Electronic Supplementary Material (ESI) for CrystEngComm.

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

Junhyung Lee*

Korea Transformer Co., Ltd., 415, Siheung Dae-ro, Geumcheon-gu, Seoul 08523, Korea

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 = 1.541Å) 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 SiO_2 coated FeMn(fur) particles

A precursor solution was prepared by disperison 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-Fe_2O_3 hollow silica (FeMn@SiO_2-500)

SiO_2 coated FeMn(fur) particles were moved in ceramic boats and then moved into a furnace. The FeMn(fur)@SiO_2 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. Hearafter, the prepared products are called FeMn@SiO_2-X, where X indicates the calcination temperature.

Preparation of manganese doped amorphous iron oxides

Mn-doped β-Fe_2O_3@SiO_2 (FeMn@SiO_2-500) particles were immersed in 1M of NaOH solution and then were sonicated for 2h at 60 ℃. The products were washed with deionized water and ethanol by centrifugation to remove residues.

Preparation of manganese doped mixed Fe_2O_3 (FeMn-500)

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

Preparation of manganese doped α-Fe_2O_3 (NH_4OH-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 ℃ for 2 hr. Aqueous ammonica solution treated FeMn(fur) particles were isolated by filtration and then washed with deinoized wated, ethanol and acetone 2 times and then dried. The precipitates were calcined at 500 ℃ under air atmosphere with a heating rate of 5 °C /min and then naturally cooled down to room temperature.

