Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

Shape control of core–shell MOF@MOF and derivate MOF nanocage via ion modulation in one-pot strategy

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This ESI for *J. Mater. Chem. A*, 2018, **6**, 18234-18241, originally published on 6th September 2018, was updated on 11th January 2019, to correct an error in the units in Table S1.

Supplemental Figures and Discussions

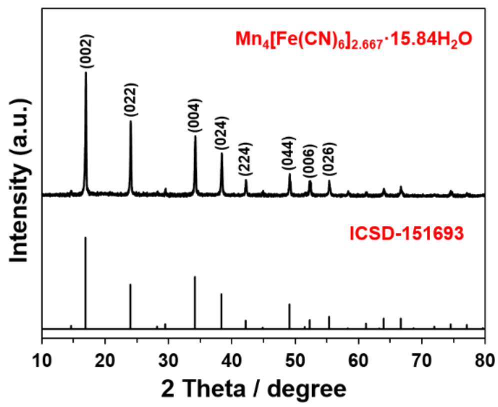

Fig. S1 XRD pattern of the original $Mn_4[Fe(CN)_6]_{2.667}$ (Mn/Fe PBA) nanocubes.

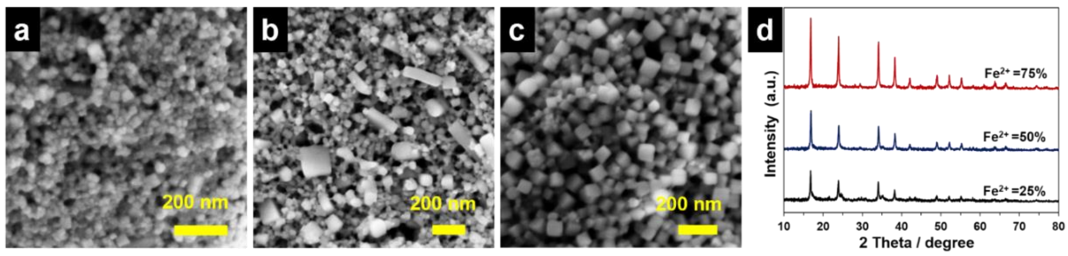

Fig. S2 (a-c)Overview SEM images and (d) XRD patterns of irregular Mn-Fe PBA nanoparticles obtained from the synthetic procedure using different doses of Fe^{2+}: (a) 75%, (b) 50%, (c)25%.

