Supporting information

Stabilized the Layered Manganese Oxide by Cationic ion Substitution Doping

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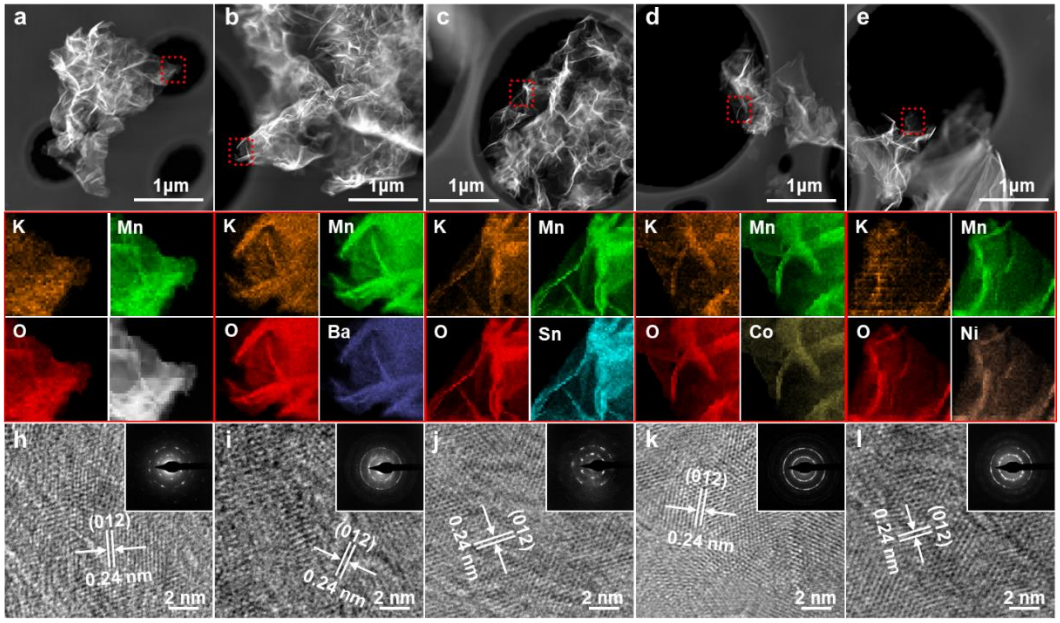

Fig. S1. Morphology and structure of 2D KMnO and 2D M-KMnO for a reaction time of 10 minutes. The HAADF-TEM images and the corresponding mapping images of a) 2D KMnO, b) 2D Ba-KMnO, c) 2D Sn-KMnO, d) 2D Co-KMnO and e) Ni-KMnO. The HR-TEM images of h) 2D KMnO, i) 2D Ba-KMnO, j) 2D Sn-KMnO, k) 2D Co-KMnO and l) 2D Ni-KMnO; insert shows the SAED patterns.

