

Exchange Bias Effect in Au-Fe₃O₄ Nanocomposites

Journal:	<i>Nanotechnology</i>
Manuscript ID:	NANO-101553.R1
Manuscript Type:	Paper
Date Submitted by the Author:	06-Dec-2013
Complete List of Authors:	Chandra, Sayan; University of South Florida, Department of Physics Huls, N.A.; University of South Florida, Department of Physics Phan, Manh-Huong; University of South Florida, Department of Physics Srinath, S; University of Hyderabad, School of Physics Garcia, Miguel; Consejo Superior de Investigaciones Cientificas, Institute for Ceramic and Glass Lee, Youngmin; Brown University, Wang, Chao; Brown University, Sun, Shouheng; Brown University, Iglesias, Oscar; Universitat de Barcelona, Departament de Fisica Fonamental Facultat de Fisica Srikanth, Hariharan; University of South Florida, Materials Physics Laboratory
Article Keywords:	magnetic nanoparticles, exchange bias, magnetic anisotropy, nanocomposites, Monte Carlo simulations
Abstract:	We report exchange bias (EB) effect in the Au-Fe ₃ O ₄ composite nanoparticle system, where one or more Fe ₃ O ₄ nanoparticles are attached to an Au seed particle forming "dimer" and "cluster" morphologies, with the clusters showing much stronger EB in comparison with the dimers. The EB effect develops due to the presence of stress at the Au-Fe ₃ O ₄ interface which leads to the generation of highly disordered, anisotropic surface spins in the Fe ₃ O ₄ particle. The EB effect is lost with the removal of the interfacial stress. Our atomistic Monte-Carlo studies are in excellent agreement with the experimental results. These results show a new path towards tuning EB in nanostructures, namely controllably creating interfacial stress, and opens up the possibility of tuning the anisotropic properties of biocompatible nanoparticles via a controllable exchange coupling mechanism.

Exchange Bias Effect in Au-Fe₃O₄ Nanocomposites

*Sayan Chandra¹, N.A. Frey Huls¹, M. H. Phan¹, S. Srinath^{1,2}, M. A. Garcia³, Youngmin Lee⁴,
Chao Wang⁴, Shouheng Sun⁴, Òscar. Iglesias⁵, and H. Srikanth^{1,*}*

¹Physics Department, University of South Florida, Tampa, FL 33620 USA

²School of Physics, University of Hyderabad, Hyderabad 500046, India

³Instituto de Cerámica y Vidrio - CSIC & IMDEA Nanociencia, 28049 Madrid, Spain

⁴Department of Chemistry, Brown University, Providence, RI 02912 USA

⁵Departament de Física Fonamental and Institut de Nanociència i Nanotecnologia (IN²UB),
Universitat de Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain

KEYWORDS: magnetic nanoparticles, exchange bias, magnetic anisotropy, nanocomposites,
Monte Carlo simulations.

1
2
3 ABSTRACT
4
5
6

7 We report exchange bias (EB) effect in the Au-Fe₃O₄ composite nanoparticle system, where one
8 or more Fe₃O₄ nanoparticles are attached to an Au seed particle forming “dimer” and “cluster”
9 morphologies, with the clusters showing much stronger EB in comparison with the dimers. The
10 EB effect develops due to the presence of stress at the Au-Fe₃O₄ interface which leads to the
11 generation of highly disordered, anisotropic surface spins in the Fe₃O₄ particle. The EB effect is
12 lost with the removal of the interfacial stress. Our atomistic Monte-Carlo studies are in excellent
13 agreement with the experimental results. These results show a new path towards tuning EB in
14 nanostructures, namely controllably creating interfacial stress, and opens up the possibility of
15 tuning the anisotropic properties of biocompatible nanoparticles via a controllable exchange
16 coupling mechanism.
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1. Introduction

There has been a lot of interest in the search for multifunctional nanocomposites which forecast a promising future for the next generation nanotechnology applications.^{1,2} The goal is to artificially synthesize or fabricate a multicomponent nanostructure with controlled optical, electromagnetic and magnetic responses to suit various applications. Recently, with the advances in different chemical synthesis techniques, it has been demonstrated that one can design and chemically grow bifunctional nanostructures, called magnetic-plasmonic nano-heterostructures (MP-NHs), which are both magnetically and optically active.¹⁻³ Such heterostructures can be synthesized into a core/shell geometry, where the magnetic component (core) is contained within a chemically inert noble metal (shell), thereby enabling surface functionalization with biomolecules, while maintaining chemical stability against surface oxidation⁴ or in different arrangements, namely heterodimers, nanoflowers, nanotriangles, nanotadpoles etc.^{1, 3, 5, 6} Interestingly, the epitaxial growth of one component on the other at the nano-scale leads to the manifestation of fascinating properties⁷⁻⁹. However, little is known about the influence of the shape and size of the constituent nanoparticles on their functional properties, knowledge of which is essential to attain better control.

In particular, Au-Fe_xO_y MP-NHs have attracted a lot of attention and are thought of as potential candidates for applications in magnetic resonance imaging, magnetic/photo-induced hyperthermia, DNA sensing, cell sorting by method of magnetic separation, etc.^{7, 9} Recent reports have shown evidence of direct interaction due to spin polarization transfer between the magnetic moment and the non-magnetic plasmonic counterpart, thereby inducing finite magnetization in Au.⁴ Simultaneously, it has been reported that the magnetic properties of Fe₃O₄ are influenced due to the presence of Au in direct contact, which is evidenced as exchange bias

1
2
3 (EB) effect, modified magnetization response to alternating fields, enhanced blocking
4 temperature etc.^{8,10}
5
6

7
8 The EB effect in nanostructures has been an area of intense research over the last few
9 decades.^{11, 12} It manifests as a horizontal shift in the hysteresis loop accompanied by an increase
10 in coercivity after cooling in a magnetic field, a well-known phenomenon observed typically in
11 ferromagnet-antiferromagnet (FM-AFM) bilayer films¹². EB has been reported also in many
12 core-shell nanoparticles of different compositions, most notably Co-CoO¹³, CrO₂-Cr₂O₃¹⁴, FeO-
13 Fe₃O₄¹⁵, and Fe- γ Fe₂O₃¹⁶. However, loop shifts have also been reported in single component
14 magnetic nanoparticles (NiFe₂O₄¹⁷, CoFe₂O₄¹⁸) and they are usually attributed to a “shell” of
15 disordered surface spins formed in nanoparticles with a high surface-to-volume ratio that results
16 in EB due to coupling to core spins. The origin of this behavior is the fraction of surface spins
17 with decreased co-ordination (and thus weaker bonding) that increases when particle size
18 decreases. These disordered spins can take on a number of configurations that are quasi-
19 degenerated in energy due to randomness and frustration induced by the competition between
20 exchange coupling and surface anisotropy.¹⁹ This degeneracy can be usually broken by applying
21 a magnetic field while cooling the particles and, thus, EB is induced. Consequently, EB can be
22 introduced in nanostructures mainly by (i) the growth of two different magnetic phases with
23 competing anisotropies, or (ii) diminishing the particle size of a single magnetic material (< 5 nm
24 in case of ferrites), such that the surface anisotropy exceeds the anisotropy of the bulk material
25 by several orders of magnitude. For example, in the case of Fe₃O₄, it has been theoretically
26 predicted that EB can develop in particles with diameter ~ 2.5 nm or below, and ceases to exist
27 for bigger particle sizes.²⁰
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 In this article, we show a remarkable EB effect in Au-Fe₃O₄ composite nanoparticles, where
4 Fe₃O₄ nanoparticles were epitaxially grown on one or more facets of the Au particle forming the
5 corresponding “dimer” and “cluster” morphologies. The observation of exchange bias in case of
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

In this article, we show a remarkable EB effect in Au-Fe₃O₄ composite nanoparticles, where Fe₃O₄ nanoparticles were epitaxially grown on one or more facets of the Au particle forming the corresponding “dimer” and “cluster” morphologies. The observation of exchange bias in case of 8 nm Au – 9 nm Fe₃O₄ nanostructures is rather perplexing. For Fe₃O₄ nanoparticles with mean size ~ 8 nm, it has been reported that no additional surface or shape anisotropy exists and, hence, no EB effect is observed.²¹ This suggests that, in the Au-Fe₃O₄ system, EB is induced in ~ 9 nm Fe₃O₄ by the epitaxial growth of a non-magnetic metal on it. This phenomenon of the development of EB in magnetic nanoparticles, just by the introduction of a non-magnetic material on its surface is uncommon and its origin from a fundamental point of view is not understood. We investigate this by performing a series of systematic magnetometry experiments along with atomistic Monte-Carlo simulations to gain insights into the complex physics associated with this system leading to EB.

