

Supporting Information

Synthesis and ORR Electrocatalytic Activity of Mixed Mn-Co oxides Derived from Divalent Metal-based MIL-53 Analogues

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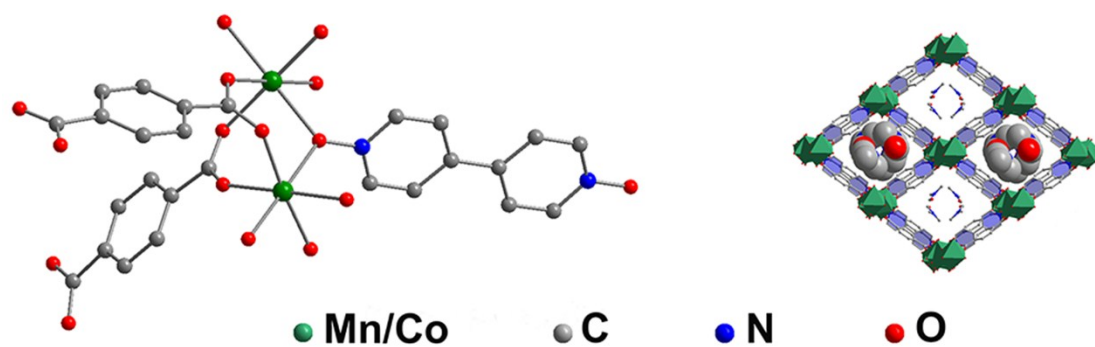


Fig. S1 Structural unit (left) and three dimensional open structure (right) of Mn/Co MIL-53. The hydrogen atoms are omitted for clarity. The occluded guest molecules in the right structure are DMF with ball-and-stick and space-filling models (quoted with permission from Ref. S1. Copyright 2010 American Chemical Society).

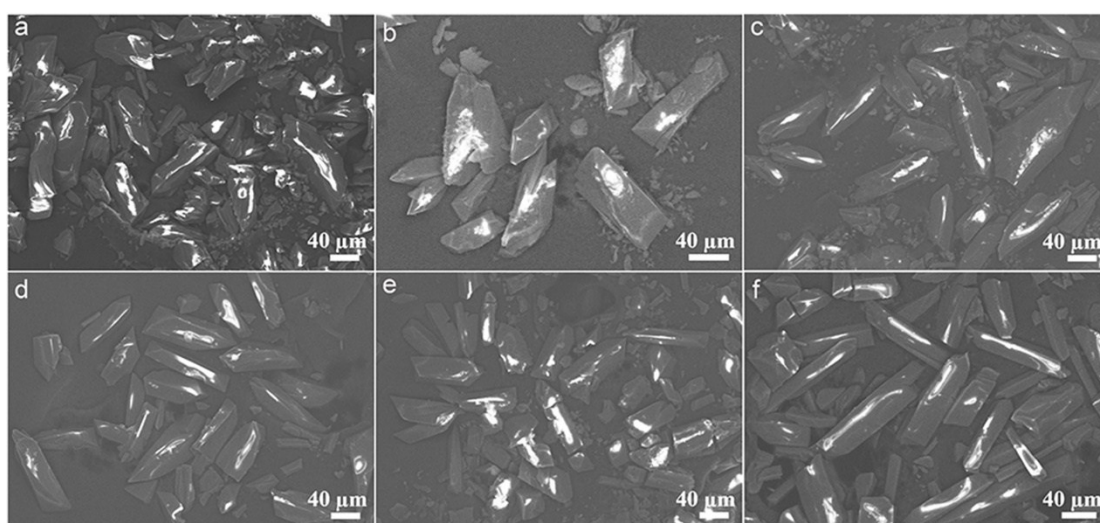


Fig. S2 SEM images of (a) Co-MOF, (b) Co₂Mn-MOF, (c) CoMn-MOF, (d) CoMn₂-MOF, (e) CoMn₄-MOF and (f) Mn-MOF, respectively.

