Selective Magnetic Evolution of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ Nanoplates

Hyon-Min Song, Jeffrey I. Zink, and Niveen M Khashab

J. Phys. Chem. C, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcc.5b01938 • Publication Date (Web): 27 Apr 2015

Downloaded from <http://pubs.acs.org> on May 3, 2015

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications
High quality. High impact.

The Journal of Physical Chemistry C is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036
Published by American Chemical Society. Copyright © American Chemical Society.
However, no copyright claim is made to original U.S. Government works, or works
produced by employees of any Commonwealth realm Crown government in the course
of their duties.

Selective Magnetic Evolution of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ Nanoplates

Hyon-Min Song,^{†,‡,§,} Jeffrey I. Zink,[‡] and Niveen M. Khashab^{§,*}*

[†]Department of Chemistry, Dong-A University, Busan 604-714, South Korea

[‡]Department of Chemistry and Biochemistry, University of California, Los Angeles, California
90095-1569

[§]Division of Physical Sciences and Engineering, and Center for Advanced Membranes and
Porous Materials (AMPM), 4700 King Abdullah University of Science and Technology, Thuwal
23955-6900, Kingdom of Saudi Arabia

ABSTRACT Iron-manganese oxide ($\text{Mn}_x\text{Fe}_{1-x}\text{O}$) nanoplates were prepared by thermal decomposition method. Irregular development of crystalline phases was observed with the increase of annealing temperature. Magnetic properties are in accordance with their respective crystalline phases, and the selective magnetic evolution from their rich magnetism of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ and MnFe_2O_4 is achieved by controlling the annealing conditions. Rock-salt structure of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ (space group $Fm-3m$) is observed in as-synthesized nanoplates, while MnFe_2O_4 and $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ with significant magnetic interactions between them are observed at 380 °C. In nanoplates annealed at 450 °C, soft ferrites of $\text{Mn}_{0.48}\text{Fe}_{2.52}\text{O}_4$ with $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ are observed. It is assumed that the differential and early development of crystalline phase of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$, and the

1
2
3 inhomogeneous cation mixing between Mn and Fe cause this rather extraordinary magnetic
4 development. In particular, the prone nature of divalent metal oxides to cation vacancy and the
5 prolonged annealing time of 15 hours which enables ordering are also thought to contribute to
6 these irregularities.
7
8
9
10

11 Introduction

12
13
14 Creation of anisotropy, hence the increase of coercivity is an important way of diversifying the
15 utility of soft ferrites.¹ The decrease of saturation magnetization follows, but the compensation is
16 that the increased coercivity can be used for many applications from biomedical to magnetic
17 storage technology.²⁻⁴ One of the explored methods is the hybridization of soft ferrites with hard
18 magnets,⁵ for example, hard ferrite magnet CoFe_2O_4 as cores with MnO shell.⁶ This method in
19 some materials requires additional annealing step to obtain desired coercivity and magnetization,
20 as seen in tetrahedral FePt from as-synthesized cubic phase. The other method of enhancing the
21 utility of soft ferrites is the hybridization with other metal oxides, which are mostly
22 antiferromagnetic (AFM) and create exchange bias when coupled with soft ferrites.⁷⁻⁹
23 Manganese oxides are one of those AFM materials for the hybridization with ferromagnetic
24 (FM) materials, for example, as outer shells of FM cores.¹⁰ They create exchange bias by the
25 interaction with FM, such as core-shell $\text{MnO@Mn}_3\text{O}_4$,¹¹ and $\text{Mn}_2\text{O}_3\text{@Mn}_3\text{O}_4$,¹² or equally
26 importantly they create intrinsic exchange bias in perovskite manganites such as
27 $\text{La}_{0.25}\text{Ca}_{0.75}\text{MnO}_3$,¹³ $\text{Y}_{0.2}\text{Ca}_{0.8}\text{MnO}_3$,¹⁴ and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.¹⁵ The versatility of manganese oxides
28 stems from their easy synthesis, their tendency to make ternary metal oxides, and their diverse
29 magnetism from FM to AFM depending on the stoichiometry.
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 With such diverse magnetism, selective magnetic development at certain condition will be an
55 interesting study, as magnetization of metal oxides is always associated with their electrical
56
57
58
59
60

properties. If that magnetism is governed by the hybrid between AFM and FM, enhanced magnetic properties are achievable by AFM-FM interaction. First-row divalent transition metal oxides are well-known AFM materials. With similar ionic radius, and based on the radius ratio rule, they are categorized into NaCl-type rock salt structure. Most notable are MnO and FeO. MnO has been utilized in many different areas from chemical sensor to electrode materials.¹⁶⁻¹⁸ MnO has also been studied for energy conversion, such as an anode material for Li-ion batteries,¹⁹⁻²¹ and even as the commercial Li-MnO batteries. FeO, however, is not broadly used primarily due to its metastable structure. Non-stoichiometry is another feature, as it is vulnerable to the oxidation and very rarely exists as FeO at room temperature. Despite these limitations, nanosize FeO with partial oxidation has been synthesized as various shapes.²²⁻²⁵ In nanosize, there is a deviation from equilibrium, and it is thought that this deviation is well agreeable with the off-stoichiometric nature of FeO.

In this study, iron-manganese oxide ($\text{Mn}_x\text{Fe}_{1-x}\text{O}$) nanoplates (NPs) were prepared in one step, and their magnetism was studied with increasing annealing temperature. Several shapes of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ nanoparticles were prepared by thermal decomposition method, such as nanospheres,²⁶ concave shape nanoparticles,²⁷ nanocubes,^{28,29} and hexagonal shape nanoparticles.³⁰ The advantage of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ is its resistance to oxidation in air compared to MnO and FeO, which makes it a good candidate for magnetic contrast agent.²⁶ Plate shape $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ nanoparticles have not been synthesized, and experimental conditions are modified as 2-dimensional (2D) plate shape is controlled by MnO, and the magnetic activity is enhanced by hybridizing with FeO. Rock salt structure of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ was observed in as-synthesized NPs, whereas nearly stoichiometric MnFe_2O_4 appeared at 380 °C with $\text{Mn}_x\text{Fe}_{1-x}\text{O}$. At 450 °C, $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ with a minor contribution from spinel ferrites was observed. Magnetic behaviour follows this

progress with dominant AFM at 320 °C and 450 °C, and major FM at 380 °C. During this magnetic progress, magnetic phenomena such as exchange bias under zero-field-cooled (ZFC) measurement, multiple transition temperatures, and spin glass-like states were observed.