2. Experimental section

The Au-Fe₃O₄ dimer nanoparticles were prepared by decomposing iron pentacarbonyl, Fe(CO)₅, over the surface of Au nanoparticles, followed by oxidation in air. The Au nanoparticles were formed in situ by injecting HAuCl₄ solution into the reaction mixture. By changing the solvent from a nonpolar hydrocarbon to a slightly polarized solvent (e.g. diphenyl ether), flower-like cluster nanoparticles were synthesized. Further details of the synthesis are presented elsewhere⁵. The important feature of this synthesis is that the sizes of the Au and the Fe₃O₄ components can be independently tuned to create a variety of size combinations with the Au phase stable up to 8 nm and the Fe₃O₄ stable up to 20 nm. Samples for TEM analyses were prepared by evaporating a drop of diluted colloidal dispersion onto carbon

1
2
3 coated copper grids. Low-resolution and high resolution TEM images were acquired
4
5
6 respectively on a Philips EM 420 (120 kV) and a JEOL 2010 (200 kV).
7

8
9 Samples were prepared for magnetic measurements by evaporating nanoparticle suspensions
10
11 into a gelatin capsule. Since the surfactant on the particles also acts as an adhesive, the dried
12
13 particles made a paste in the gelcap and we are confident that there was no movement during
14
15 measurement. Magnetization versus temperature measurements were performed on a
16
17 physical properties measurement system (PPMS) by Quantum Design by first cooling the
18
19 samples from room temperature in zero field to 2 K. A field of 1 mT was then applied and the
20
21 magnetization measured upon warming at 2 K/min to room temperature wherein the
22
23 temperature was lowered at 2 K/min to 2 K.
24
25
26
27

28
29 Field cooled M-H curves were performed on the spherical Fe_3O_4 , Au- Fe_3O_4 dimers and Au-
30
31 Fe_3O_4 clusters by cooling in a field from above room temperature to the lowest temperature
32
33 and then and then incrementally increasing the temperature and carrying out a hysteresis loop
34
35 measurement at each step using a PPMS. The same protocol was used for a second Au- Fe_3O_4
36
37 dimer sample and the etched Au- Fe_3O_4 dimers using a superconducting quantum interference
38
39 device, magnetic properties measurement system (MPMS, Quantum Desgin).
40
41
42

43
44 Optical absorption measurements were performed at room temperature with a Shimadzu
45
46 3100 double-beam spectrophotometer attached with an integrating sphere in the transmission
47
48 mode. Samples were deposited onto a glass substrate and placed in the beam path. The beam
49
50 spot was 4 mm x 4 mm at the sample surface. A linear background was subtracted to account
51
52 for other contributions to the absorption spectrum.
53
54
55
56
57
58
59
60

RESULTS AND DISCUSSION

8 nm Au – 9 nm Fe₃O₄ dimer- and cluster-shaped nanoparticles were synthesized following the method outlined in reference.⁵ For comparison purposes, 9 nm spherical Fe₃O₄ nanoparticles of the same size were synthesized following the same procedure in the absence of Au seed particles. We also examined Fe₃O₄ particles that were obtained after the chemical etching of the Au off the Au-Fe₃O₄ dimers resulting in a dented morphology. Figures 1a and 1b show the dimer and cluster nanoparticles respectively, while Figure 1c shows the Fe₃O₄ particles after the chemical etching of the Au from the dimers. High resolution transmission electron microscopy of a dimer particle (Figure 1d) reveals the epitaxial growth of single crystalline Fe₃O₄ on the Au seed. It has been reported that Au-Fe₃O₄ composite nanoparticles show a red-shift of the surface plasmon of the Au owing to an electron deficient population arising from its contact with the Fe₃O₄.⁵ We avail this optical property as a tool to characterize the quality of the samples. Consistent with previous reports, the surface plasmon resonance (SPR) absorption spectra for the dimers (Figure 1e) exhibits a red shift of the absorption peak compared to that of the Au seeds which have an absorption frequency of ~ 520 nm. For the Au-Fe₃O₄ clusters, it is worth noting that no meaningful results could be obtained from SPR measurements, the electronic oscillations being so damped by the modified electronic structure as to render the quantitative results unusable. This indicates enhanced interface communication between Au and Fe₃O₄.⁹

Figure 2 shows the temperature dependence of magnetization in an applied field of 0.01 mT after zero-field cooled (ZFC) and field-cooled (FC) procedures. In the limiting case of single-domain monodispersed particles, the ZFC magnetization exhibits a peak (T_B) which is associated with the blocking phenomenon of the nanoparticles. The spherical particles have T_B ~ 36 K, and, although, the dimers and the clusters are constituted by similar ~ 9nm Fe₃O₄ particles, they

1
2
3 exhibit an increase in T_B up to ~ 65 K (Fig. 2b) and 90 K (Fig. 2c) respectively. This feature,
4 together with the increase in T_B also associated with broadening of the peak, are typically
5 associated with enhancement of magnetic anisotropy or inter-particle interactions.^{22, 23} The
6 contributions of the shape and surface anisotropies to the effective magnetic anisotropy play a
7 vital role in determining the blocking temperature. In case of spherical Fe_3O_4 nanoparticles, it
8 has been reported that the contribution of shape anisotropy cancels out owing to its symmetry.²⁴
9
10 As it can be seen from the TEM images in figure 1, the shape of the Fe_3O_4 nanoparticles in case
11 of the dimers and the clusters deviate from that of an ideal sphere. Moreover it is not clear if the
12 epitaxial growth of the Fe_3O_4 nanoparticles on the Au seeds in case of the dimers and clusters
13 modify and alter their surface anisotropy.
14
15
16
17
18
19
20
21
22
23
24
25
26

27 The blue squares in Figure 3 show the ZFC magnetization versus magnetic field (M-H) curves
28 for the Fe_3O_4 spherical particles (3a), the Au- Fe_3O_4 dimers (3b) and the Au- Fe_3O_4 clusters (3c)
29 taken at 2 K. In the insets we provide complete FC hysteresis loops for the respective samples.
30
31 Each type of particle morphology has different properties, with the M-H curve for the spheres
32 being similar to other reports of Fe_3O_4 in the same size range.²⁵ The coercivity (H_C) increases
33 with the introduction of the Au with the dimers having a higher H_C (64 mT) than the spheres (39
34 mT) and the clusters having the highest H_C of the three (124 mT). We also note for the clusters a
35 slow approach to saturation and a low remanent magnetization (M_R).
36
37
38
39
40
41
42
43
44
45

46 Hysteresis loops were also measured for all three samples after field cooling (FC) to 2 K
47 in 1 T and the results appear as red circles in Figure 3. While no EB is observed for the Fe_3O_4
48 nanoparticles, both the dimers and the clusters are found to exhibit substantial exchange fields
49 (H_E) which were calculated using the expression:
50
51
52
53
54

$$55 \quad H_E = \frac{-(H_{C1} + H_{C2})}{2}$$

56
57
58
59
60

1
2
3 where H_{C1} and H_{C2} are the coercive fields measured along the descending and ascending
4 branches respectively. The dimers display a H_E of 26 mT, while the clusters have an H_E of 50
5 mT. The dimers and clusters also show a slight increase in coercivity as well (73 mT versus 64
6 mT for the dimers and 130 mT versus 124 mT for the clusters) as well as a vertical shift and
7 increase in remanent magnetization. This phenomenon is frequently seen in exchange coupled
8 nanoparticle systems where the pinning layer is a metastable disordered state such as a shell of
9 disordered spins.^{11, 26} While in FM-AFM systems it is the result of uncompensated interfacial
10 spins, similarly in FM-disordered systems the net preferred direction of frozen spins lies along
11 the cooling field creating a vertical asymmetry.²⁷ The EB results suggest that there is a pinning
12 layer present somewhere in the Au-Fe₃O₄ particles (which is not present in the spherical Fe₃O₄
13 nanoparticles) and that this pinning is much stronger in the clusters than in the dimers.
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28

