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Magnetic Gold Confined in Ordered Mesoporous Titania Thin Films: a Noble Approach for Magnetic devices

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Abstract

In the last 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 due to 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 ~150 nm and pore diameter ~5 nm), and we studied their magnetic properties under confinement. We present here the results of the magnetization as a function of temperature and magnetic field for this system,

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3 *which are consistent with the previously reported for free (unconfined) thiol-capped*
4 *gold nanoparticles. The successful inclusion of stable magnetic Au nanoparticles within*
5 *transparent mesoporous thin films opens the gates for the application of these*
6 *nanocomposites in 2D microdevices technology and magneto-optical devices.*
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INTRODUCTION

Gold nanoparticles (GNPs) have been intensively studied due to their wide possibilities of applications in optics, catalysis and sensing, among other fields. In the last 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 nanoparticles size or surface functionalization, and many different GNPs systems have been studied by magnetometry techniques.^{2,3,4} Although the details are still to be clarified, the chemically induced magnetism is considered the main 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} It is nowadays well established that in general noble metal nanoclusters 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 non-magnetic metals (*i.e.* Au, Ag, Cu, Pd or Pt).^{7,8,9}

Although some works have proposed alternative mechanisms, such as self-sustained persistent currents of conduction electrons, at this moment there is 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 related with 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 non-zero magnetic moment.⁶ **Maitra *et al.*⁹ evidenced experimentally that the saturation magnetization increases with capping and depends on the strength of the metal-sulfur bond.** Although the origin of GNPs magnetism has not been fully elucidated yet, and there is a lack of reproducibility of the magnetic behavior between reports, nowadays 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 Au thin layer of superconducting spin valves.¹⁴ In the light of these findings, magnetic structures based in noble metal nanoparticles is becoming a growing field, and might inspire the design of novel magnetic, opto-magnetic and spintronic devices.

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

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

27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 **EXPERIMENTAL**

46 *Synthesis of mesoporous titania thin films*

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48 Mesoporous TiO₂ thin films (MTTF) were synthesized by dip-coating, using a titania
49 sol in the presence of a supramolecular polymer template.²³ A stock solution of TiCl₄ in
50 ethanol was prepared by adding 19 g of TiCl₄ in 181 g of absolute ethanol in a cold
51 bath. To 20 g of this solution, it was added 0.56 g of Brij58 as supramolecular template
52 and 1.8 g of water to promote the hydrolysis of the Ti precursor. The molar ratio
53 between components TiCl₄:Brij58:H₂O:EtOH was 1:0.05:10:40.
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3 The prepared sol was heated up to 32 °C and dip coated at a withdrawal speed of 3.0
4 mm·s⁻¹ in a controlled environment of 35% relative humidity (RH). Double side
5 polished silicon wafers (University Wafers, USA) were used as substrates, therefore
6 mesoporous films were deposited simultaneously over the two sides of the substrates.
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8 After deposition, the films were kept for 24 hours in a chamber at 50% RH to promote
9 stabilization of the mesostructure, and then submitted to 60 °C for 30 minutes, 130 °C
10 for additional 30 minutes and finally calcined at 350 °C for 2 h.²⁵ Films were then
11 washed with acetone and immersed for two hours in an ethanol:water 1:1 v:v mixture
12 under strong agitation in order to remove any residue from the pyrolysis of the
13 surfactant. Films were finally dried at 130 °C. Mesoporous TiO₂ films templated with
14 Brij 58 will be referred hereafter as TB.
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22 *Loading mesoporous films with Au nanoparticles*