Experimental Section

Analytical grades of chemicals and solvents were used. Powder X-ray diffraction (XRD) measurements were performed with a Pananalytical X'Pert Pro X-ray powder diffractometer using CuK α radiation (40 V, 40 mA, $\lambda = 1.54056 \text{ \AA}$) in a θ - θ mode from 25 to 100 degrees (2θ). Transmission electron microscopy (TEM) images were obtained with either JEOL JEM 2010F operating at 200 kV, or FEI Titan 80-300 kV S/TEM using field emission gun operating at 300 kV. Mn $_x$ Fe $_{1-x}$ O NPs were dispersed in 0.1 mL of hexane and sonicated for 30 seconds before dropcasting onto carbon-coated Cu grids. Scanning electron microscopy (SEM) images were taken with the FEI NovaNano SEM 630 FESEM at an operating voltage of 2–5 kV. SEM samples were prepared by casting aqueous dispersions of samples on the aluminum plate of 1.5 cm diameter and were dried under vacuum for 1 hour before being loaded into the SEM chamber. Magnetic properties were measured by superconducting quantum interference device (SQUID, Quantum Design).

Synthesis of Mn $_x$ Fe $_{1-x}$ O NPs Under the standard Schlenk line, mixture of Fe(acac) $_3$ (acac: acetylacetonate, 0.99 g, 2.8 mmol), Mn(acac) $_2$ (1.2 g, 4.7 mmol), oleylamine (1.5 mL, 4.6 mmol), oleic acid (1.5 mL, 4.8 mmol), and 1,2-hexadecanediol (1.3 g, 5.0 mmol) was stirred with octyl ether (8.0 mL) in a three-neck round-bottomed flask (25 mL). Reaction temperature was increased to 200 °C under N $_2$ atmosphere, and the mixture was stirred for 2.5 hours at 200 °C. Temperature was further increased to 320 °C, and stirring continued for 0.5 hours. After

cooling down, the products were collected by adding 8 mL of hexane and 20 mL of ethanol, followed by centrifugation at 4000 rpm for 5 minutes. Washing and precipitation steps were repeated to obtain $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ NPs. As-synthesized $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ NPs were dried under vacuum for 1 hour before annealing. Thermal annealing was conducted under N_2 atmosphere. The rate of temperature increase was $5\text{ }^\circ\text{C}/\text{min}$, and the target temperatures were $380\text{ }^\circ\text{C}$, or $450\text{ }^\circ\text{C}$. After reaching the target temperature, annealing lasted for 15 hours.

Results and Discussion

As other $3d$ divalent metal oxides such as TiO , VO , ZnO , CoO , and NiO , both FeO and MnO adopt a rock salt structure ($Fm-3m$) with a cell parameter of $a = 4.326\text{ \AA}$ for FeO ,³¹ and $a = 4.446\text{ \AA}$ for MnO .³²⁻³⁴ Most of these metal oxides are AFM materials, as superexchange interaction exists via oxygen anions situated between metal cations and the spins align antiferromagnetically in an alternate fashion along the $\langle 111 \rangle$ directions.^{35,36} Another common feature is that they are liable to be nonstoichiometric due to the presence of excessive oxygen atoms, and the metal cations are susceptible to being vacant.^{37,38} Therefore, other species of metal cations with similar size can occupy those defect sites. MnO nanoparticles have been synthesized by solvothermal decomposition of manganese cupferronate with a stainless autoclave at $325\text{ }^\circ\text{C}$ in toluene,³⁹ or thermal decomposition of manganese acetate in the presence of triocylamine and oleic acid.⁴⁰ When the molar ratio between $\text{Fe}(\text{acac})_3$ and $\text{Mn}(\text{acac})_2$ is 1:1.7, plate-shape $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ nanoparticles were obtained, which were identified in TEM (Figures 1a,1b,1d) and SEM (Figure 2) images. On TEM grids, 2D plates are shown perpendicular to the electron beam (Figure 1a), or parallel to the beam, where partial self-assembly is observed (Figure 1b). In the high resolution TEM (HRTEM) images, $\{100\}$ planes were identified from rock-salt face-centered-

cubic (fcc) structure (Figures 1e,1f). This NaCl-type fcc structure of as-synthesized NPs is also observed in the selected area electron diffraction (SAED) pattern (Figure 1c). In the energy-dispersive X-ray spectroscopy (EDX, Figure 2d) of as-synthesized NPs, Mn K_{α} -edge at 5.890 keV and Fe K_{α} -edge at 6.400 keV were observed with a molar ratio of 0.55 to 0.45 (Mn : Fe). Similar plate shape nanoparticles of single phase MnO were prepared by reacting manganese acetate in oleylamine at 200 °C.⁴¹ Mn(OH)₂ plates were also prepared by solvothermal autoclave method at 180 °C. These plates are used as precursors for the multistep synthesis of MnO@C core-shell NPs.⁴² In another study, Fe₃O₄/MnO₂ plates were prepared in one step by hydrothermal method at 90 °C, but the phase of MnO₂ is amorphous and thus limits their utilities.¹⁰ Synthetic method of MnO plates⁴¹ was modified by conducting the reaction for 2.5 hours rather than 15 minutes at 200 °C.⁴¹ The formation of plate-shape Mn_xFe_{1-x}O is contributed from MnO during this prolonged reaction at 200 °C (Scheme 1).