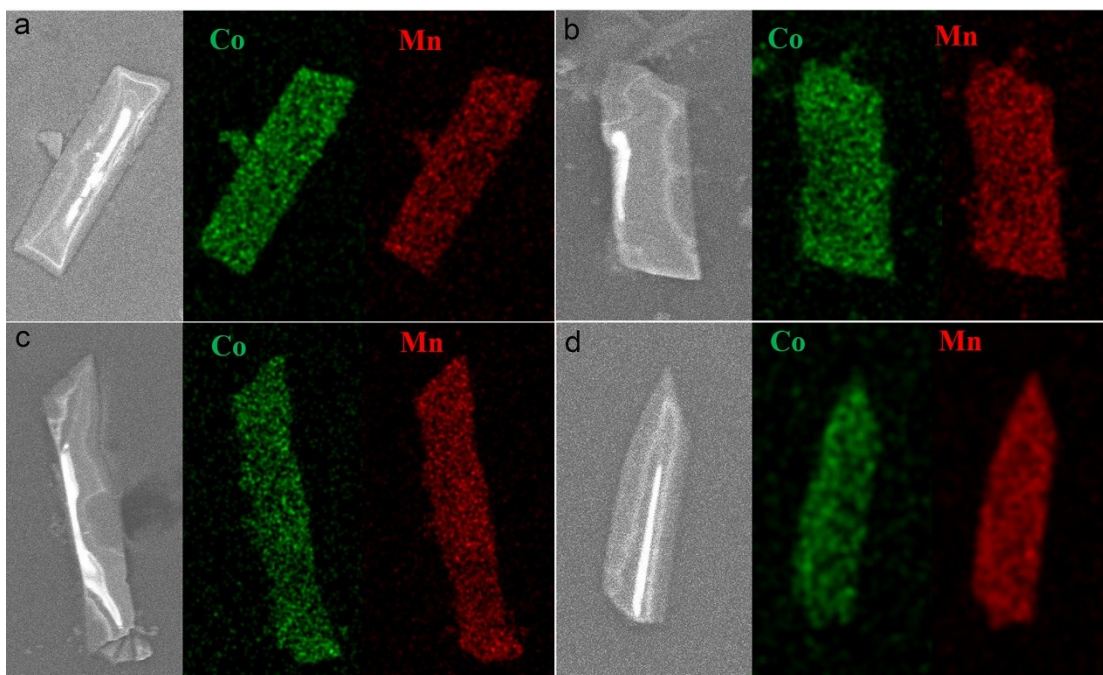


Fig. S3 Elemental mappings of (a) Co₂Mn-MOF, (b) CoMn-MOF, (c) CoMn₂-MOF and (d) CoMn₄-MOF.

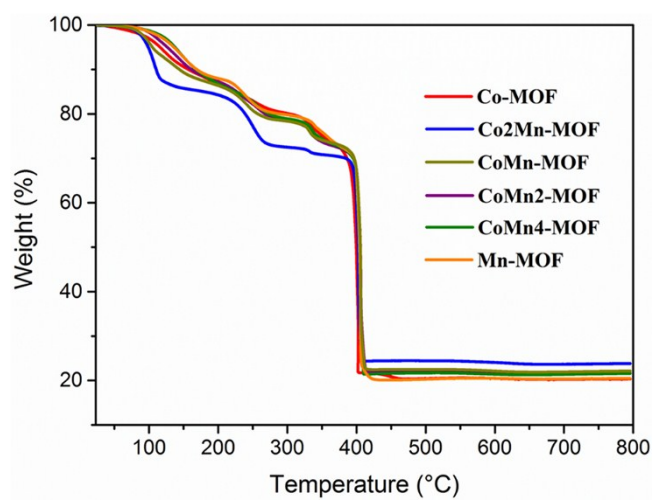


Fig. S4 TGA curves of Co-MOF, Co₂Mn-MOF, CoMn-MOF, CoMn₂-MOF, CoMn₄-MOF and Mn-MOF.