23 Mesoporous TiO₂ films were loaded with Au by controlling the nucleation and growth
24 of GNPs in cycles of adsorption and reduction of AuCl₄⁻. The procedure, described and
25 analyzed in detail in previous work,²⁶ was performed by immersing the films in a 1 mM
26 aqueous solution of HAuCl₄·3H₂O at pH 4, controlled by addition of NaOH. After 1
27 minute, films were extracted, washed with deionized water, and immersed in NaBH₄ 10
28 mM aqueous solution for another minute. This reduction step cycle (RS) was repeated
29 16 times in total. An intermediate step was added after each two reduction steps to favor
30 the adsorption of a thiol molecule by immersing the films in an ethanol solution of
31 octanethiol (OT, Sigma-Aldrich, 98.5%) 10 μM for 30 minutes. The objective of this
32 procedure was to limit the growth of the GNPs by thiol capping, and favor the
33 development of new nucleation sites instead. Particular care was set in avoiding contact
34 of the precursor solutions and samples with iron or any other magnetically active
35 substances during the synthesis and measurement procedures, in order to discard the
36 presence of magnetic impurities.
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48 *Thin Film Characterization*

49 Mesoporous thin films thickness, optical constants and porosity were characterized by
50 spectroscopic ellipsometry in a commercial SOPRA GES5 multispectral ellipsometer in
51 microspot configuration; the data was analyzed by the use of Winelli II software.
52 Ellipso-porosimetry was performed in order to determine film pore volume and pore
53 diameter, by means of controlled condensation of water vapor inside porosity and
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3 measure of the subsequent change in refractive index of the film, following Boissière et
4 al.²⁷
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7 Field emission-scanning electron microscopy (FE-SEM) images were obtained with a
8 ZEISS LEO 982 GEMINI field emission electron microscope using an in-lens detector
9 to improve resolution. Energy Dispersive Spectroscopy (EDS) was performed at the FE-
10 SEM, to quantify the amount of Au in the samples by resolving the atomic ratio
11 Au:Ti(*r*). High resolution transmission electron microscopy (HR-TEM) was performed
12 in a Philips CM 200 electron microscope operating at 200 kV equipped with a LaB₆
13 emission filament and an ultra-thin objective lens for high resolution images. Samples
14 for HR-TEM measurements were prepared by depositing a small amount of pieces
15 scratched off the films onto an ethanol drop placed on carbon coated copper grids.
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18 Magnetization of the GNP@MTTF sample was measured in a MPMS Quantum Design
19 SQUID magnetometer. It was studied as a function of temperature (T) and applied
20 magnetic field (H) in the ranges of 5 – 300 K and up to 5 T respectively.
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23 RESULTS

24 Spectroscopic ellipsometry was used to determine the thickness and refractive index at
25 633 nm and 0% relative humidity (RH) of the TB films, finding values of 147 ± 6 nm
26 and 1.701 ± 0.004 respectively. By controlling the RH in a closed chamber around the
27 sample, ellipsometry could be used to obtain a water adsorption isotherm from which
28 the porosity and the pore size distribution (PSD) could be extracted. The results
29 presented in Fig. 1 show a type IV isotherm with an H2 hysteresis loop, characteristic of
30 a mesoporous structure formed by pores with restrictions. The porous volume fraction
31 obtained of 32% is formed by pores of 4.9 ± 0.9 nm in diameter, connected by open
32 necks of 3.2 ± 0.4 nm wide. Spectroscopic ellipsometry²⁸ was also exploited to study
33 the optical properties of GNP@MTTF at 0% RH. It was found that the plasmonic
34 features of GNPs are retained together with the magnetic properties. This subject is
35 discussed in-depth at the SI.
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53 Electronic microscopy was used to analyze the framework of MTTF and the
54 GNP@MTTF samples (see Fig. 2). The characteristic long range highly ordered
55 mesoporous structure obtained for TB films²³ is displayed by TEM (Fig. 2-A) and small
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angle X-Ray scattering (SAXS) at 3° grazing incidence (inset of Fig. 2-A). The GNP@MTTF nanocomposite displays a homogeneous dispersion of 4-6 nm spherical GNPs located evenly across and along the film thickness (Fig. 2-B to 2-F, calculated from TEM images, average of 200 nanoparticles).

