c \approx 10$  nm estimated for spherical iron NPs [6].

Figure 3 shows a representative HRTEM micrograph of single particle regions, revealing that the synthesis procedure produces NPs of high crystallinity and structural homogeneity. There can be distinguished different sets of fringes, coming from the different crystalline planes in each NP and also the different relative orientation between the NPs. Two interplanar distances have been measured in the HRTM Fe@Au NP images,  $d_1 =$ 2.4 Å and  $d_2 = 2.0$  Å, indicated in the Fig., belonging to Au {111} and Au {200} planes, and Fe {110} planes,



Fig. 4. (Color online) EDXS analysis showing the chemical composition of Fe@Au samples indicating the presence of Fe, Au and Cu (from the Cu grid).

respectively.

#### 2. Chemical Composition

In Fig. 4 the EDXS analysis performed on Fe@Au samples shows their chemical composition. It can be observed the presence of Fe, Au and Cu (from the TEM grids). Since EDXS is a surface analytical technique, the largest presence of gold compared to the marginal presence of iron, indicates the core (Fe)-shell (Au) structure of the NPs.

#### 3. UV-Vis Absorption

Au sphere NPs behave as an electric dipole and presents an absorption peak due to the surface plasmon resonance (SP) originated by collective excitations of Drude-like conduction or d-band electrons that are optically excited [11]. The resonance peak is located in wavelengths range  $\lambda_{SPR} = [515-530]$  nm depending on the particle's size and shape, solvent dielectric constant, etc. Whereas isolated, solid, spherical and homogenous NPs present sharp resonances shifted to the blue spectra, aggregated, non-spherical or polydisperse samples, present broad peaks which are red-shifted.

Core@shell nanostructures present absorption spectra that have been reported to depend on core and shell thickness, geometry and dielectric permittivity [1]. Tuning of the peak can be done by controlling the ratio of



Fig. 5. (Color online) UV-Vis absorbance spectra of Fe@AuNPs suspended in solvents with different polarity, toluene ( $\varepsilon = 2.38$ ), a mixture of water ( $\varepsilon = 80$ ) & thiol ( $\varepsilon = 2.1$ ) and water ( $\varepsilon = 80$ ).

the core radius to the total radius. Studies on the SP resonance in core@Au-shell NPs [12–14] show that the plasmon resonance of NPs with a thin shell results in a red-shifted broad spectra while thick shells produce a blue-shifted and sharp spectra [15].

Figure 5 shows the UV-Vis absorbance spectra of samples of Fe@Au NPs dispersed in solvents with different polarity: toluene ( $\varepsilon = 2.38$ ), a mixture of water & thiol ( $\varepsilon = 80 \& \varepsilon = 2.1$ , respectively) and water ( $\varepsilon = 80$ ), in order to assess their stability and perform optical characterizations.

Dried samples of Fe@Au were dispersed in water, but the solution was unstable with the formation of large aggregates, as it can be readily observed by their broad and red-shifted spectra [11]. With the addition of MUA (11-mecapto undecanoic acid) a stable and well dispersed solution is obtained since thiol groups attach the gold surface and avoid the aggregation processes, obtaining correspondingly a blue-shifted and sharp SP resonance located on  $\lambda_{SPR}^{Fe@Au(MUA)} = 534$  nm, very close to SP resonance  $\lambda_{SPR}^{SPR} = 520$  nm for solid and isolated gold NPs below d = 20 nm [15].

The third sample, dispersed in toluene, produced a slightly more wide resonance peak located on  $\lambda_{SPR}^{tol.} = 582$  nm, which can be explained by the different dielectric constant.

It has to be noticed that the SP resonance  $\lambda_{SPR}^{Fe@Au(MUA)}$  (for Fe@Au NPs in the water & MUA mixture), practically coincides with that of pure gold  $\lambda_{SPR}^{Au}$ , where the small difference observed of about  $\Delta \lambda = 14$  nm, can be ascribed to the iron core that magnetically affects the dielectric environment of the surface plasmon [15]. Moreover, taking into account that iron NPs are known to produce only a broad absorption band decreasing from  $\approx 200$  nm [16]; NPs with corners or irregularities (as it could be the case in an irregular and incomplete gold shell) would produce a broad and

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Fig. 6. (Color online) FC-ZFC curves for Fe@Au NPs maintained at different magnetic fields H = [100,500,1000] Oe.

red shifted spectrum [1]. Therefore, the fact that the absorption spectrum peak of the Fe@Au samples coincides in shape and location with that of a spherical gold NP,  $\lambda_{SPR}^{Fe@Au} \approx \lambda_{SPR}^{Au}$ , allows us to assume that the gold shell has widely, homogeneously and effectively coated the iron core.

### **IV. MAGNETIC PROPERTIES**

Dried samples of Fe@Au NPs have been magnetically characterized performing cycles of FC and ZFC on fixed field values, H = [100,500,1000] (Oe) as it is shown in Fig. 6.