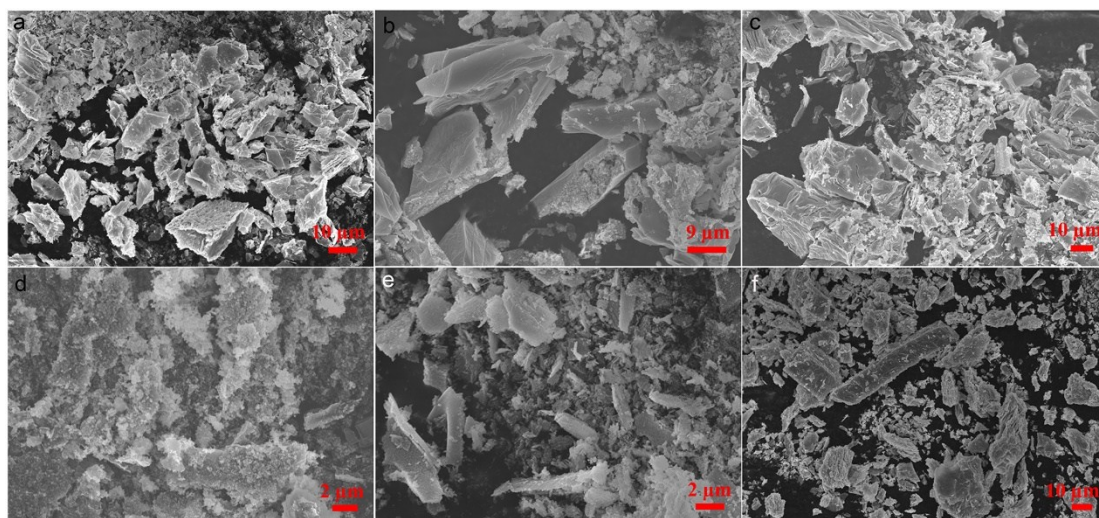


Fig. S5 SEM images of as-obtained metal oxides: (a) Co_3O_4 , (b) $\text{Co}_2\text{Mn-O}$, (c) CoMn-O , (d) $\text{CoMn}_2\text{-O}$, (e) $\text{CoMn}_4\text{-O}$ and (f) Mn_2O_3 .