29 It is well established that EB may develop in nanoparticles by way of exchange coupling
30 of the core moments with the surface spins.²⁸ A prerequisite for EB is the presence of two
31 magnetic phases, one that reverses with the external field, and one that does not. In case of
32 nanoparticles, if the surface anisotropy is high compared to the anisotropy of the core moments,
33 then the surface spins may behave as pinning centers necessary for EB. In case of the dimers and
34 clusters, if the development of EB is indeed due to the enhancement of the surface
35 anisotropy, then we should observe an increase in the effective magnetic anisotropy of the
36 dimers and clusters in comparison to the spherical particles.
37
38
39
40
41
42
43
44
45
46
47

48 To elucidate this, we have performed radio-frequency transverse susceptibility (TS)
49 experiments on these systems. The TS has been a largely successful technique for directly
50 probing magnetic anisotropy in assemblies of single domain particles.^{29, 30} This method measures
51 the susceptibility by means of a perturbing alternating current field (H_{AC}) oriented perpendicular
52
53
54
55
56
57
58
59
60

1
2
3 to a changing direct current (DC) magnetic field, H_{DC} . In the theoretical paper on the transverse
4 susceptibility of a Stoner Wohlfarth particle, Aharoni *et al.* calculated that three singularities
5 would be observed in the transverse susceptibility when H_{DC} was scanned from positive to
6 negative saturation.³¹ Two of these peaks were located precisely at the positive and negative
7 effective anisotropy fields (H_K) and the third peak at the switching field (H_S). In the experimental
8 set up of TS, the sample is inserted in a coil whose axis is perpendicular to H_{DC} and produces a
9 small perturbing AC magnetic field ($H_{AC} \approx 1$ mT) perpendicular to H_{DC} . The coil is part of a
10 self-resonant circuit driven by a tunnel diode oscillator which oscillates at a frequency of around
11 2.6 MHz. The coil is inserted into the PPMS such that it can operate within a temperature range
12 of 5 K – 300 K and a DC magnetic field range of ± 7 T. As H_{DC} is swept, the permeability of the
13 sample sitting in the coil changes and thereby changes the inductance of the coil. This results in a
14 shift in the oscillating frequency which is recorded within an accuracy of one 1 Hz in 1 MHz.
15 Because the change in frequency of the circuit is a direct consequence of the change in
16 inductance as the sample is magnetized, Δf is directly proportional to $\Delta\chi_T$. We are therefore
17 most interested in the quantity

$$\frac{\Delta\chi_T}{\chi_T} (\%) = \frac{|\chi_T(H) - \chi_T^{sat}|}{\chi_T^{sat}} \times 100$$

18 as a function of H_{DC} where χ_T^{sat} is the TS at the saturating field H_{sat} . This quantity, which
19 represents a figure of merit, does not depend on geometrical parameters and is useful for
20 comparing the TS data for different samples, or for the same sample under different conditions.

21 The left panel of Figure 4 shows the magnified view of the bipolar TS curves (positive
22 saturation field to negative saturation field and back) of the spheres (a), dimers (b) and clusters
23 (c) to illustrate the peaks corresponding to the anisotropy fields ($\pm H_K$). In the middle panel
24 (Figure 4 d, e, f), a family of unipolar TS scans at selected temperatures are provided for the
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 three samples. We observe that while the anisotropy peaks for the spherical particles are
4 symmetric, the dimers exhibit asymmetric TS curves, and the asymmetry increases in case of the
5
6 symmetric, the dimers exhibit asymmetric TS curves, and the asymmetry increases in case of the
7
8 clusters. In experimental measurements of arrays of nanoparticles, certain deviations are
9
10 observed such as asymmetry and broadening of the $\pm H_K$ peaks and the merging of H_S with the
11
12 second anisotropy peak.^{13, 23} This merging, along with asymmetry in peak height and field
13
14 placement require us to distinguish between the anisotropy peak observed upon reducing the
15
16 field from saturation (henceforth $\pm H_{K1}$) and the peak observed upon increasing the field after
17
18 crossing through $H = 0$ ($\pm H_{K2}$) which is frequently the combination of the switching and
19
20 anisotropy peaks. These deviations can be attributed to the size distribution in the nanoparticles
21
22 and the dipolar interactions between the nanoparticles.²⁹ However, since $H_{K1} \neq H_{K2}$ due to the
23
24 merging of the switching peak with the H_{K2} , we exclusively use the $\pm H_{K1}$ peak to quantify the
25
26 anisotropy field, whereas we use the $\pm H_{K2}$ peak to make qualitative observations regarding the
27
28 switching behavior of the nanoparticle assembly. The right panel in figure 4 shows the evolution
29
30 of $\pm H_{K1}$ with temperature for the three samples. The anisotropy field value for the spherical
31
32 particles (Figure 4g) at 10 K (~ 64 mT) is found to be less than that of the dimers ~ 78 mT
33
34 (Figure 4h). Considering that the magnetic volume of the spherical particles and the dimers is the
35
36 same, the increase in anisotropy field in case of the dimers can be attributed to enhanced surface
37
38 anisotropy. This suggests that in case of the dimers, perhaps, the seed mediated growth of Fe_3O_4
39
40 on Au results in a different magnetic configuration of the surface spins with higher anisotropy as
41
42 compared to spherical Fe_3O_4 . Interestingly, the anisotropy field for the clusters at 10 K (~ 400
43
44 mT) is significantly higher than the dimers, which can be attributed to the complex morphology
45
46 and shape of each cluster particle. Similar to previous studies, as the temperature is increased, the
47
48 anisotropy field decreases for all three samples and vanishes above their respective blocking
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 temperatures.^{23, 32} Hence, the TS experiments allow us to conclusively infer that the Fe₃O₄
4
5 particles in the dimers and the clusters have higher surface anisotropy compared to spherical
6
7 Fe₃O₄. To this point, *the question that arises is: how does the seed mediated growth of Fe₃O₄ on*
8
9 *Au affect its surface magnetization?*
10
11

12
13 It is well known that there exists a slight lattice mismatch between the lattice parameter of Au
14
15 (4.08 Å) and Fe₃O₄ (8.4 Å) at the interface. The lattice mismatch can be estimated to be ~ 2.9%
16
17 which is significantly large to develop an interfacial stress. The development of strain due to
18
19 lattice compression or elongation is commonly observed in vertically aligned nanocomposite thin
20
21 films.³³ In an earlier study, we have reported the development of stress at the heterogeneous
22
23 interface in Au-Fe₃O₄ dimers.³⁴ The mechanical modeling analysis revealed that the development
24
25 of stress occurred due to different thermal expansion coefficients of Au and Fe₃O₄ at the
26
27 interface of Au-Fe₃O₄, and was of the order of 1 – 5 GPa. This further enhances the interfacial
28
29 stress as the temperature is lowered. It has also been reported that compacting Fe₃O₄
30
31 nanoparticles under external pressure (1 – 5 GPa) can result in the development of surface spin
32
33 disorder and hence replicate a core/shell magnetic structure.³⁵ In such a scenario, EB has been
34
35 observed in Fe₃O₄ nanoparticles up to 20 nm. We would like to point out that the magnitude of
36
37 external stress applied to the Fe₃O₄ nanoparticles of reference 35 is of the same order as that
38
39 generated across the Au-Fe₃O₄ interface of the dimers We hypothesize that as a consequence of
40
41 the interfacial stress, the Fe₃O₄ particles in the dimers develop surface spin disorder by way of
42
43 energy minimization. Perhaps, as a result of the interfacial stress, a spin glass layer may develop
44
45 at the interface which forms a part of the total disordered surface spin structure, and collectively
46
47 behaves as a surface spin glass. The disordered surface spins are highly anisotropic, which is
48
49 consistent with the rise in effective magnetic anisotropy of the dimers as seen in Figure 4. The
50
51
52
53
54
55
56
57
58
59
60