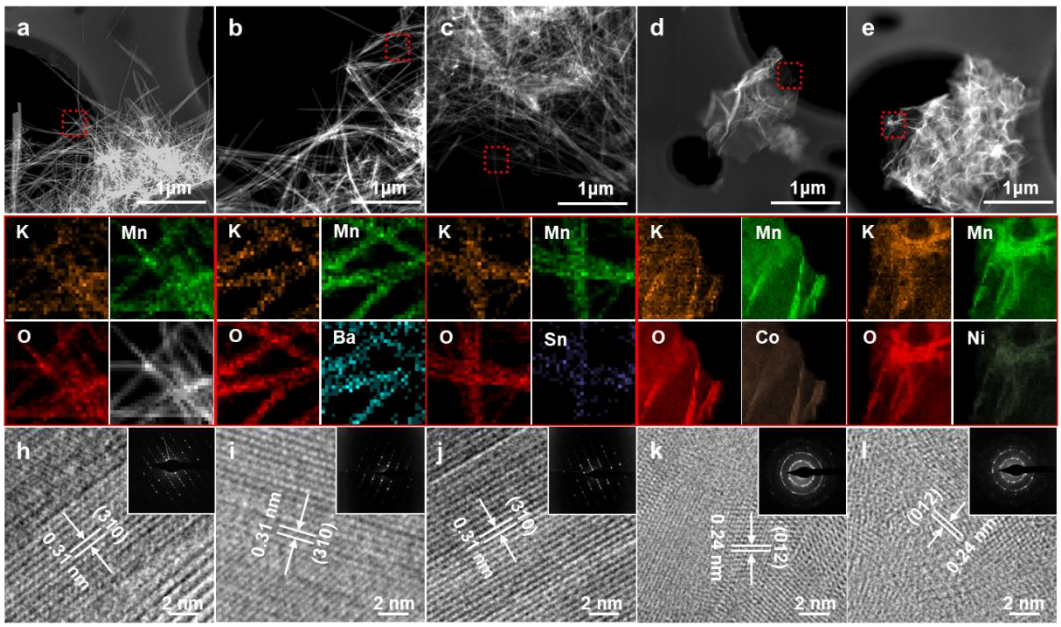

Fig. S2. Morphology and structure of KMnO-30 and M-KMnO-30 for a reaction time of 30 minutes. The HAADF-TEM images and the corresponding mapping images of a) KMnO-30, b) Ba-KMnO-30, c) Sn-KMnO-30, d) Co-KMnO-30 and e) Ni-KMnO-30. The HR-TEM images of h) KMnO-30, i) Ba-KMnO-30, j) Sn-KMnO-30, k) Co-KMnO-30 and l) Ni-KMnO-30; insert shows the SAED patterns.

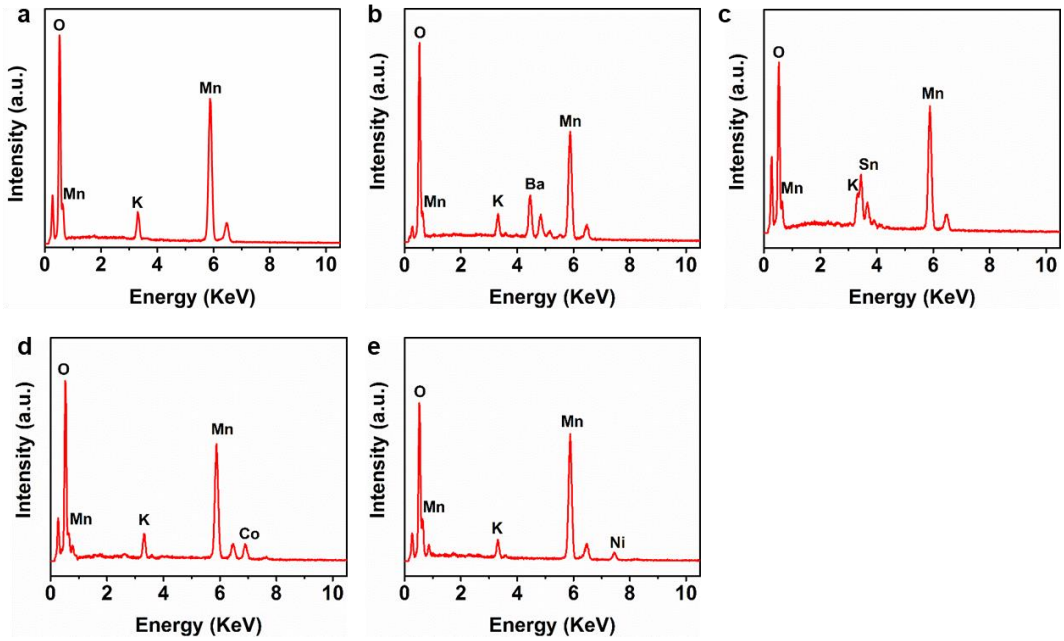

Fig. S3. EDS patterns for a) 2D KMnO, b) 2D Ba-KMnO, c) 2D Sn-KMnO, d) 2D Co-KMnO and e) 2D Ni-KMnO.

