Imaging Large Iron-Oxide Nanoparticle Clusters by Field-Dependent Magnetic Force Microscopy

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Abstract: Iron-oxide nanoparticles are intensively considered for high-performance biomedical applications, where simultaneous functionalities, such as magnetic state, large surface area for maximal protein/enzyme binding, high magnetization values to provide large signals, and good dispersion in liquid media, are usually required. In this context, the association of individual nanoparticles into large clusters is of particular interest. Here, we present a magnetic force microscopy (MFM) approach capable to image individual nanoparticulate clusters as large as 350 nm at room temperature and under variable magnetic fields. It is shown that an in situ removal of electrostatic interactions—particularly important for large particle sizes supported by dielectric substrates—in MFM experiments based on phase detection allows us to image the magnetic state of individual clusters. After taking into account the magnetization behavior of the microscope tip, the phase signal reveals a gradual and uniform rotation of the magnetization with the magnetic field and the absence of a hysteretic behavior for all investigated clusters.

Introduction

Various applications in bio-nanomedicine, (1–3) bio-separation, (4,5) drug delivery, (6–8) magnetic hyperthermia, (9–11) magnetic resonance, (11–13) or magnetic resonance imaging, (14,15) rely on the magnetic state of iron-oxide nanoparticles (NPs). (16–18) Generally, iron-oxide NPs display small magnetic moments triggering weak magnetic responses in magnetic fields, a drawback for their potential use in applications. (19,20) A way to overcome this limitation is to enhance the magnetic moment by increasing the particle size. (21–25) One particularly promising solution is the formation of porous or nanoparticulate clusters by self-assembling or self-aggregation. (26–30) Hence, inter-nanoparticle interactions within the clusters and the collective behavior can activate higher magnetic moments, (31–34) enhancing the magnetic responses while providing larger surface areas for binding functional biomolecules, as needed for instance in drug delivery. (35)

Clusters made of NPs can be formed in a two-step process, including first the synthesis of the NPs and then their assembling through colloidal (solvo-phobic) interactions mediated by ligands. [\(36\)](#) The method allows tuning the NP interactions with a good control. Alternatively, a clustering process can be produced through a direct aggregation of NPs during synthesis. [\(37,38\)](#) The polyol method has extensively been used in the last decade for this purpose. [\(39,40\)](#) Its versatility enables the formation of different types of aggregates with controlled morphologies ranging from nanoclusters to nanoflowers and hollow spheres. [\(41–48\)](#) The major inconvenience of this method when applied for mass production is however the long reaction time (6 h to 24 h or even more). It has been shown that increasing the synthesis temperature above the boiling point of the polyols reduces the reaction time down to 1 h. [\(49\)](#) Such a temperature rise also triggers the development of ferromagnetic atomic crystal phases [\(50\)](#) requiring systematic magnetic investigations.

A good understanding of the magnetic state of clusters made from NPs can be obtained by monitoring the collective magnetic response with superconducting quantum interference devices (SQUID) [\(51\)](#) or vibrating sample (VSM) magnetometers. [\(52\)](#) Such magnetic measurements performed on dried powders or colloidal suspensions are necessary for optimizing the chemical synthesis, as well as for concluding about the magnetic state. MFM [\(53\)](#) on the other hand is a technique able to image individual clusters and to address their magnetization states at the nanometer scale. [\(54–57\)](#) This technique has been used for revealing magnetic properties of individual NPs [\(58–61\)](#) and of magnetically correlated grain systems. [\(62\)](#) Nevertheless, MFM has also the potential to qualitatively investigate the magnetization state of clusters made of several NPs, in addition to their morphology, size characteristics, and separation. [\(63,64\)](#) Moreover, in some cases, the magnetic interaction forces measured by the microscope can also be used for quantitative magnetization studies under magnetic fields. [\(65,66\)](#)

