

Magnetic Gold Confined in Ordered Mesoporous Titania Thin Films: A Noble Approach for Magnetic Devices

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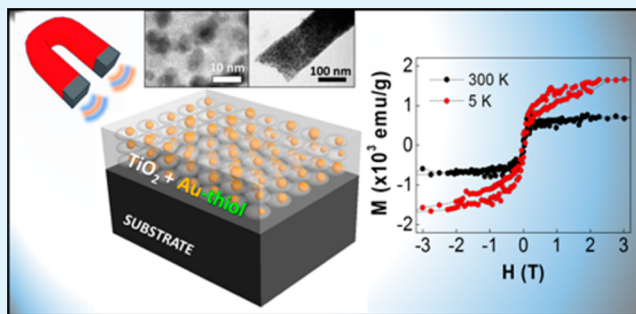
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Supporting Information

ABSTRACT: In the past decade, the surprising magnetic behavior of gold nanoparticles has been reported. This unexpected property is mainly attributed both to size and surface effects. Mesoporous thin films are ideal matrices for metallic nanoparticles inclusion, because of their highly accessible and tailorable pore systems that lead to completely tunable chemical environments. Exploiting these features, we synthesized Au nanoparticles within mesoporous titania thin films (film thickness of ~ 150 nm and pore diameter of ~ 5 nm), and we studied their magnetic properties under confinement. Here, we present the results of the magnetization as a function of temperature and magnetic field for this system, which are consistent with the previously reported for free (unconfined) thiol-capped gold nanoparticles. The successful inclusion of stable magnetic Au nanoparticles within transparent mesoporous thin films opens the gates for the application of these nanocomposites in two-dimensional (2D) microdevices technology and magneto-optical devices.

KEYWORDS: gold nanoparticles, mesoporous thin films, noble metals magnetism, chemical induced magnetism, gold-titania nanocomposites



INTRODUCTION

Gold nanoparticles (GNPs) have been studied intensively, because of their wide possibilities of applications in optics, catalysis, and sensing, among other fields. In the past decade, it was surprisingly found that GNPs could also present magnetic properties, which has opened a thriving research area.¹ These unusual magnetic properties have been ascribed to the size of the nanoparticles or their surface functionalization, and many different GNP systems have been studied by magnetometry techniques.^{2–4} Although the details are still to be clarified, the chemically induced magnetism is considered to be the main factor responsible for the magnetic moment in GNPs or clusters. The emergence of the magnetic properties has been studied by varying the stabilizing ligand.^{5,6} Currently, it has been well-established that, in general, noble metals, nano-clusters and nanoparticles can form high spin states, and a size dependence of the magnetic properties has been observed in

surface-capped nanoparticles or clusters, based on nonmagnetic metals (i.e., Au, Ag, Cu, Pd, or Pt).^{7–9}

Although some works have proposed alternative mechanisms, such as self-sustained persistent currents of conduction electrons, at this moment, there is a general consensus about the orbital nature of this magnetic moment.^{1,10} The appearance of magnetization in capped GNPs was proposed to be associated with a spin symmetry breaking that was related to the 5d and 6s electrons of the Au atoms involved in the chemical bond with the ligands. The presence of the capping agents at the surface changes the number of uncompensated spins, which, in turn, modifies the relative spin densities at the Fermi energy, thus creating a nonzero magnetic moment.⁶

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Maitra et al.⁹ evidenced experimentally that the saturation magnetization increases with capping and is dependent on the strength of the metal–sulfur bond. Although the origin of GNP magnetism has not been fully elucidated yet, and there is a lack of reproducibility of the magnetic behavior between reports, currently, the magnetism of gold at the nanoscale is accepted.^{1,11}

At present, the role of the surface and the interface of noble metal thin layers are being particularly considered in magnetic devices research. As an example, magnetic proximity effects have been reported at the Pt/Y₃Fe₅O₁₂ interfaces in magnetoresistance devices.^{12,13} Moreover, it was recently found that magnetization is induced in the thin gold layer of superconducting spin valves.¹⁴ In light of these findings, magnetic structures based on noble metal nanoparticles is becoming a growing field, and might inspire the design of novel magnetic, opto-magnetic, and spintronic devices.