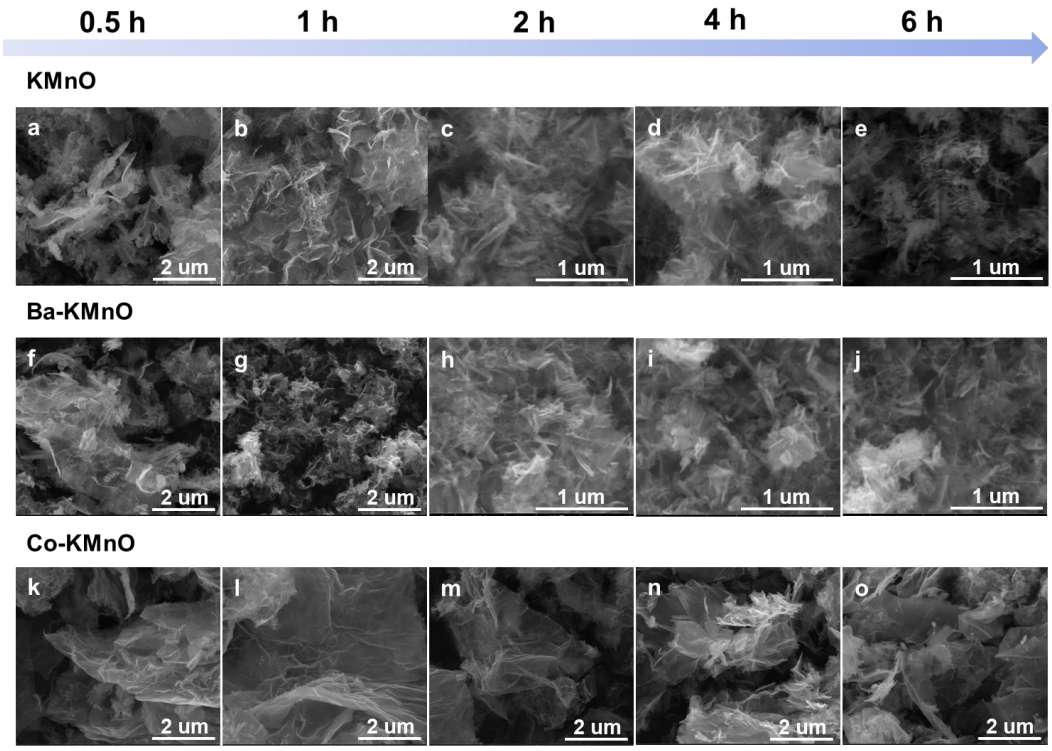

Fig. S4. Morphology conversion of the 2D KMnO, 2D Ba-KMnO and 2D Co-KMnO samples under heat treatment at 400 °C for varying times. a-e) SEM images of 2D KMnO under heat treatment from 0.5 to 6 h. f-j) SEM images of Ba-KMnO under heat treatment from 0.5 to 6 h. k-o) SEM images of 2D Co-KMnO under heat treatment from 0.5 to 6 h.

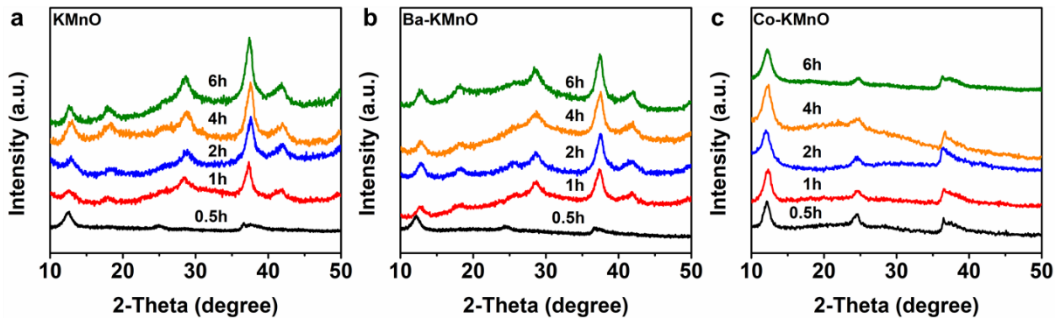

Fig. S5. Structure conversion of 2D KMnO, 2D Ba-KMnO and 2D Co-KMnO samples under heat treatment at 400 ℃ for varying times. a) XRD patterns for 2D KMnO under heat treatment from 0.5 to 6 h. b) XRD patterns for 2D Ba-KMnO under heat treatment from 0.5 to 6 h. c) XRD patterns for 2D Co-KMnO under heat treatment from 0.5 to 6 h.

