Physicochemical Studies of Complex Silver–Magnetite Nanoheterodimers with Controlled Morphology

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ABSTRACT: This work discusses the influence of synthesis conditions on self-assembly capability and morphology of obtained Ag–Fe₃O₄ nanoheterostructures. Samples were synthesized in two steps: first silver nanoparticles were synthesized and then used as seeds for the growth of iron oxide nanoparticles in a second step. The silver nanoparticle size was tuned, changing the oleylamine (OAm) and oleic acid (OA) ratio, which enables us to study the influence of chemical agents and seed size on the final magnetic nanoparticle morphology. The mechanism during the formation of these heterostructures has been discussed by several authors; however, it remains an open issue. In this paper we extend the discussion and advance on the understanding of synthesis conditions, related to silver sizes, chemical agents, and physical properties on the obtained nanoparticles. In our Ag–Fe₃O₄ system, two types of heterostructures were obtained: dimer, flower, or combination of the two. We have found that the final shape depends on silver seed size, as well as the polarity of the chemical agents used during the synthesis. We made an exhaustive study of the relationship between magnetic properties and structural features. The morphology and size distributions of the heterostructures were analyzed with transmission electron microscopy (TEM).

INTRODUCTION

Noble metal–iron ferrite nanoheterostructures are interesting bifunctional materials, in which nanoparticles of magnetic iron oxide and noble metal are stuck together. In this way, it is possible to combine the optical properties of a noble metal, like silver or gold, and the high magnetization and superparamagnetic properties associated with the iron ferrite nanoparticles. These heterodimer nanoparticles, sometimes called Janus nanoparticles, have enormous potential for biomedical application such as hyperthermia treatment, magnetic resonance imaging contrast agents, and magnetic separation, among others. They can also be used in 43 technological applications, taking advantage of the incorporation of the metal ions into iron oxide nanoparticles, for example, in switch contacts, welding, and catalysis, among others.

Diverse routes for synthesizing Ag (or Au)–MFe₂O₄ (M = Fe, Co, or Mn) have been reported. One pioneering work reported by L. Zhang et al. suggests that the heterodimer structure is determined through epitaxial growth of Ag on the Fe₃O₄ seeds in nonpolar solution. With a similar synthesis, more contemporary work shows that changing reaction times and noble metal (Au instead of Ag) makes it possible to obtain core–shell Fe₃O₄@Au structures. Since then, several articles have been published, varying the route of synthesis, concentration of seed nanoparticles, as well as the type and size of the iron oxide used, aiming to improve and explain observed magnetic, optical, and electrical properties. Nevertheless, the formation mechanism was not sufficiently studied, thus leaving unfinished questions.

In this paper, we report the synthesis of Ag–Fe₃O₄ heterodimer structures, first varying the polarity of the chemical agents and second using different Ag seed sizes. The main objective is to go further into the mechanism of the formation...
of these structures. Also we present magnetic properties of these systems related to the final structure obtained.

**EXPERIMENTAL SECTION**

General Synthesis of Ag–Fe$_3$O$_4$ Heterostructures. Ag–Fe$_2$M$_{0.5}$O$_{1.5}$ (M = Fe$^{3+}$) heterodimer nanoparticles were synthesized by thermal decomposition of organometallic precursors. The first reaction involves the synthesis of Ag nanoparticles, namely, Ag seeds, which in a second step, will be used as seeds for growing magnetite nanoparticles by an in situ procedure, forming a nanosized heterostructure.

Synthesis of Ag Seeds. Ag nanoparticles, namely, Ag seeds throughout this manuscript, were obtained by thermal decomposition of Ag(PPh$_3$)$_2$NO$_3$ in benzyl ether solution. The silver complex was prepared from stoichiometric amounts of silver nitrate and triphenylphosphine (PPh$_3$) in acetonitrile. A white solid is obtained after heating the solution at 80 °C. Subsequently, the white solid is dispersed in benzyl ether, oleylamine (OAm), and oleic acid (OA). To obtain different samples, different quantities of OA were added to produce specific Ag particle size and surface charge. The mixture is loaded into a three-neck round-bottom flask with a reflux condenser, a thermometer, and a magnetic stir bar in an argon atmosphere. The reaction mixture was heated at a rate of 3 °C/min up to 100 °C and then at a rate of 2 °C/min up to 300 °C. In both thermal treatments, after the temperature was stabilized, reaction conditions were maintained for 30 min. Ag nanoparticles were centrifuged several times with toluene–ethanol solution and dried in vacuum. Ag seeds are labeled as OA6-Ag, OA10-Ag, and OA14-Ag, for samples prepared with OAm:OA (molar ratios) of 6:6, 6:10, and 6:14, respectively.