Materials with highly controlled pore size are very interesting matrices for the immobilization of magnetic metallic nanospecies. Platinum clusters have been immobilized in zeolites, which affect the hydrogen adsorption properties, leading to controlling the catalytic and magnetic behaviors.¹⁵ Very recently, the magnetism of GNPs within hollow mesoporous silica particles has been exploited in multifunctional nanoparticles for theranostics.¹⁶ In order to fully exploit their potential in two-dimensional (2D) magnetic devices such as magnetic sensors and memory devices, GNPs must be efficiently incorporated into thin films, permitting an easy positioning and handling of the magnetic species, which is still a challenge.¹⁷ Ordered mesoporous thin films¹⁸ arise as a promising matrix to solve this limitation, by using them as robust frameworks to be filled with the desired nanoparticles, which results in enhanced nanoparticle stability and high accessibility for analytes.^{19,20} In addition, simple and affordable patterning methods that rely on chemical or lithographic routes can be applied to these composites in order to specifically locate the nanoparticles in the micrometer or submicrometer scale.^{21,22}

In this work, we present an efficient and robust method to incorporate magnetic GNPs within the pore system of highly ordered mesoporous titania thin films²³ combining a soft reduction method and thiol capping. Controlled reduction and capping process were essential toward obtaining stable magnetic GNPs confined inside the mesopores. The method is highly reproducible and leads to protected GNPs, whose magnetic properties are constant throughout the samples and conserved along time. These nanocomposites lead to magnetically functionalized mesoporous thin films, and open the gate for exploiting GNPs properties in thin-film-related applications such as opto-magnetic²⁴ and spintronic devices.

■ EXPERIMENTAL SECTION

Synthesis of Mesoporous Titania Thin Films. Mesoporous TiO₂ thin films (MTTF) were synthesized by dip-coating, using a titania sol in the presence of a supramolecular polymer template.²⁰ A stock solution of TiCl₄ in ethanol was prepared by adding 19 g of TiCl₄ in 181 g of absolute ethanol in a cold bath. To 20 g of this solution was added 0.56 g of Brij58, as a supramolecular template, and 1.8 g of water, to promote the hydrolysis of the Ti precursor. The molar ratio between components (TiCl₄:Brij58:H₂O:EtOH) was 1:0.05:10:40.

The prepared sol was heated up to 32 °C and dip-coated at a withdrawal speed of 3.0 mm s⁻¹ in a controlled environment of 35% relative humidity (RH). Double-side polished silicon wafers (University Wafers, USA) were used as substrates; mesoporous films were then deposited simultaneously over both sides of the substrate. After deposition, the films were kept for 24 h in a chamber at 50% RH to promote stabilization of the mesostructure, and then subjected to a temperature of 60 °C for 30 min, then 130 °C for additional 30 min, and finally calcined at 350 °C for 2 h.²⁵ Films were then washed with acetone and immersed for 2 h in an ethanol:water 1:1 v:v mixture under strong agitation in order to remove any residue from the pyrolysis of the surfactant. Films were finally dried at 130 °C. Mesoporous TiO₂ films that were templated with Brij 58 will be referred hereafter as TB.

Loading Mesoporous Films with Gold Nanoparticles.

Mesoporous TiO₂ films were loaded with gold by controlling the nucleation and growth of GNPs in cycles of adsorption and reduction of AuCl₄⁻. The procedure, which has been described and analyzed in detail in a previous work,²⁶ was performed by immersing the films in a 1 mM aqueous solution of HAuCl₄·3H₂O at pH 4, controlled via the addition of NaOH. After 1 min, films were extracted, washed with deionized water, and immersed in a 10 mM NaBH₄ aqueous solution for another minute. This reduction step (RS) cycle was repeated a total of 16 times. An intermediate step was added after each two reduction steps, to favor the adsorption of a thiol molecule by immersing the films in an ethanol solution of octanethiol (OT) (Sigma–Aldrich, 98.5%) (10 μM) for 30 min. The objective of this procedure was to limit the growth of the GNPs by thiol capping and favor the development of new nucleation sites instead. Particular care was used to avoid contacting the precursor solutions and samples with iron or any other magnetically active substances during the synthesis and measurement procedures, in order to minimize the presence of magnetic impurities.