1
2
3 disordered surface spins undergo exchange coupling with the core moments resulting in the EB
4 effect in the dimers and the clusters. It is to be mentioned that the manifestation of the EB effect
5 in both intrinsically and externally strained systems is not uncommon. It has been shown in case
6 of Pt₃Fe single crystals that plastic deformations can lead to superlattice dislocations, thereby
7 inducing growth of FM domains within an AFM matrix, which couple magnetically to exhibit
8 EB effect.³⁶ In another study, the EB effect was found to diminish with the application of
9 external mechanical strain on FM/AFM heterostructures.³⁷

10
11
12
13
14
15
16
17
18
19
20 With regard to the present study, one can argue, that if EB in the dimers is solely due to the
21 development of interfacial stress induced surface spin disorder, then, EB should vanish if the
22 source of the interfacial stress were to be removed. To test this, we removed the interfacial stress
23 by chemically etching away the Au seed in the dimers, resulting in dented Fe₃O₄ etched particles
24 (Figure 1c). Figure 5a shows a magnified view of the ZFC and 1 T FC hysteresis loops for the
25 etched dimers taken at 2 K. The inset shows the complete 1T FC loop. We find that H_C of the
26 etched dimers for the ZFC loop (35 mT) is similar to the spherical Fe₃O₄ particles shown in
27 Figure 3a (39 mT). In the case of the etched dimers, field cooling actually reduced the H_C to 28
28 mT and resulted in an improvement in the remanent magnetization. We tested this result using
29 several different cooling fields and no EB was seen in fields as low as 0.1 T. Figure 5b shows
30 normalized ZFC hysteresis loops for the spherical, dimers and etched particles. Usually magnetic
31 nanoparticles with negligible surface anisotropy or surface spin canting exhibit a (i) low coercive
32 field, and (ii) quick approach to saturation. In case of the spheres and the etched dimers, we
33 observe both properties, however, the hysteresis loop for the dimers is found to exhibit a rather
34 slow approach to saturation. The non-saturating behavior of the dimers is consistent with the
35 idea of highly anisotropic disordered surface spins which resist aligning even at large magnetic
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 fields.³⁸ After etching, as the interfacial stress in the dimers is lost, the surface spin disorder
4
5 diminishes. Hence, the etched dimers attain saturation, similar to spherical Fe₃O₄. In fact, the
6
7 magnitude of the coercive fields for the etched dimers and the spherical Fe₃O₄ particles are
8
9 identical, and less compared to the dimers (inset of Figure 5b). It is to be mentioned that the
10
11 shape asymmetry in the etched dimers does not enhance disordering of spins in the surface layer
12
13 and lead to the consequent development of EB. This is in agreement with earlier experimental
14
15 results proving that surface or shape contributions to effective magnetic anisotropy are negligible
16
17 in spherical Fe₃O₄ nanoparticles down to 8 nm, giving a natural explanation for the absence of
18
19 EB in this system.²¹ The cartoon shown in Figure 5c summarizes the different scenarios
20
21 encountered in the Au-Fe₃O₄ composite system. The presence of significantly disordered surface
22
23 in the dimers and clusters is depicted by a darker shade.
24
25
26
27
28

29 To complement our experimental results, we have performed Monte Carlo (MC) simulations
30
31 of an atomistic model of Fe₃O₄ for Heisenberg spins similar to our studied samples. Monte Carlo
32
33 simulations using the standard Metropolis algorithm are based on Heisenberg classical spins
34
35 representing Fe ions placed on the nodes of the real crystal lattice of magnetite with the
36
37 following interaction Hamiltonian:
38
39

$$40 \quad \mathbf{H} / k_B = - \sum_{\langle i,j \rangle} J_{ij} (\vec{S}_i \cdot \vec{S}_j) - \sum_i \vec{h} \cdot \vec{S}_i + E_{\text{anis}}$$

41
42
43
44
45 which includes the exchange interactions (J_{ij}), the Zeeman energy with $h = \mu H / k_B$ (H is the
46
47 magnetic field and μ the magnetic moment of the magnetic ion), and the magnetocrystalline
48
49 anisotropy energy E_{anis} . Values for the J_{ij} between spins with tetrahedral and octahedral
50
51 coordination have been taken from the available literature.^{20, 39}
52
53
54
55
56
57
58
59
60

1
2
3 Fe ions with reduced coordination with respect to bulk are considered to be surface spins with
4 Néel type anisotropy and anisotropy constant K_S , while core spins have uniaxial anisotropy along
5 the field direction with anisotropy constant K_C . Therefore, E_{anis} has the form:
6
7
8
9

$$10 \quad E_{\text{anis}} = -k_S \sum_{i \in S} \sum_{j \in \text{nn}} (\vec{S}_i \cdot \hat{r}_{ij})^2 - k_C \sum_{i \in C} (\vec{S}_i \cdot \mathbf{n}_i)^2$$

11
12
13
14 where \hat{r}_{ij} is a unit vector joining spin i with its nearest neighbors j and \mathbf{n}_i is the anisotropy axis
15 of each crystallite. The value of the anisotropy constants, expressed in units of K/spin have been
16 taken as $K_C = 0.01$ and K_S varying in the range 0.01- 30. As for the particle geometries, the
17 dimer particle has been modeled has a sphere of radius $5.5a$ (' a ' is the unit cell size) truncated by
18 a sharp facet where the magnetite contacts the Au. The cluster-shaped particle is formed by four
19 overlapping spheres of radius $5a$ surrounding a spherical hole that stands for the central Au
20 component.
21
22
23
24
25
26
27
28
29
30
31

32 The simulated hysteresis loops after a FC process at $h_{FC} = 100$ K for the spherical-, cluster-, and
33 dimer- shaped nanoparticles are shown in the main panels of Fig. 6. In our simulations, we can
34 recreate the effect of interfacial stress and consequential disorder in the surface spins by
35 assigning Néel surface anisotropy with an increased value ($k_S = 30$) as compared to the core
36 spins which are assumed to have the same anisotropy as the bulk ($k_C = 0.01$).
37
38
39
40
41
42
43

44 The inclusion of increased surface anisotropy ($k_S = 30$, red circles in Figure 6 a, b) results in a
45 slower approach to saturation and high field irreversibility, along with the expected observation
46 of EB, which is practically absent for the case in which surface and core anisotropies are the
47 same, $k_S = k_C$ (blue squares in Figure 6 a,b). Moreover, the horizontal shift of the loops is
48 noticeably higher for the clusters than for the dimers, as also observed experimentally, which
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 demonstrates that the EB can be tuned by the increase of the contact interfaces between Au and
4
5 the magnetic NPs.
6
7

8 The case for the etched dimers can be recreated by assigning the same anisotropy values to the
9
10 surface and core moments. We observe that for Fe_3O_4 in the cluster and etched dimer geometries,
11
12 with surface anisotropy equal to the core value ($k_s = k_c = 0.01$), neither loops exhibit horizontal
13
14 shifts after a FC (blue squares in Figure 6 a, b). The absence of EB in the asymmetric etched
15
16 dimers (dashed lines in Figure 6b) is consistent with the experimental data shown in Figure 5a.
17
18

19 Note that the hysteresis loops for $k_s = 0.01$ have more squared shape than those for $K_s = 30$,
20
21 which display high field linear susceptibility, irreversibility and lack of saturation both for
22
23 dimers and clusters, as also observed experimentally. This last point can be ascribed to the
24
25 contribution of surface spins (green squares in the inset of Figure 6b) that presents an hysteresis
26
27 loop typical of a frustrated material and dominates the magnetization reversal of the whole
28
29 particle. However, core spins (yellow circles in the inset of Figure 6b), reverse in a more
30
31 coherent fashion although influenced also by the ones at the surface. The higher value of the
32
33 remanent magnetization for the dimers than for the clusters is also in agreement with the
34
35 experimental results. The high degree of disorder at the particle surface is corroborated by the
36
37 snapshots of the spin configurations displayed in Figure 6(c-f), where one can notice that, even
38
39 after the high FC process (Figures 6c and 6e) only the core spins (drawn in lighter colors) are
40
41 aligned along the anisotropy axis while surface spins remain highly disordered even at low
42
43 temperatures. Snapshots taken near the coercive field (Figures 6d and 6f) demonstrate a more
44
45 coherent reversal of core spins that are dragged by the disordered shell of surface spins (drawn in
46
47 darker tones).
48
49
50
51
52
53
54
55
56
57
58
59
60

CONCLUSIONS

We have performed a systematic study to understand the origin of EB in 8 nm Au – 9 nm Fe₃O₄ nanocomposites with two configurations, namely dimers and clusters. The dimers and the clusters exhibit enhanced magnetic anisotropy compared to 9 nm spherical particles, which, has been directly probed by transverse susceptibility measurements. Exchange bias effect is observed in the dimers and the clusters, as opposed to the spherical, and the etched dimer particles. The increase in effective magnetic anisotropy and the development of EB in the dimers and clusters are attributed to the presence of highly disordered surface spins which foster as a result of stress (order of ~ few GPa) across the Au-Fe₃O₄ interface. We also show that EB vanishes with the removal of the interfacial stress in case of the etched dimers. Our experimental results are well supported by atomistic Monte-Carlo simulation studies which provide conclusive evidence of the manifestation of EB solely due to highly anisotropic disordered surface spins.