Here, we present a MFM study on individual large iron-oxide nanoparticle clusters by operating the microscope under a variable magnetic field. The aim is to develop a microscopy method capable to address the magnetization behavior of individual clusters, without the adverse impact of electrostatic fields. In particular, the goal of this study is to demonstrate that individual clusters display a SP behavior at room temperature with specific MFM imaging characteristics. The study is realized on individual clusters with diameters of the order of 300 nm. They are composed of crystalline nanoparticles of about 14 nm. The clusters were deposited on a non-magnetic carbon-membrane grid (as used in electron microscopy). This allows the investigation of the same clusters by TEM and MFM, using a nanometric correlative approach. In particular, it will be shown that field-dependent (FD) MFM signals acquired after an in situ removal of electrostatic contributions can inform about the magnetization state of individual clusters as large as several hundreds of nanometres. In the limit of the magnetic fields used in the present study, the hysteresis loops indicate a superparamagnetic (SP) state for all investigated clusters.

Experimental Details

Synthesis The synthesis of magnetic clusters has been performed with the following products: iron(III)chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (Roth, $\geq 98\%$), ethylene glycol (EG) (Roth, $\geq 99\%$), polyethylene glycol 1000 (PEG1000) (Roth, $\geq 99\%$), and sodium acetate trihydrate (NaAc) (Roth, $\geq 99.5\%$). Iron oxide NPs have been synthesized according to the following procedure: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.27 g), NaAc (1.2 g), and PEG1000 (0.5 g) were mixed and dissolved in 40 mL of EG. The solution was stirred at room temperature for 30 min and then transferred in a 60 mL round-bottom flask. Prior to sealing the reaction vessel, the solution was degassed with a flux of nitrogen gas for 5 min. The solution was

heated to 300 °C with a constant heating rate of 5 °C/min and kept at this temperature for 1 h. A series of multiple ultrasonication/magnetic separation cycles, in order to remove the excess of ligands and unreacted precursors, were applied. The increase of the temperature at 300 °C during the synthesis, which is well above the boiling point of EG (200 °C), enables the formation of iron-oxide clusters in only 1 h, as compared to previous synthesis which require longer reaction times. (41,42) As shown in the inset of Figure 1 and Figure S1a, the resulting iron-oxide clusters exhibit on average a spherical-like shape with diameters in the range of hundreds of nanometers

Methods TEM was carried out on a JEOL-2100F microscope working at 200 kV. A 5 μ L drop of an aqueous solution containing clusters was deposited on a copper grid covered with a carbon membrane. XRD measurements (Figure 1a) were carried out on powder with a Bruker D8 ADVANCE diffractometer, using Cu K α radiation. Magnetic measurements (Figure 1b) were performed on powder in magnetic fields up to 2 T, using a VSM. Atomic force microscopy (AFM) and MFM experiments have been performed in ambient conditions by means of a modified ICON-AFM apparatus controlled by Nanoscope V electronics from Bruker. Low magnetic moment probes (PPP-MFMR–NanoSensors) with a coercive field of 25 mT were used. Prior to the experiments, the analyzed clusters were not exposed to any magnetic field. The spring constant of the cantilevers was between 2 and 3 N m⁻¹, and their resonance quality factor ranged between 500 and 1000. The magnetic field, normal to the substrate plane, was given by a home-built electromagnet, calibrated with a Hall probe.

Results and Discussion

Figure 1c shows three clusters which have been individually analyzed by both TEM and MFM. The isolated upper cluster, labeled S, has a diameter of 350 nm, while the lower two clusters, labeled C1 and C2, have sizes of about 280 and 330 nm, respectively. The mean crystalline size inside the clusters (Figure 1d), calculated using Scherrer's equation and a fit of the (220), (311), and (440) diffraction peaks, is around 14 nm, indicating a multicore structure of the clusters. Moreover, the XRD pattern confirms the presence of a pure inverse spinel crystalline phase ascribed to magnetite–Fe₃O₄ (PDF no: 88-0315 (67)), as can also be seen in Figure 1e. In addition, the corresponding atomic lattice parameter is very close to that of bulk magnetite ($a = 0.8375$ nm). As shown by EDX analysis [Figure 1f–h], the iron (Fe) and oxygen (O) elements within the clusters are homogeneously distributed.