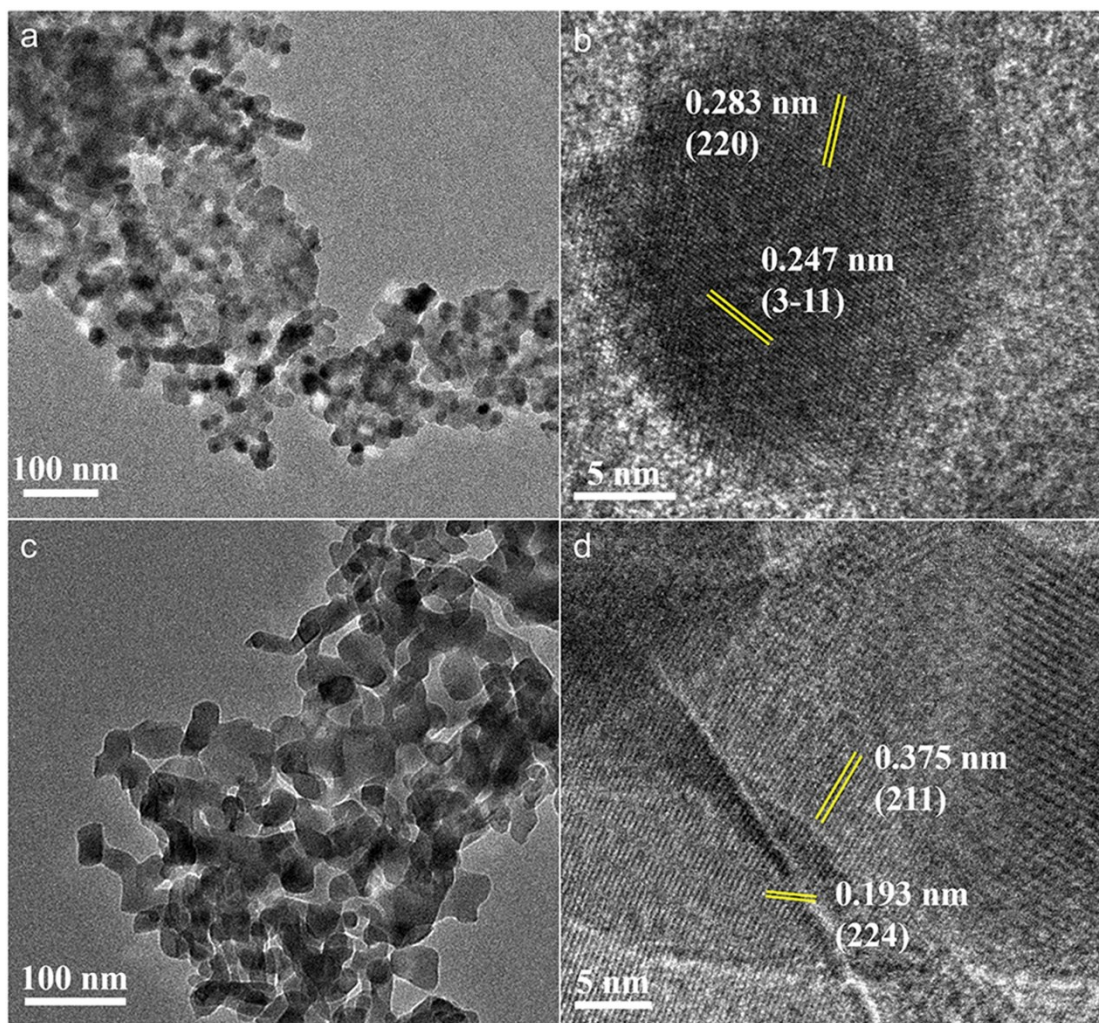


Fig. S6 Low-magnification TEM and HRTEM images of (a and b) Co_3O_4 and (c and d) Mn_2O_3 , respectively.