Energy-filtered TEM (EFTEM) images of as-synthesized Mn_xFe_{1-x}O NPs prove the distribution of Fe and Mn atoms in NPs. Zero-loss EFTEM image is the image obtained from the atoms which do not lose their kinetic energies during the pass of electron beam through the sample (Figure 3a). Green indicates manganese (Figure 3b), and red indicates iron (Figure 3c), while merged image displays the distribution of two atoms (Figure 3d). For acquiring Mn signals, Mn L_{2,3}-edge was used and for acquiring Fe signals, Fe L_{2,3}-edge was used. Inhomogeneous distribution of Mn and Fe was observed in as-synthesized NPs, while the degree of this localization is complicated to decide. There is a study about the phase separation of Mn and Fe at high temperature in a sol-gel synthesis of manganese ferrite.⁴³ Within the silica matrix, Mn and Fe separate from each other and form noncrystalline structure at 450 °C, while the desirable MnFe₂O₄ phase was observed at 750 °C.⁴³

Crystallinity and phase of as-synthesized and annealed NPs were examined by XRD. As-synthesized NPs maintain rock-salt structure ($Fm-3m$) with a cell parameter of $a = 4.380 \text{ \AA}$ (Figure 4a).³² Detailed examination by Rietveld refinement reveals that they exist as $\text{Mn}_{0.482}\text{Fe}_{0.508}\text{O}$ (Figure 4c) with a slight cation vacancy. Generally, $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ has a tendency to be non-stoichiometric, as neutron diffraction study resolved several structures of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$.⁴⁴ Mn and Fe occupy randomly at the position of $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with oxygen occupying at the position of $(0, 0, 0)$, or vice versa. Although the position of Fe/Mn is random, it is a crystalline structure of single phase $\text{Mn}_x\text{Fe}_{1-x}\text{O}$. In the annealed NPs at 380°C , well-defined pattern of nearly stoichiometric MnFe_2O_4 ($Fd-3m$, $a = 8.491 \text{ \AA}$) appears along with $\text{Mn}_x\text{Fe}_{1-x}\text{O}$. Peak deconvolution with Pseudo-Voigt curve fitting indicates that there is a slight peak shift to low angle in $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ ($x \sim 0.490$, $a = 4.382 \text{ \AA}$). The appearance of MnFe_2O_4 is more likely played by FeO rather than MnO in $\text{Mn}_x\text{Fe}_{1-x}\text{O}$. The off-stoichiometric nature of FeO places it in the metastable equilibrium with Fe_3O_4 .⁴⁵ There are also Fe^{3+} ions in the vacancy-prone FeO in order to balance the overall charge. During the prolonged annealing time of 15 hours, transformation of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ into MnFe_2O_4 is affected by oxidation-vulnerable $\text{Mn}_x\text{Fe}_{1-x}\text{O}$. In fact, Fe_3O_4 accompanies during the synthesis of FeO.²²⁻²⁵ With the formation of MnFe_2O_4 , vacancy filling by Mn^{2+} is thought to occur in $\text{Mn}_x\text{Fe}_{1-x}\text{O}$. The structure is also thought more stoichiometric at 380°C , although there is little change of cell parameters.

At the annealing temperature of 450°C , two characteristics were observed. One is the narrower peaks due to the coalescence of nanoparticles, and the other is the shift of (311) plane of MnFe_2O_4 into high angle and the slight low angle shift of (111) plane of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$. After curve fitting, $\text{Mn}_{0.48}\text{Fe}_{2.52}\text{O}_4$ ($a = 8.459 \text{ \AA}$)⁴⁶ and $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ ($x \sim 0.500$, $a = 4.383 \text{ \AA}$) were identified. Generally, FeO is known stoichiometry over 560°C . With approaching stoichiometry

at the annealing temperature of 450 °C, there are more Fe^{3+} ions from $\text{Mn}_x\text{Fe}_{1-x}\text{O}$, and these produce Fe-rich manganese ferrite. The resemblance of FeO and Fe_3O_4 is reflected in the vacancy clusters of FeO, and it is known that off-stoichiometric FeO always contains microdomains of Fe_3O_4 .²³ $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ obtained at 450 °C is believed more stoichiometric and more ordered structure.

Unit cell of as-synthesized $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ is depicted with oxygen residing on (111) plane, and Mn/Fe residing randomly on (222) plane (Figure 4d), or with oxygen on (11-1) plane, and Mn/Fe on (22-2) plane (Figure 4e). Spins of metal cations align in the same direction in (222) plane (Figure 4d), or (22-2) plane (Figure 4e), but antiparallel with respect to the other. Spin alignment is alternative along $\langle 111 \rangle$ direction, therefore makes overall AFM structure. Based on the Rietveld refinement of as-synthesized NPs, 3D slant-plane Fourier map was obtained with $\langle 111 \rangle$ projection view (Figure 4f). Each atom in the unit cell has isotropic thermal factors at room temperature, although many AFM materials display differently at low temperature with the appearance of new peaks due to the magnetic transition.⁴⁷ In 2D electron density map with z-axis perpendicular to the plane, two representative maps were observed in as-synthesized $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ NPs with one taken at the planes of (0,0,8/n) (n: odd number, Figure 4g) and the other taken at the planes of (0,0,8/n) (n: even number, Figure 4h).

In the field-dependent magnetization (M - H) curve of as-synthesized NPs at 5 K (blue curve, Figure 5a), the magnetic behaviour is dominated by AFM. Hysteresis extended up to 50 kOe, which is usual hard magnetic behaviour of AFM materials. In addition, the magnetic moment does not reach saturation even at the applied field of 50 kOe, and this is another indication of major AFM. In addition, noticeable hysteresis shift along the field direction was observed when measured at 5 K in ZFC condition, which is due to the interaction between major AFM and

minor FM (inset blue curve, Figure 5a). This soft FM is thought from Fe_3O_4 or MnFe_2O_4 . Especially, Fe_3O_4 is known accompanying during the synthesis of FeO .²²⁻²⁵ Relatively large M_0 value (1.40 emu) at zero applied fields at 5 K is another indication of the presence of FM component. In the hysteresis at 300 K (blue curve, Figure 5b), AFM from $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ is dominant with a steep drop of magnetization at zero applied fields. A small contribution from soft FM is thought one of reasons, although this sharp drop of magnetization is observed in a single phase AFM nanomaterial.³⁹ In dM/dH curve in as-synthesized NPs, a peak is observed at zero applied fields, which implies that there is a slope in dM/dH curve and this is a strong indication of the presence of FM component (inset, Figure 5b).