Synthesis of Ag–Fe$_3$O$_4$ (Samples M$_{OA:6}$, M$_{OA:10}$, and M$_{OA:14}$) Using As Seeds Ag Nanoparticles Previously Synthesized. These Ag–Fe$_3$O$_4$ heterostructures were obtained by mixing the aforementioned Ag seeds, Fe(acac)$_3$, OAm, OA, 1,2-hexadecanediol, and benzyl ether in a molar relation of 3:2:1:6:6:10:263, respectively. The reaction mixture was kept at 80 °C in an argon atmosphere for 30 min. Then, the temperature was slowly raised to 300 °C with a heating rate of 2 °C/min. After 40 min of reaction, the heater was turned off, and the solution was brought to room temperature. The samples were dispersed and then precipitated and after centrifugation with toluene–ethanol several times and finally dried in vacuum. Throughout this paper the following nomenclature for samples is used: M$_{OA:6}$, M$_{OA:10}$, and M$_{OA:14}$ for samples prepared with OAm:OA molar ratios of 6:6, 6:10, and 6:14, respectively.

Synthesis of Ag–Fe$_2$O$_4$ (Samples S$_{PH}$ and S$_{OT}$) Keeping Ag Seed Size and Using Two Solvents with Different Polarity. Some changes were introduced with respect to the previous synthesis. The main difference involves the use of two different solvents: octadecene and phenyl ether (see Supporting Information for synthesis details). S$_{OT}$ and S$_{PH}$ correspond to samples prepared with octadecene and phenyl ether, respectively.

Characterization. Structural characterization was carried out via X-ray diffraction (XRD), in a commercial diffractometer, and with small-angle X-ray scattering (SAXS), measured at the SAXS line (National Synchrotron Light Laboratory, LNLS, CNPEM, Campinas, Brazil). Morphology and size distribution of the samples have been obtained by transmission electron microscopy (TEM). Magnetic properties were studied by SQUID magnetometry between 5 and 300 K.

**RESULTS AND DISCUSSION**

Ag Seed Size Distributions. Ag seeds were studied by XRD (see Supporting Information, Figure S.1) and SAXS to confirm the phase of the Ag seed and to obtain a detailed analysis of particle size distributions and aggregation state. Figure 1a and c shows the particle size distributions of OA10-Ag and OA14-Ag samples obtained from SAXS measurements (red lines) and size distribution histograms with their corresponding log-normal fits, obtained by analyzing TEM images. (b and d) Size distribution and its log-normal fit for Fe$_3$O$_4$ nanoparticles in heterostructures.

Ag and OA14-Ag samples (obtained from SAXS measurements, red lines), respectively. SAXS size distribution was calculated using Gnom software. Two major peaks were observed for each size distribution profile. The OA10-Ag sample shows a narrow peak at D = 23 nm, and a small peak is observed at D = 77 nm. For the OA14-Ag sample, a peak is observed at D = 32 nm, and a second peak, broader and less defined, has a maximum at D = 120 nm.

TEM size distribution histograms were obtained from several TEM images of Ag–Fe$_3$O$_4$ samples. Their fit to a log-normal curve (black lines) is also displayed in Figure 1a and c. It is worth noting that in Ag seed size distribution profiles obtained by SAXS (red line) and TEM are similar for the first peak. As expected, this agreement confirms that the size of Ag NPs is preserved in the synthesis final step. Also from TEM images, only individual particles of mean value 23 and 32 nm were observed, for OA10-Ag and OA14-Ag, respectively. This confirms that the second correlation length population could be caused by nanoparticle agglomerations, through electrostatic interaction of the first population during the colloidal suspension in the SAXS acquisition. This is the first evidence of possible charge compensation mediated by a stabilization agent, from where on the OA14-Ag the charge compensation would be greater than the OA10-Ag.