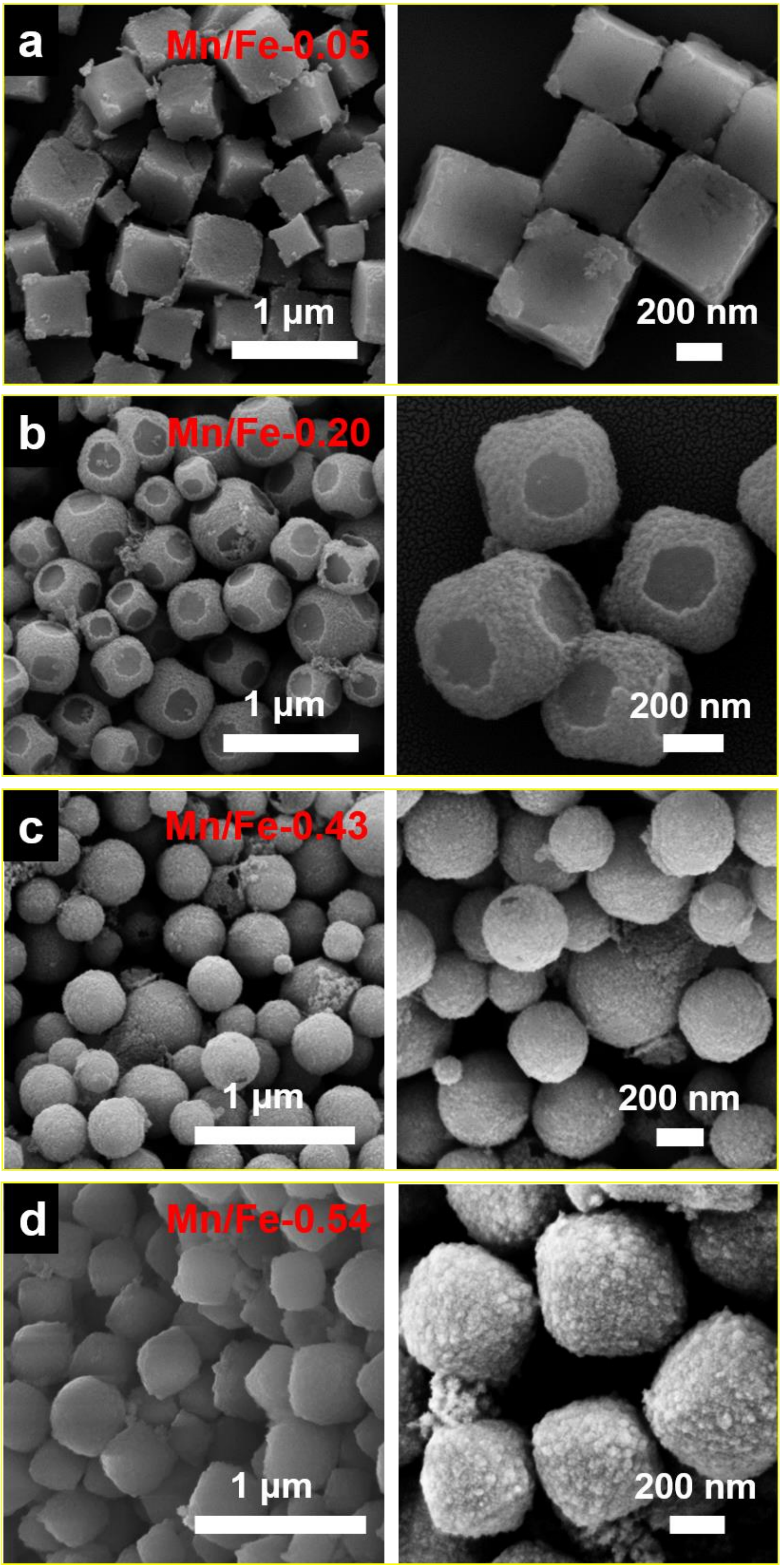

Fig. S3 Large-scale SEM images of (a) Mn/Fe-0.05, (b) Mn/Fe-0.2, (c) Mn/Fe-0.43, and (d) Mn/Fe-0.54.

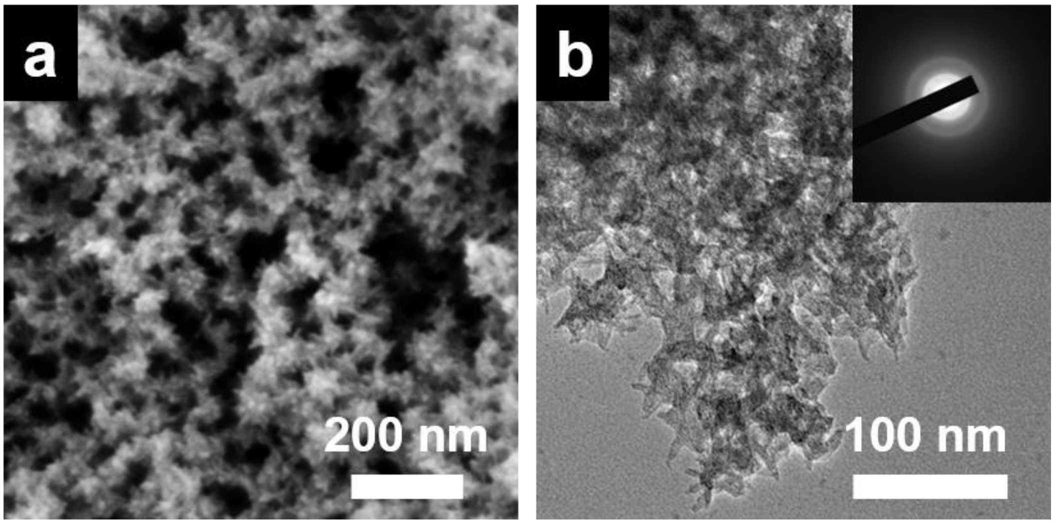

Fig. S4 (a) SEM and (b) TEM images of nanoclusters obtained from the synthetic procedure in the presence of >67% Fe^{3+} (inset: SAED pattern of nanocluster). SAED pattern indicates the amorphous characteristic of obtained nanocluster.