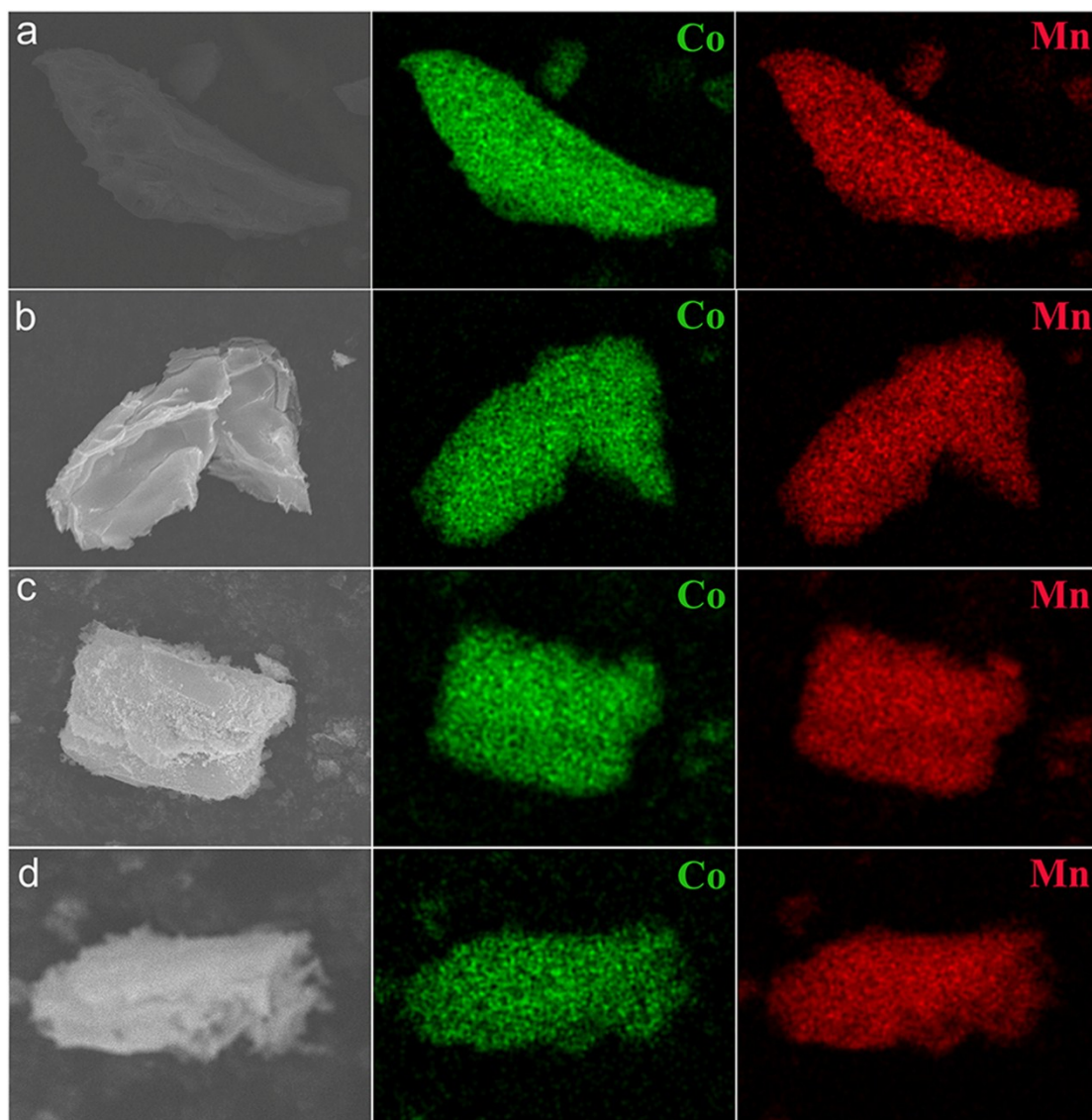


Fig. S7 Elemental mapping patterns of EDX spectra for as-obtained (a) Co₂Mn-O, (b) CoMn-O, (c) CoMn₂-O and (d) CoMn₄-O, respectively.

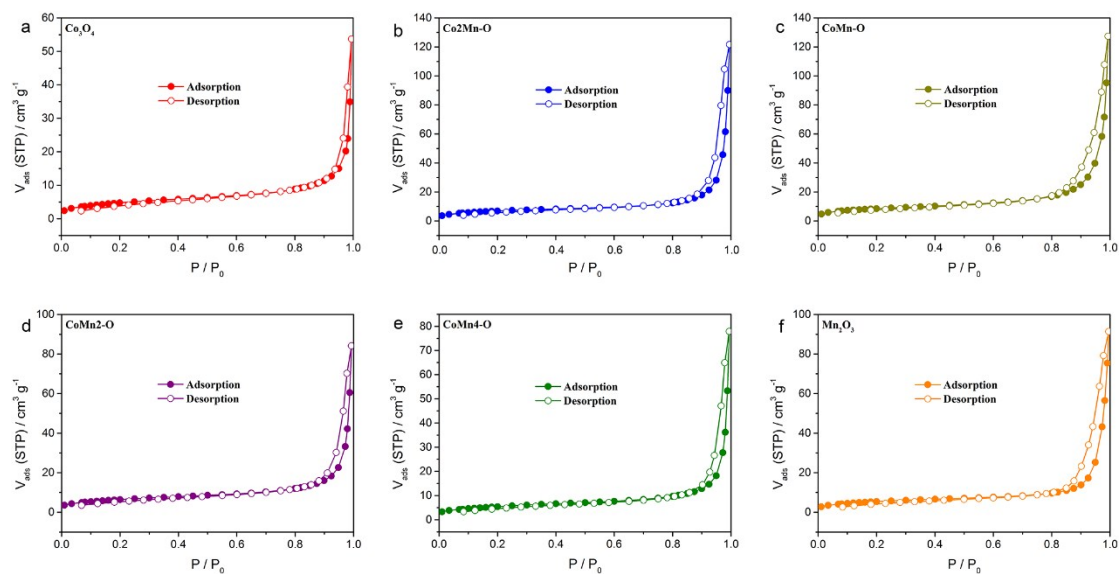


Fig. S8 Nitrogen adsorption-desorption isotherms of as-prepared metal oxides: (a) Co_3O_4 , (b) $\text{Co}_2\text{Mn-O}$, (c) CoMn-O , (d) $\text{CoMn}_2\text{-O}$, (e) $\text{CoMn}_4\text{-O}$ and (f) Mn_2O_3 , respectively.