Our study reveals a new path to deliberately engineer EB into nanoparticles with high magnetization, by actuating a local stress in its environment in the form of a noble metal nanoparticle. Consequently, the interfacial stress, and hence the EB field can be tuned by varying the size of both the Au and Fe₃O₄ particles. The capability to induce controlled EB effect in Fe₃O₄ up to 20 nm large particles opens the possibility of various applications involving EB which, were otherwise limited by low magnetization of smaller nanoparticles. Furthermore, depending on the size of the magnetic particle in such nanocomposites, one can gain control over the onset temperature of EB as well.

FIGURES

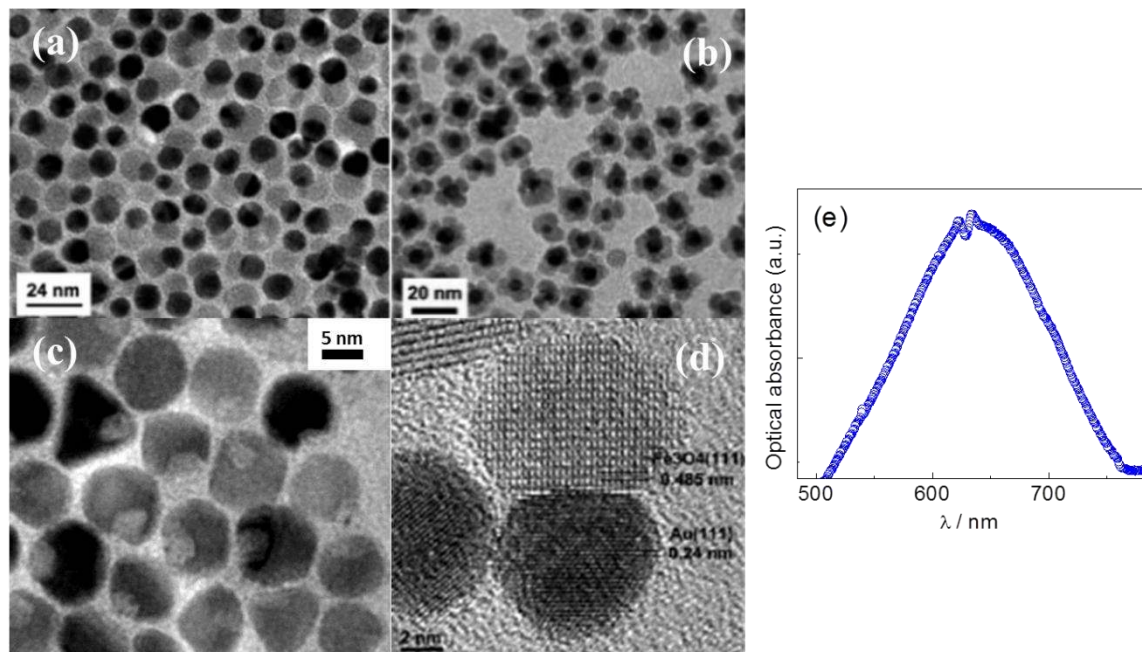


Figure 1. TEM images of (a) Au-Fe₃O₄ dimers⁵, (b) Au-Fe₃O₄ clusters⁵, (c) dimers after Au etching, (d) shows the HRTEM image of an Au-Fe₃O₄ dimer showing single crystalline Au and Fe₃O₄ grown epitaxially⁵, and (e) Surface Plasmon resonance absorption spectra of the Au-Fe₃O₄ dimer nanoparticles.

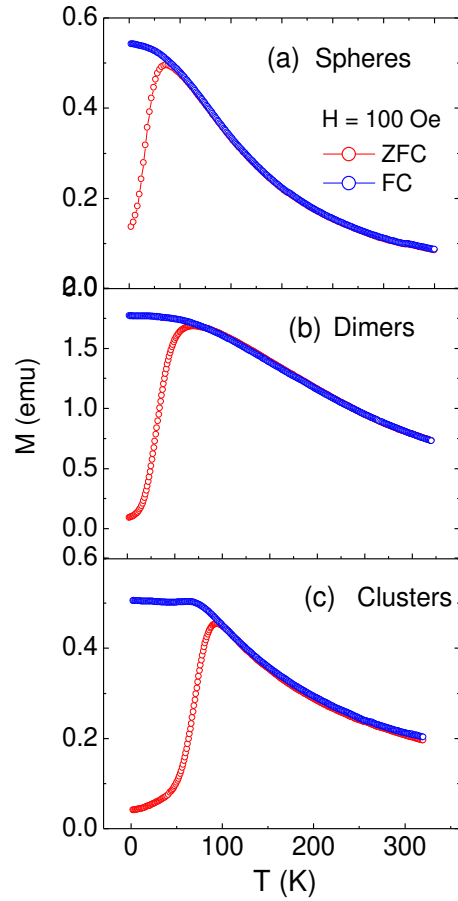


Figure 2. Temperature dependence of magnetization in the zero-field cooled and field cooled protocols for (a) spheres, (b) dimers, and (c) clusters.

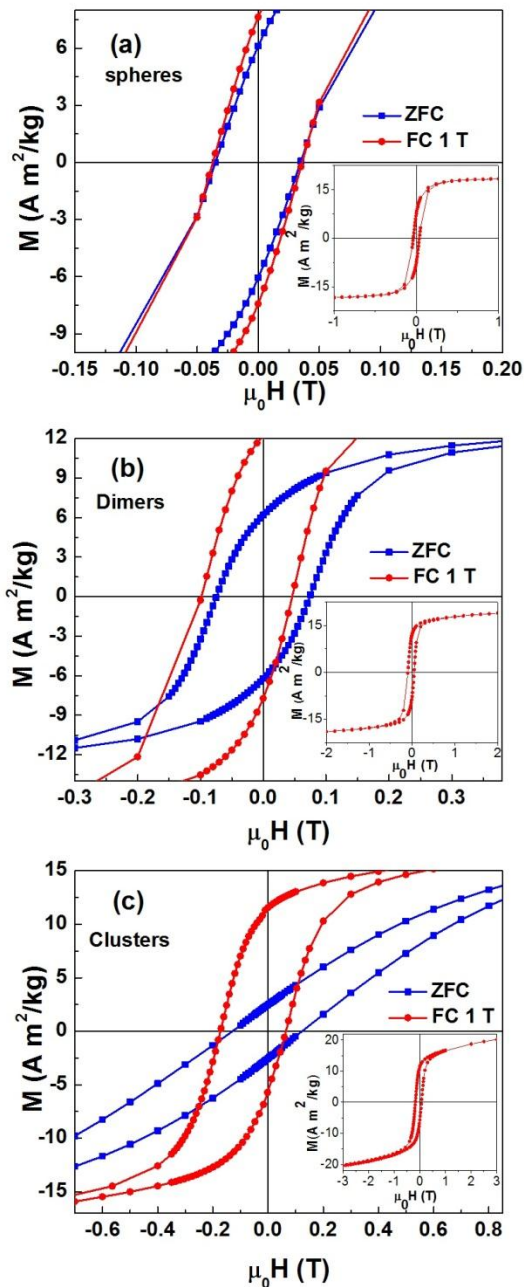


Figure 3. Zero field cooled (blue squares) and 1 T field cooled (red circles) magnetization versus field (M-H) curves taken at 2 K for (a) Fe_3O_4 spheres, (b) Au- Fe_3O_4 dimers, and (c) Au- Fe_3O_4 clusters. Insets of (a, b, c) show complete FC hysteresis loops for respective samples.