At 4 K, the VSM hysteresis loop [Figure 1b] measured on powders shows a ferromagnetic character with a saturation magnetization of 78 emu/g, a remnant magnetization of 20 emu/g, and a coercive field of 28 mT. At 300 K, the saturation magnetization decreases considerably to 62 emu/g, owing to spin-canting effects. (68) The remnant magnetization is of about 6 emu/g with a coercive field of 10 mT, which suggests the presence of ferromagnetic phases.

The collective magnetic properties of the clusters have been further addressed by temperature dependences of magnetization (Figure S1c). From zero-field cooling (ZFC) curve, the onset of the ferromagnetic to SP transition (blocking temperature T_B) can be identified around 175 K. However, the peak in the ZFC curve is very broad extending above 300 K. This indicates a gradual transition to the SP state which is not completed at 300 K as the ZFC curve displays a magnetization value of 35 emu/g. The field cooled (FC) curve coincides with ZFC curve in a very short temperature range from 300 to 280 K, which represents the so-called irreversibility temperature (T_{IRR}), while below 280 K, it reaches a plateau. It is worth noticing that for monodispersed and non-interacting single-domain magnetic nanoparticles, the T_{IRR} coincides with T_B forming a narrow ZFC peak, with both ZFC and FC curves decreasing progressively toward zero, becoming even negative in the vicinity of room temperature.

(69) For our samples, the behavior of ZFC and FC curves is therefore typical for an assembly of nanoparticles with a non-negligible distribution in the magnetic properties. This might be induced by interparticle interactions and/or residual ferromagnetic phases.

Figure 1. (a) X-ray diffraction (XRD) diffraction pattern of a powder of Fe_3O_4 particle-based clusters. (b) Magnetization curves of the powder at 4 and 300 K. Inset is a transmission electron microscopy (TEM) image ($3 \times 5 \mu\text{m}^2$) of a cluster assembly on a carbon substrate. (c) TEM image of three clusters studied by magnetic force microscopy (MFM), labeled S, C1, and C2. (d) TEM image of a border crystallite with the corresponding fast Fourier transform pattern (e) showing the presence of well-defined crystallographic structure. (f,g) Chemical maps obtained by EDX spectroscopy of iron and oxygen distribution within the Fe_3O_4 cluster, respectively. (h) Relative chemical map with the distributions of both iron and oxygen within the clusters.

For accurate magnetic state measurements by MFM, it is essential to first evaluate the electrostatic interactions between the microscope probe and the sample. Indeed, the phase signal measured by MFM may contain a significant contribution from non-magnetic electrostatic forces, which arise from topographic effects and from inhomogeneous surface potentials between the clusters and substrate surface. (70–73) Therefore, we began our study by precisely evaluating the electrostatic contributions to the phase signal acquired in MFM. Our approach is to monitor the phase shift of the cantilever oscillation at specific tip-sample distances as a function of a bias voltage applied between the tip of the microscope and the sample substrate (Figure 2a).

In the absence of electrostatic interactions, the phase signal as a function of the applied tip bias is expected to have a quadratic shape (parabola) centered at 0 V. As shown in Figure 2a (also see Figure S2), the parabolas are not symmetric with respect to 0 V, as their maxima are shifted to about +1 V. This suggests the presence of an important intrinsic electrostatic contribution to the phase signal. It is also seen that, although the parabolas progressively flatten with tip-sample distance, they persist to at least 900 nm. The parabolas recorded in the presence of an external out-of-plane magnetic field ranging from 15 to 55 mT are shown in Figures 2b and S2. As seen, the parabolas do not change with respect to the magnetic field, which confirms the possibility of compensating the electrostatic interactions by applying a bias voltage of +1 V to the tip. Insights into the magnetic state of the clusters were gained by recording FD MFM images. Two sets of MFM images have been recorded: one without electrostatic compensation (0 V, presented in Figure S3) and another with an electrostatic compensation (+1 V), as shown in Figures 3 and S4.