In M - H curve of NPs annealed at 380 °C (red curve, Figure 5a), soft FM from MnFe_2O_4 dominates with the saturation magnetization (M_S) of 40.6 emu/g at 5 K and 27.9 emu/g at 300 K (Table 1). Coercivity measured at 5 K is 0.05 T, which is quite large value considering its soft magnetism (Table 1). This large coercivity is due to the interaction between FM and AFM, and this interaction causes slight hysteresis shift along the field direction in ZFC measurement. AFM-FM interaction is also reflected in the difficulty to reach saturation at both 5 K and 300 K. However, M - H curve at room temperature follows more likely superparamagnetism rather than

Table 1. Summary of the magnetization data

	M_S (emu/g) ^d		M_0 (emu/g) ^e				H_C (T) ^f			
	5 K	300 K	5 K		300 K		5 K		300 K	
As-syn ^a	14.0	7.4	1.34	-0.71	0.10	-0.11	-0.21	0.10	-0.005	0.005
380 ^b	40.6	27.9	8.61	-7.31	0.68	-0.65	-0.06	0.04	-0.003	0.003
450 ^c	10.6	8.6	0.59	-0.79	0.52	-0.50	-3E-4	3E-4	-0.004	0.004

^a as-synthesized NPs, ^b NPs annealed at 380 °C, ^c NPs annealed at 450 °C
^d magnetization measured at the applied magnetic field of 5 T
^e magnetization at the applied magnetic field of 0 T on the hysteresis curves
^f Coercivity measured as tesla (T)

1
2
3 soft FM. This would be from the hard magnetic nature of more ordered AFM $\text{Mn}_x\text{Fe}_{1-x}\text{O}$,^{48, 49} or
4
5 from the small grain size of MnFe_2O_4 (12.7 nm from Scherrer equation).
6
7

8 In M - H of NPs annealed at 450 °C, the pattern follows the sum of FM and AFM rather than
9
10 AFM/FM hybrid (green curve, Figure 5a). $\text{Mn}_{0.48}\text{Fe}_{2.52}\text{O}_4$ and $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ ($x \sim 0.500$) are
11
12 observed in the XRD pattern. With the major AFM $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ host, $\text{Mn}_{0.48}\text{Fe}_{2.52}\text{O}_4$ experiences
13
14 limited interaction. During the annealing at 450 °C, $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ is thought more stoichiometric
15
16 and more ordered, thus producing stronger AFM. Major AFM with minor FM, yet with little
17
18 interaction between them, is revealed in M - H curve with small coercivity (3×10^{-4} T, 5 K, Table
19
20 1). In addition, saturation is hard to achieve and M_s (10.6 emu/g, 5 K) is smaller compared to the
21
22 NPs annealed at 380 °C (M_s , 40.6. emu/g). Both as-synthesized NPs and the NPs annealed at 450
23
24 °C are regarded dominant AFM, but the different hysteresis is thought partly from the size effect.
25
26 As-synthesized NPs with small grain size (12.1 nm from Scherrer equation) contain substantial
27
28 number of surface spins. They interact ferromagnetically with FM component, and contribute to
29
30 the increase of magnetization as well as coercivity. Magnetization is 14.0 emu/g (M_s , 5 K, As-
31
32 syn, Table 1), and it is larger than 10.6 emu/g of the NPs annealed at 450 °C. NPs annealed at
33
34 450 °C contain larger grains (23.2 nm in $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ from Scherrer equation) due to thermal
35
36 annealing. The number of surface spins is smaller, and the stronger AFM is observed with much
37
38 smaller coercivity (3×10^{-4} T, 5 K), which is an indication of major AFM. The increase of FM
39
40 component with the decrease of AFM at small size regime is also seen in stoichiometric
41
42 perovskite manganites.⁵⁰
43
44
45
46
47
48
49

50 In M - T curve of as-synthesized NPs, there are two transition temperatures of 157 K and 59 K
51
52 (Figure 6c). Sharp increase of magnetic moment in ZFC measurement around 157 K is typical of
53
54 AFM-PM transition. This PM transition is obvious in $1/M$ vs T (inset, Figure 6c), where over 157
55
56
57
58
59
60

K linear pattern conforming to Curie-Weiss law is observed. The transition at 157 K stems from AFM FeO, as seen in several examples of FeO^{22,23,25} and Mn_xFe_{1-x}O.^{27,28} FeO is known AFM with T_N of 198 K, but the increase of Mn causes the shift of T_N to lower temperature^{27,29} For example, T_N appears at 173 K in Mn_{0.29}Fe_{0.71}O nanoparticles.²⁹ The other transition at 59 K is thought from the interaction between AFM and FM. In many AFM/FM materials, this broad transition at low temperature is observed.^{51,52} With the hysteresis shift in M - H curve, and with the appearance of peaks in the derivative curves under ZFC condition (Figure 7), spinel ferrites exist in as-synthesized NPs. The interaction between FM and AFM causes magnetic transition at 59 K. One characteristic of this transition is its broadness, which is thought from the broad size distribution of as-synthesized Mn_xFe_{1-x}O NPs, or from many different interactions between soft FM and Mn_xFe_{1-x}O with different stoichiometry.

In M - T curve of NPs annealed at 380 °C, MnFe₂O₄ with more ordered Mn_xFe_{1-x}O ($x \sim 0.490$) exists. There is AFM-FM interaction between them, and this interaction causes magnetic transition at around 60 K (Figure 6b), which is clearly observed in the derivative curves (Figure 7). In addition, both FC and ZFC measurements follow the smooth pattern of ferrite nanomaterial.⁵³ Major contribution is from MnFe₂O₄, but there is also a minor contribution from Mn_xFe_{1-x}O, as shown in the small mound around 151 K in both ZFC and FC measurements. The broad up-turn in inverse $M(T)$ curve (inset, Figure 6b) is another indication of major FM. Divalent oxides of Mn_xFe_{1-x}O in our study are hardly thought as stoichiometric, as deviation from stoichiometry is well known in FeO along with first-row divalent metal oxides. The degree of divalent cation vacancy is complicated to decide, but with the annealing at high temperature, the stoichiometry is believed also variable. This variable stoichiometry affects the appearance of MnFe₂O₄ with little change of cell parameter of Mn_xFe_{1-x}O. The other to consider is the ordering

of cation vacancy while annealing for 15 hours. In as-synthesized NPs, the vacancy is disordered and while off-stoichiometric, locally crystalline Mn-rich and Fe-rich phases contribute to major AFM. However, in NPs annealed at 380 °C, ordering of metal vacancy and ordering of mixed metal cations disrupt AFM, therefore the transition at 157 K is not as distinct.