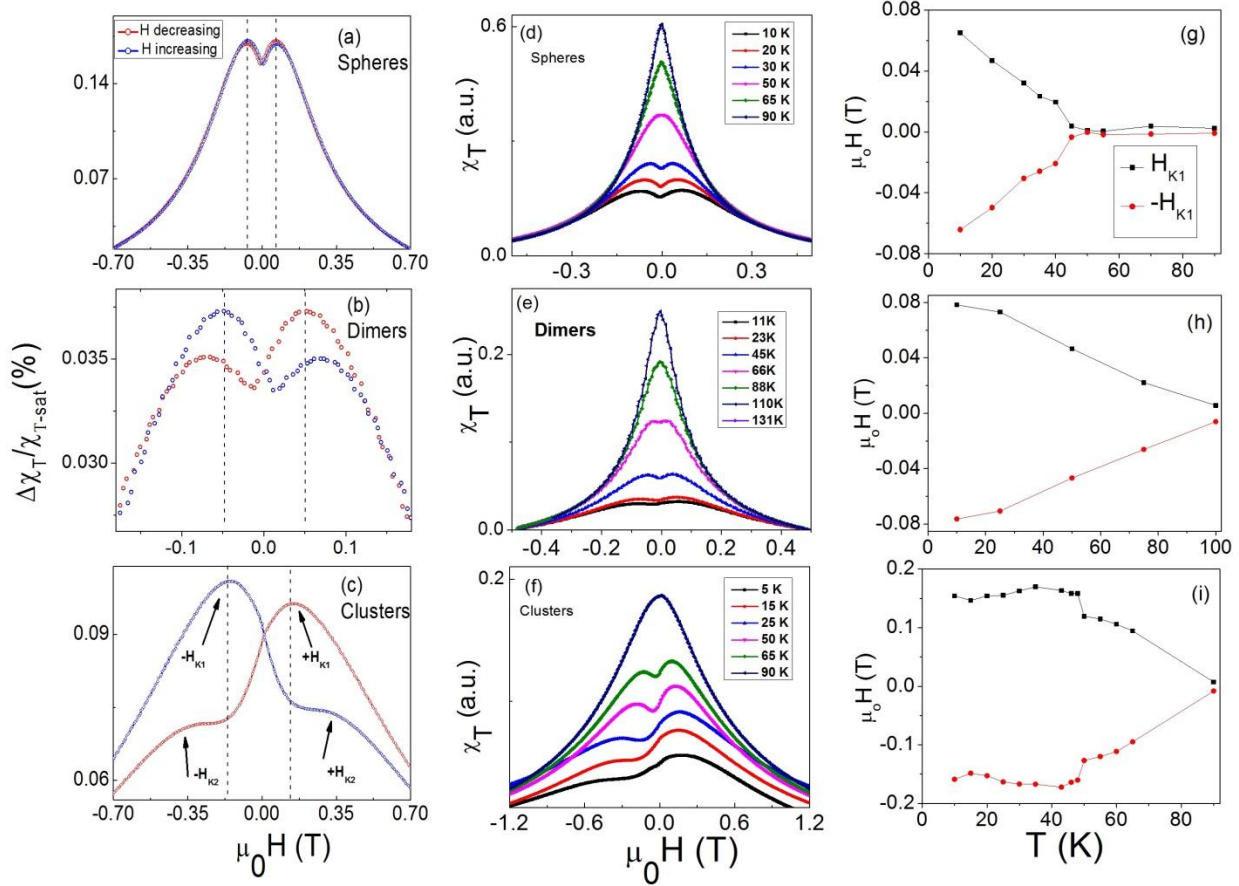


Figure 4. Representative bipolar TS curves measured at 20 K for (a) spheres, (b) dimers, and (c) clusters. Selected unipolar TS curves to illustrate the evolution of anisotropy peaks with temperature for (d) spheres, (e) dimers, and (f) clusters; Evolution of first anisotropy field with temperature for (g) spheres, (h) dimers and (i) clusters.

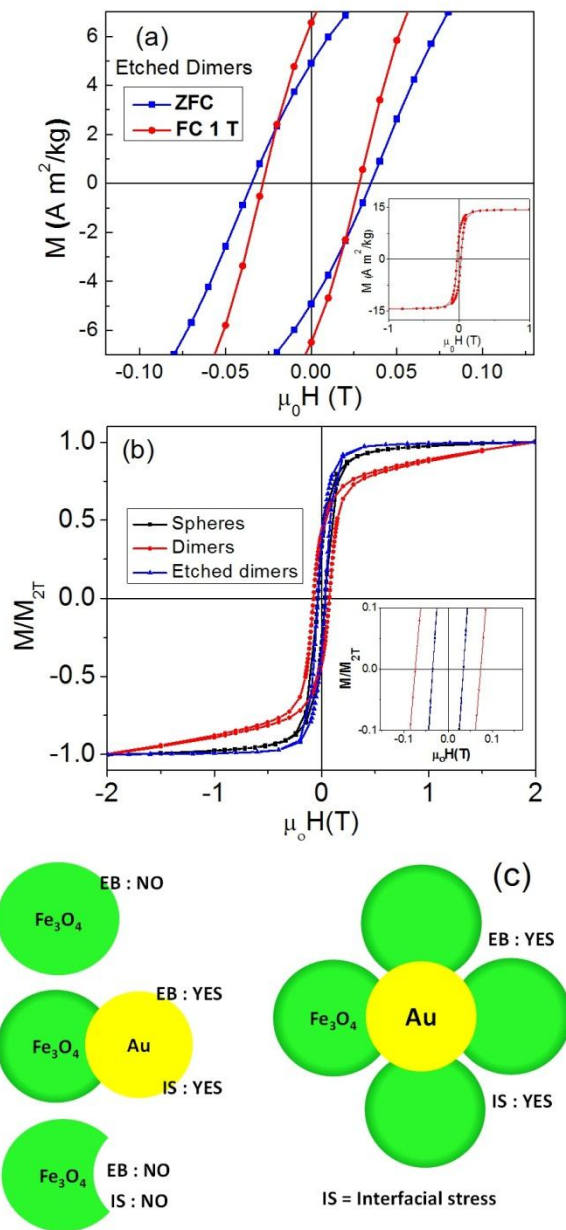


Figure 5. (a) Zero field cooled (blue squares) and 1 T field cooled (red circles) magnetization versus field (M-H) curves taken at 2 K for etched dimers; (b) comparison of zero-field cooled hysteresis curves for spheres, dimers, and etched dimers; (c) Schematic representation of the Au-Fe₃O₄ morphologies studied. Inset of (a) shows a complete 1 T field cooled loop, and (b) shows a magnified view of hysteresis curves at low field.