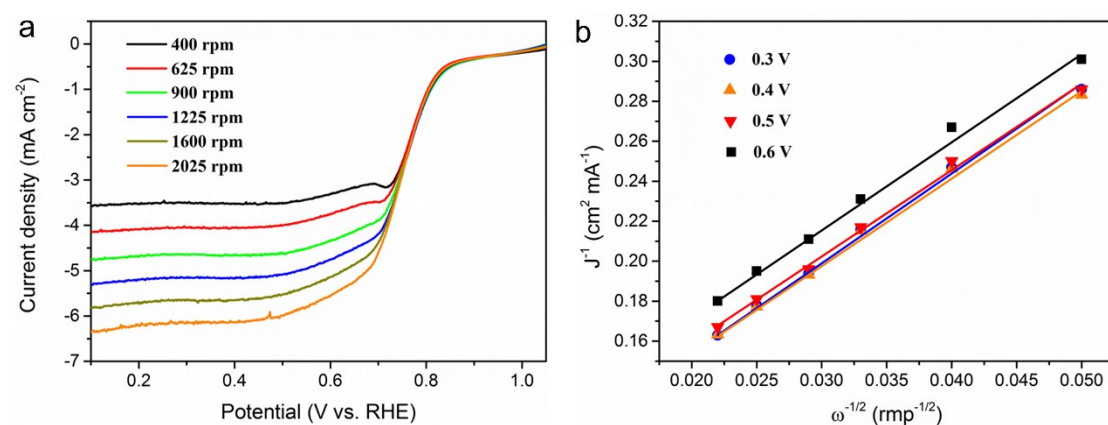


Fig. S9 (a) RDE voltammograms of $\text{Co}_2\text{Mn-O}$ in O_2 -saturated 0.1 M KOH at different rotation rates and (b) corresponding Koutecky-Levich plots at potential 0.3 to 0.6 V (vs. RHE).

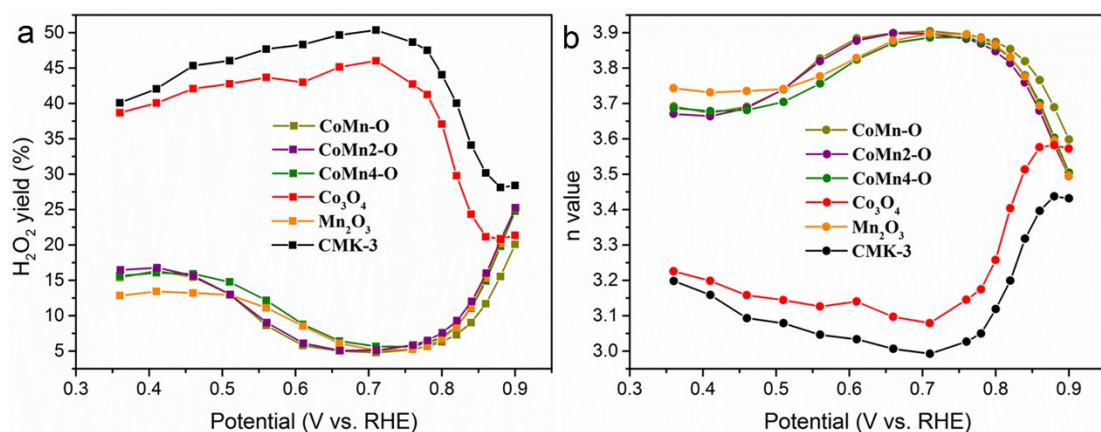


Fig. S10 (a) H_2O_2 yields and (b) electron transfer number of CoMn-O, CoMn2-O, CoMn4-O, Co_3O_4 , Mn_2O_3 and CMK-3, respectively.

