Two-, Three-, and Four-Component Magnetic Multilayer Onion Nanoparticles Based on Iron Oxides and Manganese Oxides

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Supporting Information

ABSTRACT: Magnetic multilayered, onion-like, heterostructured nanoparticles are interesting model systems for studying magnetic exchange coupling phenomena. In this work, we synthesized heterostructured magnetic nanoparticles composed of two, three, or four components using iron oxide seeds for the subsequent deposition of manganese oxide. The MnO layer was allowed either to passivate fully in air to form an outer layer of Mn3O4 or to oxidize partially to form MnO|Mn3O4 double layers. Through control of the degree of passivation of the seeds, particles with up to four different magnetic layers can be obtained (i.e., FeO|Fe3O4|MnO|Mn3O4). Magnetic characterization of the samples confirmed the presence of the different magnetic layers.

Magnetic nanoparticles are very attractive for their novel fundamental properties and numerous current and potential applications.1–3 The advances in chemical methods of synthesis have allowed the production of relatively large amounts of narrowly size-distributed nanoparticles with a broad range of compositions and morphologies.4–7 Recently, besides single-component nanoparticles, the interest in two-component nanoparticle systems has steadily increased because of the appealing novel properties and promising applications arising from the simple combination of properties of their constituents or the interaction between them (e.g., refs 8 and 9 and references therein). Since the report on the use of exchange bias to overcome the antiferromagnetic interaction (AFMs) FeO and MnO and ferrimagnets Fe3O4 and Mn3O4. The multicomponent nanoparticles were fabricated by the heterogeneous growth of manganese oxide shells on iron oxide cores using the latter as seeds, as depicted schematically in Figure 1.

Figure 1. Schematic 2D projections (top) and 3D representations (middle) and the corresponding chemical path of the formation of multicomponent onion nanoparticles (bottom).

The particles were truncated nanocubes with an edge length (l) of 11 ± 1 nm consisting of a more electron dense inner core with a size of ~5 nm and a less electron dense edge of ~3 nm.24 Phase analysis of the X-ray diffraction (XRD) measurements suggested two components that could be associated with either Fe3O4 or γ-Fe2O3 and FeO.24 Quantitative analysis of the Fe L3/L2 integrated intensity ratio obtained by electron energy loss spectroscopy (EELS) resulted in a ratio of 4.9, indicating that the CS particles had an average composition between FeO and Fe3O4.24 The passivation of the surface layer indicates that the original particles were composed of FeO, which upon exposure to air oxidized to Fe3O4 in agreement with previous reports (although the presence of γ-Fe2O3 as a result of lattice strains cannot be completely ruled out).26–28