Fe$_3$O$_4$ Size Distributions Obtained from Analysis of TEM Images. Size distribution profiles show that the Fe$_3$O$_4$ nanoparticles in the heterostructure have a narrow size distribution with a mean size of 7 and 8 nm for M$_{OA:10}$ and M$_{OA:14}$.
TEM Information on the Ag–Fe₃O₄ System (Samples M₉OA:10 and M₉OA:14)

Images of the Ag–Fe₃O₄ systems (Figure 2) show nanoparticles with two different contrasts associated with two different materials (silver and magnetite). The darkness profile in TEM images of a particle with homogeneous density is proportional to atomic number, Z. Hence, Ag particles, which have higher Z compared with Fe₃O₄ particles, exhibit darker contrast.

TEM images reveal that Fe₃O₄ nanoparticles nucleate, grow, and self-assemble (during the synthesis final step) using Ag nanoparticles as fixed seeds. This evolution leads to the formation of two types of heterostructures, dimer or “flower” (Figure 2). These two types of structures were obtained in the studied samples. In the M₉OA:10 sample, the dimer or dumbbell-like structure predominates, while in M₉OA:14, the flower-like structure is the one that prevails. These possible structures, dimer or “flower”, are derived from the atom-by-atom growth of the magnetite nanoparticles on the Ag seeds.

Our interpretation is that when Fe₃O₄ nanoparticles start to nucleate on the Ag surface a charge in the polarized plane at the interface is induced. This new deficiency must be compensated, in this case by free electrons from the Ag nanoparticles. The way in which compensation is carried out can lead to the formation of distinct heterostructures.

In previous work, Heng Yu et al. demonstrated that for Au–Fe₃O₄ systems the solvent polarity plays an important role in the final conformation structure. They argue that the increase in solvent polarity could compensate the charge induced by the polarized plane growth of the Fe₃O₄ nanoparticles, allowing the nucleation on multiple facets. Under this perspective, the mechanism of charge compensation induced by a specific compound in the reaction mixture (solvent or a stabilization agent) is a crucial issue to define the heterostructure conformation. Also it will determine the final structure and shape, as well as the magnetic and electronic properties.

In the samples under study (M₉OA:10 and M₉OA:14), the amount of solvent (benzyl ether) is kept constant; therefore, the differences in the charge compensation process are associated with the amount of stabilizing agent (OA) used in the synthesis. In Ag nanoparticles synthesized by the employed method, the interaction with the metal surface is mediated by the electron-dense carboxylic group of the OA. A denser presence of these groups over the surface will produce a charge compensation needed to allow nucleation on multiple facets. This type of charge compensation causes the formation of flower-like heterostructures in the sample M₉OA:14, the one with the biggest amount of OA. On the other hand, in the M₉OA:10 sample, the charge compensation induced by the stabilization agent (OA) is not enough to allow multiple facet growth, thus producing dumbbell-like heterostructures. Also, as will be discussed later, the difference in the Ag seed size between the two samples can contribute to the formation of these two types of heterostructures.

To verify that the formation of different heterostructures occurs when the amount of stabilizing agent (OA) is constant (OA concentrations in the same order of OA14-Ag sample) and the compensating charge is modified by varying the solvent, two other samples were synthesized (SPHE and SOTD). For this, two solvents with different polarity were employed. First Ag–Fe₃O₄ (SPHE) heterostructure was synthesized using phenyl ether as solvent. It is known that this organic compound, with increased polarity, contains an ether group which acts as a charge compensator. On the other hand, the second Ag–Fe₃O₄ heterostructure (SOTD) was synthesized using octadecene as solvent, and this compound is known for being nonpolar.

Figure 3 shows TEM images of the as-prepared Ag–Fe₃O₄ heterostructures (SPHE and SOTD). As in previous samples, the darker regions correspond to Ag NPs and low contrast structures correspond to Fe₃O₄ NPs. From the images the formation of dimer-like heterostructures can be observed when octadecene is used as solvent, while when phenyl ether is used instead, “flower”-like heterostructures are obtained.