Considering the film porosity, the density of the TiO₂ matrix and the atomic ratio Au:Ti(*r*) obtained by EDS, an estimated value of the gold filling fraction (*F*) can be calculated using Eq. 1,²⁶ where *V_p* is the accessible porous fraction (*V_p* = 0.32 from Fig. 1), *δ_{Au}* and *M_{Au}* are respectively the bulk density and the molecular weight of gold (19.3 g cm⁻³, 196.96 g mol⁻¹), *δ_{TiO2}* is the bulk density of anatase TiO₂ (3.8985 g cm⁻³), which is the main crystallographic phase present in the films,**Error! Bookmark not defined.** and *M_{TiO2}* is the molecular weight (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 (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.

$$F(\%) = \frac{r\delta_{TiO_2}M_{Au}(1-V_p)}{\delta_{Au}M_{TiO_2}V_p} \times 100 \quad \text{Eq. 1}$$

<i>F</i> (%)	VFF (%)	Atomic ratio Au:Ti	Au atoms/mm ²
22.6	7.3	0.27	6.3×10 ¹⁴

Table 1 Composition of MTTF after gold infiltration and thiol capping analyzed by ellipsometry and EDS.

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 made up 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

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3 obtained from the magnetometer is shown, for 300 K and 5 K, at the inset of Fig. 3-B.
4 The magnetic response is governed by a linear negative-slope which is independent of
5 temperature, due to the diamagnetic contribution of the TiO₂ film, the Si substrate and
6 the sample mounting. Fig. 3-A and 3-B display the magnetization results once the
7 diamagnetic slope was subtracted. Note that the resolution range used to measure in the
8 magnetometer is conditioned by the whole magnetic signal (Inset of Fig. 3-B), which is
9 about ten times higher than the non-linear features extracted from them (Fig. 3-A and 3-
10 B). Therefore these measurements of the magnetization of GNPs included inside the
11 thin film oxide matrix are more indirect, and consequently more noisy and weaker, than
12 the measurements of the GNPs alone, which are already widely reported.
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20 Within this framework, it was confirmed that the magnetization results displayed here
21 are reproducible from sample to sample and the magnetic properties of the samples
22 were preserved along the several months that the experiments lasted. In Fig 3-A and 3-B
23 are compared two session measurements for 300 K and 5 K respectively, where it can be
24 appreciated clear differences with temperature. These are important results considering
25 sample-to-sample reproducibility and the stabilization of the GNPs embedded in the
26 porous matrix, which is a well documented feature in metal nanoparticle-mesoporous
27 oxide nanocomposite systems.²⁰
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34 The magnetic behavior of the TB films without GNPs was also studied. It was found
35 that the magnetization is mostly independent of temperature and that there are no clear
36 differences between the zero field cooling (ZFC) and field cooling (FC) curves (Figure
37 4). Slight deviations from the diamagnetic behavior at low temperatures are consistent
38 with the electronic characteristics previously reported for TiO₂^{29,30} and doped
39 silicon.^{31,32} Following the same analysis performed with the GNP@MTTF results, the
40 negative linear contribution was deducted from the m(H) curves (inset A of Fig. 4) of
41 the TB film. Comparing with the obtained for GNP@MTTF, which saturates at 8×10^{-4}
42 emu/g at 300 K (normalized by the sample mass), the non-linear component of the m(H)
43 of the TB film (see Inset B of Fig. 4) is independent of T and does not exceed 4.88×10^{-4}
44 emu/g. Therefore, it should not be interpreted as a hysteresis loop or any other reliable
45 magnetic behavior. It is known that for small magnetic signals, the measurements are
46 very sensitive to some measurements settings. One of the most critical is the SQUID
47 center procedure, what introduces in many cases very confusing artifacts.³³
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3 With the aim of comparing our findings with those already reported for other GNPs
4 systems, we estimated the magnetic moment (M) per Au atom from the Au content
5 obtained by EDS (see Table 1). Figure 5-A displays M(H) results measured at different
6 temperatures between 300 K and 5 K. It can be observed that M increases and the
7 hysteresis appears with the decrease of temperature. The coercive field (H_c) reaches a
8 value of $H_c = 0.045$ T at 5 K (see inset of Fig. 5-A), in good agreement with the values
9 previously reported in literature.^{1,4,5} The saturation magnetic moment (m_s) is $\sim 0.07 \mu_B /$
10 *Au atom* at 5 K. Regarding the small mass of GNPs present in the MTTF structure and
11 the $\sim 50\%$ uncertainty involved in the estimation, it is remarkable that the m_s obtained is
12 well included within the wide range, 0.002 to $0.3 \mu_B / Au atom$, reported for similar
13 thiol-capped GNPs.^{1,4,16}