Results and Discussion

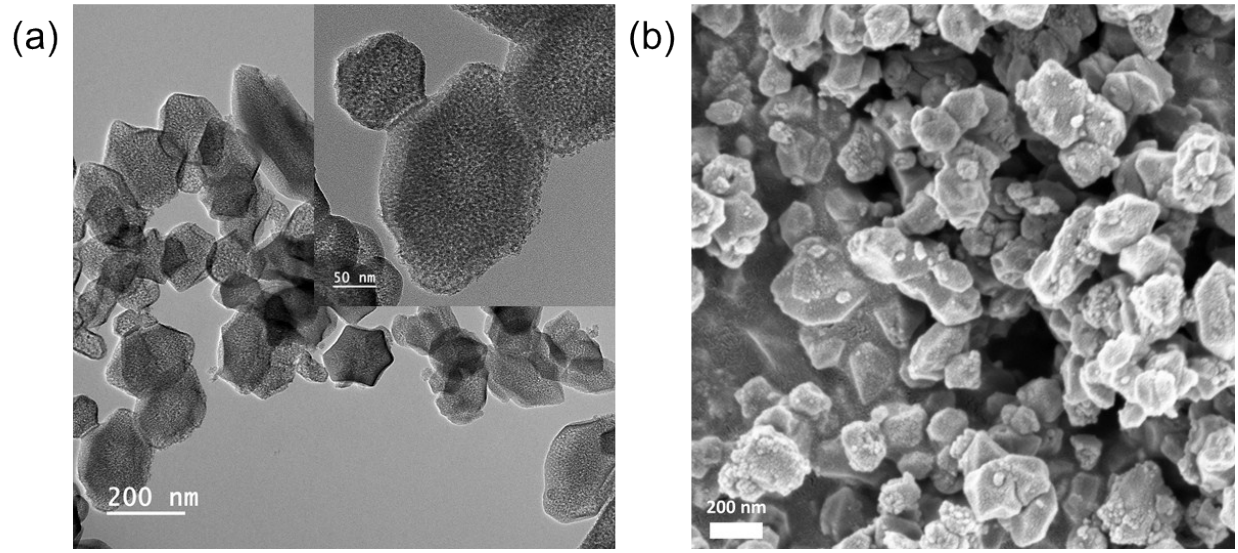

Fig. S1. (a) TEM and (b) SEM images of FeMn(fur)@SiO2 particles

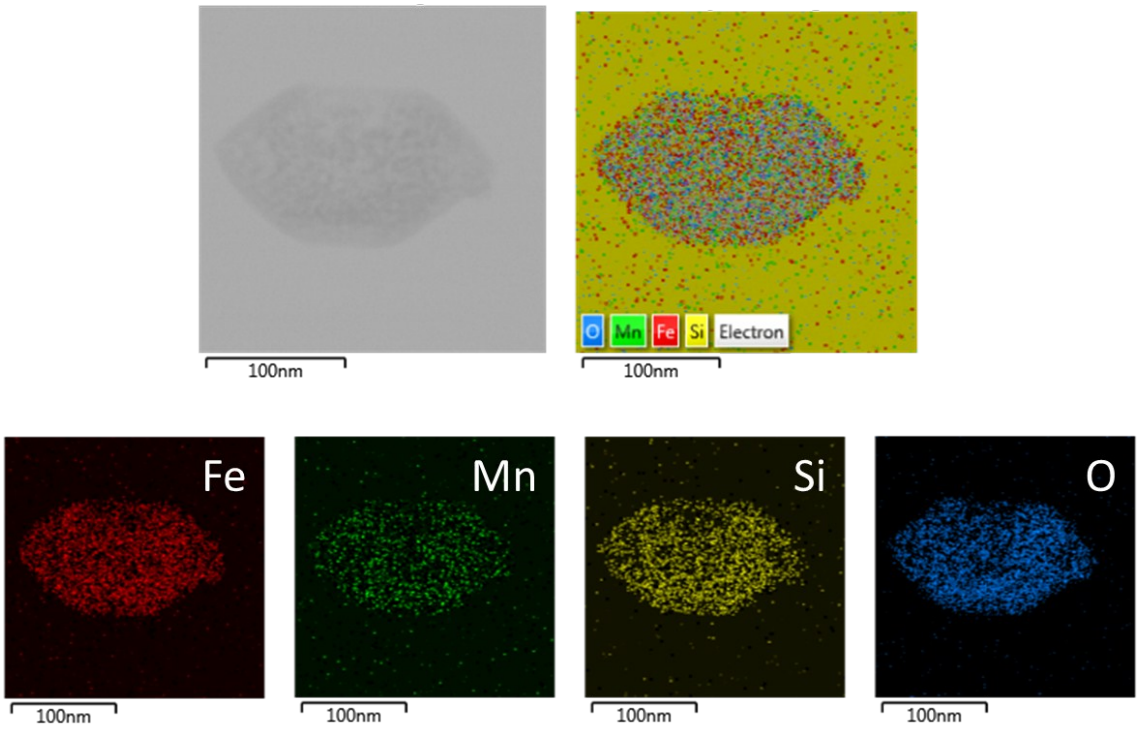

Fig. S2. The scanning transmission electron microscopy (STEM)-EDS maps showing the distribution of Fe, Mn, Si and O of FeMn(fur)@SiO_2 particles.