Then, our results prove that synthesis performed with different polarity organic solvents leads to different heterostructure conformations. Unlike the samples M₉OA:10 and M₉OA:14, on SPHE and SOTD samples charge compensation is influenced by the polarity of the solvent. In that way, if a solvent with increased polarity is used, their charges act to allow nucleation...
of iron oxide NPs on multiple facets on the surface of Ag NPs. When a nonpolar solvent is used, charge compensation is carried out by the stabilizing agent (OA). These results correlate with results shown by Yu et al. for Au–Fe₃O₄ heterostructures. Moreover, several studies have analyzed other conditions that lead to the different final conformations of M–Fe₃O₄ heterostructures. For example, Ag seeds of same size but varying concentration could change the final structure of this complex nanoparticle. In this sense, a high concentration of Ag seeds produces dimeric structures, while low concentrations produce flower-like heterostructures. Also, the size of the Ag seed has great influence on the final conformation. This assumption is based on the fact that the electron delocalization influences differently when Ag seeds are large or small; i.e., if the seeds are small, the delocalization could affect different facets on the surface, leaving them unsuitable for multi-nucleation, while if the seeds are larger, the delocalization affects the Ag nanoparticle core. Considering that Ag seed size would influence the charge compensation, we synthesized silver nanoparticles of greater size. These seeds are labeled as OA6-Ag. Figure 4a shows the particle size distribution from SAXS with the first peak showed by SAXS size distributions. Also in TEM images, no Ag nanoparticles with D > 250 nm are observed. Figure 4b displays the size distribution of the Fe₃O₄ NPs on the Mₐₒ₆₋ sample. The size distribution was obtained by measuring more than 300 nanoparticles (joined to Ag seeds and alone). From the analysis of these images, these nanoparticles have a size distribution slightly broader compared to the distributions reported for samples Mₐₒ₁₀ and Mₐₒ₁₄. Figure 4c and d show the TEM images of the Ag–Fe₃O₄ heterostructures (Mₐₒ₁₀) prepared using OA6-Ag as seeds. In the as-synthesized heterostructure a mix of dumbbell and flower-like structures (multiple facets) is observed.

To expand the discussion regarding the influence of Ag size on the formation of the achieved structures, the results obtained above were compared with the results presented for samples Mₐₒ₁₀ and Mₐₒ₁₄. For this purpose, and considering the low charge compensation by a stabilization agent, only the size of Ag seeds would influence the charge compensation and hence the formation of different heterostructures. Subsequently, we can see that the approximated condition 2 ≤ sizeAg seed/sizeFe₃O₄ ≤ 4 favors the formation of a dimer or dumbbell-like structure, also noted in others works. On the other hand, when the size of the Ag seeds is slightly greater than the previous condition, “flower” (or core–satellite) nanoparticles are the predominant heterostructure. This type of structure has been previously reported for similar systems in which the reported condition was 3 ≤ sizeAg seed/sizeFe₃O₄ ≤ 5. In our results we note that the conditions previously described are conserved in almost all cases.

As described above, there may be different forms of charge compensation in Mₐₒ₁₀, Mₐₒ₁₄, and Mₐₒ₁₄ samples: by size and/or by stabilization agent. Table 1 shows the influence of the charge compensation mechanisms and the final heterostructure obtained.

Table 2 shows the influence of the charge compensation mechanism on Sₒ₉₁₀ and Sₒ₉₁₂ samples. In these two samples, (red line) and TEM (black line and histogram) of the OA6-Ag sample. From SAXS size distributions two peaks are observed: the first corresponds to Ag nanoparticles with mean diameter of 73 nm. Another peak, observed at D = 266 nm, is electrostatic agglomerates of particles of the first populations. From TEM, only one peak is revealed (78 nm), which is in good agreement with the following factor.

**Table 1. Influence of the Charge Compensation Mechanisms**

<table>
<thead>
<tr>
<th>Sample (OA:m:OA ratio)</th>
<th>M₁₀₁₀</th>
<th>M₁₀₁₂</th>
<th>M₁₀₁₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–Fe₃O₄ (6:6)</td>
<td>M₁₀₁₀</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Ag–Fe₃O₄ (6:10)</td>
<td>M₁₀₁₂</td>
<td>low</td>
<td>medium</td>
</tr>
<tr>
<td>Ag–Fe₃O₄ (6:14)</td>
<td>M₁₀₁₄</td>
<td>low-medium</td>
<td>high</td>
</tr>
</tbody>
</table>

**Note:** The influence by size and by stabilization agent is not taken into account since parameters such as the Ag seed size and amount of stabilizing agent were kept constant.