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16 In order to understand the magnetic behavior involved in these systems, the M(H)
17 curves of Fig. 5-A were plotted together as a function of H/T in Fig. 5-B. It can be noted
18 that the M(H/T) reversible loops merge into the same curve above 100 K indicating the
19 presence of a superparamagnetic state. At low temperatures, it can be appreciated in Fig.
20 5-B that M(H/T) curves deviates from this behavior and hysteresis in M(H) appears
21 below 50 K, suggesting that the system would become blocked.

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24 As a complement of the former observations, Figure 6 displays the results of the
25 magnetization as a function of temperature, performed with $H = 0.1$ T, for the Zero
26 Field Cooling (ZFC) and Field Cooling (FC) measurement modes. It can be seen that
27 ZFC and FC curves join into the same M(T) above 150 K, reinforcing the idea of a low
28 temperature blocked state. Dutta *et al.*³⁴ had previously reported a blocking temperature
29 of ~ 50 K in ~ 5 nm dodecanethiol-caped GNPs. Looking more in detail, a peak can be
30 appreciated at ~ 80 K and ~ 45 K respectively for FC and ZFC curves. This behavior has
31 been previously observed in thiol-capped GNPs and seems to be directly associated
32 with the magnetic mechanisms present in these systems.^{9,35}

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

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3 Regarding the consensus about a chemically induced magnetism, favored by the
4 interactions with OT at the Au-S bonding,^{4,6} the main contribution to the magnetization
5 for each particle could be originated at the superficial Au atoms.⁹ In this direction, we
6 could consider only the external monatomic Au shell of the particles, calculated for the
7 particle size distribution (inset of Fig. 2-B). The value we obtained for m_s in this way is
8 $\sim 0.3 \mu\text{B}/\text{superficial Au atom}$, which is significantly higher than the one reported by
9 Crespo *et al.*, who estimated $0.036 \mu\text{B}/\text{Au-S bonding}$ for dispersed thiol-capped GNPs
10 of 1.4 nm size.⁵

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

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35 In summary, we present here for the first time the magnetic response of GNPs
36 embedded and *in-situ* generated in semiconductor TiO₂ mesoporous thin films. We
37 demonstrate that the magnetic results obtained from the GNP@MTTF are consistent
38 with previous reports for dispersed thiol-capped GNPs systems, manifesting low
39 temperature remnant magnetization. These highly stable and reproducible magnetic
40 nanostructures formed in ordered mesoporous thin films, are compatible with current
41 microelectronics fabrication processes. These results also show the importance of the
42 materials processing (in this case, the *in-situ synthesis*-reduction-capping cycle) in the
43 magnetic properties of the nanocomposite system. Inclusion of stable GNPs in
44 accessible mesoporous matrices opens the door to extending the applications of GNPs
45 beyond the present nanoparticle domains, inspiring the design of novel magnetic and
46 opto-magnetic thin film devices.
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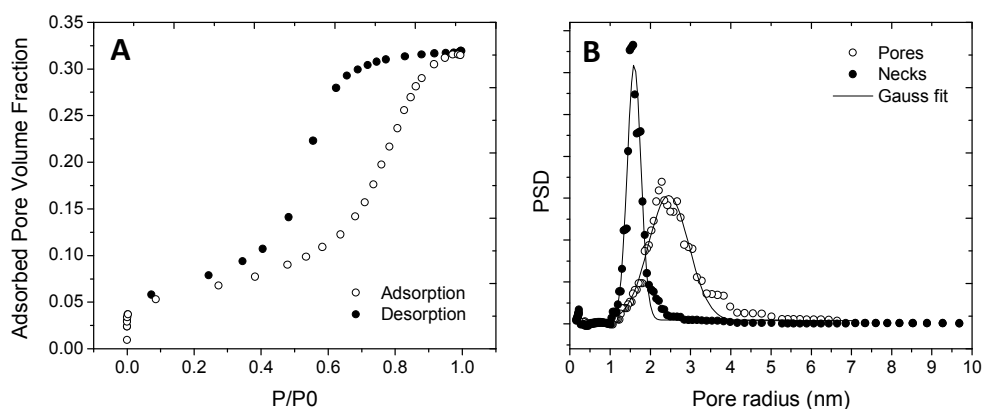