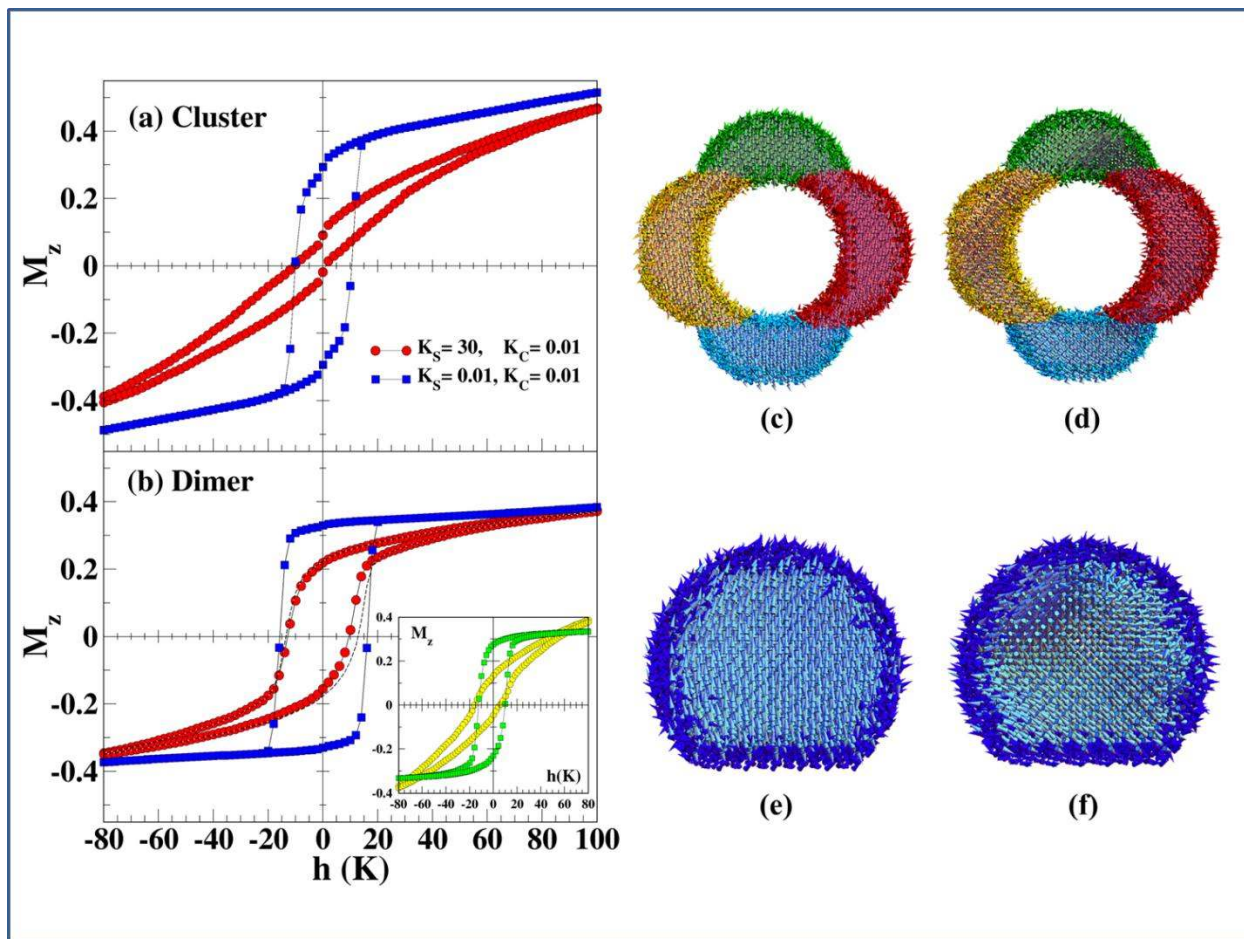


Figure 6. Low temperature hysteresis loops simulated after a cooling in a magnetic field $h_{FC} = 100$ K as computed by MC simulations of individual nanoparticles with cluster (a) and dimer (b) geometries. The non-magnetic metal is simulated as a hole in the middle for the cluster geometry and a sharp facet for the cluster. Panels (a) and (b) show hysteresis loops of a particle with cluster and dimer geometry, respectively, for two different values of the surface anisotropy constant: $k_s = 0.01$ (blue squares) equal to the core value $k_c = 0.01$, and increased surface anisotropy $k_s = 30$ (red circles). The dashed lines in (b) stand for a spherical particle of the same size as the dimer. The Inset displays the contribution of the surface (yellow circles) and core (green squares) spins of a dimer particle to the hysteresis loop for $k_s = 30$. Snapshots of the spin configurations for cluster (c and d panels) and dimer (e and f panels) particles for $k_s = 30$ (red

1
2
3 circles) obtained at the end of the FC process (c and e panels) and at the coercive field point of
4
5 the decreasing field branch (d and f panels) of the hysteresis loops displayed in Figure 6 (a) and
6
7 (b). For clarity, only a slice of width $4a$ along the applied field direction and through the central
8
9 plane of the particles is shown. Surface spins have darker colors and core spins have been
10
11 colored lighter.
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 ASSOCIATED CONTENT
45
6 AUTHOR INFORMATION
78
9 **Corresponding Author**10
11 *sharihar@usf.edu
1213
14
15 **Author Contributions**
1617 N.F.H., S. Srinath, H.S., and S. Sun jointly conceived the study. C. W., Y.L. and N.F.H.
18 synthesized the nanoparticles. S.C., N.F.H., S. Srinath, and M.H.P. performed magnetic
19 measurements and data analysis. M.A.G. performed optical measurements. Ò.I. performed
20 magnetic simulations. S.C., N.F.H., M.H.P., Ò. I., and H.S. wrote the paper.
21
22
23
24
25
2627
28 ACKNOWLEDGMENT
2930
31 Work at USF supported by DOE through grant number DE-FG02-07ER46438. HS also
32 acknowledges support from the Center for Integrated Functional Materials through grant
33 USAMRMC-07355004. Work done at Brown was supported through NSF DMR 0606264. Ò.I.
34 acknowledges funding by the Spanish MINECO (projects MAT2009-0866 and MAT2012-
35 33037), Catalan DURSI (project 2009SGR856), European Union FEDER funds (Una manera de
36 hacer Europa) and CESCA and CEPBA under coordination of C4 for computer facilities.
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

REFERENCES

1. Cortie, M. B.; McDonagh, A. M. Synthesis and Optical Properties of Hybrid and Alloy Plasmonic Nanoparticles. *Chemical Reviews* **2011**, 111, 3713-3735.
2. Armelles, G.; Cebollada, A.; Garcia-Martin, A.; Garcia-Martin, J. M.; Gonzalez, M. U.; Gonzalez-Diaz, J. B.; Ferreiro-Vila, E.; Torrado, J. F. Magnetoplasmonic nanostructures: systems supporting both plasmonic and magnetic properties. *Journal of Optics a-Pure and Applied Optics* **2009**, 11, 114023.
3. Leung, K. C.-F.; Xuan, S.; Zhu, X.; Wang, D.; Chak, C.-P.; Lee, S.-F.; Ho, W. K. W.; Chung, B. C. T. Gold and iron oxide hybrid nanocomposite materials. *Chemical Society Reviews* **2012**, 41, 1911-1928.
4. Pineider, F.; Fernandez, C. d. J.; Videtta, V.; Carlino, E.; al Hourani, A.; Wilhelm, F.; Rogalev, A.; Cozzoli, P. D.; Ghigna, P.; Sangregorio, C. Spin-Polarization Transfer in Colloidal Magnetic-Plasmonic Au/Iron Oxide Hetero-nanocrystals. *Acs Nano* **2013**, 7, 857-866.
5. Yu, H.; Chen, M.; Rice, P. M.; Wang, S. X.; White, R. L.; Sun, S. H. Dumbbell-like bifunctional Au-Fe₃O₄ nanoparticles. *Nano Letters* **2005**, 5, 379-382.
6. Wang, Z. F.; Shen, B.; Zou, A. H.; He, N. Y. Synthesis of Pd/Fe₃O₄ nanoparticle-based catalyst for the cross-coupling of acrylic acid with iodobenzene. *Chemical Engineering Journal* **2005**, 113, 27-34.
7. Xie, J.; Zhang, F.; Aronova, M.; Zhu, L.; Lin, X.; Quan, Q.; Liu, G.; Zhang, G.; Choi, K.-Y.; Kim, K.; Sun, X.; Lee, S.; Sun, S.; Leapman, R.; Chen, X. Manipulating the Power of an Additional Phase: A Flower-like Au-Fe₃O₄ Optical Nanosensor for Imaging Protease Expressions In vivo. *Acs Nano* **2011**, 5, 3043-3051.
8. Frey, N. A.; Srinath, S.; Srikanth, H.; Wang, C.; Sun, S. Static and dynamic magnetic properties of composite Au-Fe₃O₄ nanoparticles. *Ieee Transactions on Magnetics* **2007**, 43, 3094-3096.
9. Lee, Y.; Angel Garcia, M.; Huls, N. A. F.; Sun, S. Synthetic Tuning of the Catalytic Properties of Au-Fe₃O₄ Nanoparticles. *Angewandte Chemie-International Edition* **2010**, 49, 1271-1274.
10. Frey, N. A.; Phan, M. H.; Srikanth, H.; Srinath, S.; Wang, C.; Sun, S. Interparticle interactions in coupled Au-Fe₃O₄ nanoparticles. *Journal of Applied Physics* **2009**, 105, 07B502.
11. Iglesias, O.; Labarta, A.; Batlle, X. Exchange bias phenomenology and models of core/shell nanoparticles. *Journal of Nanoscience and Nanotechnology* **2008**, 8, 2761-2780.
12. Nogues, J.; Schuller, I. K. Exchange bias. *Journal of Magnetism and Magnetic Materials* **1999**, 192, 203-232.
13. Chandra, S.; Khurshid, H.; Phan, M. H.; Srikanth, H. Asymmetric hysteresis loops and its dependence on magnetic anisotropy in exchange biased Co/CoO core-shell nanoparticles. *Appl. Phys. Lett.* **2012**, 101, 232405.
14. Zheng, R. K.; Liu, H.; Wang, Y.; Zhang, X. X. Cr₂O₃ surface layer and exchange bias in an acicular CrO₂ particle. *Applied Physics Letters* **2004**, 84, 702-704.
15. Khurshid, H.; Chandra, S.; Li, W.; Phan, M. H.; Hadjipanayis, G. C.; Mukherjee, P.; Srikanth, H. Synthesis and magnetic properties of core/shell FeO/Fe₃O₄ nano-octopods. *Journal of Applied Physics* **2013**, 113, 17B508.
16. Chandra, S.; Khurshid, H.; Li, W.; Hadjipanayis, G. C.; Phan, M. H.; Srikanth, H. Spin dynamics and criteria for onset of exchange bias in superspin glass Fe/gamma-Fe₂O₃ core-shell nanoparticles. *Physical Review B* **2012**, 86, 014426.