**Table 2. Influence of the Charge Compensation Mechanisms on Sₒ₉₁₀ and Sₒ₉₁₂ Samples**

<table>
<thead>
<tr>
<th>Sample (solvent)</th>
<th>charge compensation by size</th>
<th>charge compensation by stabilization agent</th>
<th>heterostructure conformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–Fe₃O₄ (octadecene)</td>
<td>low</td>
<td>medium</td>
<td>dimer and flower</td>
</tr>
<tr>
<td>Ag–Fe₃O₄ (phenyl ether)</td>
<td>high</td>
<td>high</td>
<td>flower</td>
</tr>
</tbody>
</table>

This influence is labeled as high, medium, or low according to the impact of each mechanism in the sample preparation. Notice that for the Mₒ₁₄ sample charge compensation by size was considered as “low-medium”, but could be little bigger than the Mₒ₁₀ sample because of a small difference on sizes.
the influence by size and by stabilizing agent is not taken into account since parameters such as the Ag seed size and amount of stabilizing agent were kept constant.

Magnetic Measurements of Samples $M_{OA:6}$, $M_{OA:10}$, and $M_{OA:14}$. Experimental field-dependent magnetization curves (symbols) at $T = 300$ K and $T = 5$ K are shown in Figure 5a, b, and c. From these measurements of Ag–Fe₃O₄ at 300 K the superparamagnetic behavior is confirmed, with low coercive fields of 4, 20, and 19 Oe for $M_{OA:6}$, $M_{OA:10}$, and $M_{OA:14}$ samples, respectively. The temperature dependence of the coercive fields $H_c(T)$ for the Ag–Fe₃O₄ samples are shown at the top left inset of Figure 5a, b, and c. In all samples, and at temperatures below 50 K, the coercive field has a dependence typical for a system with random distributions of anisotropies. At low temperatures, hysteresis loops show that increased coercive fields, e.g., at $T = 5$ K, are obtained at $H_c$ values of 370 Oe for sample $M_{OA:6}$, 322 Oe for sample $M_{OA:10}$, and 394 Oe for sample $M_{OA:14}$. Above 50 K, $H_c(T)$ behavior deviates from the $T^{1/2}$ curve, suggesting that the process is influenced by other effects, like dipolar interaction. H$_s$ values at low temperature (5 K), reported in Table S.1 (see Supporting Information), are similar for all Ag–Fe₃O₄ samples. The obtained magnetization saturation values ($M_s$) for Ag–Fe₃O₄ samples were 3.2, 6.5, and 5.8 emu/g for the 6:6, 6:10, and 6:14 OAm:OA ratios, respectively. The significant small value of $M_s$ in comparison with Fe₃O₄ in bulk (84 emu/g), is due to the relative low mass percentage of the Fe₃O₄ component in these heterostructures and the small sizes of the magnetic nanoparticles. Similar superparamagnetic Fe₃O₄ nanoparticles with an average size of 7 nm have a saturation magnetization ($M_s$) of about 26 emu/g at $T = 300$ K. Considering that the magnetite nanoparticles in the heterostructure have a narrow size distribution with a maximum of around 7 nm (Figure 1b, d, and Figure 4b), we can consider 26 emu/g as a reference value to calculate, in a first approximation, the relative amount of magnetite nanoparticles present in Ag–Fe₃O₄ samples. On the basis of this assumption the obtained values were 13, 25, and 21 wt % for $M_{OA:6}$, $M_{OA:10}$, and $M_{OA:14}$ samples, respectively. Reduction in saturation magnetization is usually attributed to the effect of the nanometer scale of the particle size on the surface/volume ratio, resulting in spin canting due to the spin frustration or poor crystallization of the Fe₃O₄ phase which reduces the magnetic moment of the iron oxide nanoparticles. Furthermore, TEM images show some isolated Fe₃O₄ nanoparticles with size below 3 nm, which gives a superparamagnetic contribution to the measures and lower magnetic moment per particle than for the 7 nm ones.