Thin Film Characterization. Mesoporous thin films thickness, optical constants, and porosity were characterized by spectroscopic ellipsometry in a commercial SOPRA GESS multispectral ellipsometer in microspot configuration; the data were analyzed by the use of Winelli II software. Ellipsoporosimetry was performed in order to determine film pore volume and pore diameter, by means of controlled condensation of water vapor inside the porosity and measurement of the subsequent change in refractive index of the film, following the work of Boissière et al.²⁷

Field-emission scanning electron microscopy (FE-SEM) images were obtained with a Zeiss Model LEO 982 Gemini FE-SEM system that used an in-lens detector to improve resolution. Energy-dispersive spectroscopy (EDS) was performed at the FE-SEM device, to quantify the amount of gold in the samples by resolving the Au:Ti atomic ratio. High-resolution transmission electron microscopy (HR-TEM) was performed, using a Philips Model CM 200 electron microscope that was operating at 200 kV and was equipped with a LaB₆ emission filament and an ultrathin objective lens for high-resolution images. Samples for HR-TEM measurements were prepared by depositing a small amount of pieces scratched off the films onto an ethanol drop placed on carbon-coated copper grids.

Magnetization of the GNP@MTTF sample was measured in an MPMS Quantum Design SQUID magnetometer. It was

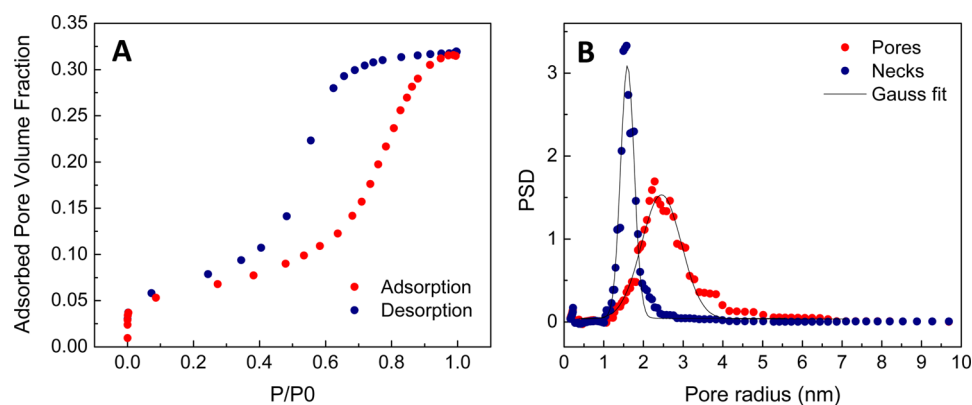


Figure 1. (A) Water adsorption–desorption isotherm and (B) pore size distribution (PSD) of a mesoporous thin film TB/Si dip-coated at a rate of 3 mm s^{−1}, obtained via spectroscopic ellipsometry.

