Template-assisted self-assembly of individual and clusters of magnetic nanoparticles

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Abstract
The deliberate control over the spatial arrangement of nanostructures is the desired goal for many applications such as, for example, in data storage, plasmonics or sensor arrays. Here we present a novel method to assist the self-assembly process of magnetic nanoparticles. The method makes use of nanostructured aluminum templates obtained after anodization of aluminum discs and the subsequent growth and removal of the newly formed alumina layer, resulting in a regular honeycomb-type array of hexagonally shaped valleys. The iron oxide nanoparticles, 20 nm in diameter, are spin-coated onto the surface of honeycomb nanostructured Al templates. Depending on the size, each hexagon site can host up to 30 nanoparticles. These nanoparticles form clusters of different arrangements within the valleys, such as collars, chains and hexagonally closed islands. Ultimately, it is possible to isolate individual nanoparticles.

The strengths of the magnetic interaction between particles in a cluster are probed using the memory effect known from the coupled state in superspin glass systems.

1. Introduction
Magnetic nanoparticles (NPs) are recognized as promising systems with a high potential for several technological applications, e.g. in magnetic data storage media and spintronic devices or in plasmonic, photonic or nanomedical systems [1–4]. At present, large efforts are being devoted in order to investigate and control their chemical and physical properties [5]. The magnetic properties of NP assemblies are proven to depend on their degree of packing and ordering, which might result in different particle-to-particle interactions having both short range and long range effects [6–9]. Various synthesis methods have been developed in order to control the formation, packing and self-assembly of NPs at the nanoscale, ranging from inorganic materials (e.g. metallic or metal oxide NPs), macromolecules and biomolecules on 1D and 2D surfaces, and on 3D patterned substrates [10–14]. Many of these methods, including lithography-based techniques and/or other complex nanoengineering routes, require very sophisticated experimental equipment and high operational costs when accurate sub-100 nm ordered structures are to be achieved [15]. However, one low-cost, easy-to-manipulate and well-reproducible technique to form highly ordered 2D to 3D patterned nanostructures over large areas is based on nanoporous anodic alumina membranes (NAAMs) [16, 17]. In this work we present a new composite nanomaterial obtained by combining two nanostructured materials, namely iron oxide NPs, prepared by a chemical route [18], and nanostructured aluminum templates obtained by means of an electrochemical route after the preparation process of NAAMs [19, 20]. The templated aluminum substrate is successfully used to control the relative distance between isolated clusters of magnetic nanoparticles as well as of individual NPs.
2. Experimental details

2.1. Material preparation

High purity Al foils (Goodfellow, 99.999%) were cleaned by sonication in isopropanol and ethanol for 5 min. The surface of the starting Al substrate was then smoothed by double-sided electropolishing in a 1:3 vol. perchloric acid and ethanol mixture at 5°C during 15 min, and by applying a constant dc potential of 20 V between the sample and a Pt mesh. The electropolished Al foils were mounted in a homemade electrochemical anodization cell serving as the anodic electrode. A Pt mesh was kept at a distance of about 10 mm from the anode and was used as the cathode. Anodization was performed under potentiostatic conditions using different applied voltages and acidic electrolytes that were kept at fixed temperatures and moderately stirred during the entire process. This procedure allows us to prepare several self-ordered NAAMs having different geometrical parameters. During the course of the anodization process, the nanostructured growth of NAAMs develops nanopatterns at the metal interface, the parameters of which depend on the anodization conditions and are closely related to the NAAM lattice parameters. In all cases the final nanostructured Al templates consist of highly ordered hexagonal nanocups disposed in a honeycomb lattice, the center of each hexagon defining the pore site. A schematic drawing of all synthesis steps is shown in figures 1(a) and (b).

Following the anodization process, the oxide layer is removed from the nanopatterned Al substrate by selective chemical etching in an aqueous solution of CrO$_3$ 0.18 M and H$_3$PO$_4$ (0.61 M), as indicated in figure 1(c).

Afterwards, iron oxide nanoparticles were spin-coated on top of the aluminum substrate in cycles of two consecutive steps of 3 s and 30 s at a rotational speed of 300 rpm and 2000 rpm, respectively (figure 1(d)).

2.2. Magnetic and structural characterization

Structural characterizations of the samples were performed by means of an FEI Quanta 200 FEG scanning electron microscope (SEM), and the magnetic properties analyzed by zero-field-cooling (ZFC) and field-cooling (FC) magnetization measurements using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer in the temperature range between 330 and 15 K, and applied fields up to 50 kOe.