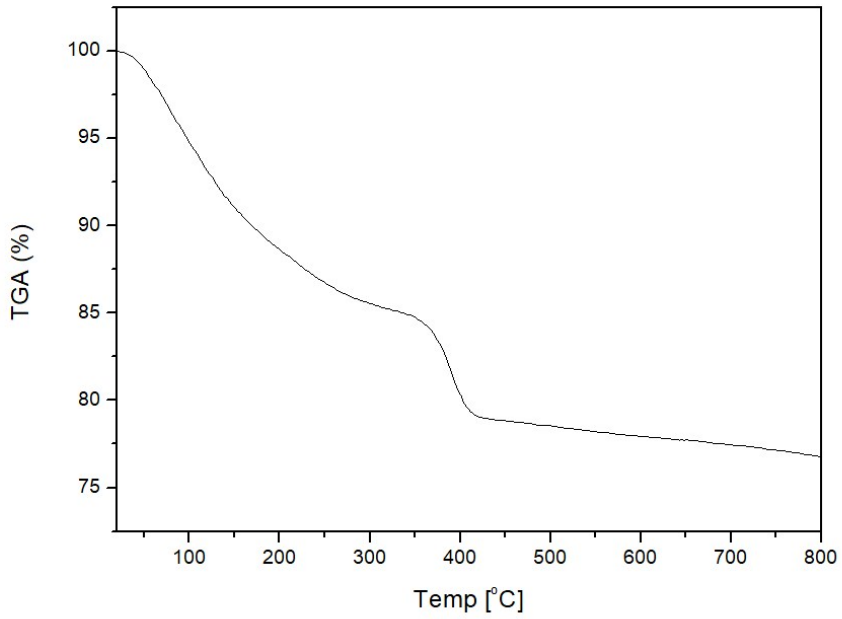

Fig. S3. TGA curve of FeMn(fur)@SiO_2

	α-Fe_2O_3	**β-Fe_2O_3**	**γ-Fe_2O_3**	**ε-Fe_2O_3**
Crystal System	Rhombohedral	Cubic	Tetragonal	Monoclinic
Space Group	R-3 (148)	Ia-3 (206)	P43212 (6)	P
a (Å)	5.033 Å	8.144 Å	8.34 Å	8.44 Å
b (Å)	5.033 Å	8.144 Å	8.34 Å	10.21 Å
c (Å)	13.74 Å	8.144 Å	25.02 Å	12.97 Å
V ($Å^3$)	301.37 $Å^3$	415.82 $Å^3$	1740.28 $Å^3$	1112.82 $Å^3$

Table S1. The crystallographic parameter for (a) α-Fe_2O_3 (ICDD No. 04-006-6579) (b) β-Fe_2O_3 (ICDD No. 00-039-0238) (c) γ-Fe_2O_3 (ICDD No. 00-025-1402) and (d) ε-Fe_2O_3 (ICDD No. 00-016-0653)