Figure 1. Water adsorption-desorption isotherm (A) and PSD (B) of mesoporous thin film TB/Si dip-coated at $3 \text{ mm} \cdot \text{s}^{-1}$ obtained by spectroscopic ellipsometry.

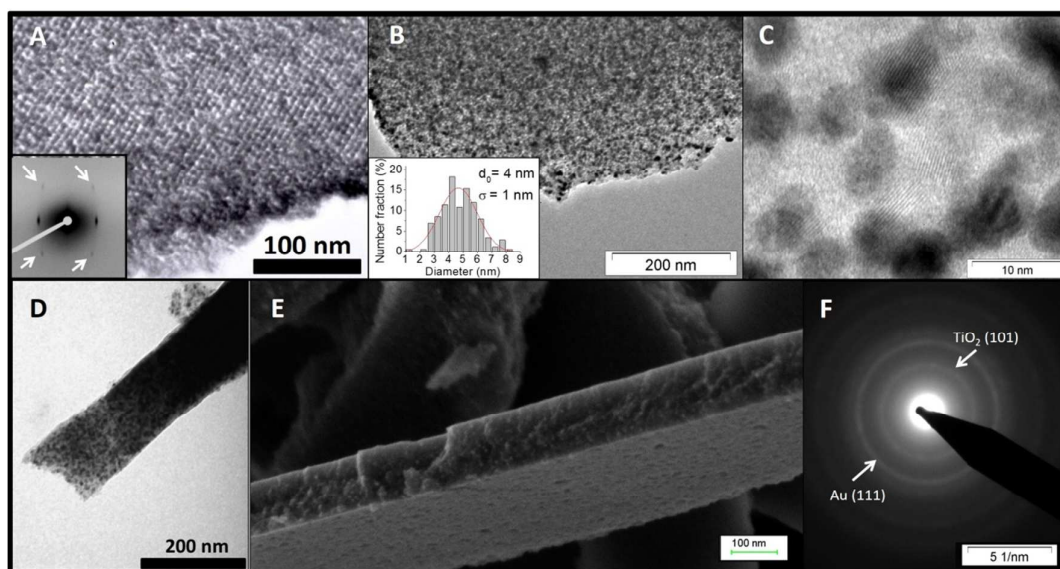


Figure 2. TEM image of a highly ordered MTTF deposited on glass (A) and small angle x-ray scattering (SAXS) at 3° grazing incidence showing the large-scale mesoporous order of these systems (inset). Large scale (B) and high magnification (C) TEM images of GNP@MTTF. Inset: particle size distribution extracted from multiple images. Cross section view of the mesoporous GNP@MTTF sample revealing the homogeneous distribution of particles across the film thickness as view by TEM (D) and FE-SEM (E). Selected Area Electron Diffraction showing the crystalline nature of the titania matrix (anatase) and GNPs (F).