Since the synthesis procedure of gold coated iron nanoparticles is a successive steps one-pot method, no information about the size of iron core is directly available. Indirect calculation has been performed by using the equations developed by Chantrell *et al.* [17] which hold for a system of magnetic non-interacting nanoparticles, monodisperse and in the SPM regime. The NP's magnetic core NP  $(D_{Mag})$ , and its deviation  $(\sigma)$  can be obtained by fittings to the following equations:

$$D_{Mag} = \left[\frac{18k_BT}{\pi M_s} \sqrt{\frac{\chi_i}{3m_s} \frac{1}{H_0}}\right]^{1/3}$$
(2)

$$\sigma = \frac{1}{3} \left[ \ln \left( \frac{3\chi_i}{m_s} / \frac{1}{H_0} \right) \right]^{1/2} \tag{3}$$

where  $M_s$  and  $m_s$  are, respectively, the saturation magnetization of the bulk material and nanoparticles;  $X_i$  is the initial susceptibility at low fields, where M follows a linear relationship with H; The saturation magnetization for each temperature,  $M_{sat}(T)$ , was determined by extrapolating  $H^{-1} \to 0$  from the magnetization data using fields  $H \leq 10$  kOe and the value  $1/H_0$  as the location where the tangent crosses the horizontal axes.



Fig. 7. (Color online) M versus H/T for 5 to 100 K where collapsing of curves happens for SPM regime at T > 25 (K).

Following the criterion that, for a system of noninteracting particles above the blocking temperature, the hysteresis cycles of magnetization versus H/T overlaps [18], we have plotted in Fig. 7 the magnetization of Fe@Au samples for a set of temperatures T = [5,100]in order to choose the adequate experimental conditions to fit the Chantrell's equation.

In Fig. 7, magnetization M is represented versus H/T showing that almost all curves overlapped, indicating that our system consists of non-interacting NPs. A clear superparamagnetic (SPM) behavior is observed only at the highest temperatures T > 25 (K), where coercive forces and remanence are zero and, correspondingly, M versus H/T collapse, as it can be clearly observed in the inset of this Fig. This is in good agreement with the XRD and TEM results, which evidenced that the Fe core of the NPs does not exceed the critical size of single- to multi-domain limit for iron NPs ( $d_c \approx 10$  nm). For lower temperatures  $T \leq 25$  (K), there is an obvious widening of the coercive field and mismatching of saturation magnetization values.

We obtained all the quantities involved in Chantrell's equation from the experimental data on the SPM regime, at T = 50 (K), and computed the estimated value of the core diameter as:  $D_v = 3.0$  nm;  $\sigma = 0.5$  nm. With this data of the iron core radius, r = 1.5 nm, and the gold shell thicknes  $\delta = 1.5$  nm, the magnetic mass of the samples has been computed and, after correction of the magnetic data by subtracting the non-magnetic mass corresponding to the gold shell (that represents a large % of the total mass), the saturation value to iron mass,  $M/m_{Fe}$  has been obtained. The maximum values of saturation magnetization obtained, for low T, are  $M_{sat}^{NP} \approx 50 \text{ emu}/g_{Fe}$  which is approximately four times lower than bulk iron saturation magnetization,  $M_{sat}^{bulk} = 210 \text{ emu}/g_{Fe}$ . The large difference between  $M_{sat}^{NP}$ and  $M_{sat}^{bulk}$  can partially be explained by the contribution of surface effects, which in ultrasmall NPs may be of paramount importance [6]. In fact, the ratio of surface to volume ions for iron nanoparticles with  $d \approx 3$  nm may be very large,  $\approx 50$  %. Therefore, surface spin magnetism becomes the main contribution to the NP's magnetic properties.

In addition, it has been reported that magnetic properties of gold coated iron nanoparticles become highly reduced due to the chemical bonding effect of gold on the magnetism of the surface electrons, which makes this issue as one of the most discouraging side effects [5] in the synthesis of Fe@Au NPs.

In spite of the reduction of the magnetization values to  $M_{sat}^{NP} \sim 50 \text{ emu}/g_{Fe}$  these core-shell NPs can be of interest in hyperthermia applications by comparison to reported heating achieved with NPs with comparable magnetization values and sizes [19], which are able to produce increases of temperatures about  $\Delta T = 30$  °C, depending on the time of the magnetic field exposure, and which are enough for killing cancer cells (T = 42 - 45 °C).

#### V. CONCLUSIONS

A simple successive one-pot procedure based on a microemulsion method for the synthesis of Fe@Au NPs has successfully been performed to obtain ultra-small gold coated iron NPs. Purified product, after several washing processes and magnetic separation, has been morphologically, structurally, optically and magnetically studied. Highly monodisperse, nearly spherical core@shell NPs have been obtained. The size of the NPs has been characterized by TEM giving a monodisperse set of ultra-small particles (< d > = 6 nm), with an iron core ( $d_c \sim 3$  nm), obtained from magnetic data, well below the single domain size for iron NPs, that makes them especially suitable for MRI. By HRTEM and XRD, good crystallinity and homogeneity as well as absence of iron oxides have been observed.

They present a sharp absorption resonance under UV-Vis spectra due to the metallic shell of gold that endow the particles with surface plasmonic response, making them useful for sensing applications.

Moreover, the iron magnetic core adds magnetic functionally to the ensemble. In fact, Fe@Au have been measured to present SPM behavior at room temperature with a maximum saturation around 50 emu/ $g_{-Fe}$ that allows the core@shell NPs to be useful for remotelycontrolled magnetic applications as magnetic hyperthermia or magnetic separation applications. The combination of the magneto plasmonic response of this ultrasmall core-shell Fe@Au makes them very useful for nanomedicine and nanosensing applications taking into account all the benefits of biocompatibility and surface functionality of the gold shell.

In this sense, more efforts will have to be done in the synthesis procedure, in order to obtain larger iron cores with better magnetic performances and tunable gold shell thickness to be able to control the final magnetoplasmonic responses.

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