The iron oxide CS nanoparticles were used as seeds for the heterogeneous growth of manganese oxide.24 Figure 2a shows...
The synthesis relies in air oxidation of some of the components. Unlike the seeds with cubic morphology, these particles are larger and seem to have lost the corners to form, probably, cuboctahedrons or truncated octahedrons. Moreover, the self-assembly of the onion nanoparticles leads to the formation of hexagonal arrays, in contrast to the square arrays formed by the seeds.5,24 The inset of Figure 2a shows a cuboctahedron with an edge length \( l_{\text{cs}} \) of \( \sim 14 \) nm, indicating that it practically embeds a cubic particle with an edge length of \( \sim 11 \) nm. The formation of the cuboctahedrons (or truncated octahedrons) instead of cubes must arise from an increasing surface chemical potential of the \{111\} faces relative to the \{100\} faces.29 Indeed, it has been shown that MnO nanoparticles tend to crystallize in the form of octahedrons with \{111\} faces.5,30–33 It is expected that upon exposure to air, the manganese monoxide should oxidize to a higher oxide, i.e., Mn_{3}O_{4} (or \( \gamma\)-Mn_{2}O_{3} \), in a similar fashion to the MnO|Mn_{3}O_{4} system.34–36 On the basis of the Mn \( L_{3}/L_{2} \) ratio and the characteristic shape of the O K absorption edge from the corresponding EEL spectra,24 the composition of the manganese oxide layer was estimated to be Mn_{3}O_{4}. 2–3 nm thick manganese outer shell was confirmed by electron-filtered TEM (EFTEM) images taken at the Fe and Mn \( L_{3} \) edges (Figure 2d–f). The growth of manganese oxide on the surface of the two-component seeds renders three-component onion nanoparticles with composition FeO|Fe_{3}O_{4}|MnO, which passivate toward FeO|Fe_{3}O_{4}|Mn_{3}O_{4}. XRD results are consistent with this structure.24 The synthesis relies in air oxidation of some of the components. Previous reports have shown that the composition thus attained can be stable for months and even be size-dependent.34,36,39 Thicker manganese oxide layers (>20 nm) can be grown on the CS seeds using higher decomposition temperatures than in the three-component case (see Figure 3).35 The manganese-containing layer was confirmed by EFTEM images taken at the Fe and Mn \( L_{3} \) edges (Figure 3b–d). On the basis of the characteristics of the MnO|Mn_{3}O_{4} system,35 these particles are expected to be formed from four components, i.e., FeO|Fe_{3}O_{4}|MnO|Mn_{3}O_{4}. The presence of both MnO and Mn_{3}O_{4} was determined from magnetization data, as discussed below. A proper differentiation between the different manganese oxides using the XRD and EEL spectra was not possible, as MnO dominates the signal because of its large volume fraction.24 These nanoparticles present a slightly concave geometry, reminiscent of a tetracube. Hofmann et al.40 argued that the formation of this type of concave geometry is due to the presence of water during the reaction, which induces some etching of defective areas on the \{100\} faces. Water then helps solubilize some metal (oxy)hydroxide, which recrystallizes on the edges and along the corners according to the Berg effect.41 The final size and shape of the three-component nanoparticles, FeO|Fe_{3}O_{4}|MnO, is likely to depend on three interrelated mechanisms: (i) seeded growth, which can be discussed in the framework of the Gibbs–Thomson effect and is influenced mainly by the size and curvature of the seeds (FeO|Fe_{3}O_{4}) and the monomer concentration;42 (ii) the formation of a heterogeneous layer (MnO) on the initial seeds as manganese oxide is deposited on iron oxide, thereby creating an interface, which can be understood as the spherical case of the Frank–van der Merwe (FM) or Volmer–Weber (VW) regimes43 and is affected mostly by the difference in surface energy, lattice mismatch, and degree of supersaturation of the monomer;44 and finally (iii) the growth rates of the different crystal faces of the manganese oxide layer, which are likely to be dependent on the type and concentration of surfactant and the initial shape of the seeding particle according to the Wulff–Gibbs criteria of equilibrium.45 The use of faceted seeds

Figure 2. TEM images of the three-component FeO|Fe_{3}O_{4}|Mn_{3}O_{4} onion nanoparticles. (a) Bright-field TEM image of the particles forming hexagonal arrays. In the inset, the marked particle is an octahedral particle with a cubic core, and the scale bar represents 20 nm. (b) Schematic representation of the composition of the particle highlighted in the inset of (a) and a cartoon showing how the CS seed becomes progressively coated with a manganese oxide layer to form an octahedral particle. (c) Bright-field TEM image of the three-component nanoparticles. (d–e) Corresponding EFTEM micrographs acquired at the (d) iron and (e) manganese \( L_{3} \) edges. (f) Overlay map showing the distribution of iron and manganese in the particles.

Figure 3. (a) Bright-field TEM image of the four-component FeO|Fe_{3}O_{4}|MnO|Mn_{3}O_{4} onion nanoparticles. (b–d) EFTEM micrographs corresponding to (b) iron and (c) manganese and (d) an overlay map showing the distribution of cations in the particles. The arrows in (a) indicate the position of excess two-component CS seeds. The dark inner corona in (c) and (d) is due to diffraction contrast.
serves a twofold purpose: First, it delays the deposition of manganese oxide monomer, which preserves the very narrow size distribution of the seeds.\textsuperscript{8,29} This becomes more apparent upon comparison of the particles shown in Figure 2a with those prepared without the seeds (see ref 35). Second, the morphology of the particles (i.e., truncated cubes) provides well-defined high-energy \{111\} corners where the manganese oxide can be deposited (see Figure 2b). Hence, as the manganese oxide monomer is deposited on the truncated high-energy \{111\} corners of the iron oxide, these grow and the \{100\} planes dissolve to produce a cuboctahedron or truncated octahedron, as illustrated by the cartoon in Figure 2b. For the growth of a continuous coating on the seeds, both the outermost layer (mainly Fe\textsubscript{3}O\textsubscript{4}) and the developing shell (most probably MnO) must accommodate a relatively large lattice mismatch of \(\sim 5\%\). The simplest way to do this is by creating a graded defective interface that is rich in iron and poor in manganese (i.e., Mn\textsubscript{3}Fe\textsubscript{5−x}O\textsubscript{x}) and enriched toward MnO at the outermost layer with a low manganese occupancy (i.e., Mn\textsubscript{1−x}O). The formation of such a defective structure then facilitates its oxidation toward a distorted Mn\textsubscript{3}O\textsubscript{4} to release further the internal stresses, similar to the MnO|Mn\textsubscript{3}O\textsubscript{4} system.\textsuperscript{34−36} The formation of the larger four-component nanoparticles proceeds likewise using higher decomposition temperatures.\textsuperscript{34}