According to Kechrakos et al., dipolar interactions act to decrease the magnetic response of the system, suggesting that magnetization approximates to saturation slower than the corresponding noninteracting superparamagnetic systems. Hence, in the case of the sample, $M_{OA:10}$ which is already saturated at $H = 16$ kOe, should present a smaller influence of dipolar interactions. It is important to notice that the majority of the heterostructures found in this sample presents a dumbbell-like structure.

In contrast, and due to the possible existence of stronger dipolar interactions among Fe₃O₄ nanoparticles, the samples $M_{OA:6}$ and $M_{OA:14}$ do not reach saturation even at $H = 20$ kOe.
and $T = 5$ K. Due to the shape of these samples (containing flower-like or core–satellite heterostructures), we can infer that the existence of this type of heterostructure promotes the increase in the strength of dipolar interactions. Then, based on the theory proposed in the cited reference and comparing $M$ vs $H$ curves at $T = 300$ K of these two samples, the $M_{OA:14}$ sample should have a greater influence of dipolar interactions between the magnetic nanoparticles.

To better understand the role of magnetic interactions in our systems, more quantitative analysis was performed. The Langevin equation was used to fit the $M$ vs $H$ curves, from which size distribution histograms were obtained (Figure 1b, d and Figure 2b). These indicated that the samples have size distributions which follow a log-normal distribution. Therefore, the magnetization contribution of the unblocked (superparamagnetic) Fe$_3$O$_4$ nanoparticles, $M(H,T)$, is described by

$$M(H,T) = \int_{-\infty}^{\infty} \mu_{app}(H) d\mu_{app}$$

(1)

where $L(\mu_{app}H)/(kbT)$ is the Langevin function; $kb$ is the Boltzmann constant; $T$ is the temperature; $\mu_{app}$ is the apparent magnetic moment (called apparent because the fit does not take into account interactions among nanoparticles); and $f(\mu_{app})$ represents the log-normal distribution function of the apparent moments which is given by

$$f(\mu_{app}) = \frac{N}{\sqrt{2\pi} \cdot \mu_{app} \sigma} \exp\left(\frac{-\ln^2(\mu_{app}/\mu_0)}{2\sigma^2}\right)$$

(2)

where $\mu_0$ is the median of the distribution and $\sigma$ is the standard deviation. The mean of the apparent magnetic moments is given by $\langle \mu_{app} \rangle = \mu_{app} \exp(\sigma^2/2)$.$^33$ In this way, the parameters $\mu_{app}$ and $\sigma$ were obtained, and their corresponding fitting curves (black continuous lines) are displayed in Figure 5a, b, and c. The apparent mean magnetic moments $\langle \mu_{app} \rangle$ obtained at $T = 300$ K are in good agreement with values reported for superparamagnetic systems.$^34$

Figure 5 c, d, and f (gray symbols) shows the $\langle \mu_{app} \rangle$ values obtained by eq 1. The obtained values increase with $T$ until a certain value is reached. However, in correspondence with the behavior of $M_s$ as a function of $T$, the particle magnetic moments are expected to remain almost constant for low temperatures and decrease as the temperature approaches the Curie temperature. This unrealistic behavior was reported and explained by Allia et al.$^35$ for magnetic systems with dipolar interactions between particles. To obtain the thermal dependence of a real magnetic moment, they introduce a phenomenological approach modifying the temperature on the standard Langevin function, in a model known as $T^*$ or the Allia model. They suggested the existence of a dipolar field which acts by altering in a random way the magnetic moments, their directions, sign, and magnitude. This effect is analogous to the effect produced by the temperature, such that the 418 temperature in the Langevin function can be written as $T_s = 419 T + T^*$ when $T^*$ is related to the dipolar energy, $\varepsilon_D = 420 k_BT^* = 421 \alpha M_s^2/k_BT$, where $\alpha$ is a proportionality constant. On the basis of previously mentioned results, it is possible to assume that in our systems the magnetization is described by a modified 423 Langevin function

$$M(H,T) = \int_{-\infty}^{\infty} \mu_{app}(H) f(\mu_{app}) d\mu_{app}$$

(3)

The above equation represents the magnetic regime in which the dipolar interaction effect is taken into account and where $\mu_{app}$ represent the true magnetic moment.