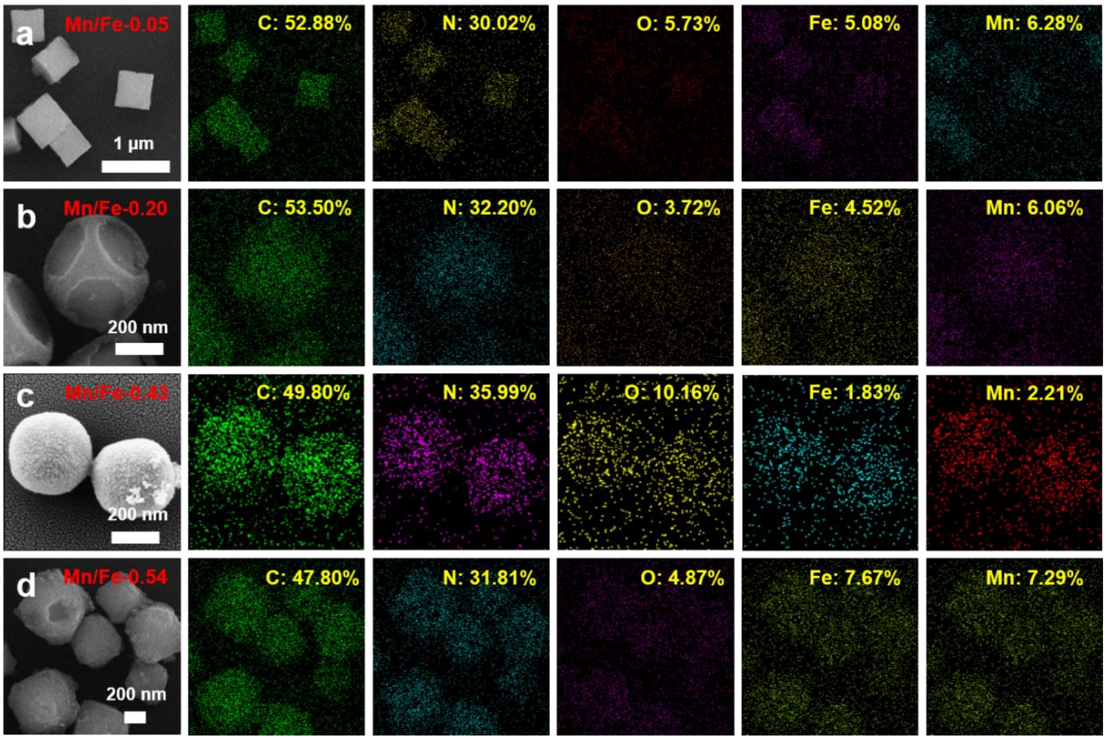

Fig. S5 Elemental mappings (C, N, O, Fe and Mn) of (a) Mn/Fe-0.05, (b) Mn/Fe-0.2, (c) Mn/Fe-0.43, and (d) Mn/Fe-0.54, respectively.