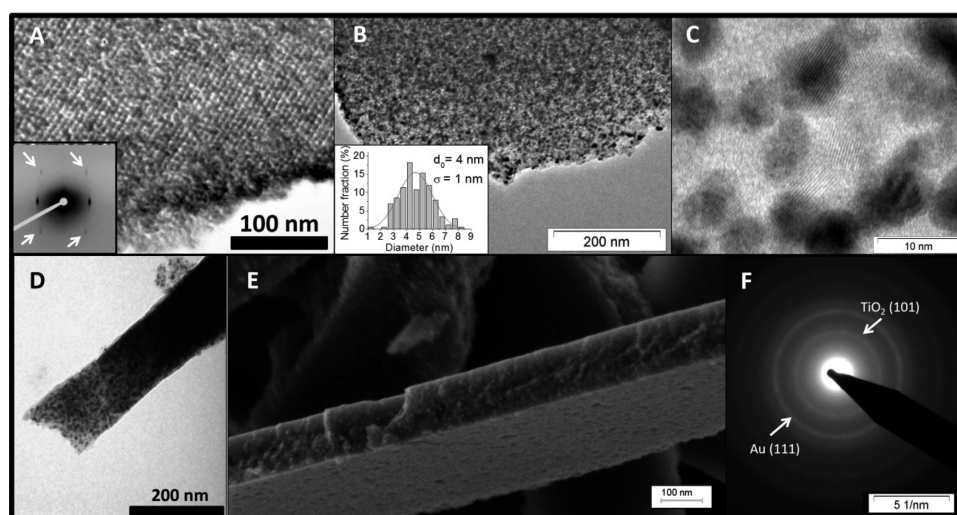


Figure 2. (A) TEM image of a highly ordered MTTF deposited on glass; small-angle X-ray scattering (SAXS) at 3° grazing incidence, showing the large-scale mesoporous order of these systems, is depicted in the inset. (B) Large-scale and (C) high-magnification TEM images of GNP@MTTF. Inset in panel (B) shows a particle size distribution extracted from multiple images. Also shown are cross-sectional views of the mesoporous GNP@MTTF sample, revealing the homogeneous distribution of particles across the film thickness, as viewed via (D) TEM and (E) FE-SEM. (F) Selected-area electron diffraction (SAED), showing the crystalline nature of the titania matrix (anatase) and GNPs.

studied as a function of temperature (T) and applied magnetic field (H), in the ranges of 5–300 K and up to 5 T, respectively.

RESULTS

Spectroscopic ellipsometry was used to determine the thickness and refractive index at 633 nm and 0% RH of the TB films, finding values of 147 ± 6 nm and 1.701 ± 0.004 , respectively. By controlling the RH in a closed chamber around the sample, ellipsometry was used to obtain a water adsorption isotherm from which the porosity and the pore size distribution (PSD) was extracted. The results presented in Figure 1 show a type IV isotherm with an H2 hysteresis loop, characteristic of a mesoporous structure formed by pores with restrictions. The porous volume fraction obtained of 32% is formed by pores 4.9 ± 0.9 nm in diameter, connected by open necks 3.2 ± 0.4 nm wide. Spectroscopic ellipsometry²⁸ was also exploited to study the optical properties of GNP@MTTF at 0% RH. It was found that the plasmonic features of GNPs are retained together with the magnetic properties. This subject is discussed in-depth in the Supporting Information (see Figures S2 and S3).

Electronic microscopy was used to analyze the framework of MTTF and the GNP@MTTF samples (see Figure 2). The

characteristic long-range highly ordered mesoporous structure obtained for TB films²⁰ is displayed by TEM (Figure 2A) and small-angle X-ray scattering (SAXS) at 3° grazing incidence (inset of Figure 2A). The GNP@MTTF nanocomposite displays a homogeneous dispersion of 4–6 nm spherical GNPs located evenly across and along the film thickness (Figures 2B–F, calculated from TEM images, over an average of 200 nanoparticles).

Considering the film porosity, the density of the TiO₂ matrix, and the Au:Ti atomic ratio (r) obtained by EDS, an estimated value of the gold filling fraction (F) can be calculated using eq 1:²⁰

$$F (\%) = \frac{r\delta_{\text{TiO}_2}M_{\text{Au}}(1 - V_p)}{\delta_{\text{Au}}M_{\text{TiO}_2}V_p} \times 100 \quad (1)$$

where V_p is the accessible porous fraction ($V_p = 0.32$ from Figure 1), δ_{Au} and M_{Au} are, respectively, the bulk density and the molecular weight of gold ($\delta_{\text{Au}} = 19.3$ g cm^{−3} and $M_{\text{Au}} = 196.96$ g mol^{−1}); δ_{TiO_2} is the bulk density of anatase TiO₂ ($\delta_{\text{TiO}_2} = 3.8985$ g cm^{−3}), which is the main crystallographic phase present in the films;¹⁸ and M_{TiO_2} is the molecular weight (M_{TiO_2}

= 79.89 g mol⁻¹). The filling fraction (F) represents the volume fraction of the porosity (V_p) of the film occupied by GNPs, from which the total film volume occupied by GNPs (defined as the volume filling fraction, VFF) is calculated. The number of Au atoms in each square millimeter of film, 147 nm thick, was also calculated. The resulting values of the EDS analysis, F and VFF, are summarized in Table 1. (The EDS spectra obtained for GNP@MTTF is displayed in Figure S1 in the Supporting Information.)