Figure 2. (a) Phase signal acquired above the cluster S from [Figure 1c](#) as a function of tip bias for different tip lifts. (b) Phase signal taken above the cluster C2 as a function of tip bias and external magnetic field (lift 200 nm). The dashed lines indicate the center of the parabolas located in each case at about +1 V tip bias.

Figure 3. MFM images acquired on the isolated cluster from [Figure 1c](#) at different values of external magnetic field ranging between +55 and -55 mT (tip lift = 200 nm and +1 V tip bias). Black and blue arrows represent the magnetization of the tip, while the brown arrows denote the cluster magnetization. The red arrows indicate the reversal of the tip magnetization.

[Figure 3](#) shows FD-MFM images of the isolated cluster labeled S in [Figure 1c](#), taken at +1 V (full series of images in [Figure S3](#)). Starting at a magnetic field of +55 mT, a dark (negative) contrast is observed over the cluster, which corresponds to an attractive interaction due to the parallel alignment of tip and cluster magnetization.

Decreasing the external magnetic field toward zero results in a decrease of the phase contrast. This indicates a decrease of the cluster magnetization along the z-axis (normal to the substrate plane), since the tip magnetization is constant in the respective magnetic field range (see below). A more complex situation is present in the field interval between 0 mT and the coercive field of the tip at -25 mT. In this interval, one could expect that the cluster magnetization aligns with the external field, that is, in the opposite direction with respect to the tip magnetization. The absence of bright contrast over the

cluster nevertheless shows that this is not the case. In turn, the dark contrast reveals an attractive interaction, indicating that the magnetization components of the cluster and the tip are still oriented in the same direction (as depicted by arrows in [Figure 3](#)). This shows that the magnetization of the cluster is influenced by the stray field of the magnetic tip that overcomes the external magnetic field in this interval. In fact, variations of the sample magnetization induced by MFM magnetic tips have been observed in MFM experiments, [\(74–78\)](#) while the axial stray field of the tips have indeed been found in the mT range. [\(79,80\)](#)

Based on the above observations, the magnetization of the cluster is schematized in [Figure 3](#) by arrows (brown) of various thicknesses, while the magnetization of the tip is represented by black and blue arrows. It can thus be deduced that at 0 mT, the dark MFM contrast (attractive interaction) is caused by the tip magnetic stray-field that induces a residual magnetization in the cluster. At -25 mT (red arrow in [Figure 3](#)), the tip coercive field is reached, and the tip magnetization suddenly reverses. The stray field of the tip points then along the same direction as the external field, explaining the larger MFM signal below the position indicated by the red arrow. It is then followed by a progressive increase of the dark contrast as the external magnetic field is swept toward more negative values.

The contrast dynamics over the cluster follows the same trend when sweeping back the external magnetic field from -55 to +55 mT. The tip coercive field is reached at +25 mT (red arrow in [Figure 3](#)). Along the entire magnetic cycle, a dominant dark contrast is therefore observed in FD-MFM images corresponding to a single magnetic domain configuration. This is consistent with a coherent rotation of the spins of multiple parts forming the cluster, indicating that the cluster behaves as a macro-spin. In addition, the observed uniform dark contrast induced by tip stray-field, that is, in the absence of an external magnetic field reflects a low value of the overall anisotropy energy of the cluster.