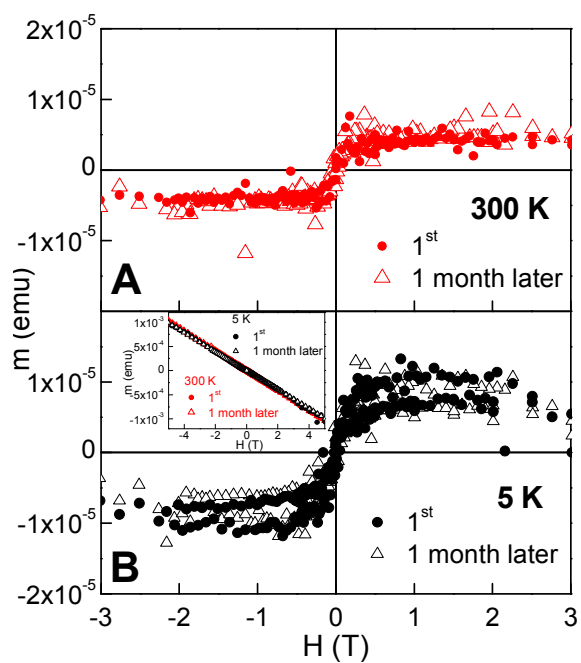


Figure 3. Magnetization (m) as a function of the applied magnetic field (H) at 300 K (A) and 5 K (B) for GNP@MTTF comparing measurements performed at different times, where the linear contribution was previously subtracted. Inset: $m(H)$ results for 300 K (red) and 5 K (black) as obtained directly from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

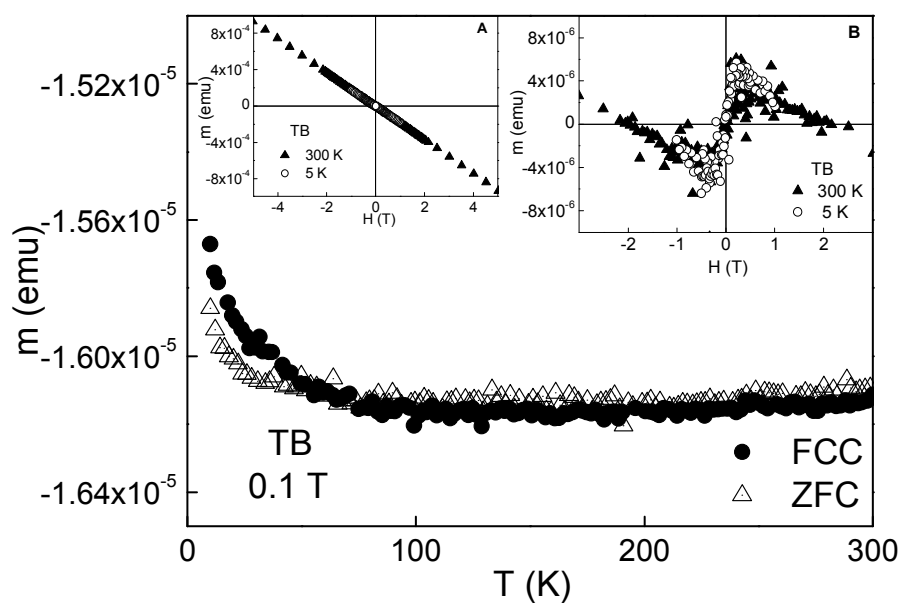


Figure 4. Magnetization (m) as a function of temperature (T) for the TB film, measured in field cooling (FC) and zero field cooling (ZFC) modes with $H = 0.1$ T. Inset A: $m(H)$ as obtained from the SQUID for 300 K and 5 K. Inset B: The same $m(H)$ results after the subtraction of the negative slope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