Table 1. Composition of MTTF after Gold Infiltration and Thiol Capping, Analyzed by Ellipsometry and EDS

parameter	value
gold filling fraction, F	22.6%
volume filling fraction, VFF	7.3%
Au:Ti atomic ratio	0.27
Au	6.3×10^{14} atoms/mm ²

The magnetization (m), as a function of the applied magnetic field (H), was measured at different temperatures for the GNP@MTTF sample. The magnetization measurements of film samples are always comprised by the sum of the film and the substrate contributions. In our case, we aimed to elucidate the relevant features of the magnetic results inherent to the GNPs, which are confined within the TB film deposited on both sides of a double-side polished (DSP) silicon substrate. The crude data information obtained from the magnetometer is shown, for 300 and 5 K, at the inset of Figure 3B. The magnetic

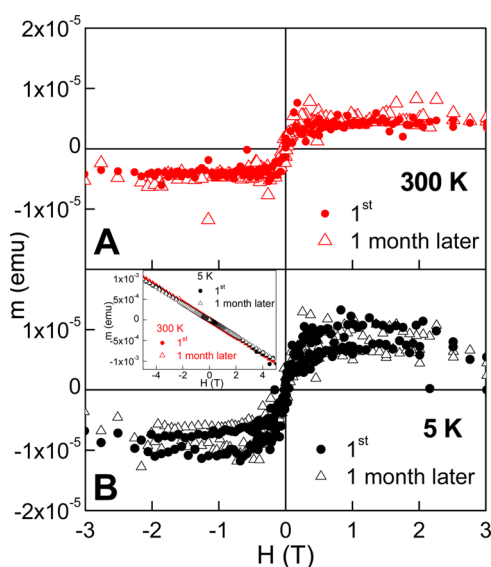


Figure 3. Magnetization (m) as a function of the applied magnetic field (H) at (A) 300 K and (B) 5 K for GNP@MTTF comparing measurements performed at different times, where the linear contribution was previously subtracted. Inset shows $m(H)$ results for 300 K (red) and 5 K (black) as obtained directly from the SQUID, without any data processing.

response is governed by a linear negative slope which is independent of temperature, because of the diamagnetic contribution of the TiO₂ film, the Si substrate, and the sample mounting. Figures 3A and 3B display the magnetization results once the diamagnetic slope has been subtracted. Note that the resolution range used to measure in the magnetometer is conditioned by the entire magnetic signal (see the inset of

Figure 3B), which is ~ 10 times higher than the nonlinear features extracted from them (Figures 3A and 3B). Therefore, these measurements of the magnetization of GNPs included inside the thin film oxide matrix are more indirect—and, consequently, are more noisy and weaker—than the measurements of the GNPs alone, which are already widely reported.

Within this framework, it was confirmed that the magnetization results displayed here are reproducible from sample to sample and the magnetic properties of the samples were preserved along the several months that the experiments lasted. Figures 3A and 3B compare two session measurements for 300 and 5 K, respectively, where clear differences with temperature can be appreciated. These are important results, considering the sample-to-sample reproducibility and the stabilization of the GNPs embedded in the porous matrix, which is a well-documented feature in metal nanoparticle–mesoporous oxide nanocomposite systems.²⁰

The magnetic behavior of the TB films without GNPs was also studied. It was found that the magnetization is mostly independent of temperature and that there are no clear differences between the zero field cooling (ZFC) and field cooling (FC) curves (Figure 4). Slight deviations from the