By a one-by-one analysis of the FD-MFM images, an average phase signal over the cluster can be obtained. [Figure 4a,b](#) shows the variation of the average phase signal as a function of the external magnetic field, for a tip bias of 0 and +1 V, respectively. A butterfly-like loop is observed in both cases. At +1 V, the compensation of electrostatic effects induces a downward shift of the butterfly loop, providing a clearer magnetic signal of the sample. It might be expected that the magnetic field of the tip adds to the external field, resulting in a shift of the magnetic field axis and in a deformation of the MFM hysteresis curves. However, the magnetization of the clusters follows the magnetization direction of the tip (interaction always attractive). This means that the resulting MFM hysteresis loop reflects the tip magnetization behavior rather than of the cluster. As a consequence, in the limit of our field resolution, a shift of the MFM hysteresis loop is not observed.

The electrostatic contribution interferes with the “magnetic” phase signal. As seen in [Figure 4a](#) in the interval -10 and -25 mT, the values of the magnetic phase shift are positive, which in principle must denote a repulsive interaction experienced by the tip. This is a clear visualization of the effect of the electrostatic field. Without the electrostatic interaction as shown in [Figure 4b](#), the butterfly loop is fully located at negative values as the tip stray-field and the external magnetic field maintains an attractive magnetic interaction. The second effect induced by electrostatic interactions and observed in [Figure 4a](#) is the asymmetry of the butterfly loop, when the external field is reversed. Indeed, when the electrostatic contribution is compensated [\[Figure 4b\]](#), the butterfly loop is far more symmetric, also being less distorted. These effects brought by the electrostatic fields can be seen even better when looking at the hysteresis loops obtained after considering the sharp reversal of the tip magnetization at ± 25 mT [\[Figure 4c,d\]](#).

Figure 4. (a,b) FD-MFM average phase signals at 0 and +1 V, respectively, acquired over the isolated cluster from [Figure 1c](#). Tip lift: 200 nm. (c,d) Corresponding hysteresis loops obtained by considering the tip magnetization reversal. Arrows indicate back and forth sweeping of the external magnetic field.

Figure 5. FD-MFM images acquired on the two adjacent clusters from [Figure 1c](#) at different values of external magnetic field ranging between +55 and -55 mT (tip lift = 200 nm and +1 V tip bias). Black and blue arrows represent the magnetization of the tip, while the brown arrows denote the cluster magnetization. The red arrows indicate the reversal of the tip magnetization.

The resulting hysteresis loop from [Figure 4d](#) has a shape given mainly by the magnetization reversal of the microscope tip. Before further strengthening this conclusion by presenting results on highly anisotropic CoPt nanoislands (coercive fields > 300 mT and close to 100% of remnant magnetization), we hereafter present the findings on the two clusters seen in the lower part of [Figure 1c](#). As above, the FD-MFM images were recorded with and without electrostatic contributions. FD-MFM images taken at +1 V are shown in [Figure 5](#), full series of images at +1 V and 0 V can be seen in [Figures S6 and S15](#), respectively. The dark contrast in [Figure 5](#) shows a similar trend as before for the isolated cluster. The tip magnetization reversal for both, back and forth magnetic sweeping directions, takes place at -25 and $+30$ mT, respectively. The dark contrast is uniform over both clusters along the entire magnetic cycle, which speaks in favor of a SP behavior of both clusters as in the case of the isolated cluster.

Phase butterfly-like loops are observed for both clusters [labeled C1 (largest) and C2 (smallest), [Figure 6a,b](#)]. No positive value of the magnetic phase shift is detected over the entire cycle, suggesting weaker electrostatic effects [[Figure 6a](#)]. Indeed, they are expected to be reduced by the proximity of the two clusters, which decreases the topographic variations. (70) Consequently, the downward shifts of the butterfly-like loops [[Figure 6a,b](#)] and of the resulting hysteresis loops [[Figure 6c,d](#)] are not so pronounced when compensating the electrostatic contribution, as compared to the isolated cluster. The fact that the phase signal delivered by the two clusters is higher with respect to the isolated cluster can also play a role. Above adjacent clusters, the tip collects a higher magnetic signal, the phase values being greater as compared to an isolated cluster. This observation strengthens the above conclusions that the hysteresis loops reflect the magnetic reversal of the tip.