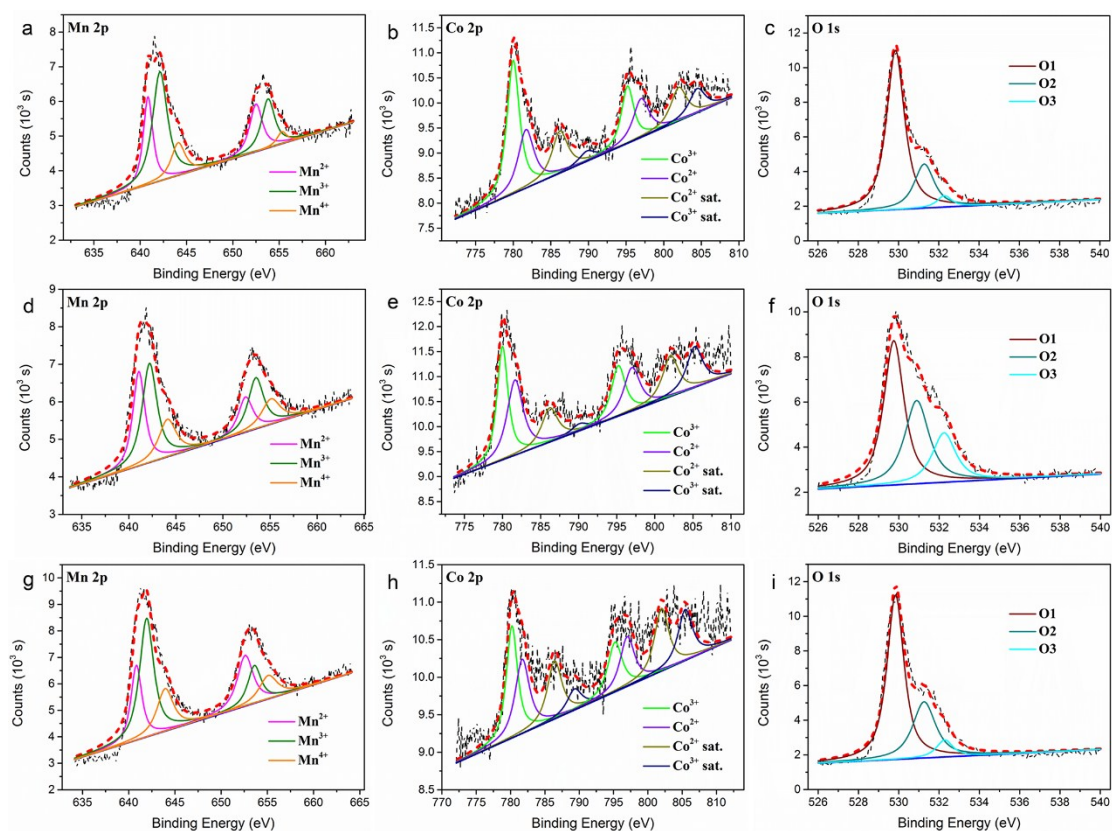


Fig. S11 XPS spectra of (a-c) CoMn-O, (d-f) CoMn2-O and (g-i) CoMn4-O for Mn 2p, Co 2p and O 1s, respectively.