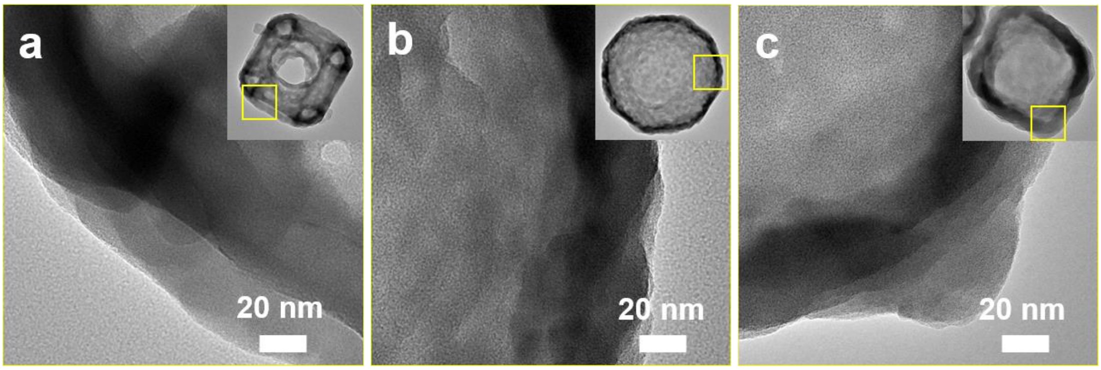

Fig. S6 HRTEM images of (a)Mn/Fe-0.2E, (b)Mn/Fe-0.43E, and (c)Mn/Fe-0.54E, respevtivley.

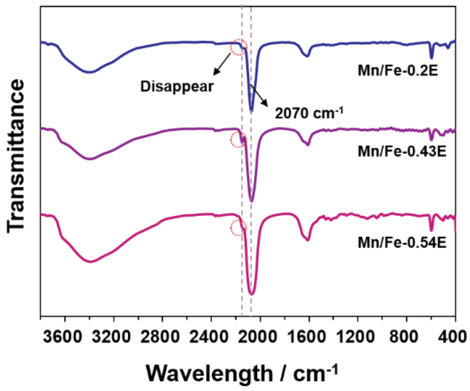

Fig. S7 FT-IR spectra of Mn/Fe-X-E (X=0.2, 0.43, 0.54).

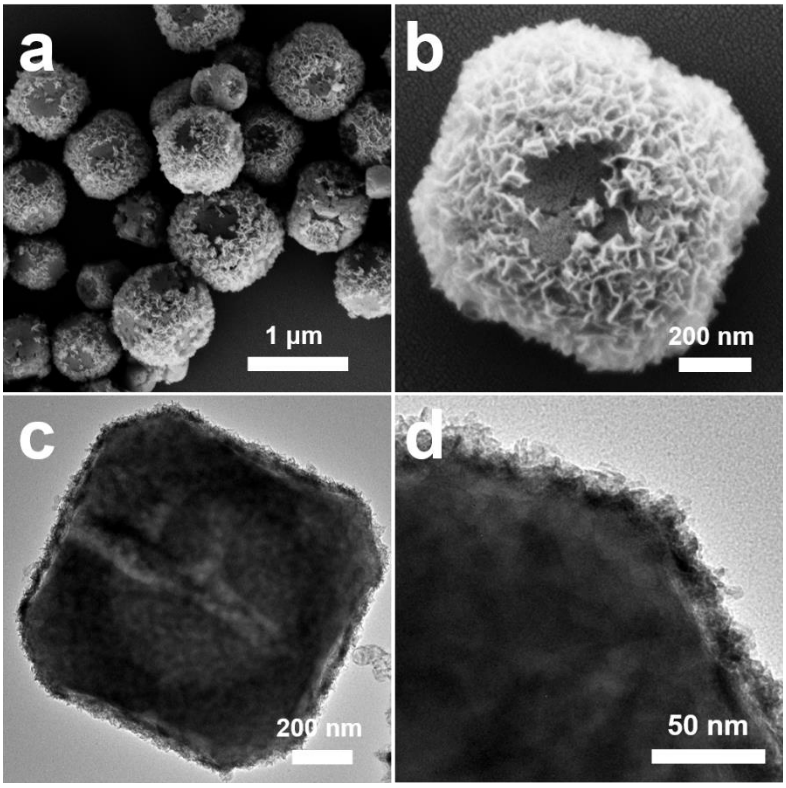

Fig. S8 (a) Low-, (b) high-magnification SEM images, and (c) Low-, (d) high-magnification TEM images of Mn/Fe-0.2 after treated by NH_4F.