Figure 6. (a,b) FD-MFM average phase signals at 0 and +1 V acquired on C1 [right-hand cluster in the “dimer” from [Figure 1c](#)] and on C2 [left-hand cluster in the “dimer” from [Figure 1c](#)], as a function of the external magnetic field. Tip lift: 200 nm. (c,d) Corresponding hysteresis loops considering the tip magnetization reversal. Arrows indicate the back and forth sweeping of the external magnetic field.

To support these findings, we conducted experiments on hard magnetic samples consisting on CoPt islands of 45 nm in height and 200 nm in diameter [[Figure 7a](#)]. Due to the strong spin–orbit coupling,

these islands have a large out-of-plane anisotropy, and a large coercive field in the range 350–550 mT, which is more than ten times larger than the tip coercive field. [81] As a consequence, the magnetization of the CoPt islands is blocked at room temperature and constant in the field interval explored in the present MFM study. [81] Changes in phase contrast with the external magnetic field can then be exclusively ascribed to the variation/reversal of the tip magnetization. With a zero external magnetic field, the magnetic contrast is either dark (negative) or bright (positive) [Figure 7b], denoting a parallel or antiparallel orientation of the magnetization, respectively. The quartz substrate supporting the CoPt islands has a different dielectric constant as compared to the carbon TEM grid and a far larger thickness of about 1 mm. For this reason, the maxima of the parabolas are shifted to approximately -5.0 V, which is significant [Figure 7c]. The electrostatic contribution to the magnetic signal is therefore expected high.

Figure 7. (a) Topographic AFM image ($6 \times 1 \mu\text{m}^2$) and its corresponding MFM phase image (b) taken at 200 nm lift and a tip bias of -5.0 V. The numbers label the CoPt islands. (c) Phase signal as a function of applied tip bias, recorded at lifts ranging from 100 to 1200 nm. The black dashed lines indicate that the center of the parabolas are located at -5.0 V tip bias. (d) Phase profiles along the four CoPt islands displayed in (a) as a function of external magnetic field (lift of 200 nm and tip bias of -5.0 V). (e) MFM hysteresis loops obtained by measuring the CoPt islands (island 1 and island 2) at a lift of 200 nm and a tip bias of -5.0 V. Insets show the phase images of the islands recorded at $+55$ mT and -55 mT, highlighting the magnetic contrast inversion owing to tip magnetization reversal.

An MFM image of four CoPt islands acquired with -5.0 V applied to the tip is shown in [Figure 7b](#). At the maximum applied magnetic field of $+55$ mT, a dark contrast is observed over the island 1 and 4, while islands 2 and 3 exhibit a bright (positive) contrast [[Figure 7d](#)]. The phase signal recorded over all islands reverses when reaching a magnetic field of -28 mT [[Figure 7d](#)]. Sweeping backward the external magnetic field, the initial phase signal is recovered when applying $+30$ mT ([Figure S7](#)).

The average phase signal as a function of the external magnetic field for both types of magnetized islands therefore results in typical hysteresis loops of the tip ([Figure 7e](#)). This is because the CoPt magnetization is strictly constant in this field interval. In addition, the sudden switch of the signal over CoPt islands reveals that the reversal of tip magnetization occurs in a reduced field range, suggesting a strong bimodal state of the tip magnetization, that is, up and down. These conclusions, along with the fact that the phase contrast reverses above the clusters at the same fields (-28 and $+30$ mT) again demonstrate that the hysteresis loops acquired on the clusters can be directly associated to the tip magnetization behavior.

