Supporting Information for

**Metastable Iron(III) Oxides Polymorph derived from Fe/Mn Bimetallic Coordination Polymer Particles in Confined Space: SiO$_2$ Shell Effect on Crystal Phase Transition**

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**Materials and Instrumentation**

All chemicals obtained from commercial resources that were used without further purification. The morphologies and particle shapes of synthesized materials was investigated by field-emission scanning electron microscopy (FE-SEM, Carl Zeiss SUPRA 55VP), operated at an accelerating voltage of 3.0 kV and equipped with energy-dispersive spectroscopy (EDS) capabilities. All scanning and high-resolution transmission electron microscopy (STEM and HR-TEM respectively) images and electron diffraction (ED) patterns were obtained using a JEOL JEM-2000EXII and JEM-ARM200F instruments operated at 200 kV. X-ray diffraction studies for the crystal structure were conducted using a XRD equipped with a Cu-Kα radiation (50kV, 100 mA, λ = 1.541 Å) at room temperature. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q500 at up to 800 °C with a heating rate of 10 °C under air. The field-dependent magnetization of each sample was measured ranging from -15 to 15 kOe using a Lake Shore 7410 vibrating sample magnetometer (VSM). The synthesis of FeMn bimetallic coordination polymer particles (FeMn(fur)) were carried out following the reported literature with the modification.¹

**Synthesis of SiO₂ coated FeMn(fur) particles**

A precursor solution was prepared by dispersion of FeMn(fur) particles (2.4 g) in a mixture of water (40 mL) and ethanol (160 mL). 6 mL of an aqueous ammonia solution was added into the mixed solution. After stirring for 10 min, 1 mL of tetraethyl orthosilicate (TEOS) in 10 mL of ethanol was added dropwise to the reaction mixture. The mixture was stirred at 60 °C for 2 hr. The final brown precipitates were isolated by filtration and then washed with deionized water, ethanol, and acetone several times.

**Preparation of manganese doped β-Fe₂O₃ hollow silica (FeMn@SiO₂-500)**

SiO₂ coated FeMn(fur) particles were moved in ceramic boats and then moved into a furnace. The FeMn(fur)@SiO₂ particles were calcinated at 500, 700, 800, 900 and 1000 °C under air atmosphere with a heating rate of 5 °C/min and then naturally cooled down to room temperature. Hereafter, the prepared products are called FeMn@SiO₂-X, where X indicates the calcination temperature.

**Preparation of manganese doped amorphous iron oxides**

Mn-doped β-Fe₂O₃@SiO₂ (FeMn@SiO₂-500) particles were immersed in 1M of NaOH solution and then were sonicated for 2h at 60 °C. The products were washed with deionized water and ethanol by centrifugation to remove residues.

**Preparation of manganese doped mixed Fe₂O₃ (FeMn-500)**

FeMn-MOFs were placed in ceramic boats and then moved into a furnace. The products were prepared via thermal treatment at 500 °C under air atmosphere with a heating rate of 5 °C/min and then naturally cooled down to room temperature.

**Preparation of manganese doped α-Fe₂O₃ (NH₄OH-FeMn-500)**

FeMn(fur) particles (2.4g) were dispersed in a mixture of deionized water (40 mL) and ethanol (160 mL). 6 mL of an aqueous ammonia solution was added into the mixed solution and then stirred at 60 °C for 2 hr. Aqueous ammonica solution treated FeMn(fur) particles were isolated by filtration and then washed with deionized water, ethanol and acetone 2 times and then dried. The precipitates were calcined at 500 °C under air atmosphere with a heating rate of 5 °C/min and then naturally cooled down to room temperature.
Results and Discussion

Fig. S1. (a) TEM and (b) SEM images of FeMn(fur)@SiO$_2$ particles.

Fig. S2. The scanning transmission electron microscopy (STEM)-EDS maps showing the distribution of Fe, Mn, Si and O of FeMn(fur)@SiO$_2$ particles.
Table S1. The crystallographic parameter for (a) $\alpha$-Fe$_2$O$_3$ (ICDD No. 04-006-6579) (b) $\beta$-Fe$_2$O$_3$ (ICDD No. 00-039-0238) (c) $\gamma$-Fe$_2$O$_3$ (ICDD No. 00-025-1402) and (d) $\varepsilon$-Fe$_2$O$_3$ (ICDD No. 00-016-0653)
Fig. S4. XRD pattern of FeMn@SiO₂-500

Fig. S5. (a) The average length and (b) the average width of FeMn@SiO₂-500 particles

Average length = 205.7 nm
Average width = 143.05 nm
Fig. S6. (a) TEM and (b) HRTEM images of Fe/Mn removed FeMn@SiO$_2$-500

Fig. S7. (a) The average length and (b) the average width of void space of FeMn@SiO$_2$-500 particles
Fig. S8. Powder X-ray diffraction patterns of SiO$_2$ coated Mn-doped iron oxides structures annealed at 500, 700, 800, 900, and 1000 °C for 30 min.
Fig. S9. TEM images of (a) FeMn@SiO2 – 700 (b) FeMn@SiO2 – 800 (c) FeMn@SiO2 – 900 (d) FeMn@SiO2 – 1000
Fig. S10. Energy dispersive X-ray spectroscopy (EDS) mapping of (a) FeMn@SiO₂-700 (b) FeMn@SiO₂-800 (c) FeMn@SiO₂-900 (d) FeMn@SiO₂-1000
Fig. S11. EDS spectra of (a) FeMn@SiO$_2$-500 (b) FeMn@SiO$_2$-700 (c) FeMn@SiO$_2$-500 (d) FeMn@SiO$_2$-900 and (e) FeMn@SiO$_2$-1000
Fig. S12. (a,b) TEM images of SiO$_2$ removed FeMn@SiO$_2$-500 particles and (c,d) NH$_4$OH-FeMn-500
<table>
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<th>Compound</th>
<th>Average Peak Position (eV)</th>
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<tr>
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<td>Fe 2p$_{1/2}$</td>
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<td>Fe$_2$O$_3$ (Fe$^{3+}$)</td>
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<tr>
<td>Fe$_3$O$_4$ (Fe$^{2+}$ and Fe$^{3+}$)</td>
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Table S2. Average peak positions of the XPS for Fe$_2$O$_3$ (Fe$^{3+}$), Fe$_2$SiO$_4$ (Fe$^{3+}$), and Fe$_3$O$_4$ (Fe$^{2+}$ and Fe$^{3+}$).

References