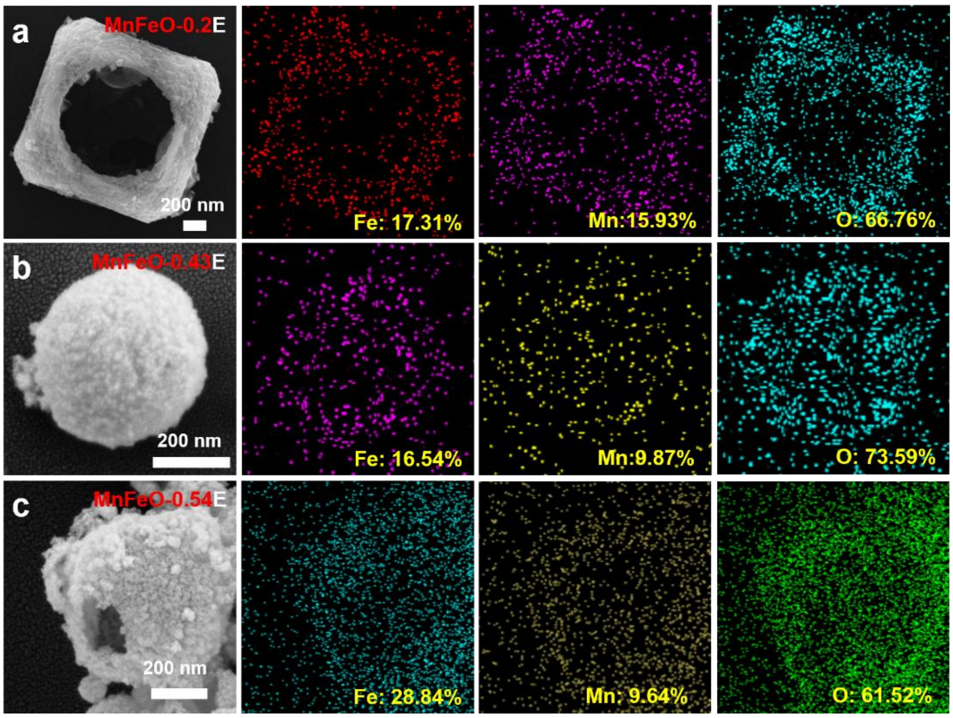

Fig. S9 Elemental mappings of (a) MnFeO-0.2E, (b) MnFeO-0.43E and (c) MnFeO-0.54E, respectively.

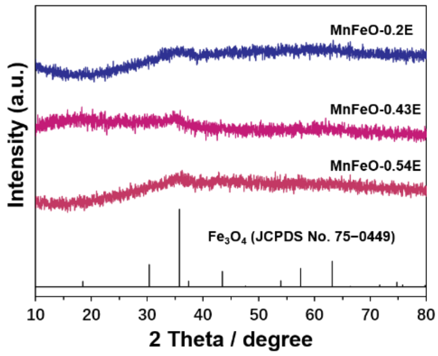

Fig. S10 XRD patterns of MnFeO-X-E (X=0.2, 0.43, 0.54).

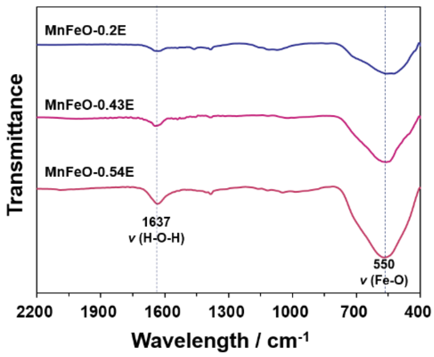

Fig. S11 FT-IR spectra of MnFeO-X-E (X=0.2, 0.43, 0.54).