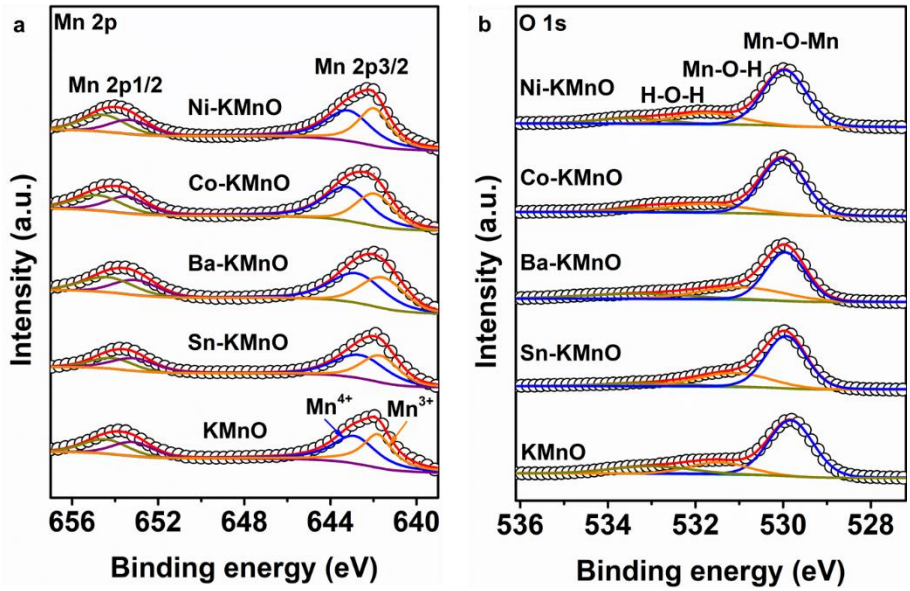

Fig. S6. XPS patterns for 2D KMnO and 2D M-KMnO. a) Mn 2p. b) O 1s.

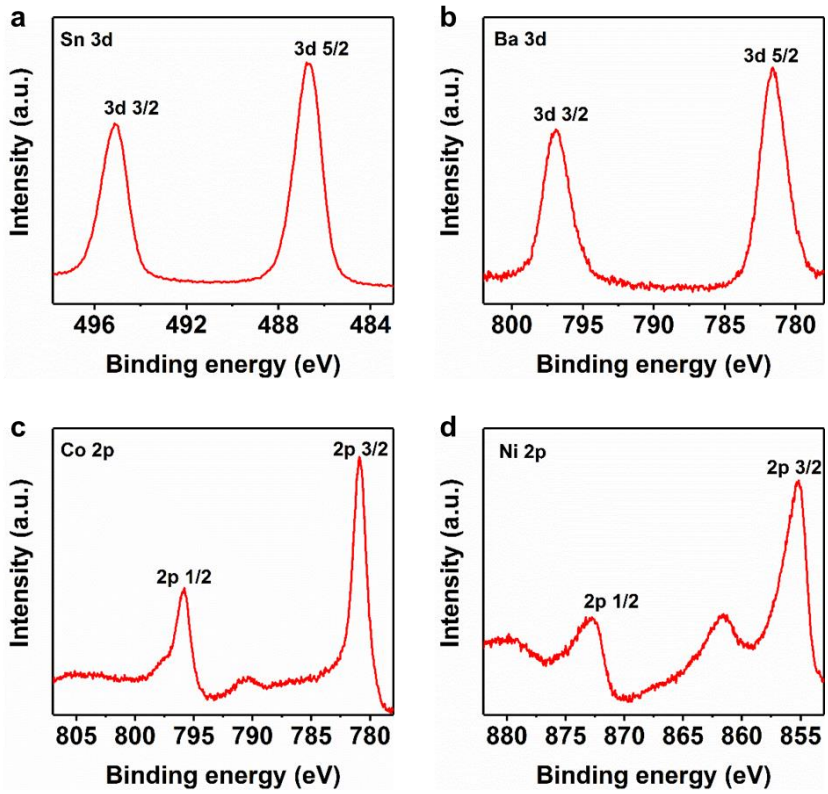

Fig. S7. XPS patterns for a) Sn 3d, b) Ba 3d, c) Co 2p and d) Ni 2p.