In M - T curve of NPs annealed at 450 °C, two characteristics are observed. One is the sharp drop of magnetization at low temperature in ZFC measurement, and the other is the broad mound around 155 K in both ZFC and FC measurements. In inverse $M(T)$ curve (inset, Figure 6a) this transition is obvious around 155 K. Both these observations are characteristics of spin-glass state, especially its broadness.⁵⁴⁻⁵⁸ Localized FM is randomly distributed in AFM host such as Fe-doped manganite $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$,⁵⁹ heterostructured Fe/CoO thin films,⁶⁰ and Fe/FeO core-shell nanoparticles.⁶¹ Exchange bias is occasionally observed in spin glass states, particularly in FM/AFM interfaces.^{51,62} In our study, there are $\text{Mn}_{0.48}\text{Fe}_{2.52}\text{O}_4$ and $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ ($x \sim 0.500$) in NPs annealed at 450 °C. With the formation of Fe-rich manganese ferrites, $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ is thought more stoichiometric and more ordered structure, hence acts as a major AFM host. With the major AFM matrix, and with its limited interaction with FM, broad transition appears due to the competition between FM and AFM, followed by sharp drop of magnetization at low temperature, which is caused by the collapse of this competition and by the random orientation of spins under ZFC condition.⁶³ This is spin glass state without the exchange bias. Nearly zero coercivity as seen in M - H curve (Figure 5a) is another indication of the absence of exchange bias.

Derivatives of M - T curves of as-synthesized NPs (blue), NPs annealed at 380 °C (green), and NPs annealed at 430 °C (red) reveal the magnetic transitions (Figure 7). Noteworthy is the transition at 130-150 K. This transition is due to FeO in $\text{Mn}_x\text{Fe}_{1-x}\text{O}$. The highest transition temperature in as-synthesized NPs (blue) is thought from non-stoichiometric and disordered

$\text{Mn}_x\text{Fe}_{1-x}\text{O}$. The other characteristic is the appearance of transition at 50-65 K in ZFC, but not in FC. This implies that AFM-FM interaction becomes more obvious in ZFC measurement, in which sample is cooled under zero applied fields after demagnetization at 300 K. With a small applied field ($H_C = 100$ Oe) at 5 K and with an increase of temperature, spins are aligned locally or they fluctuate especially in AFM-FM interfaces. In soft ferrites with a small anisotropy, small applied field is enough to align those spins, thus there is a change of magnetization. Under FC condition, however, sample is cooled in the presence of the applied field, and spins are locked oriented during cooling, in particular the spins in soft magnets. It is not easy to disturb the orientation of spins, especially at low temperature where thermal energy is not high enough to orient those frozen spins.⁶⁴ There will be little change of magnetization under FC condition.

Conclusion

Along with their first synthesis, irregular development of crystallinity is observed in $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ nanoplates. Though irregular, they are consistent with their respective magnetic behaviours. As-synthesized nanoplates are disordered, and soft ferrites are accompanied due to the partial oxidation of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$. At 380 °C, the interaction between soft FM (MnFe_2O_4) with AFM ($\text{Mn}_x\text{Fe}_{1-x}\text{O}$) causes an increase of coercivity with the shift of hysteresis. At the annealing temperature of 450 °C, spin-glass state is observed with nearly zero coercivity from the major AFM host of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$. Plate shape is governed by MnO, whereas the magnetization and crystallinity are governed by the off-stoichiometric nature of FeO. Disordered and vacancy-prone as-synthesized nanoplates transformed into more ordered and more stoichiometric nanoplates with the increase of annealing temperature. Metal oxides which are composed of Fe and Mn are probably one of the most common oxides, and this work demonstrates rare aspect of the progress

of diverse magnetism of these iron-manganese oxides with the increase of annealing temperature.

ASSOCIATED CONTENT

Supporting Information. Additional TEM, SEM, and EFTEM images of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ nanoplates are available free of charge at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

* E-mail: hyonmin1@dau.ac.kr, niveen.khashab@kaust.edu.sa

Notes

The authors declare no competing financial interest.

Funding Sources

The authors gratefully acknowledge the support from Dong-A University, King Abdullah University of Science and Technology (KAUST), and NSF Grant DBI-1266377. The work at UCLA also leveraged the support provided by the National Science Foundation and the Environmental Protection Agency under Cooperative Agreement Number, DBI 0830117. We also acknowledge Dr. Wan-Seop Kim for his help in the analysis of experimental data.

REFERENCES

1. Giri, S.; Patra, M.; Majumdar, S., Exchange bias effect in alloys and compounds. *J. Phys.: Condens. Matter* **2011**, *23*, 073201.
2. Kolhatkar, A. G.; Jamison, A. C.; Litvinov, D.; Willson, R. C.; Lee, T. R., Tuning the Magnetic Properties of Nanoparticles. *Int. J. Mol. Sci.* **2013**, *14*, 15977-16009.
3. Pankhurst, Q. A.; Connolly, J.; Jones, S. K.; Dobson, J., Applications of magnetic nanoparticles in biomedicine. *J. Phys. D: Appl. Phys.* **2003**, *36*, R167-R181.
4. Wu, H.-C.; Mryasov, O. N.; Abid, M.; Radican, K.; Shvets, I. V., Magnetization States of All-Oxide Spin Valves Controlled by Charge-orbital Ordering of Coupled Ferromagnets. *Sci. Rep.* **2013**, *3*, 1830.
5. Suzuki, Y.; van Dover, R.; Gyorgy, E.; Phillips, J.; Felder, R., Exchange coupling in single-crystalline spinel-structure $(\text{Mn,Zn})\text{Fe}_2\text{O}_4/\text{CoFe}_2\text{O}_4$ bilayers. *Phys. Rev. B* **1996**, *53*, 14016-14019.
6. Masala, O.; Seshadri, R., Spinel Ferrite/MnO Core/Shell Nanoparticles: Chemical Synthesis of All-Oxide Exchange Biased Architectures. *J. Am. Chem. Soc.* **2005**, *127*, 9354-9355.
7. Finazzi, M.; Duò, L.; Ciccacci, F., Low-Dimensional Antiferromagnetic Oxides: An Overview. In *Magnetic Properties of Antiferromagnetic Oxide Materials: Surfaces, Interfaces, and Thin Films* Duò, L., Finazzi, M. and Ciccacci, F., Ed. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2010; pp 1-23.