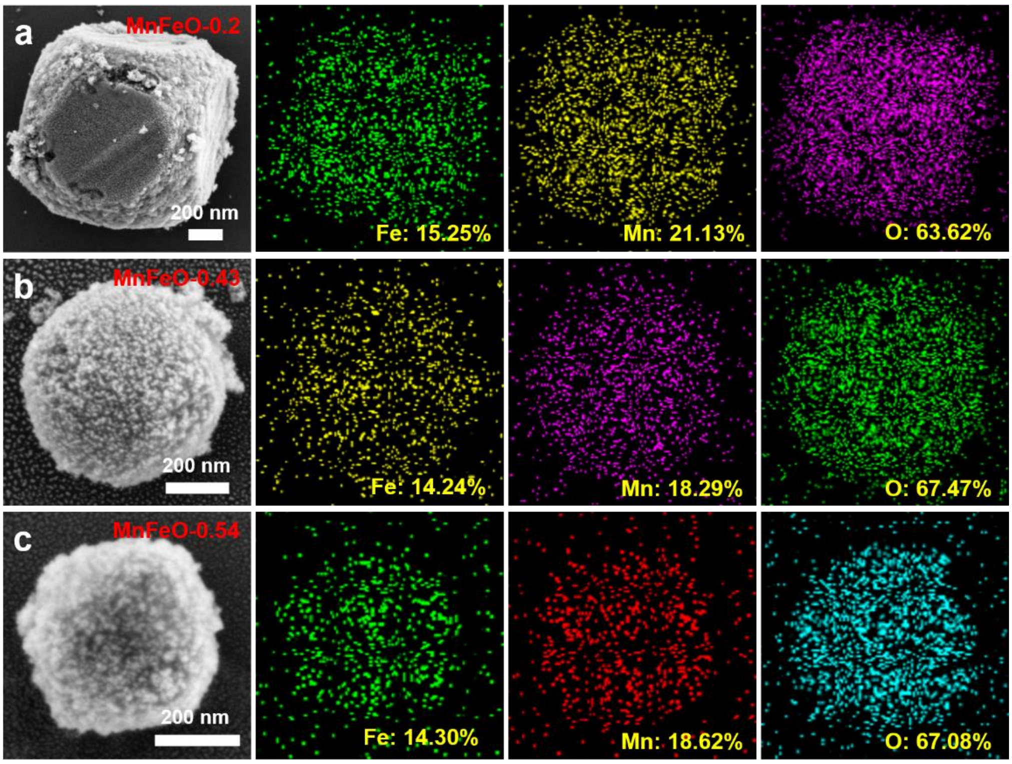

Fig. S12 Elemental mappings of (a) MnFeO-0.2, (b) MnFeO-0.43 and (c) MnFeO-0.54, respectively.

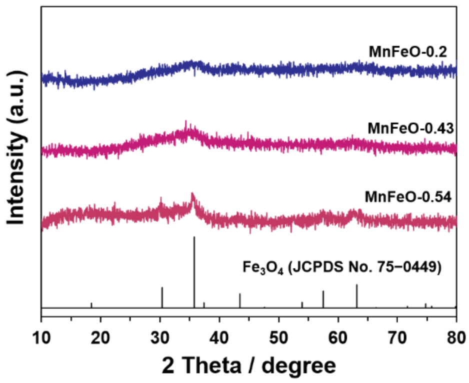

Fig. S13 XRD patterns of MnFeO-X (X=0.2, 0.43, 0.54).

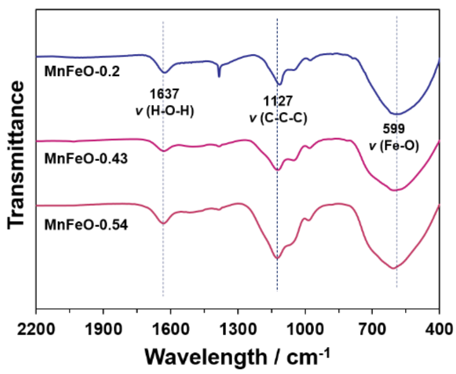

Fig. S14 FT-IR spectra of MnFeO-X (X=0.2, 0.43, 0.54).