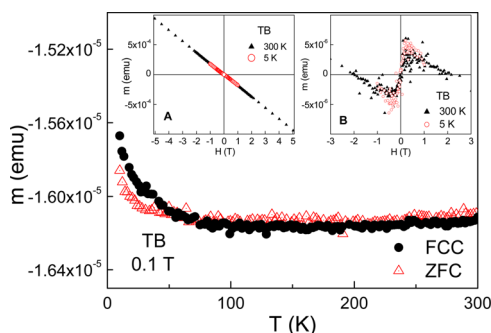


Figure 4. Magnetization (m) as a function of temperature (T) for the TB film, measured in field cooling (FC) and zero field cooling (ZFC) modes with $H = 0.1$ T. Inset A shows $m(H)$ as obtained from the SQUID for 300 and 5 K. Inset B shows the same $m(H)$ results after the subtraction of the negative slope of the diamagnetic contribution.

diamagnetic behavior at low temperatures are consistent with the electronic characteristics previously reported for TiO₂^{29,30} and doped silicon.^{31,32} Following the same analysis performed with the GNP@MTTF results, the negative linear contribution was deducted from the $m(H)$ curves (see inset A in Figure 4) of the TB film. Comparing with the obtained for GNP@MTTF, which saturates at 8×10^{-4} emu/g at 300 K (normalized by the sample mass), the nonlinear component of the $m(H)$ of the TB film (see Inset B of Figure 4) is independent of T and does not exceed 4.88×10^{-4} emu/g. Therefore, it should not be interpreted as a hysteresis loop or any other reliable magnetic behavior. It is known that for small magnetic signals, the measurements are very sensitive to some measurements settings. One of the most critical is the SQUID center procedure, what introduces in many cases very confusing artifacts.³³

With the aim of comparing our findings with those already reported for other GNPs systems, we estimated the magnetic moment (M) per Au atom from the Au content obtained by EDS (see Table 1). Figure 5A displays $M(H)$ results measured at different temperatures between 300 K and 5 K. It can be observed that M increases and the hysteresis appears as the

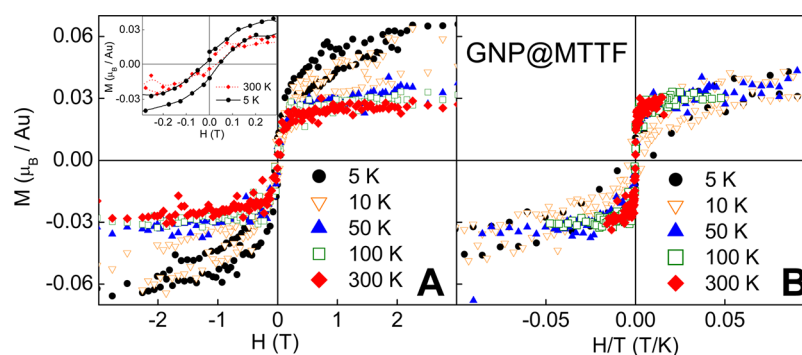


Figure 5. (A) Magnetic moment (M) of the GNP@MTTF sample, measured as a function of the applied magnetic field (H) at different temperatures (T) and (B) displayed as M vs H/T . Inset shows a comparison of $M(H)$ results in the low H region for the 5 K and 300 K curves.

temperature decreases. The coercive field (H_c) reaches a value of $H_c = 0.045$ T at 5 K (see inset in Figure 5A), in good agreement with the values previously reported in the literature.^{1,4,5} The saturation magnetic moment (m_s) is $\sim 0.07 \mu_B/\text{Au}$ atom at 5 K. Regarding the small mass of GNPs present in the MTTF structure and the $\sim 50\%$ uncertainty involved in the estimation, it is remarkable that the m_s obtained is well-included within the wide range, $0.002\text{--}0.3 \mu_B/\text{Au}$ atom, reported for similar thiol-capped GNPs.^{1,4,16}

In order to understand the magnetic behavior involved in these systems, the $M(H)$ curves of Figure 5A were plotted together, as a function of H/T in Figure 5B. Note that the $M(H/T)$ reversible loops merge into the same curve above 100 K, indicating the presence of a superparamagnetic state. At low temperatures, Figure 5B shows that the $M(H/T)$ curves deviate from this behavior and hysteresis in $M(H)$ appears at < 50 K, suggesting that the system would become blocked.