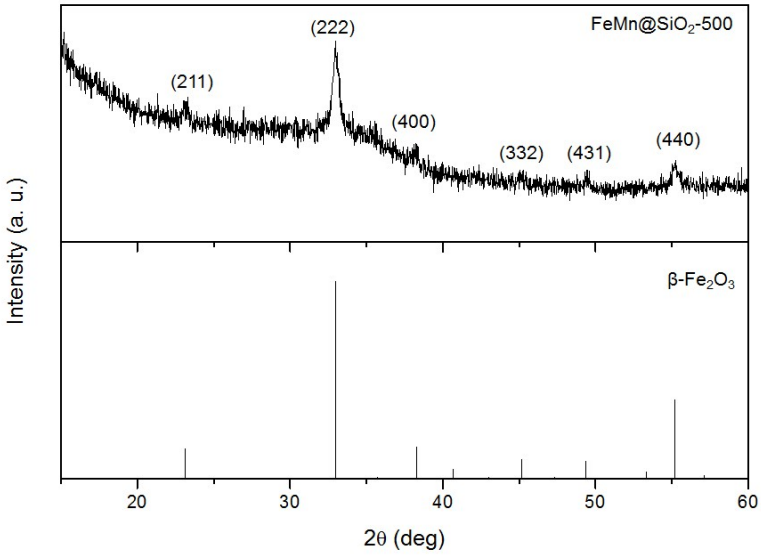

Fig. S4. XRD pattern of FeMn@SiO2-500

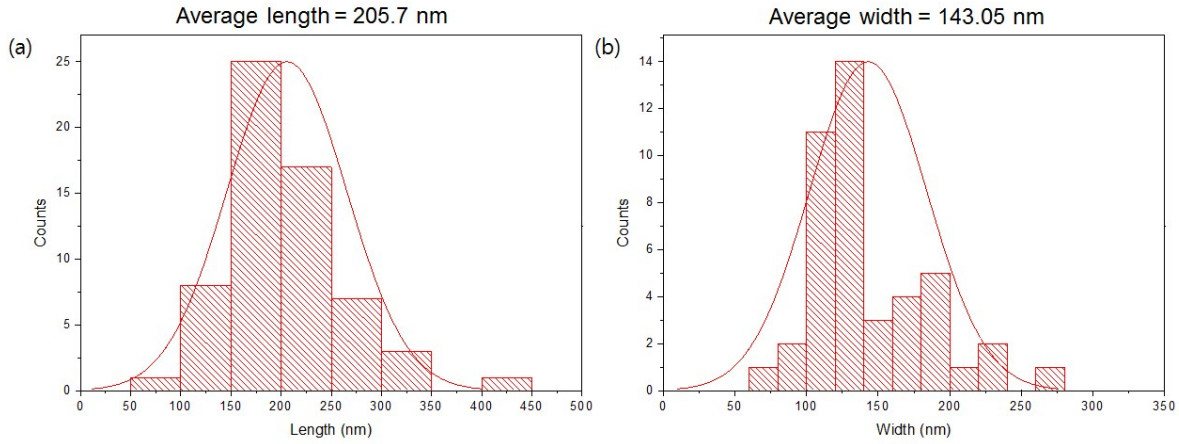

Fig. S5. (a) The average length and (b) the average width of FeMn@SiO_2-500 particles