$T^*$ determination is carried out starting from the low-field susceptibility equation for interacting superparamagnetic systems: $\chi = ((N\mu^2)/(3k_BT^*))$. Using the conditions $Nd^2 = 1$ ($d$ is average distance between particles) and $M_s = N\mu$, it is simple to obtain

$$\rho = 3k_BT^2$$

(4)

where $\rho$ is related to the distribution moments defined as $\rho = 354 \langle \mu^2 \rangle/\langle \mu \rangle^2$. In all samples a linear dependence of $\rho/\chi$ as a function of $T/M_s^2$ was observed, with the exception of the data obtained at $T = 5$ K. This deviation could be ascribed to a model failure when the system is completely blocked. However, the linear trend of the other data allowed us to determine $\alpha$ and therefore $T^*$.

On the basis of the above-mentioned $T^*$ model and using the fitting procedure of ref 34 ($\mu_{app}$) as a function of $T$ was calculated (Figure Sd, e, and f, black symbols). In all cases, at low temperature ($\mu_{app}$) values are larger than $\langle \mu_{app} \rangle$ ones, while at $T = 200$ and 300 K the values are closer. It is well-known that the true mean magnetic moment value at $T = 5$ K presents a deviation from expected behavior because at this temperature 448
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The majority of Fe₃O₄ nanoparticles are in the blocked regime.

In Table S1 (see Supporting Information), the parameters obtained through the fit with eq 1 and 3 are reported.

The (μₓ) tendencies obtained for M₀A₁₀ and M₀A₁₄ have a monotonic decrease, except for the data obtained at T = 5 K.

This behavior is related with the shape of the heterostructures, where in these two samples a dominant heterostructure persists, dimer or flower for M₀A₁₀ and M₀A₁₄, respectively.

On the other hand, the mean true magnetic moment values (μₓ) of the sample M₀A₁₀ are greater in comparison with those of the M₀A₁₄ sample (Figure 5e and f) at all temperatures. This corresponds with our previous hypothesis, where a smaller effect of dipolar interactions (dimer configuration) gives rise to a higher magnetic response. Also, it reinforces the fact that in the M₀A₁₄ sample (flower configuration) the contact between surfaces of the Ag–Fe₃O₄ and Fe₃O₄–Fe₃O₄ nanoparticles generates an increase in exchange coupling and in dipole-dipole interactions. This assumption is also in agreement with M vs H measurements in which the M₀A₁₄ sample reaches saturation at a higher magnetic field and with lower values of the mean true magnetic moment (⟨μₓ⟩) obtained for this sample. The decrease of the true magnetic moment in sample M₀A₁₆ is steeper because of the presence of the two types of heterostructures (dimer and flower). This would give rise to a more complex magnetization process, such that the information obtained for the M₀A₁₆ sample from the standard and modified Langevin equation cannot be corrected. Moreover, it should be noted that the dipolar interactions would have positive implications on hyperthermia treatment. Recent studies show that such interactions increase the specific absorption rate (SAR) due a crossover between Neel and Brown dynamics.

Figure 6a, b, and c shows the T dependence of magnetization for M₀A₉, M₀A₁₀ and M₀A₁₄ samples. Measurements were performed in a zero-field cooling (ZFC) and field-cooling (FC) modes with H = 50 Oe from 5 to 300 K. ZFC-FC curves for the three samples are typical of superparamagnetic systems. However, some differences were observed, which are associated with the shape of the structure achieved. All M_ZFC curves exhibit a well-defined maximum, ascribed to the blocking temperature (T_B). The system can be defined as blocked for values of T < T_B and superparamagnetic if T > T_B. The obtained values for T_B are 35, 63, and 22 K for samples M₀A₉, M₀A₁₀, and M₀A₁₄, respectively. In sample M₀A₁₀ (T_B = 63 K), the curve is distributed over a broad range of temperatures in comparison to the other two Ag–Fe₃O₄ samples.

At first glance, one might believe that these differences are due to an increased interaction strength (of dipolar type) or a greater size distribution of Fe₃O₄ nanoparticles in sample M₀A₁₀. However, these assumptions can be discarded because:

(1) The histograms obtained from the TEM images show a narrow size distribution of the Fe₃O₄ nanoparticles, even slightly narrower in comparison to the other two Ag–Fe₃O₄ samples (M₀A₆ and M₀A₁₄).