3. Results and discussion

3.1. Aluminum nanostructured template preparation and definition

Patterned templates of nanostructured alumina were obtained by following an electrochemical procedure, as detailed above in section 2.

Three sets of NAAMs were prepared, acting as precursors for the patterned Al substrates. Two of them were prepared following the well-established mild-anodization (MA) process [19, 20], and a third one was prepared through the hard-anodization (HA) process [21]. In the latter case the use of high anodization potentiostatic voltages provides higher nanoporous alumina growth rates, together with higher geometrical dimensions of lattice parameters (nanopore diameter and interpore distance). The experimental conditions for the synthesis procedure of NAAM templates are listed in table 1.

In all cases, during the controlled ‘bottom-up’ anodization process of the NAAMs, the initial randomly disordered pores growing on the top surface of the alumina develop a highly ordered hexagonal structure via self-assembly of the nanopores, which penetrate all the way through the alumina layer (schematically shown in figure 1(b)) [22]. In order to achieve a high degree of order of both the nanoporous alumina
layer (figure 1(b)) and the nanopatterned aluminum templates (figure 1(c)), the anodization time was extended up to 1 h and 96 h for HA NAAMs and MA NAAMs templates, respectively. After chemical removal of the alumina layer, the residual nanostructured Al patterned substrate (figure 1(c)), is used as a template for the magnetic NP assembly. The exposed top surface of the nanostructured Al template forms a honeycomb lattice of semispherical valleys, as shown schematically in figure 1(c), with sizes ranging from 50 up to 250 nm depending on the parameters of the anodization process. Nanostructured templates with a disc diameter of 17 mm have been produced.

Commercial iron oxide NPs were purchased from NN-Labs. They were prepared by thermal decomposition of metallic plates and have a nominal diameter of 20 nm with a size distribution of about 10%. The as-received NPs were annealed at 170 °C in air for 20 min in order to obtain predominantly single-phase maghemite ($\gamma$-Fe$_2$O$_3$), as reported in [23]. The NPs were dissolved in toluene and spin-coated on top of the Al-patterned substrates at 300 rpm for 3 s and subsequently at 2000 rpm for 30 s, following the method described in [23]. A monolayer film of the same kind of NPs, spin-coated on a (100) Si substrate, was also prepared for comparison.

Three different types of nanostructured aluminum templates prepared with three different lattice parameters as shown in figure 2, were used as the substrate during spin-coating of iron oxide NPs. The nanostructured aluminum is characterized by a honeycomb arrangement of nanocups with diameters $d =$ 280 nm (figure 2(a)), $d =$ 105 nm (figure 2(b)) and $d =$ 72 nm (figure 2(c)) for samples obtained by oxalic HA, oxalic MA and sulfuric MA, respectively. Obviously the smallest pattern exhibits a number of structural defects.

For simplicity, the composite samples will be labeled as D280, D105 and D72, referring to the size of the patterned nanostructure characteristic of the specific anodization conditions used for their preparation. Spin-coating of NPs results in different filling factors depending on the patterned substrate used. SEM observations over the whole surface of the samples, from their center to the outer diameter, showed that for all three templates the packing density within the same sample remains constant over the whole area considered.

### 3.2. Organization of nanoparticles on Al templates

After spin-coating on Al templates, the magnetic NPs arrange in small clusters at the bottom of each hexagon valley, as found in the SEM images of figures 3(b)–(d). The number of NPs in each hexagon site varies from 2 up to $\sim$30. If the number of particles per cluster is less than 10 particles, then the NPs arrange in different packing geometries, sometimes in closed collars or open chains; for clusters composed of more than 10 NPs a hexagonally ordered packing is observed, similar to the self-assembly of particles spin-coated on a polished Si substrate, as shown in figure 3(a). For patterns with the smallest lattice parameter (sample D72) the number of particles per host site varies between one and four, but also a large portion of sites remains empty, as can be found in figure 3(d).

More information can be obtained from the histograms of the NP population on the sites in the three templates shown in figure 4, where $N_S$ is the number of sites which are occupied by specific clusters and $N_{NP}$ is the number of NPs per cluster. The histograms were obtained from several images of the samples, each covering areas ranging from 1 to 2 $\mu$m$^2$. The largest distribution of NP-cluster population is found in D280 samples, as can be observed in figure 4(b), where an average of 17 NPs per site is found, with 30% of the occupied sites hosting between 21 and 25 NPs. A narrower size distribution is found in sample D105 (figure 4(c)), where the average number of particles per cluster is 6 and 50% of the occupied sites host between 5 and 8 NPs. Samples D72 have the narrowest size distribution, with an average number of particles per site of 2 and 86% of the occupied sites hosting between 1 and 3 NP, with 46% of the total sites hosting individual NPs (figure 4(c)). Isolated NPs are found to preferentially sit at the center of each site with an average distance between nearest-neighbor NPs of approximately 70 nm, in good agreement with the lattice parameter of the D72 substrate. In this sample, vacant sites account for approximately 11% of the total.