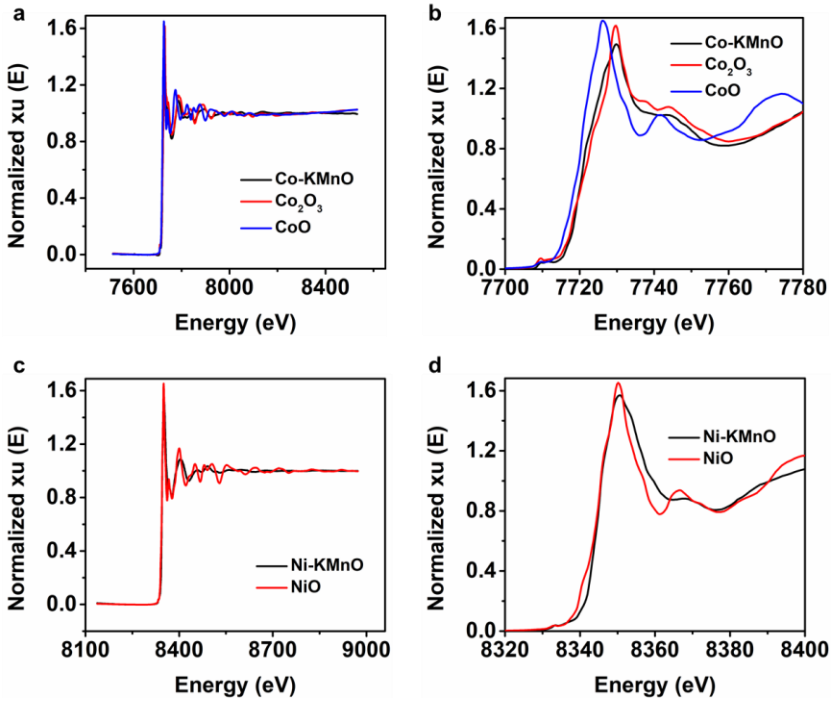

Fig. S8. a) XANES patterns for 2D Co-KMnO, Co_2O_3 and CoO. b) XANES patterns for 2D Co-KMnO, Co_2O_3 and CoO measured in the range of 7704 to 7944 eV. c) XANES patterns for 2D Ni-KMnO and NiO. d) XANES patterns for 2D Ni-KMnO and NiO in the range of 8337 to 8494 eV.

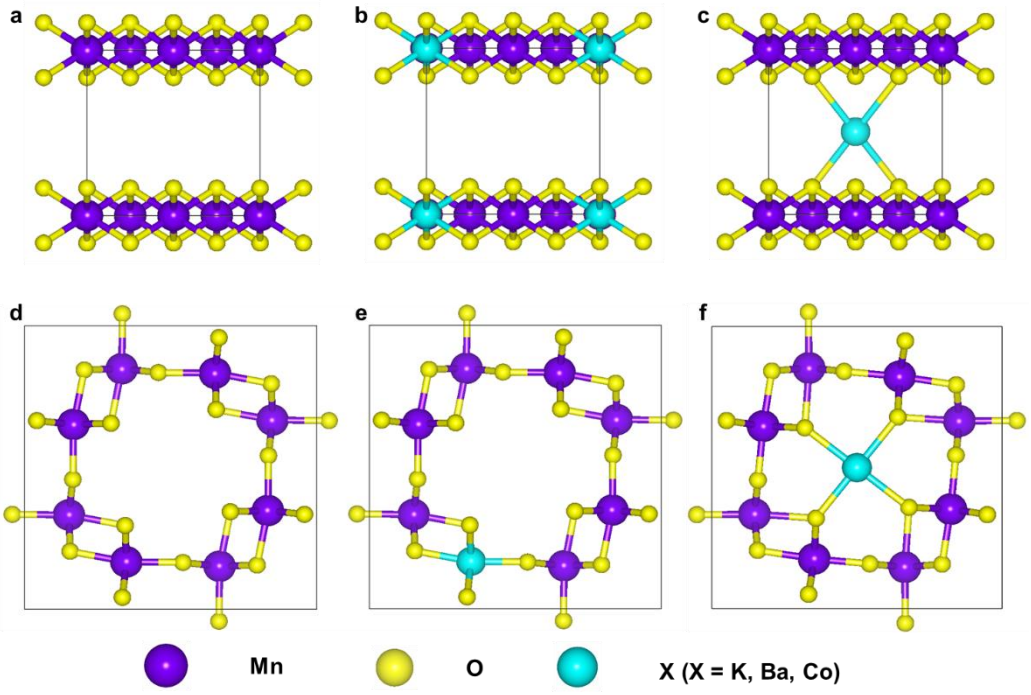

Fig. S9. Calculated Structures. a) pure δ-Mn_8O_{16}; b) δ-AMn_7O_16 (A= K, Ba, Co); c) δ-AMn_8O_{16} (A= K, Ba, Co); d) pure α-Mn_8O_{16}; e) α-AMn_7O_{16} (A= K, Ba, Co) and f) α-Mn_8O_{16} (A= K, Ba, Co).