17. Kodama, R. H.; Berkowitz, A. E.; McNiff, E. J.; Foner, S. Surface spin disorder in NiFe₂O₄ nanoparticles. *Physical Review Letters* **1996**, *77*, 394-397.
18. Peddis, D.; Cannas, C.; Piccaluga, G.; Agostinelli, E.; Fiorani, D. Spin-glass-like freezing and enhanced magnetization in ultra-small CoFe₂O₄ nanoparticles. *Nanotechnology* **2010**, *21*, 125705.
19. Chandra, S.; Biswas, A.; Datta, S.; Ghosh, B.; Raychaudhuri, A. K.; Srikanth, H. Inverse magnetocaloric and exchange bias effects in single crystalline La_{0.5}Sr_{0.5}MnO₃ nanowires. *Nanotechnology* **2013**, *24*, 505712.
20. Mazo-Zuluaga, J.; Restrepo, J.; Munoz, F.; Mejia-Lopez, J. Surface anisotropy, hysteretic, and magnetic properties of magnetite nanoparticles: A simulation study. *Journal of Applied Physics* **2009**, *105*, 123907.
21. Lima, E.; Brandl, A. L.; Arelaro, A. D.; Goya, G. F. Spin disorder and magnetic anisotropy in Fe₃O₄ nanoparticles. *Journal of Applied Physics* **2006**, *99*, 083908.
22. Pal, S.; Chandra, S.; Phan, M.-H.; Mukherjee, P.; Srikanth, H. Carbon nanostraws: nanotubes filled with superparamagnetic nanoparticles. *Nanotechnology* **2009**, *20*, 485604.
23. Poddar, P.; Morales, M. B.; Frey, N. A.; Morrison, S. A.; Carpenter, E. E.; Srikanth, H. Transverse susceptibility study of the effect of varying dipolar interactions on anisotropy peaks in a three-dimensional assembly of soft ferrite nanoparticles. *Journal of Applied Physics* **2008**, *104*, 063901.
24. Bodker, F.; Morup, S.; Linderoth, S. SURFACE EFFECTS IN METALLIC IRON NANOPARTICLES. *Physical Review Letters* **1994**, *72*, 282-285.
25. Yang, T. Z.; Shen, C. M.; Li, Z.; Zhang, H. R.; Xiao, C. W.; Chen, S. T.; Xu, Z. C.; Shi, D. X.; Li, J. Q.; Gao, H. J. Highly ordered self-assembly with large area of Fe₃O₄ nanoparticles and the magnetic properties. *Journal of Physical Chemistry B* **2005**, *109*, 23233-23236.
26. Cabot, A.; Alivisatos, A. P.; Puentes, V. F.; Balcels, L.; Iglesias, O.; Labarta, A. Magnetic domains and surface effects in hollow maghemite nanoparticles. *Physical Review B* **2009**, *79*, 094419.
27. Khurshid, H.; Li, W.; Phan, M.-H.; Mukherjee, P.; Hadjipanayis, G. C.; Srikanth, H. Surface spin disorder and exchange-bias in hollow maghemite nanoparticles. *Appl. Phys. Lett.* **2012**, *101*, 022403.
28. Iglesias, O.; Battle, X.; Labarta, A. Exchange bias and asymmetric hysteresis loops from a microscopic model of core/shell nanoparticles. *Journal of Magnetism and Magnetic Materials* **2007**, *316*, 140-142.
29. Poddar, P.; Wilson, J. L.; Srikanth, H.; Farrell, D. F.; Majetich, S. A. In-plane and out-of-plane transverse susceptibility in close-packed arrays of monodisperse Fe nanoparticles. *Physical Review B* **2003**, *68*, 214409.
30. Srikanth, H.; Wiggins, J.; Rees, H. Radio-frequency impedance measurements using a tunnel-diode oscillator technique. *Review of Scientific Instruments* **1999**, *70*, 3097-3101.
31. Aharoni, A.; Frei, E. H.; Shtrikman, S.; Treves, D. Bull. Res. Counc. Isr., Sect.: **1957**; Vol. F 6A, p 215.
32. Chandra, S.; Figueroa, A. I.; Ghosh, B.; Phan, M. H.; Srikanth, H.; Raychaudhuri, A. K. Phase coexistence and magnetic anisotropy in polycrystalline and nanocrystalline LaMnO₃+delta. *Journal of Applied Physics* **2011**, *109*, 07D720.
33. Chen, A. P.; Bi, Z. X.; Jia, Q. X.; MacManus-Driscoll, J. L.; Wang, H. Y. Microstructure, vertical strain control and tunable functionalities in self-assembled, vertically aligned nanocomposite thin films. *Acta Mater* **2013**, *61*, 2783-2792.

- 1
2
3 34. Wang, C.; Wei, Y.; Jiang, H.; Sun, S. Tug-of-War in Nanoparticles: Competitive Growth
4 of Au on Au-Fe₃O₄ Nanoparticles. *Nano Letters* **2009**, 9, 4544-4547.
5
6 35. Wang, H.; Zhu, T.; Zhao, K.; Wang, W. N.; Wang, C. S.; Wang, Y. J.; Zhan, W. S.
7 Surface spin glass and exchange bias in Fe₃O₄ nanoparticles compacted under high pressure.
8 *Physical Review B* **2004**, 70, 092409.
9
10 36. Kobayashi, S.; Takahashi, S.; Kamada, Y.; Kikuchi, H. Strain-Induced Exchange Bias
11 Effects in Chemically Ordered Pt₃Fe Single Crystal. *Ieee Transactions on Magnetism* **2008**, 44,
12 4225-4228.
13 37. Zhang, X. S.; Zhan, Q. F.; Dai, G. H.; Liu, Y. W.; Zuo, Z. H.; Yang, H. L.; Chen, B.; Li,
14 R. W. Effect of mechanical strain on magnetic properties of flexible exchange biased FeGa/IrMn
15 heterostructures. *Applied Physics Letters* **2013**, 102, 022412.
16 38. Shendruk, T. N.; Desautels, R. D.; Southern, B. W.; van Lierop, J. The effect of surface
17 spin disorder on the magnetism of gamma-Fe₂O₃ nanoparticle dispersions. *Nanotechnology*
18 **2007**, 18, 455704.
19 39. Iglesias, O.; Labarta, A. Finite-size and surface effects in maghemite nanoparticles:
20 Monte Carlo simulations. *Physical Review B* **2001**, 63, 184416.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60