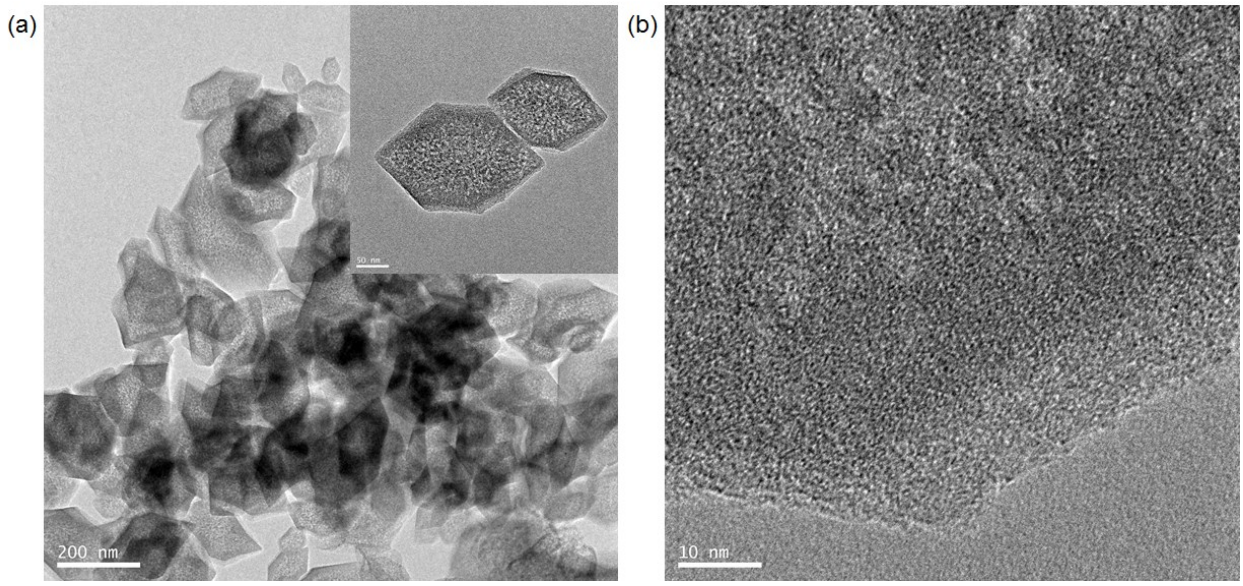

Fig. S6. (a) TEM and (b) HRTEM images of Fe/Mn removed FeMn@SiO_2-500

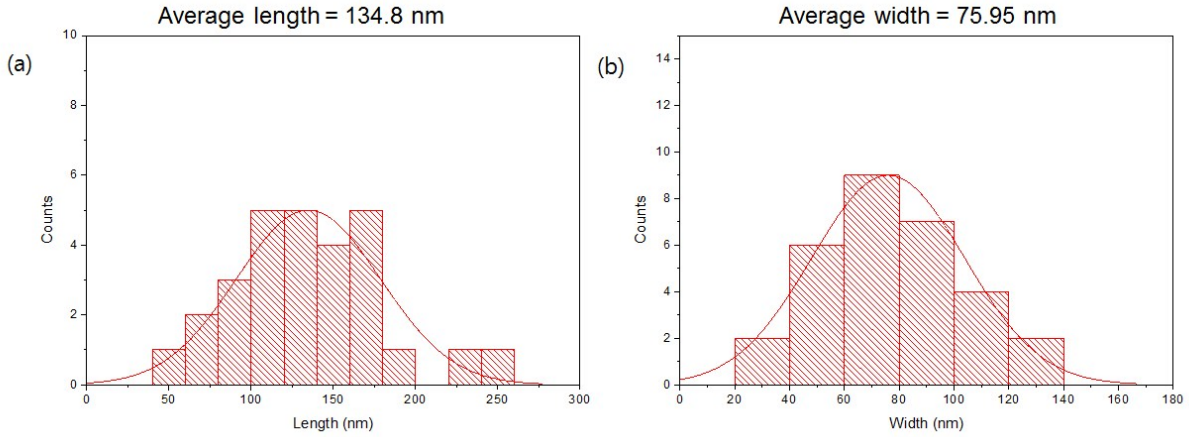

Fig. S7. (a) The average length and (b) the average width of void space of FeMn@SiO_2-500 particles

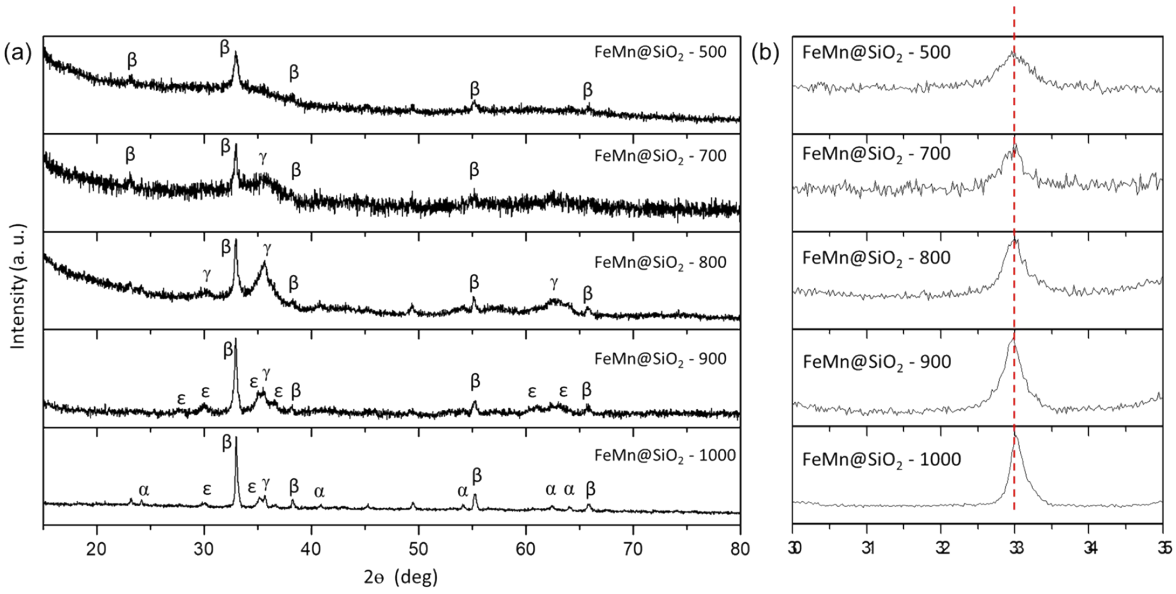

Fig. S8. Powder X-ray diffraction patterns of SiO_2 coated Mn-doped iron oxides structures annealed at 500, 700, 800, 900, and 1000 ℃ for 30 min.