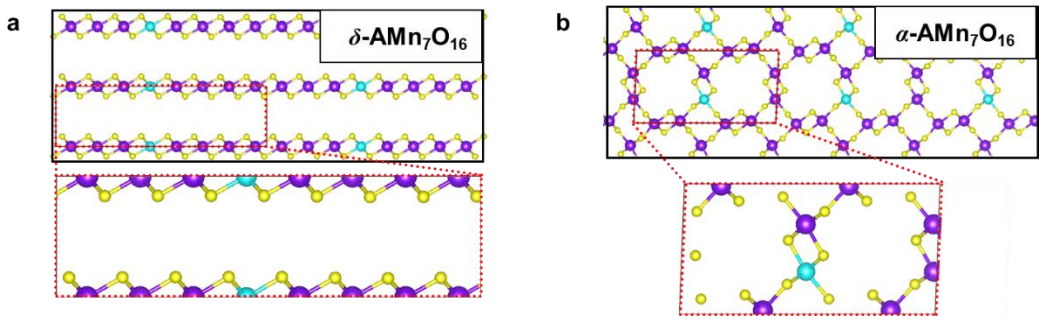

Fig. S10. Snapshots of the key states in the δ- to α-AMn_7O_{16} (A = Mn, Co) transitions. a) δ-AMn_7O_{16}; b) α-AMn_7O_{16}. A = Mn denotes pure Mn_8O_{16}.

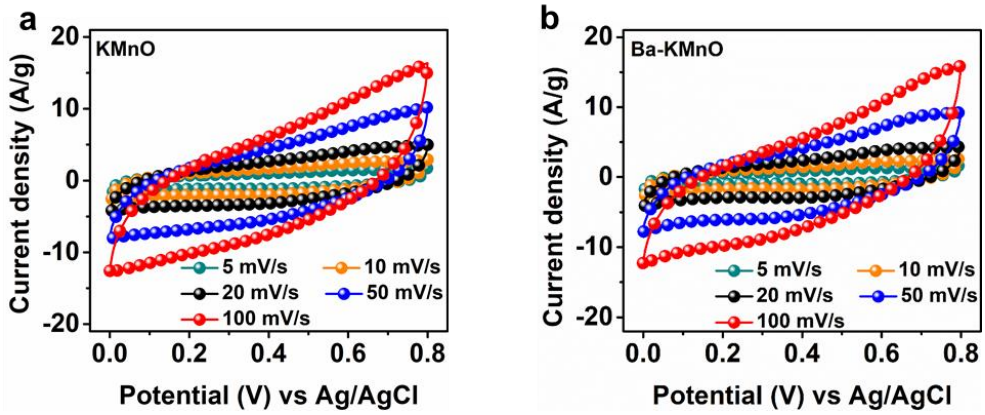

Fig. S11. CV curves for a) 2D KMnO and b) 2D Ba-KMnO at different scan rates ranging from 5 to 100 mV/s.

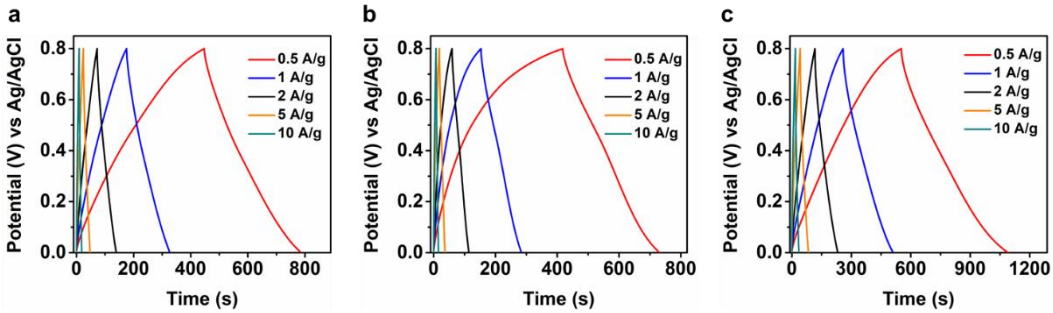

Fig. S12. Charge and discharge curves for a) 2D KMnO, b) 2D Ba-KMnO and c) 2D Co-KMnO with a current density ranging from 0.5 to 10 A/g.