8. Pebley, A. C.; Peek, A.; Pollock, T. M.; Gordon, M. J., Microplasma-Based Growth of Biphasic $\text{NiFe}_2\text{O}_4/\text{NiO}$ Nanogranular Films for Exchange Bias Applications. *Chem. Mater.* **2014**, *26*, 6026-6032.
9. Baaziz, W.; Pichon, B. P.; Lefevre, C.; Ulhaq-Bouillet, C.; Greneche, J.-M.; Toumi, M.; Mhiri, T.; Bégin-Colin, S., High Exchange Bias in $\text{Fe}_{3-\delta}\text{O}_4@\text{CoO}$ Core Shell Nanoparticles Synthesized by a One-Pot Seed-Mediated Growth Method. *J. Phys. Chem. C* **2013**, *117*, 11436-11443.
10. Zhao, Z.; Liu, J.; Cui, F.; Feng, H.; Zhang, L., One pot synthesis of tunable $\text{Fe}_3\text{O}_4\text{-MnO}_2$ core-shell nanoplates and their applications for water purification. *J. Mater. Chem.* **2012**, *22*, 9052-9057.
11. Salazar-Alvarez, G.; Sort, J.; Suriñach, S.; Baró, M. D.; Nogués, J., Synthesis and Size-Dependent Exchange Bias in Inverted Core-Shell $\text{MnO}|\text{Mn}_3\text{O}_4$ Nanoparticles. *J. Am. Chem. Soc.* **2007**, *129*, 9102-9108.
12. Wang, Z. H.; Geng, D. Y.; Hu, W. J.; Ren, W. J.; Zhang, Z. D., Magnetic properties and exchange bias in $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ nanoclusters. *J. Appl. Phys.* **2009**, *105*, 07A315.
13. Zhang, T.; Wang, X. P.; Fang, Q. F., Exchange Bias Effect and Suppression of Charge Ordering Induced by a Surface Phase Separation in $\text{La}_{0.25}\text{Ca}_{0.75}\text{MnO}_3$ Nanowires. *J. Phys. Chem. C* **2010**, *114*, 11796-11800.
14. Qian, T.; Li, G.; Zhang, T.; Zhou, T. F.; Xiang, X. Q.; Kang, X. W.; Li, X. G., Exchange bias tuned by cooling field in phase separated $\text{Y}_{0.2}\text{Ca}_{0.8}\text{MnO}_3$. *Appl. Phys. Lett.* **2007**, *90*, 012503.
15. Zhang, T.; Dressel, M., Grain-size effects on the charge ordering and exchange bias in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$: The role of spin configuration. *Phys. Rev. B* **2009**, *80*, 014435.
16. Suib, S. L., Porous Manganese Oxide Octahedral Molecular Sieves and Octahedral Layered Materials. *Acc. Chem. Res.* **2008**, *41*, 479-487.
17. Brock, S. L.; Duan, N.; Tian, Z. R.; Giraldo, O.; Zhou, H.; Suib, S. L., A Review of Porous Manganese Oxide Materials. *Chem. Mater.* **1998**, *10*, 2619-2628.
18. Arshak, K. I.; Korostynska, O.; Molloy, J.; Harris, J., Optical radiation sensing properties of MnO/TeO_2 thin films. *IEEE Sensors J.* **2006**, *6*, 656-660.
19. Li, X.; Li, D.; Qiao, L.; Wang, X.; Sun, X.; Wang, P.; He, D., Interconnected porous MnO nanoflakes for high-performance lithium ion battery anodes. *J. Mater. Chem.* **2012**, *22*, 9189-9194.
20. Mai, Y. J.; Zhang, D.; Qiao, Y. Q.; Gu, C. D.; Wang, X. L.; Tu, J. P., MnO /reduced graphene oxide sheet hybrid as an anode for Li-ion batteries with enhanced lithium storage performance. *J. Power Sources* **2012**, *216*, 201-207.
21. Zhong, K.; Xia, X.; Zhang, B.; Li, H.; Wang, Z.; Chen, L., MnO powder as anode active materials for lithium ion batteries. *J. Power Sources* **2010**, *195*, 3300-3308.
22. Lak, A.; Kraken, M.; Ludwig, F.; Kornowski, A.; Eberbeck, D.; Sievers, S.; Litterst, F. J.; Weller, H.; Schilling, M., Size dependent structural and magnetic properties of $\text{FeO-Fe}_3\text{O}_4$ nanoparticles. *Nanoscale* **2013**, *5*, 12286-12295.
23. Chen, C.-J.; Chiang, R.-K.; Lai, H.-Y.; Lin, C.-R., Characterization of Monodisperse Wüstite Nanoparticles following Partial Oxidation. *J. Phys. Chem. C* **2010**, *114*, 4258-4263.
24. Hou, Y.; Xu, Z.; Sun, S., Controlled Synthesis and Chemical Conversions of FeO Nanoparticles. *Angew. Chem. Int. Ed.* **2007**, *46*, 6329-6332.
25. Khurshid, H.; Chandra, S.; Li, W.; Phan, M. H.; Hadjipanayis, G. C.; Mukherjee, P.; Srikanth, H., Synthesis and magnetic properties of core/shell $\text{FeO}/\text{Fe}_3\text{O}_4$ nano-octopods. *J. Appl. Phys.* **2013**, *113*, 17B508.