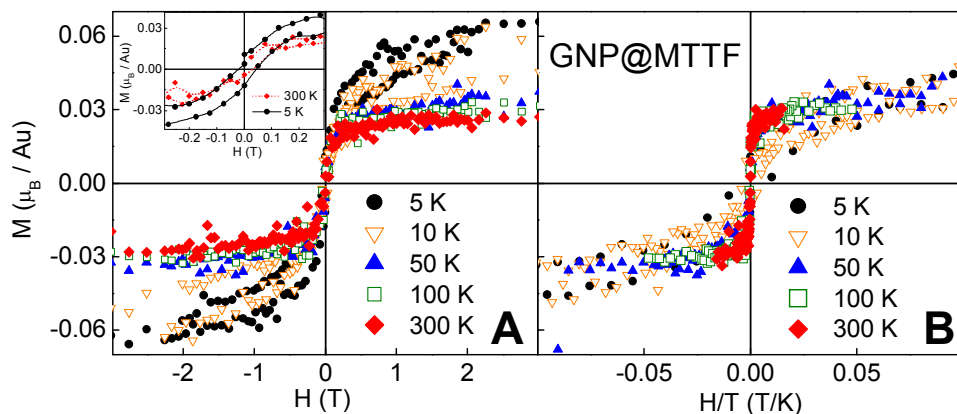


Figure 5. The magnetic moment (M) of the GNP@MTTF sample, measured as a function of the applied magnetic field (H) at different temperatures (T) (A), and displayed as M versus H/T . Inset: $M(H)$ comparing the low H region for 5 K and 300 K curves.

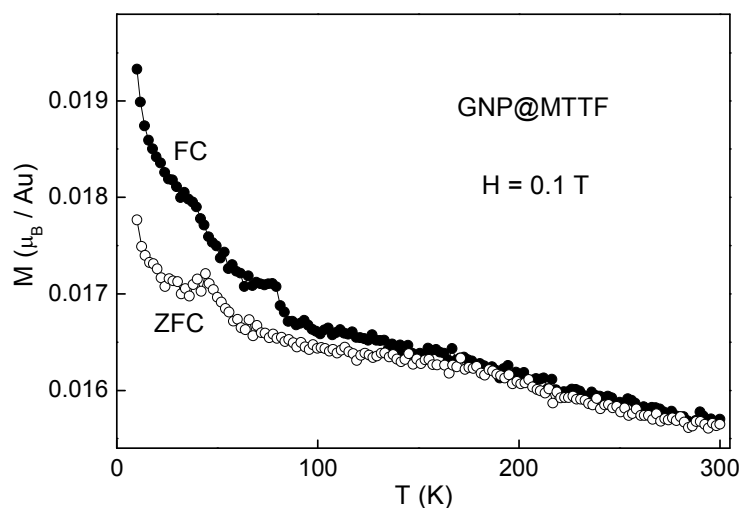


Figure 6. Zero Field Cooling (ZFC) and Field Cooling (FC) magnetic moment (M) as a function of temperature (T), measured with an applied field (H) of 0.1 T, for the GNP@MTTF sample. Hollow and filled symbols correspond to ZFC and FC curves respectively. The diamagnetic contribution was already subtracted.

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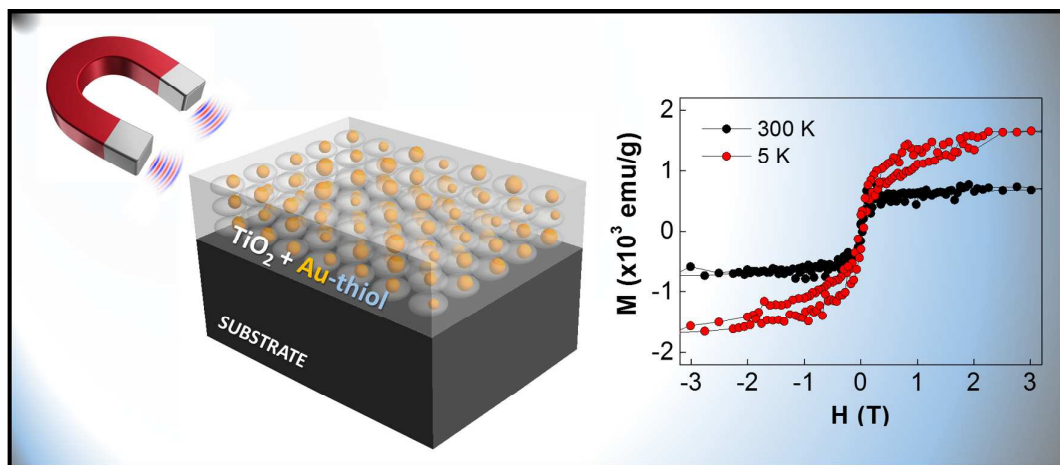
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TOC FIGURE