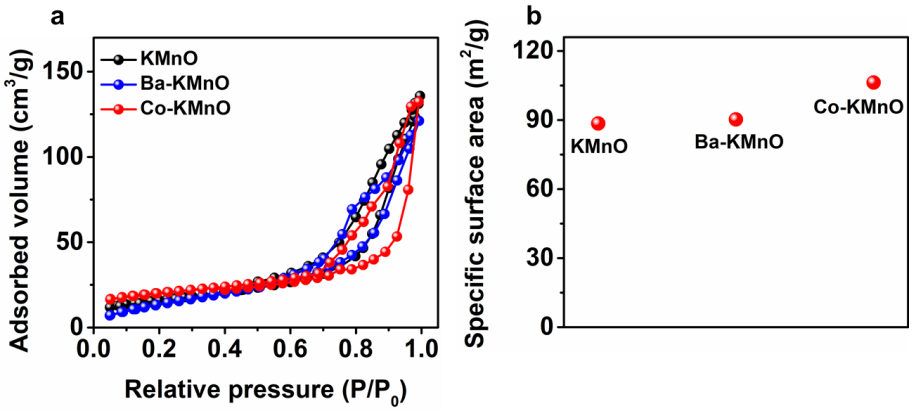

Fig. S13. a) N_2 adsorption desorption isotherms of samples 2D KMnO, 2D Ba-KMnO and 2D Co-KMnO. b) Specific surface area of 2D KMnO, 2D Ba-KMnO and 2D Co-KMnO.

Table S1. Ionic radius of different ion species.

Ion species	Mn^{4+}	Ba^{2+}	Sn^{2+}	Co^{3+}	Ni^{2+}	K^{+}
Ionic radius	54 pm	135 pm	112 pm	54.5 pm	69 pm	138 pm

Table S2. Elemental assay before and after H^{+} exchange from ICP-OES measurements.

Sample	2D KMnO		2D Ba-KMnO		2D Sn-KMnO		2D Co-KMnO		2D Ni-KMnO	
Initial	K	4.12%	K	0.87%	K	0.75%	K	1.86%	K	1.69%
			Ba	1.97%	Sn	1.76%	Co	3.62%	Ni	3.53%
After H^{+} exchange	K	0.03%	K	0.01%	K	0.02%	K	0.05%	K	0.03%
			Ba	0.02%	Sn	0.04%	Co	2.14%	Ni	1.81%

Table S3. EXAFS fitting parameters

Sample	Shell	N	R (Å)	ΔE_0 (eV)	$\sigma^2(10^{-3}Å^2)$	R-factor
KMnO	Mn-O	4.3±0.5	1.90±0.01	-6.3±1.8	4.2±1.3	0.007
	Mn-Mn	4.2±0.9	2.86±0.02	-10.7±2.3	8.3±2.2	
Ba-KMnO	Mn-O	4.2±0.5	1.90±0.01	-6.9±1.8	4.3±1.3	0.007
	Mn-X	4.3±0.9	2.86±0.02	-10.8±2.2	8.4±2.1	
Co-KMnO	Mn-O	4.2±0.6	1.90±0.01	-8.8±2.1	3.5±1.4	0.008
	Mn-X	4.2±0.8	2.84±0.01	-13.6±2.0	5.4±1.6	
	Co-O	4.3±0.4	1.92±0.01	-0.1±1.5	3.7±1.2	0.005
	Co-X	4.4±0.6	2.85±0.01	-0.6±1.5	4.3±1.1	

X presents Mn, Ba or Co; N is coordination numbers; R is the internal atomic distance; σ^2 is Debye-Waller factor; ΔE_0 is the edge-energy shift.