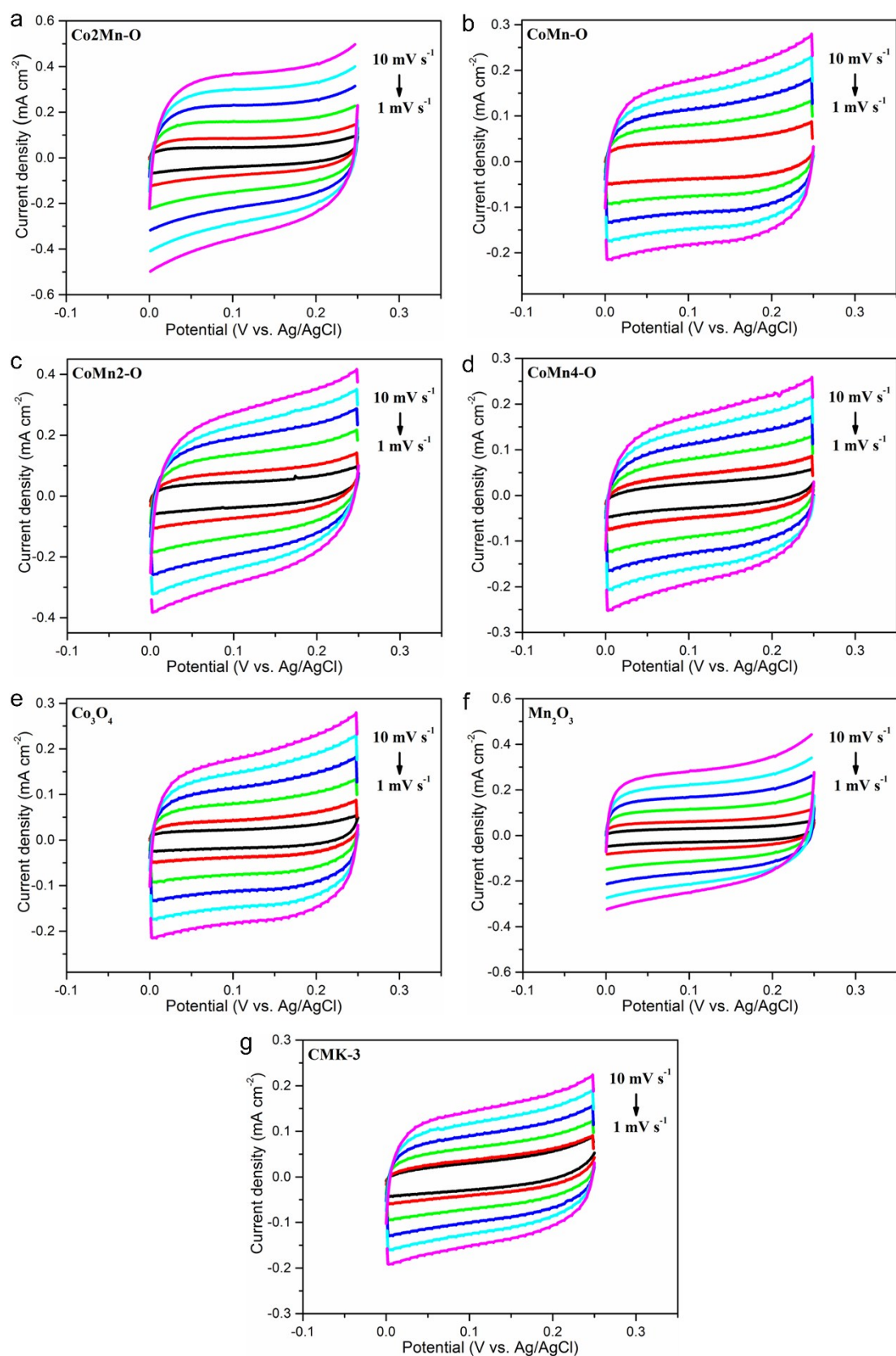


Fig. S12 CVs for different samples with scan rate ranging from 1 to 10 mV s⁻¹. (a) Co₂Mn-O, (b) CoMn-O, (c) CoMn₂-O, (d) CoMn₄-O, (e) Co₃O₄, (f) Mn₂O₃ and (g) CMK-3.

Table S1 ORR activities of different Co/Mn related electrocatalysts.

Catalyst	$E_{1/2}$ (V vs. RHE)	DLCD (mA cm ⁻²)	Reference
Co ₂ Mn-O nanoparticles	0.772	6.3	This work
CoMn-O nanoparticles	0.756	5.5	This work
CoMn ₂ -O nanoparticles	0.740	5.7	This work
CoMn ₄ -O nanoparticles	0.765	6.0	This work
Mn ₂ O ₃ nanoparticles	0.765	5.3	This work
Co ₃ O ₄ nanoparticles	0.710	5.2	This work
CMK-3 alone	0.753	4.9	This work
Co ₃ O ₄ /2.7Co ₂ MnO ₄ nanocomposite	~0.700	~5.2	Ref. S2
cubic-Co ₂ MnO ₄ nanorods	~0.720	~5.9	Ref. S3
tetragonal-CoMn ₂ O ₄ microspheres	~0.700	~5.5	Ref. S3
NiCoMnO ₄ /N-rGO ^a	0.750	~5.6	Ref. S4
NiCo ₂ O ₄ /N-rGO	-0.340*	4.2	Ref. S5
CaMn ₂ O ₄ nanorods	-0.250*	~4.3	Ref. S6
cubic-CoMn ₂ O ₄ ^b	~0.740	~4.4	Ref. S7
mesoporous-MnCo ₂ O ₄ ^a	-0.220**	~5.3	Ref. S8
CoMn ₂ O ₄ /C ^a	0.760	~5.7	Ref. S9
Mn _{0.4} Co _{2.6} O ₄	0.772	~5.5	Ref. S10
Co-Mn oxides with mixed phases	~-0.190**	~0.32	Ref. S11
MnCo ₂ O ₄ /N-rmGO	~0.820	~5.5	Ref. S12

^aThe rotating rate of electrode is 15000 rpm.

^bThe rotating rate of electrode is 900 rpm.

*These potentials are versus SCE.

**These potentials are versus Ag/AgCl.

References

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