Reconstruction of Magnetization Behavior of the Clusters

To retrace the FD magnetization behavior of the clusters, one possibility is to subtract the magnetization switching of the tip. The simplest way is to consider a square hysteresis loop for the tip. Similar to the case of diamagnetic corrections realized for weak magnetic samples, it is first required to establish a correction factor. The slope of the phase signal before the coercive fields (either flip direction) is rather constant [see black or red arrows in [Figures 4d](#) and [6d](#)]. Under these conditions, a correction factor can be the phase signal at zero magnetic field, which is slightly different for different clusters and sweeping directions.

Figure 8. FD phase signal for the three clusters from [Figure 1c](#), obtained by considering the magnetic reversal of the microscope tip. Data highlighted in (a) is for the isolated S cluster, in (b) is for C2 cluster, and in (c) is for C1 cluster. Solid lines are linear fits. Error bars are below 15% of the phase signal (not included for clarity).

[Figure 8](#) shows the phase signal of the three investigated clusters, obtained by subtracting, for each cluster, the phase shift measured at zero field. The data for all clusters drop on rather imperfect linear variations [[Figure 8a](#) isolated S cluster, (b) C2, and (c) C1]. Nonetheless, the curves from [Figure 8](#) show a progressive increase of the cluster magnetization with the magnetic field, and the absence of a hysteresis, indicating a SP behavior of these individual clusters supported by a substrate. Our magnetic field (<55 mT), as well as the impossibility to perform low-temperature experiments with our microscope does not allow us to further support this conclusion. The SP behavior revealed in the present MFM study is in agreement with the small dimension of crystallites (14 nm) composing the clusters, as the critical size of magnetite to enter ferromagnetic regime at room temperature is about 30 nm. In dried powders, as generally measured by VSM or SQUID magnetometry, the clusters are

most likely assembled in large aggregates which, upon a first exposure to an external magnetic field, are prone to develop magnetic dipolar interactions and finally ferromagnetic characteristics, as observed in our VSM curves. Dipolar interactions in highly concentrated suspensions of 13 nm maghemite NPs were in fact observed by temperature-dependent magnetization measurements. (82) However, to date, a clear picture on inter-particle interactions mediated by ligands is not yet available. In this regard, our approach based on FD-MFM investigation of individual clusters can be extended to other systems such as nanoflowers or hollow spheres. (45,48)

Conclusions

In conclusion, large iron-oxide nanoparticulate clusters have been synthesized in a quick (1 h) and one step process. According to TEM–EDX and XRD analysis, the clusters display a poly-crystalline multicore structure and an overall spherical shape with sizes of the order of few hundreds of nanometers. The magnetization state of individual clusters has been probed at room temperature by FD magnetic force microscopy. It was found that after an in situ removing of electrostatic interactions, which are known to affect the phase signals in magnetic force microscopy, it is possible to retrace the FD magnetization behavior of individual clusters in interaction with the microscope tip. The resulting magnetization loops display a typical butterfly-like shape resulting mainly from the magnetization reversal of the tip, as separately demonstrated on hard magnetic CoPt islands. After taking into account the magnetization reversals of the tip, the MFM phase signals reveal a gradual increase of the magnetization of the clusters with the magnetic field, and the absence of a hysteresis in the limit of magnetic fields below 55 mT, suggesting a SP behavior. Overall, these results show an effective experimental procedure for probing large magnetic clusters with variable sizes and shapes, as needed for many biomedical applications. Our approach can readily be used for temperature-dependent experiments or to confirm the SP character of clusters composed of crystallites of various sizes.

Supporting Information

The Supporting Information is available free of charge at <https://pubs-acscs.org.scd-rproxy.unistra.fr/doi/10.1021/acs.jpcc.1c05426>. Magnetic characterization of the clusters (in powder) as a function of magnetic field and temperature and complete series of field-dependent MFM images, as well as a characterization of the magnetic-field in the AFM microscope (PDF)

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Notes

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