Figure 4a shows the field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements carried out on the two-component CS FeO|Fe\textsubscript{3}O\textsubscript{4} seeds, the three-component FeO|Fe\textsubscript{3}O\textsubscript{4}|MnO|Mn\textsubscript{3}O\textsubscript{4} nanoparticle systems, and the four-component FeO|Fe\textsubscript{3}O\textsubscript{4}|MnO|Mn\textsubscript{3}O\textsubscript{4} onion nanoparticles. As can be seen in the figure, the initial seeds present a blocking temperature (\(T_B\)) of \(\sim 120\) K, well below the transition temperature of bulk FeO (\(T_N = 198\) K). Notably, although exchange coupling between the AFM core and the FiM shell should bring the blocking temperature of the nanoparticle toward the Néel temperature (\(T_N\)) of the AFM,\textsuperscript{40} this effect depends strongly on the size and anisotropy of the AFM counterpart.\textsuperscript{45} Surprisingly, adding a 2–3 nm thick layer of Mn\textsubscript{3}O\textsubscript{4} (with \(T_C \approx 43\) K\textsuperscript{46}) to these cubes results in an increase in \(T_B\) toward \(\sim 200\) K. This effect could have various origins: (a) There is some limited intermixing at the interface of the components (the first nanometer layer), as shown by the EFTEM images, which results in a larger effective volume of the FiM component. This is in agreement with our work on smaller particles.\textsuperscript{47} (b) The growth of the manganese layer on the surface of the cubic seeds proceeds preferentially by growth of the \{111\} faces. This directional growth creates more facets than for a cubic morphology, which can be seen as an effective rounding of the particles, leading to an increase in the effective surface anisotropy and hence \(T_B\).\textsuperscript{47} The presence of loop shifts in the hysteresis (Figure 4b), i.e., exchange bias,\textsuperscript{41} suggests the presence of AFM layers coupled to FiM layers in the particles, as designed. Figure 4b shows the hysteresis loops of the samples measured at \(T = 10\) K after cooling under a field \(H_{JC} = 50\) kOe. All of the samples show a loop shift (\(H_E\)), with the largest being that for the four-component nanoparticle system (sample O2). The temperature dependences of the coercivity and loop shift of the three different samples are shown in Figure S4 in the Supporting Information. As expected from its components, the coercivity and loop shift of the CS sample decay slowly toward the blocking temperature of the system. In the case of the Mn\textsubscript{3}O\textsubscript{4}-containing samples, the coercivity and loop shift decay very rapidly toward the Curie temperature (\(T_C^{\text{Mn3O}4} \approx 40\) K). The effect is more pronounced in the four-component nanoparticle system, where most of the magnetic volume corresponds to the AFM MnO. Thus, the coercivity decays nearly 90\%, although there is a remnant component that disappears near the Néel temperature (\(T_N^{\text{Mn3O}4} \approx 120\) K).

Taking advantage of the surface oxidation of FeO and MnO allows nanoparticles with various compositions and number of components to be produced: (i) two-component FeO|Fe\textsubscript{3}O\textsubscript{4} nanoparticles can be synthesized directly, and (ii) three-component FeO|Fe\textsubscript{3}O\textsubscript{4}|MnO|Mn\textsubscript{3}O\textsubscript{4} nanoparticles or (iii) four-component FeO|Fe\textsubscript{3}O\textsubscript{4}|MnO|Mn\textsubscript{3}O\textsubscript{4} nanoparticles can be obtained from CS FeO|Fe\textsubscript{3}O\textsubscript{4} seeds by growing a single Mn\textsubscript{3}O\textsubscript{4} layer or a MnO|Mn\textsubscript{3}O\textsubscript{4} double layer, respectively. Magnetic measurements suggest that the interfacial effects dominate in the three-component particles, whereas MnO dominates in the four-component particles.
ACKNOWLEDGMENT