The possibility of controlling the NP-cluster dispersion in an ordered arrangement over the whole surface of a patterned substrate offers a unique scenario for the investigation of competing magnetic interactions in systems with low dimensionalities. In a system of interacting single-domain NPs, two main possible magnetic behaviors can be observed.

In the first case, when the interactions between particles are sufficiently small, the magnetic behavior is dominated by the magnetic moments of the individual NPs. In this case, the system behavior is superparamagnetic (SPM) [7, 24, 25].

In the second case, for a system with a sufficiently high concentration of NPs and consequently stronger particle–particle dipolar interactions, it may be possible to observe a collectively coupled state, two prominent examples of which are the superspin glass (SSG) [2, 26–30] and the...
superferromagnetic (SFM) state [1, 31, 32]. The effect of the interparticle dipolar interaction depends on the specific type of arrangement in each cluster as well as on the number of NPs in each cluster.

3.3. Magnetic characterization of templated nanoparticles

For the analysis of their magnetic behavior, we have performed zero-field-cooling–field-cooling (ZFC–FC) measurements of the magnetization. For the ZFC protocol the sample was cooled from an initial temperature of \( T_i = 330 \text{ K} \) to a final temperature \( T_f = 15 \text{ K} \) in zero field, then a magnetic field of 50 Oe was applied and the ZFC curve measured upon warming. The FC curve is obtained directly following the ZFC curve upon cooling in the same applied field.

The results are depicted in figure 5, where for comparison purposes the ZFC–FC magnetization values are normalized to the maximum value of the \( M_{ZFC} \) curve.

The magnetic behavior of the monolayer of \( \gamma \)-Fe\(_2\)O\(_3\) NPs on the Si substrate agrees well with the results reported in previous work [23], where a detailed study of the magnetic properties of NP monolayers was performed.

In the present study the shape of the FC magnetization, \( M_{FC} \), shows features which are different from those for regular NP monolayers [7, 23] that hint at novel behavior. One finds in figure 5 that, with decreasing the temperature below the blocking temperature, \( T_b \), the magnetization for the clusters of NPs is either constant or drops slightly. This feature has been reported to originate from dipolar interactions between NPss [2, 9, 33–35]. The \( M_{FC} \) is also observed to decrease when the particles are arranged in clusters, as in the case of sample D105. This can be explained as follows: although the clusters themselves are too small to display SSG behavior, the average edge-to-edge distance between clusters (\( \sim 50 \text{ nm} \)) is of the same order of magnitude as the average cluster size. Therefore, dipolar cluster-to-cluster interactions can be expected. However, the lower slope of the \( M_{FC} \) curve in sample D105 suggests a decreasing strength of the dipolar interactions compared with the NP monolayer on an Si substrate.
On the other hand, when NP clusters are placed further apart, as in the case of sample D280, the long range interaction becomes negligible and $M_{\text{FC}}$ follows the usual SPM behavior of increasing $M_{\text{FC}}$ with decreasing temperature below $T_i$. However, although the clusters in D280 appear to be non-interacting, one has to consider the relatively wide number distribution of the clusters in this sample and therefore the possibility of interactions between large clusters that cannot be completely excluded.

Sample D72 presents some unique features. In the first place $M_{\text{FC}}$ remains constant in the temperature range from $T_i$ to $T_b$. This behavior has two possible reasons. In the first place, individual nanoparticles might be interacting with each other. As mentioned above, the average distance between particles is approximately 70 nm, being larger than the average distance between clusters in sample D105. Therefore it is reasonable to expect a weaker response. The second possibility is that the observed behavior is the result from contributions coming from the coexistence of both non-interacting individual NPs as well as dipolarly coupled clusters of NPs separated with an average edge-to-edge distance of $\sim$40 nm. A further difference is found in the value of $T_b = 125$ K, which suggests that $T_b$ is decreased, when individual particles are successfully isolated. In fact, in the case of the NP monolayer, samples D280, and D105, $T_i$ remains constant at approximately 150 K, indicating that the blocking temperature does not depend on the long range SSG-like interactions. It should be mentioned that, even within isolated small clusters of particles, dipolar interactions between the constituent particles are expected. This would explain the different $T_b$ values between samples D280 and D72.