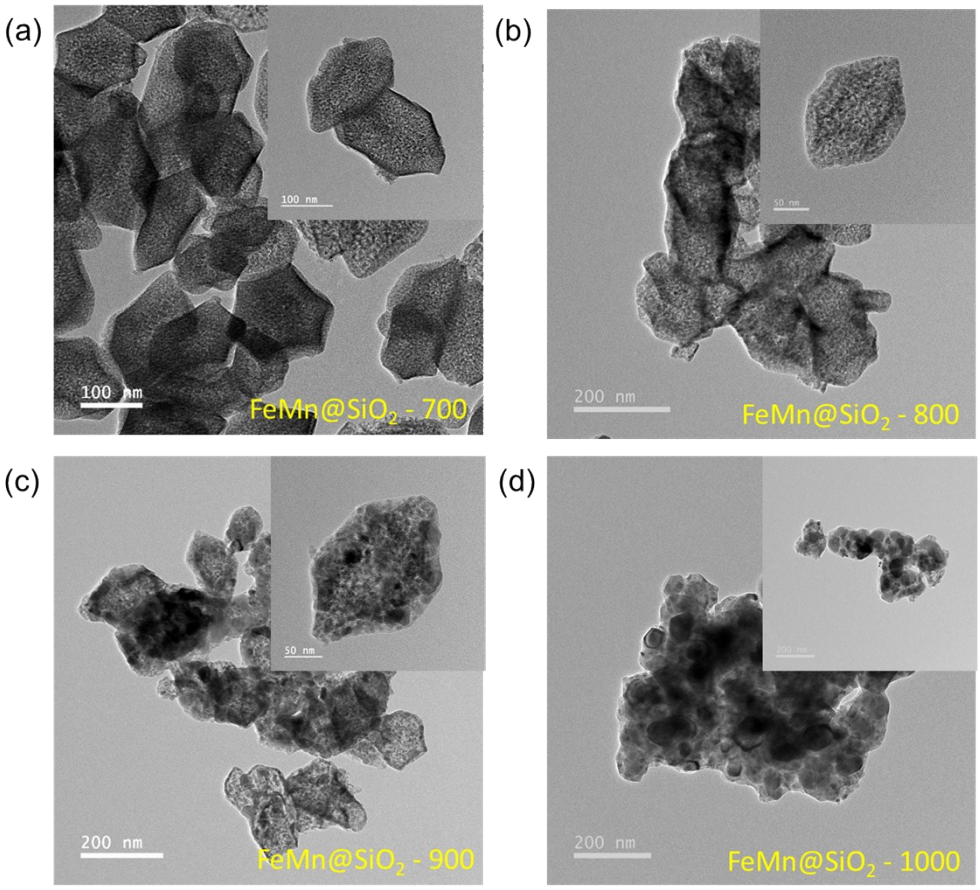

Fig. S9. TEM images of (a) FeMn@SiO2 − 700 (b) FeMn@SiO2 − 800 (c) FeMn@SiO2 − 900 (d) FeMn@SiO2 − 1000