26. Choi, D.; Han, A.; Park, J. P.; Kim, J. K.; Lee, J. H.; Kim, T. H.; Kim, S.-W., Fabrication of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ Colloidal Solid Solution as a Dual Magnetic-Resonance-Contrast Agent. *Small* **2009**, *5*, 571-573.
27. Lee, P.-Y.; Teng, H.-S.; Yeh, C.-S., Preparation of superparamagnetic $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ nanoparticles from low-index-facet cubes to high-index-facet concave structures and their catalytic performance in aqueous solution. *Nanoscale* **2013**, *5*, 7558-7563.
28. Li, Z.; Ma, Y.; Qi, L., Controlled synthesis of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ concave nanocubes and highly branched cubic mesocrystals. *CrystEngComm* **2014**, *16*, 600-608.
29. Huang, C.-C.; Chang, C.-N.; Yeh, C.-S., A thermolysis approach to simultaneously achieve crystal phase- and shape-control of ternary M-Fe-O metal oxide nanoparticles. *Nanoscale* **2011**, *3*, 4254-4260.
30. Hofmann, C.; Rusakova, I.; Ould-Ely, T.; Prieto-Centuri3n, D.; Hartman, K. B.; Kelly, A. T.; Lüttge, A.; Whitmire, K. H., Shape control of new Fe_xO - Fe_3O_4 and $\text{Fe}_{1-y}\text{Mn}_y\text{O}$ - $\text{Fe}_{3-z}\text{Mn}_z\text{O}_4$ nanostructures. *Adv. Funct. Mater.* **2008**, *18*, 1661-1667.
31. Fjellvåg, H.; Grønvold, F.; Stølen, S.; Hauback, B., On the Crystallographic and Magnetic Structures of Nearly Stoichiometric Iron Monoxide. *J. Solid State Chem.* **1996**, *124*, 52-57.
32. Morosin, B., Exchange Striction Effects in MnO and MnS. *Phys. Rev. B* **1970**, *1*, 236-243.
33. Sasaki, S.; Fujino, K.; Takeuchi, Y.; Sadanaga, R., On the estimation of atomic charges by the X-ray method for some oxides and silicates. *Acta Crystallogr. Sect. A* **1980**, *36*, 904-915.
34. Radler, M. J.; Cohen, J. B.; Sykora, G. P.; Mason, T.; Ellis, D. E.; Faber J. Jr, The defect structures of Mn_{1-x}O . *J. Phys. Chem. Solids* **1992**, *53*, 141-154.
35. Roth, W. L., Magnetic Structures of MnO, FeO, CoO, and NiO. *Phys. Rev.* **1958**, *110*, 1333-1341.
36. Ködderitzsch, D.; Hergert, W.; Szotek, Z.; Temmerman, W. M., Vacancy-induced half-metallicity in MnO and NiO. *Phys. Rev. B* **2003**, *68*, 125114.
37. Smyth, D. M., *The Defect Chemistry of Metal Oxides*. MacLaren and Sons Ltd.: New York, 2000; p 239-240.
38. Chen, C.-J.; Chiang, R.-K., Sulfidation of rock-salt-type transition metal oxide nanoparticles as an example of a solid state reaction in colloidal nanoparticles. *Dalton Trans.* **2011**, *40*, 880-885.
39. Ghosh, M.; Biswas, K.; Sundaresan, A.; Rao, C. N. R., MnO and NiO nanoparticles: synthesis and magnetic properties. *J. Mater. Chem.* **2006**, *16*, 106-111.
40. Yin, M.; O'Brien, S., Synthesis of Monodisperse Nanocrystals of Manganese Oxides. *J. Am. Chem. Soc.* **2003**, *125*, 10180-10181.
41. Du, Y.-P.; Zhang, Y.-W.; Sun, L.-D.; Yan, C.-H., Self-Assembled Ferromagnetic Monodisperse Manganese Oxide Nanoplates Synthesized by a Modified Nonhydrolytic Approach. *J. Phys. Chem. C* **2009**, *113*, 6521-6528.
42. Zhang, X.; Xing, Z.; Wang, L.; Zhu, Y.; Li, Q.; Liang, J.; Yu, Y.; Huang, T.; Tang, K.; Qian, Y.; Shen, X., Synthesis of $\text{MnO}@C$ core-shell nanoplates with controllable shell thickness and their electrochemical performance for lithium-ion batteries. *J. Mater. Chem.* **2012**, *22*, 17864-17869.
43. Carta, D.; Casula, M. F.; Mountjoy, G.; Corrias, A., Formation and cation distribution in supported manganese ferrite nanoparticles: an X-ray absorption study. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3108-3117.