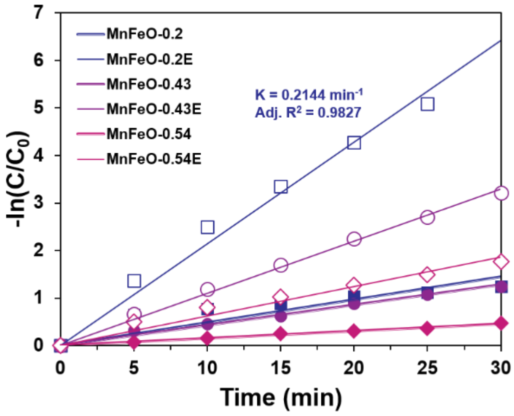

Fig. S15 Kinetic curves in different reaction systems. Reaction conditions: [BPA] = 10 mg/L, [PMS] = 0.2 g/L, [catalyst] = 0.1 g/L .

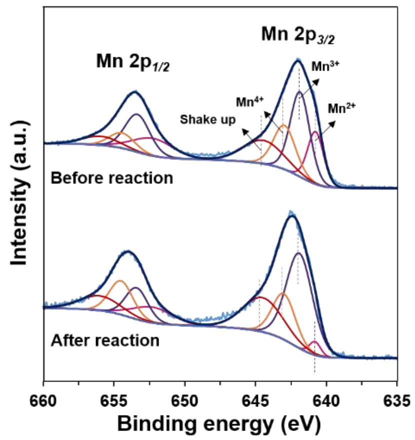

Fig. S16 Mn 2p regions of the XPS spectra of the MnFeO-0.2E sample before and after the reaction. Reaction conditions: [BPA] = 10 mg/L, [PMS] = 0.2 g/L, [MnFeO-0.2E] = 0.1 g/L.

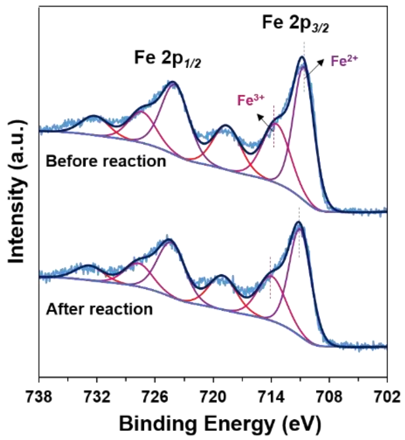

Fig. S17 Fe 2p regions of the XPS spectra of the MnFeO-0.2E sample before and after the reaction. Reaction conditions: [BPA] = 10 mg/L, [PMS] = 0.2 g/L, [MnFeO-0.2E] = 0.1 g/L.

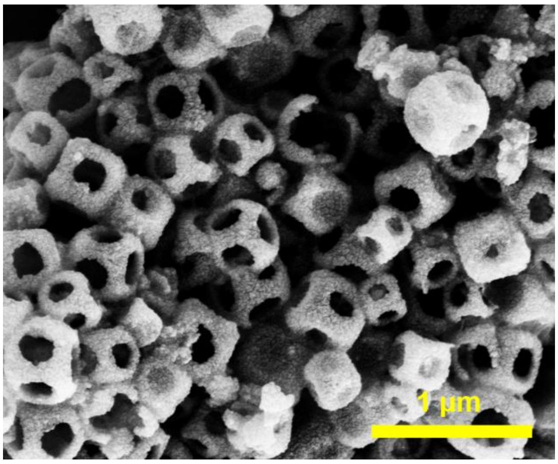

Fig. S18 SEM image of the MnFeO-0.2E sample after three-cycle reactions. Reaction conditions: [BPA] = 10 mg/L, [PMS] = 0.2 g/L, [MnFeO-0.2E] = 0.1 g/L .

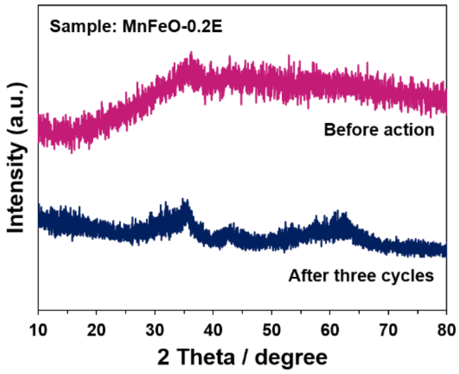

Fig. S19 XRD spectra of the MnFeO-0.2E sample before and after three-cycle reactio. Reaction conditions: [BPA] = 10 mg/L, [PMS] = 0.2 g/L, [MnFeO-0.2E] = 0.1 g/L .