(2) The results obtained from M vs H measurements demonstrate an increase in the dipolar interactions when flower-like structures are the predominant form. In this sense, these differences can be explained from the different electronic configurations due to the influence of Ag nanoparticles like major spin transfer (from the magnetite to the silver) or changes on the magnetic orbital. However, further studies are required to confirm these hypotheses. We have observed that in M₀A₁₀ and M₀A₁₄ the irreversibility temperature was near the blocking one, and no Morin (typically of hematite) was detected. For M₀A₆, the Verwey transition T_V is evident (T_V = 120 K). T_V is typically observed in well-crystallized Fe₃O₄ nanoparticle systems, at T_V = 120 K.

Temperature dependence of the inverse magnetization is also shown in the insets of Figure 6. At high temperatures, it follows the Curie–Weiss law: \( \chi = \frac{C}{T - \Theta_p} \), where \( C \) is the Curie molar constant, \( T \) the absolute temperature, and \( \Theta_p \) the Curie–Weiss temperature. The measures show that the inverse susceptibility (directly related to the magnetization with \( M = \chi H \)) is not linear in the whole temperature range as a consequence of the magnetic interparticle interactions (with greater strength in samples M₀A₆ and M₀A₁₄). Another source of deviation can be related to the spin frustration which is manifested in the surface of the nanoparticles. Even in the most diluted superparamagnetic system the ideal Curie law is never observed. Deviations from linearity at very low temperatures can be ascribed to some type of particle blocking, so that one can infer that in the M₀A₁₀ sample, which has a higher value of \( \Theta_p \) (~133 K), this blocking would be related to the dimer-like heterostructure.

To compare magnetic moments obtained from the M vs H curves, the Curie–Weiss law was used to obtain the effective magnetic moment, such that \( \mu_{eff} = (3k_B N\mu_0(1/C))^{1/2} \), where \( C \) is the Curie constant. The results obtained were 7.3 × 10⁵ \( \mu_B \) for M₀A₆, M₀A₁₀, and M₀A₁₄ samples, respectively. It is remarkable that these results have the same order of magnitude as those obtained from the M vs H curves at \( T = 300 \) K.

CONCLUSIONS

We have presented a detailed and extensive study of synthesis conditions, structural and magnetic properties, and mechanism formation of magnetic heterostructures composed by Ag–Fe₃O₄. From these studies we conclude that in a two-step synthesis Fe₃O₄ uses Ag nanoparticles as fixed seeds, to grow a shell layer. This growth is restricted to a charge distribution on the silver nanoparticle, limiting the possible facets where the oxide could nucleate and grow. In this sense, the charge compensation in the Ag seed associated with the amount of stabilizing agents in the surface will determine the final magnetic nanostructure. Also, the Ag sized nanoparticles used as seeds could affect the final structure in physical properties.

For example, high values of oleic acid (OA) and silver nanoparticles of about 32 nm create a high charge compensation and lead the formation of “flower”-type structure, whereas low amounts of OA and silver particles of 23 nm decrease this charge compensation, inhibit the Fe₃O₄ nucleation in multiple facets, and favor the dumbbell-like heterostructures.

The final shapes of the obtained nanoparticles were correlated with magnetic properties. From these studies all the samples present near superparamagnetic behavior, at room temperature. It is interesting to notice that in all cases the irreversibility temperature was near the blocking one, an observation not reported on this type of system before. To better understand the magnetic behavior of these samples a superparamagnetic-based Langevin model was considered.

From this model, we observed that the dipolar interaction strongly affected the magnetic moment of the nanoparticles. Hence, it was necessary to consider a dipolar interaction contribution on the Langevin model to obtain a more accurate value of magnetic moment as a function of temperature. On the basis of this, we show that the sample with flower structure presents a higher dipolar interaction than the heterodimer

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samples, possibly due to the proximity of the magnetic particles on the edges of the silver particles. These conformations result in a reduction of the magnetic moment per magnetic nanoparticle when the dipolar interaction increases. The effect on dipolar interaction could have a positive implication on hyperthermia treatment because the specific heat absorption is enhanced under an alternating magnetic field.

**ASSOCIATED CONTENT**

Preparation of Ag-Fe$_3$O$_4$ and Figure S1 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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