As a complement of the former observations, Figure 6 displays the results of the magnetization as a function of

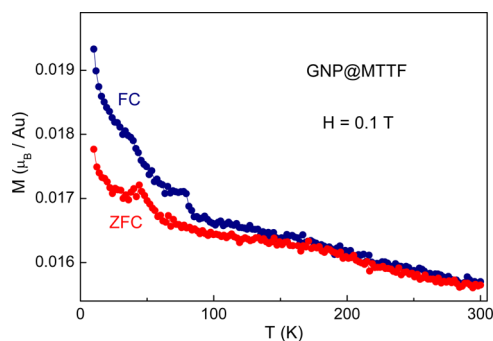


Figure 6. Zero field cooling (ZFC) and field cooling (FC) magnetic moment (M) as a function of temperature (T), measured with an applied field (H) of 0.1 T, for the GNP@MTTF sample. Hollow and filled symbols correspond to ZFC and FC curves, respectively. The diamagnetic contribution was already subtracted.

temperature, performed with $H = 0.1$ T, for the zero field cooling (ZFC) and field cooling (FC) measurement modes. It can be seen that ZFC and FC curves join into the same $M(T)$ at > 150 K, reinforcing the idea of a low-temperature blocked state. Dutta et al.³⁴ had previously reported a blocking temperature of ~ 50 K in ~ 5 nm dodecanethiol-capped GNPs. Looking more in detail, a peak can be appreciated at ~ 80 K and ~ 45 K, respectively, for FC and ZFC curves. This behavior has been previously observed in thiol-capped GNPs and seems to

be directly associated with the magnetic mechanisms present in these systems.^{9,35}

Furthermore, low-temperature magnetic interactions are evidenced in the nonzero magnetic moment for $H = 0$. Regarding the size of the GNPs, the presence of remnant magnetization and coercive field could not be related with an inner magnetic domain structure. Thus, the interactions between nanoparticles emerge as the main candidates to explain the magnetic behavior observed at low T .¹

Regarding the consensus about a chemically induced magnetism, favored by the interactions with OT at the Au–S bonding,^{4,6} the main contribution to the magnetization for each particle could be originated at the superficial Au atoms.⁹ In this direction, we could consider only the external monatomic Au shell of the particles, calculated for the particle size distribution (inset of Figure 2B). The value we obtained for m_s in this way is $\sim 0.3 \mu_B/\text{superficial Au atom}$, which is significantly higher than the one reported by Crespo et al., who estimated a value of $0.036 \mu_B/\text{Au–S bonding}$ for dispersed thiol-capped GNPs 1.4 nm in size.⁵

It is usually assumed in the literature that the m_s dispersion reported could be related with a nonhomogeneous magnetic behavior of the GNPs within a same sample. In our case, the MTTF mesostructure would confine the GNPs and limit their size. This confinement, along with the procedure design for the OT-capped GNP synthesis, would contribute together to obtain a more homogeneous magnetic behavior for our GNP@MTTF samples. Moreover, Donnio et al.³⁶ reported ferromagnetic-like behavior for dendrimer-coated GNPs self-assembled in a cubic array presumably related with the presence of the mesoscale order. This would suggest that also the order of the mesoporous matrix could be relevant in our case. Further experiments are in due course to shed light on this subject.

CONCLUSIONS

In summary, we present here for the first time the magnetic response of gold nanoparticles (GNPs) embedded and generated *in situ* in semiconductor TiO_2 mesoporous thin films. We demonstrate that the magnetic results obtained from the GNP@MTTF are consistent with previous reports for dispersed thiol-capped GNPs systems, manifesting low-temperature remnant magnetization. These highly stable and reproducible magnetic nanostructures formed in ordered mesoporous thin films, are compatible with current microelectronics fabrication processes. These results also show the importance of the materials processing (in this case, the *in situ* synthesis-reduction-capping cycle) in the magnetic properties

of the nanocomposite system. Inclusion of stable GNPs in accessible mesoporous matrices opens the door to extending the applications of GNPs beyond the present nanoparticle domains, inspiring the design of novel magnetic and opto-magnetic thin film devices.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b15189.

Details on EDS analysis of GNPs loaded samples; ellipsometric measurements and reconstructed absorption spectra of the systems (PDF)

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Notes

The authors declare no competing financial interest.

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