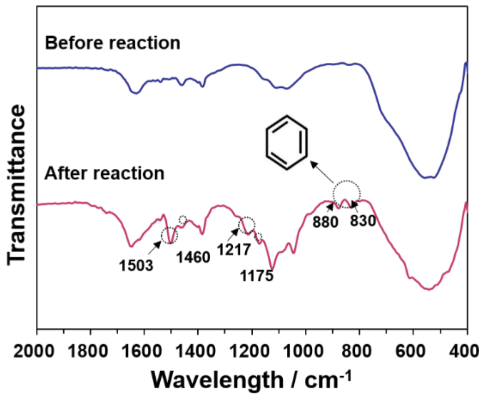

Fig. S20 FT-IR spectra of the MnFeO-0.2E samples before and after three-cycle reaction with PMS. Reaction conditions: [BPA] = 10 mg/L, [PMS] = 0.2 g/L, [MnFeO-0.2E] = 0.1 g/L .

Table S1. Dose of starting materials and code of products obtained in each step of strategy.

Starting material			Code of products			
X_{Fe}	$Fe_2(SO_4)_3$ (μmol)	$MnSO_4$ (μmol)	MOF@MOF nanocrystal	Annealed MOF@MOF	MOF nanocage	Annealed nanocage
0.05	13	479	Mn/Fe-0.05	—	—	—
0.20	48	373	Mn/Fe-0.2	MnFeO-0.2	Mn/Fe-0.2E	MnFeO-0.2E
0.43	80	213	Mn/Fe-0.43	MnFeO-0.43	Mn/Fe-0.43E	MnFeO-0.43E
0.54	93	160	Mn/Fe-0.54	MnFeO-0.54	Mn/Fe-0.54E	MnFeO-0.54E

Table S2. XPS results of the Fe 2p3/2 and Mn 2p3/2 for MnFeO-0.2E sample before and after reation.

MnFeO-0.2E	Fe $2p_{3/2}$		Mn $2p_{3/2}$		
	Fe(II)	Fe(III)	Mn(II)	Mn(III)	Mn(IV)
Before reaction	63	37	24	48	28
After reaction	66	35	4	68	28

Table S3. Comparison between MnFeO and the previously reported Mn/Fe oxide catalysts in the catalytic performance.

Catalyst Dosage (g/L)	Pollutant (mg/L)	PMS dosage (g/L)	Conversion (%)	*k* (min^{-1})	Ref.
$MnO_2/ZnFe_2O_4$ (0.2)	Phenol (20)	2.0	100%	0.032	[1]
β-MnO_2 (0.4)	Phenol (25)	2.0	100%	0.0723	[2]
α-Mn_2O_3@α-MnO_2-500 (0.15)	Phenol (25)	~0.3	100%	0.05	[3]
Corolla-like δ-MnO_2 (0.2)	Phenol (20)	2.0	100%	0.19	[4]
δ-FeOOH (0.3)	AO7 (50)	0.3	91.4%	0.099	[5]
Fe_3O_4@C/Co (0.2)	AO II (20)	1.0	99%	none	[6]
Mn_2O_3@Mn_5O_8 (0.3)	4-chlorophenol (80)	~0.5	100%	0.06836	[7]
Fe_3O_4/MnO_2 (0.2)	4-chlorophenol (50)	0.5	>95%	~0.116	[8]
Fe_3O_4 (0.8)	Acetaminophen (10)	0.06	98%	0.0118	[9]
Fe_3O_4@MnO_2 BBHs (0.3)	MB (30)	6.0	100%	0.0253	[10]
DPA-hematite (0.5)	BPA (15)	2.0	100%	0.262	[11]
$Fe_{1.8}Mn_{1.2}O_4$ (0.1)	BPA (10)	0.2	100%	0.1019	[12]
MnFeO-0.2E (0.1)	BPA (10)	0.2	100%	0.2144	[This work]

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