A unique and characteristic feature of SSG (and more generally spin glass) systems is the memory effect of the ZFC curve [27, 29, 36]. In this type of measurement, the sample is first cooled from $T_i$ to $T_b$ in zero applied external field. The magnetization is then recorded as a function of temperature in the interval $T_i$ to $T_f$. This behavior has two possible reasons. In the first place, individual nanoparticles might be interacting with each other. As mentioned above, the average distance between particles is approximately 70 nm, being larger than the average distance between clusters in sample D105. Therefore it is reasonable to expect a weaker response. The second possibility is that the observed behavior is the result from contributions coming from the coexistence of both non-interacting individual NPs as well as dipolarly coupled clusters of NPs separated with an average edge-to-edge distance of $\sim$40 nm. A further difference is found in the value of $T_b = 125$ K, which suggests that $T_b$ is decreased, when individual particles are successfully isolated. In fact, in the case of the NP monolayer, samples D280, and D105, $T_i$ remains constant at approximately 150 K, indicating that the blocking temperature does not depend on the long range SSG-like interactions. It should be mentioned that, even within isolated small clusters of particles, dipolar interactions between the constituent particles are expected. This would explain the different $T_b$ values between samples D280 and D72.

In the second step, the measurement is repeated with the difference that, during cooling in zero field, the sample is held at a stop temperature $T_s = 90$ K, with $T_s < T_i < T_f$, for a sufficiently long waiting time $t_w = 10 000$ s. The two ZFC curves (conventional $M_{\text{ZFC}}$ and $M_{\text{FC}}(T_i)$ after halting at $T_s$) are then compared. In SSG systems, the sample will ‘recall’ the treatment received at $T_s$, showing a deviation in the $M_{\text{FC}}(T_s)$ curve with respect to the regular ZFC curve.

Measurements of the memory effect were performed on the three template cluster samples as well as on the NP monolayer sample. Figure 6 shows the difference $\Delta_m = m_{\text{ZFC}} - m_{\text{ZFC}}(T_s)$. It can be found that both the NP monolayer film and sample D105 display a memory effect near $T = 90$ K, confirming an SSG behavior of the two systems.

On the other hand, samples D280 and D72 show no hint of any memory effect. Consequently no collective SSG behavior is observed. This is in agreement with the results obtained from the analysis of the ZFC–FC curves shown in figure 5, where long range dipolar interactions were only observed for the monolayer system and sample D105. It should be noted that the $\Delta m$ memory curves of the monolayer and sample D105 show an unexpected feature of a downward pointing peak near $T_i$. Usually, the memory effect in SSG systems is characterized by a relatively broad positive peak in $\Delta m$ [34, 37, 38].

To show that this feature is not simply an artifact of our measurement, we have studied another system of Co NPs for comparison. The Co NPs are formed by ion beam sputtering of Co on an Al$_2$O$_3$ buffer layer similar to the technique used in the work published in the references [29, 39, 40]. Details on the preparation and behavior of these samples will be published elsewhere. This type of system is known to display SSG behavior [29, 30].

Memory ZFC measurements were performed on this type of Co NP with $T_i = 50$ K, $T_f = 5$ K, $T_s = 20$ K, $t_w = 10 000$ s and $H = 20$ Oe. The results are shown in the inset of
figure 6. One finds the usual positive peak near to the stopping temperature.

Therefore we tentatively assume that the appearance of a downward peak at $T_a$ is a unique feature of the Fe-oxide NP systems. A possible explanation of the origin of this work is the presence of other iron oxide phases within the nanoparticles. For the NP diameter considered in this work, previous studies [23] reported the difficulty in obtaining a single phase directly from the heat treatment. However, the origin of this feature is still unclear and further work is ongoing to clarify this point.

4. Summary and conclusions

Nanostructured aluminum discs with a honeycomb pattern of different lattice parameters serve as templates for the self-assembly of Fe-oxide NPs, which have been spin-coated on the surface. By choosing the appropriate template lattice parameters the NPs can be arranged highly ordered into small clusters or even isolated on individual host sites. The number of particles per cluster, as well as the cluster-to-cluster distance, was found to strongly depend on the aluminum template used. Modifying the distance among clusters and/or individual NPs can destroy the long range magnetostatic coupling and hence inhibit the formation of a collective SSG state, otherwise often found in monolayer films of close-packed magnetic NPs. The preparation method proposed in this work can easily be extended to a different variety of NP systems, offering new possibilities for the study of both fundamental properties of magnetic NPs as well as technological applications.

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