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SUPPORTING INFORMATION

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1 Experimental section

1.1 Synthesis details

The synthesis of the iron oxide cores was carried out following a similar procedure reported earlier.[1, 2] Cubic core-shell nanoparticles with an edge $l = 11 \pm 1$ nm (Sample CS) were prepared by dissolving 7 mmol of the iron (III) oleate precursor and 3.4 mmol of oleic acid (Fluka) in 43 cm$^3$ of 1-octadecene (90 %, Aldrich) at 70 °C. The mixture was heated to 320 °C (at 3.3 °C/min) and kept for 30 min. The reaction vessel was allowed to cool down to room temperature before exposure to air and addition of ethanol to coagulate the solids. The mixture was heated to 320 °C (at 5 °C/min) under mechanical stirring at 130 rpm and kept for 30 min. The particles were retrieved by several cycles of centrifugation at 2000×g, disposal of supernatant, re-dispersion in hexane and coagulation with ethanol.[3] The manganese oxide layers were laid on the iron oxide-based nanocubes by modifying an earlier reported procedure used for the synthesis of MnO|Mn$_{3-x}$O$_4$ nanoparticles.[4] The procedure is as follows: to a given amount of iron oxide seeds (see Table S1) an equimolar amount of 1,2-hexadecanediol (HDD, Aldrich) and manganese (II) acetylacetonate (Mn(acac)$_2$, Aldrich) were added to a solution of oleic acid (OIOH, Aldrich) and oleylamine (OLNH$_2$, Fluka) in benzylether (Bz$_2$O, Fluka). The slurry was de-aerated with Ar for 15 min while heating at 100 °C. The temperature was then ramped at $\sim$ 7 °C/min to a final temperature, $T$, kept under reflux during a 45 min, and then removed from the heating source and allowed to cool down to room temperature. The particles were washed from the reaction media by subsequent steps of precipitation under ethanol, centrifugation, and re-dispersion in hexane.[3]

Table SI: Table describing the conditions used for the synthesis of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seeds (mg)</th>
<th>Mn(acac)$_2$ (mmol)</th>
<th>HDD (mmol)</th>
<th>OIOH (mmol)</th>
<th>OLNH$_2$ (mmol)</th>
<th>Bz$_2$O (cm$^3$)</th>
<th>$T$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>20</td>
<td>1</td>
<td>1</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>200</td>
</tr>
<tr>
<td>O2</td>
<td>50</td>
<td>1.5</td>
<td>1.5</td>
<td>15</td>
<td>15</td>
<td>30</td>
<td>250</td>
</tr>
</tbody>
</table>

1.2 TEM characterization

Samples for transmission electron microscopy (TEM) were prepared by drop-casting few microlitres of a diluted hexane suspension of nanoparticles onto a carbon-coated copper grid and letting the solvent evaporate. High-resolution transmission electron microscopy images (HRTEM) were obtained in a JEOL-2011 electron microscope operated at 200 kV. Particle size histograms were obtained
by manually measuring the edge length, \( l \), or diameter, \( D \), of at least 200-300 particles, respectively, on TEM micrographs. The mean size and its standard deviation, \( \sigma \), were determined by fitting the corresponding histogram with a Gaussian distribution function.

### 1.3 EELS and EFTEM characterization

Electron energy loss spectra (EELS) and energy-filtered transmission electron microscopy micrographs (EFTEM) were acquired using a F-30ST (Tecnai) operated at 300 kV equipped with a GIF2002 (Gatan) spectrometer on areas containing >50 particles. EEL spectra of the Mn and Fe L edges were acquired using a dispersion of 0.2 eV/channel. In a typical run an energy resolution of 1.5–2 eV was determined from the full width at half maximum of the zero loss peak.

### 1.4 Magnetic characterization

Magnetic measurements were carried out on loosely packed powdered samples using a superconducting quantum interference device (SQUID) magnetometer Quantum Design MPMS-7XL. The field cooled (FC) and zero field cooled (ZFC) magnetization measurements were carried out in \( H_{\text{appl}} = 50 \) Oe. The hysteresis loops were measured using maximum fields of up to 70 kOe at 10 K after field cooling from room temperature in \( H_{\text{FC}} = 50 \) kOe.

### 1.5 X-ray powder diffraction

The X-ray diffractograms shown in Figure S3 were obtained on loosely-packed powdered samples using a Philips 3050 diffractometer with Cu K\( \alpha \) radiation using the Bragg-Brentano geometry. The measurements were carried out in the 2\( \theta \) range 25 – 100 ° with a step size of 0.04 ° and collection time of 40 s.