44. Hope, D. A. O.; Cheetham, A. K.; Long, G. J., A neutron diffraction, magnetic susceptibility, and Moessbauer-effect study of the (manganese iron) oxide $((\text{Mn}_x\text{Fe}_{1-x})_y\text{O})$ solid solutions. *Inorg. Chem.* **1982**, *21*, 2804-2809.
45. Stolen, S.; Glockner, R.; Gronvold, F.; Atake, T.; Izumisawa, S., Heat capacity and thermodynamic properties of nearly stoichiometric wustite from 13 to 450 K. *Am. Mineral.* **1996**, *81*, 973-981.
46. Aoki, I., Tetragonal Distortion of the Oxide Spinel Containing Cobalt and Manganese. *J. Phys. Soc. Jpn.* **1962**, *17*, 53-61.
47. Shull, C. G.; Strauser, W. A.; Wollan, E. O., Neutron Diffraction by Paramagnetic and Antiferromagnetic Substances. *Phys. Rev.* **1951**, *83*, 333-345.
48. Gong, W. J.; Liu, W.; Li, D.; Guo, S.; Liu, X. H.; Feng, J. N.; Li, B.; Zhao, X. G.; Zhang, Z. D., Exchange bias effect in NiO/NiFe₂O₄ nanocomposites. *J. Appl. Phys.* **2011**, *109*, 07D711.
49. Kovylina, M.; del Muro, M. G.; Konstantinović, Z.; Varela, M.; Iglesias, O.; Labarta, A.; Batlle, X. Controlling exchange bias in Co-CoO_x nanoparticles by oxygen content. *Nanotechnology* **2009**, *20*, 175702.
50. Trukhanov, S. V.; Trukhanov, A. V.; Stepin, S. G.; Szymczak, H.; Botez, C. E., Effect of the size factor on the magnetic properties of manganite La_{0.50}Ba_{0.50}MnO₃. *Phys. Solid State* **2008**, *50*, 886-893.
51. Lei, S.; Liu, L.; Wang, C.; Shen, X.; Guo, D.; Wang, C.; Zeng, S.; Cheng, B.; Xiao, Y.; Zhou, L., The ferromagnetic-antiferromagnetic properties of Ni-Cr₂O₃ composite hollow spheres prepared by an in situ reduction method. *CrystEngComm* **2014**, *16*, 1322-1333.
52. Muscas, G.; Concas, G.; Cannas, C.; Musinu, A.; Ardu, A.; Orrù, F.; Fiorani, D.; Laureti, S.; Rinaldi, D.; Piccaluga, G.; Peddis, D., Magnetic Properties of Small Magnetite Nanocrystals. *J. Phys. Chem. C* **2013**, *117*, 23378-23384.
53. Mohapatra, J.; Mitra, A.; Bahadur, D.; Aslam, M., Surface controlled synthesis of MFe₂O₄ (M = Mn, Fe, Co, Ni and Zn) nanoparticles and their magnetic characteristics. *CrystEngComm* **2013**, *15*, 524-532.
54. Peddis, D.; Cannas, C.; Musinu, A.; Piccaluga, G., Coexistence of Superparamagnetism and Spin-Glass Like Magnetic Ordering Phenomena in a CoFe₂O₄-SiO₂ Nanocomposite. *J. Phys. Chem. C* **2008**, *112*, 5141-5147.
55. Wang, X. L.; James, M.; Horvat, J.; Dou, S. X., Spin glass behaviour in ferromagnetic La₂CoMnO₆ perovskite manganite. *Supercond. Sci. Technol.* **2002**, *15*, 427.
56. Fiorani, D.; Bianco, L. D.; Testa, A. M.; Trohidou, K. N., Exchange bias in disordered granular systems. *J. Phys.: Condens. Matter* **2007**, *19*, 225007.
57. Balaji, G.; Wilde, G.; Weissmüller, J.; Gajbhiye, N. S.; Sankaranarayanan, V. K., Spin-glass-like transition in interacting MnFe₂O₄ nanoparticles. *Phys. Status Solidi B* **2004**, *241*, 1589-1592.
58. Winkler, E.; Zysler, R. D.; Mansilla, M. V.; Fiorani, D.; Rinaldi, D.; Vasilakaki, M.; Trohidou, K. N., Surface spin-glass freezing in interacting core-shell NiO nanoparticles. *Nanotechnology* **2008**, *19*, 185702.
59. Levy, P.; Parisi, F.; Granja, L.; Indelicato, E.; Polla, G., Novel Dynamical Effects and Persistent Memory in Phase Separated Manganites. *Phys. Rev. Lett.* **2002**, *89*, 137001.
60. Thomas, S.; Uhlig, M.; Wiedwald, U.; Han, L.; Ziemann, P.; Albrecht, M., Super spin-glass state and exchange bias in Fe/CoO hybrid nanostructures. *Nanotechnology* **2013**, *24*, 155703.

61. Kumar, P. A.; Gurvinder, S.; Wilhelm, R. G.; Davide, P.; Erik, W.; Mathieu, R., Superspin glass state and exchange bias in amorphous Fe/FeO core/shell nanoparticles. *Mater. Res. Express* **2014**, *1*, 036103.
62. Peng, D. L.; Sumiyama, K.; Hihara, T.; Yamamuro, S.; Konno, T. J., Magnetic properties of monodispersed Co/CoO clusters. *Phys. Rev. B* **2000**, *61*, 3103-3109.
63. Trukhanov, S. V.; Trukhanov, A. V.; Vasiliev, A. N.; Balagurov, A. M.; Szymczak, H., Magnetic state of the structural separated anion-deficient $\text{La}_{0.70}\text{Sr}_{0.30}\text{MnO}_{2.85}$ manganite. *J. Exp. Theor. Phys.* **2011**, *113*, 819-825.
64. Joy, P. A.; Kumar, P. S. A.; Date, S. K., The relationship between field-cooled and zero-field-cooled susceptibilities of some ordered magnetic systems. *J. Phys.: Condens. Matter* **1998**, *10*, 11049.

Scheme 1. Illustration of the development of $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ NPs

Figure 1. (a), (b), (d) TEM images, (e), (f) HRTEM images, and (c) SAED pattern of as-synthesized $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ NPs.

Figure 2. (a,b,c) SEM images, (d) EDX spectrum of as-synthesized $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ NPs.

Figure 3. EFTEM images of as-synthesized $\text{Mn}_x\text{Fe}_{1-x}\text{O}$ NPs, (a) with zero-loss filtering, (b) with Mn map, (c) with Fe map, and (d) merged map of Mn and Fe.

Figure 4. (a) XRD patterns of (top) annealed MnFe₂O₄/Mn_xFe_{1-x}O composite NPs at 450 °C, (middle) annealed composite NPs at 380 °C, and (bottom) as-synthesized NPs. (b) Deconvoluted XRD patterns with Pseudo-Voigt fitting at (311) plane of MnFe₂O₄ and at (111) plane of Mn_xFe_{1-x}O. (c) Rietveld refinement of as-synthesized NPs. (d) Unit cell of Mn_xFe_{1-x}O with oxygen residing on (111) plane, and Mn/Fe residing randomly on (222) plane. (e) Unit cell of Mn_xFe_{1-x}O with oxygen residing on (11-1) plane, and Mn/Fe residing randomly on (22-2) plane. (f) Projection view of 3D slant-plane Fourier map along <111> direction. Electron density map perpendicular to z-axis (g) at planes of (0,0,8/n) (n: odd number) and (h) at planes of (0,0,8/n) (n: even number).

Figure 5. Field-dependent magnetization of (blue) as-synthesized NPs, (red) NPs annealed at 380 °C, and (green) NPs annealed at 450 °C. Measurements were conducted at (a) 5 K, and (b) 300 K.

Figure 6. Temperature-dependent magnetization of (a) NPs annealed at 450 °C, (b) NPs annealed at 380 °C, and (c) as-synthesized NPs.

Figure 7. Derivatives of magnetization (M) vs temperature (T) of (blue) as-synthesized NPs, (green) NPs annealed at 380 °C, and (red) NPs annealed at 430 °C. The measurement was conducted with the applied magnetic field of 100 Oe

Table of Contents Graphic and Synopsis

Development of irregular magnetism and phase