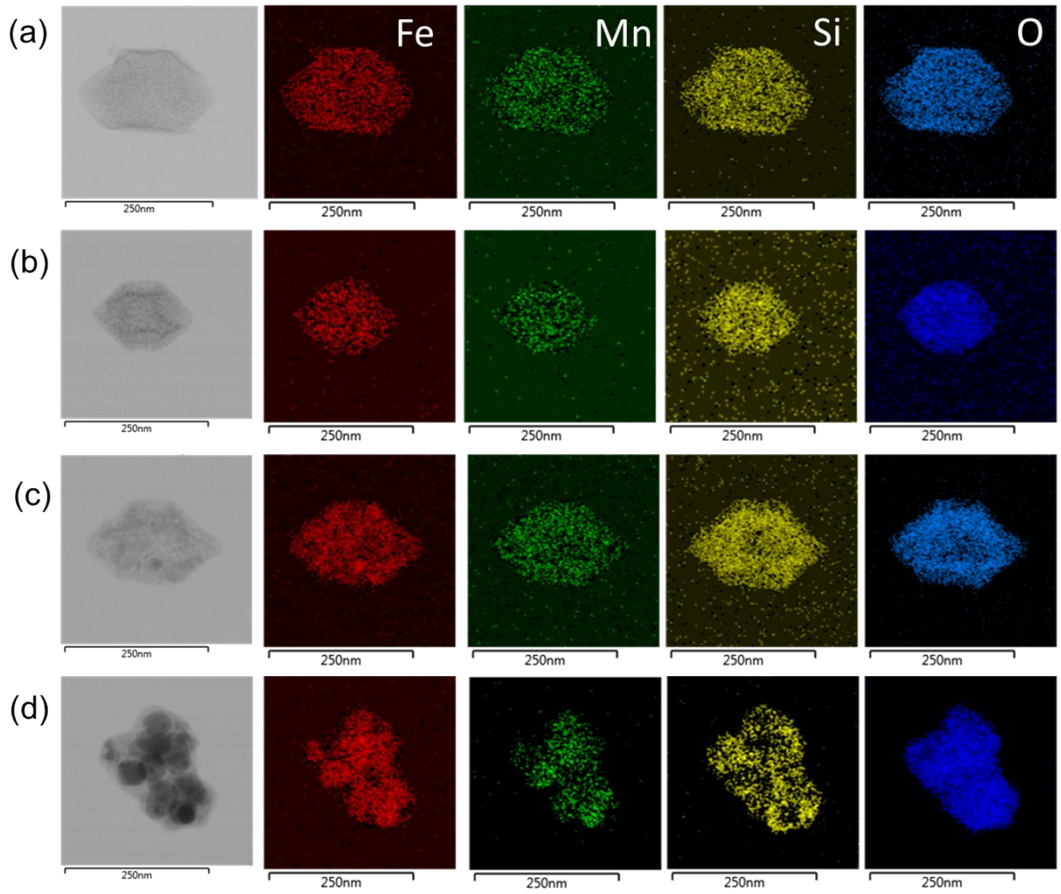

Fig. S10. Energy dispersive X-ray spectroscopy (EDS) mapping of (a) FeMn@SiO_2-700 (b) FeMn@SiO_2 -800 (c) FeMn@SiO_2-900 (d) FeMn@SiO_2 -1000

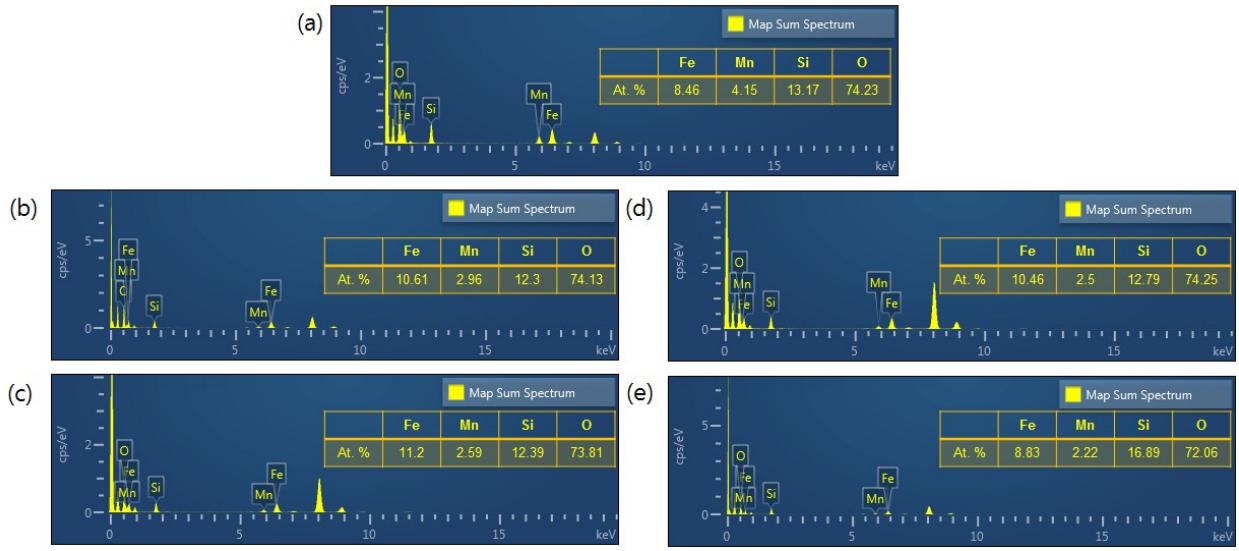

Fig. S11. EDS spectra of (a) FeMn@SiO_2-500 (b) FeMn@SiO_2-700 (c) FeMn@SiO_2-500 (d) FeMn@SiO_2-900 and (e) FeMn@SiO_2-1000