## 2 Additional results

### 2.1 EEL Spectrum analysis

The recorded spectra for the different samples showing the O-K, Mn-L and Fe-L regions are shown in Figure S2. Phase determination was carried out by comparing the \( L_3/L_2 \) ratio following the second derivative procedure described in [7]. Using the program Digital Micrograph (Gatan), the second derivative of the spectra was obtained using a numerical filter that averages over an interval \( w^+ \) units wide and subtracts half the averages in two adjacent “wings” of width \( w^- \). Then,
Table SII: Correlation of composition to $L_3/L_2$ ratio for various iron and manganese oxides. Rightmost column indicates the suggested composition of the particles in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe-$L_3/L_2$ ratio</th>
<th>Mn-$L_3/L_2$ ratio</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. [5]</td>
<td>4.6</td>
<td>–</td>
<td>FeO</td>
</tr>
<tr>
<td>Ref. [5]</td>
<td>5.2</td>
<td>–</td>
<td>Fe$_3$O$_4$</td>
</tr>
<tr>
<td>Ref. [5]</td>
<td>5.8</td>
<td>–</td>
<td>$\gamma$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Ref. [7, 6]</td>
<td>–</td>
<td>2.6, 2.8</td>
<td>Mn$_3$O$_4$</td>
</tr>
<tr>
<td>Ref. [7, 6]</td>
<td>–</td>
<td>2.3, 2.4</td>
<td>Mn$_2$O$_3$</td>
</tr>
<tr>
<td>CS</td>
<td>4.9±0.1</td>
<td>–</td>
<td>FeO-Fe$_3$O$_4$</td>
</tr>
<tr>
<td>O1</td>
<td>4.9±0.1</td>
<td>2.7±0.1</td>
<td>FeO-Fe$_3$O$_4$,Mn$_3$O$_4$</td>
</tr>
<tr>
<td>O2</td>
<td>N/A$^{[I]}$</td>
<td>3.8±0.1</td>
<td>FeO-Fe$_3$O$_4$$^{[II]}$, MnO</td>
</tr>
</tbody>
</table>

$^{[I]}$ The element’s signal is too low to be quantified.  
$^{[II]}$ Composition of the seeds is assumed to be the same as samples CS, and O1.

The spectrum is divided by the squared sum of $w^+$ and $w^-$ to yield an approximation of the second derivative with respect to energy. The $L_3/L_2$ ratio is then calculated from the ratio of the maximum intensity of the peaks at the white line position. In this work we used window widths, $w^+$ = 4 eV and $w^-$ = 2 eV. There are several reports that attempt to establish a correlation between spectral parameters (such as the intensity ratio of the white lines, position, and separation between white lines, and so on) and the stoichiometry of manganese or iron containing samples using different methods.$^{[5, 6, 7, 8, 9, 10, 11, 12, 13, 14]}$ However, although it is possible to see the general trend for the same report, there is a large scattering of data between the different reports.$^{[12]}$ The values thus obtained for the measured samples in this work as well as the probable stoichiometry given in Table SII should be taken with caution and used with a secondary parameter. Figure S2a shows the O-$K$ spectra for the different samples. The O-$K$ spectra corresponding to samples CS and O1 can be identified readily with that of a spinel oxide, i.e., Fe$_3$O$_4$ or $\gamma$-Fe$_2$O$_3$$^{[5]}$ and Mn$_3$O$_4$$^{[14]}$. 
2.2 Additional figures

Figure S1: (a) Bright field TEM micrograph of several FeO|Fe₃O₄ cubic nanoparticles. Inset: magnified view of several particles with a core|shell structure exhibiting square arrays, the scale bar represents 20 nm. FFT filtering was applied for clarity. (b) High resolution TEM image of a single nanocube showing the interplanar distances corresponding to the (220)_{spinel} (d=0.30 nm) and (400)_{spinel} or (200)_{FeO} (d=0.21 nm). (c) Particle size distribution of the particles in (a). (d) Cartoon illustrating the structure of the particle shown in (b) from a top and perspective views.
Figure S2: EEL spectra after background removal for the synthesized samples. Comparison of a) oxygen $K$ spectra and b) manganese and iron $L$-lines.
Figure S3: X-ray powder diffraction patterns corresponding to the samples shown in Table SI. The open symbols correspond to the experimental data and the line a fit to the data. Sample CS: The stars (•) show the position of the reflections corresponding to FeO, all other reflections are assigned to Fe$_3$O$_4$. Sample O1: The clovers (♠) show the position of the unassigned reflections, all other reflections correspond to Fe$_3$O$_4$ and Mn$_3$O$_4$. Sample O2: The filled circles (●) show the position of the reflections corresponding to MnO whereas the diamonds (♦) indicate traces of the peaks corresponding to Mn$_3$O$_4$. 
Figure S4: Temperature dependence of the coercivity (circles) and loop shift (squares) for samples CS1, O1, and O2 cooled under a static field, $H_{FC} = 50$ kOe, from 300 K.
References