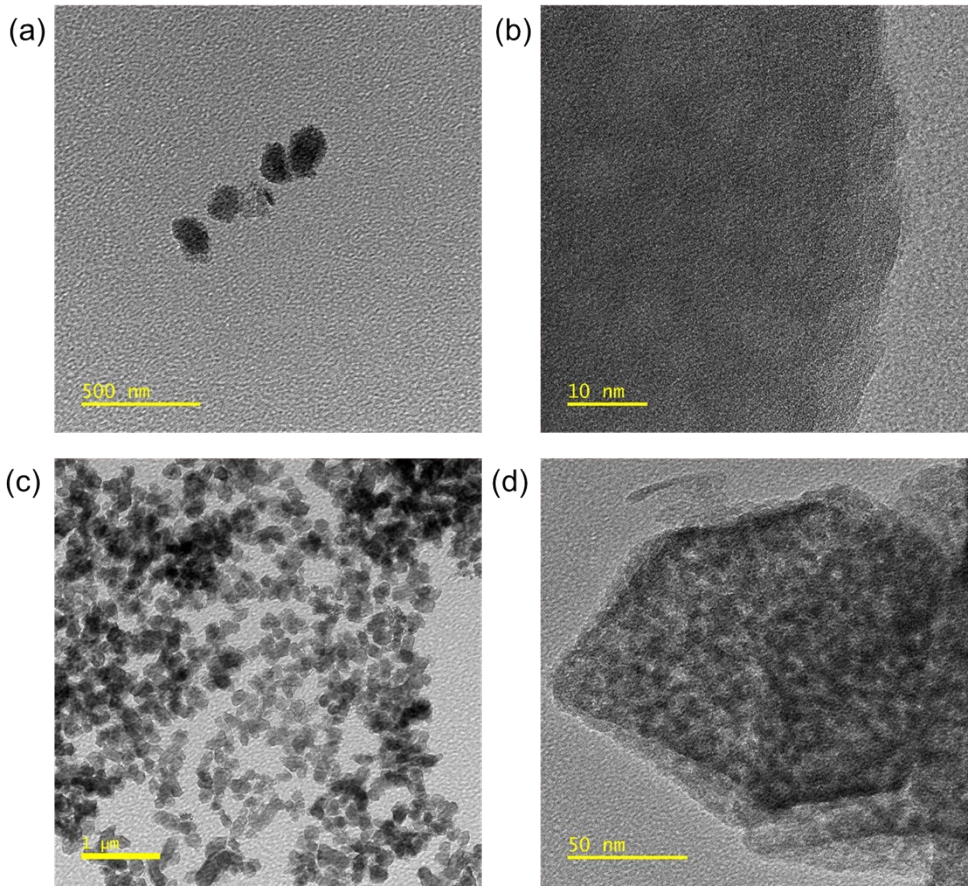

Fig. S12. (a,b) TEM images of SiO_2 removed FeMn@SiO_2-500 particles and (c,d) NH_4OH-FeMn-500

Compound	Average Peak Position (eV)	
	Fe $2p_{1/2}$	Fe $2p_{3/2}$
Fe_2O_3 (Fe^{3+})	724.6	711.0
Fe_2SiO_4 (Fe^{2+})	722.6	709.0
Fe_3O_4 (Fe^{2+} and Fe^{3+})	724.07	710.56

Table S2. Average peak positions of the XPS for Fe_2O_3 (Fe^{3+}), Fe_2SiO_4 (Fe^{2+}), and Fe_3O_4 (Fe^{2+} and Fe^{3+})[2]

References

1. J. Lee, S. Y. Kwak, *ACS Omega* 2018, **3,** 2634.
2. T. Yamashita, P. Hayes, Analysis of XPS spectra of Fe^{2+} and Fe^{3+} ions in oxide materials. *Applied Surface Science* 2008, **254**, 2441-2449