Supporting Information

Strong-electrophilic heteroatom confined in atomic CoOOH nanosheets realizing efficient electrocatalytic water oxidation

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Synthesis of Mn-confined CoOOH nanosheets.

The Mn-confined CoOOH nanosheets were synthesized by a two-step method. First, 0.8 mmol$CoCl_2 \cdot 6H_2O$ were dissolved into 40 ml ethylene glycol and deionized water mixture. Followed by being bubbled by $N_2$for 1 h, the solution was adjusted to be alkaline by adding 5 M ammonia. The solution was then was mixed with prepared Manganese chloride solutions. The mixed solution were then transferred to aTeflon-lined stainless autoclave and heated at 130 ºC for 20 h. The obtained precursor$Co(OH)_2$ were collected by centrifugation, washed with ethanol, then ultrasonic dispersed in deionized water again, and then 0.5 M NaClO solution was dropped in at 50 ºC under vigorous stirring for oxidation treatment. Finally, the precipitate was washed with water and then was ultrasonic treated to exfoliate the products into nanosheets. For comparison purpose, the pure CoOOH nanosheets were also prepared without Manganese chloride solutions. The IrO_2 and MnO_2 was commercial product obtained from Alfa Aesar.

Morphology and structure characterizations. TEM, HRTEM and EDS were performed by using a JEOL-2010 TEM with an acceleration voltage of 200 kV. XPS were acquired on Thermo ESCALAB 250 with Al *Kα* (*hv* = 1486.6 eV) as the excitation source. The XAFS data were collected at BL14W1 station in Shanghai Synchrotron Radiation Facility and 1W1B station in Beijing Synchrotron Radiation

Facility. The O *k*-edge was measured at BL12B-a beamline of National Synchrotron Radiation Laboratory in the total electron yield mode under a vacuum better than 5×10^{-6} Pa. The beam from the bending magnet was monochromatized utilizing a varied line-spacing plane grating and refocused by a toroidal mirror.

Electrochemical characterization. Electrochemical measurements were performed using an electrochemical workstation (Model CHI760D, CH instruments, Inc., Austin, TX) with a three-electrode system, operated with the modified glassy carbon disk electrode as working electrode, platinum mesh as the counter electrode, and saturated Ag/AgCl as reference electrode in 1M KOH electrolyte. The Linear Sweep Voltammetry (LSV) curves were measured at a rate of 1 mV/s without IR correction after dozens of cyclic voltammetric scans until stable. Electrochemical impedance spectroscopy (EIS) was recorded with frequency range of 0.1–1000 kHz at a bias potential of 1.6 V vs RHE. To avoid Faradaic region, the electrochemical double layer capacitance (C_{dl}) was measured at a range of 1.0–1.1Vvs RHE at rate ranging from 10 to 100 mV/s withinterval 10 mVincrement.

For electrode preparation, 2mg of fresh prepared Mn-confined CoOOH nanosheets, was dispersed in 1ml of 3:1 (v/v) DI-water/ethanol mixture solvent under ultrasonic water bath for about 30min. After that, an amount of carbon black and 20µl Nafion solution (5 wt%, Sigma-Aldrich) was added, and the mingled solution was sonicated in an ultrasonic water bath for another 30min. Subsequently, 5 µl of the dispersion was transferred onto the glassy carbon disk with a diameter of 3mm, corresponding to the catalyst loading about 0.15 mg/cm^2.

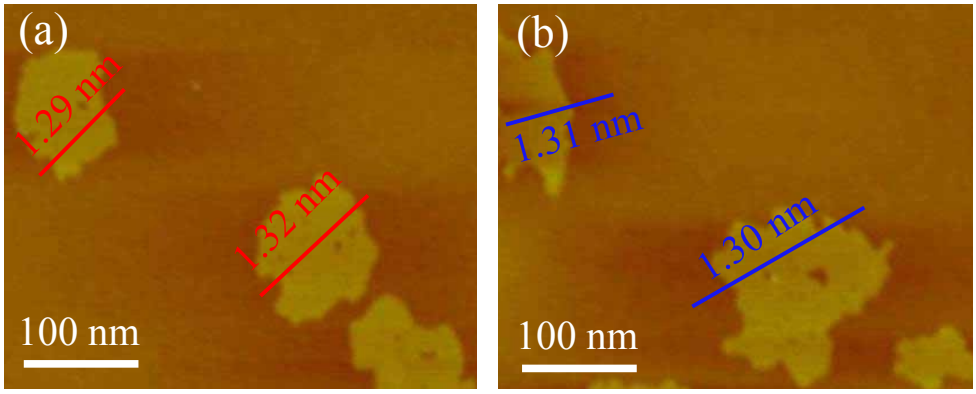

Figure S1. AFM images for (a) 2% and (b) 5% Mn-CoOOH nanosheets.

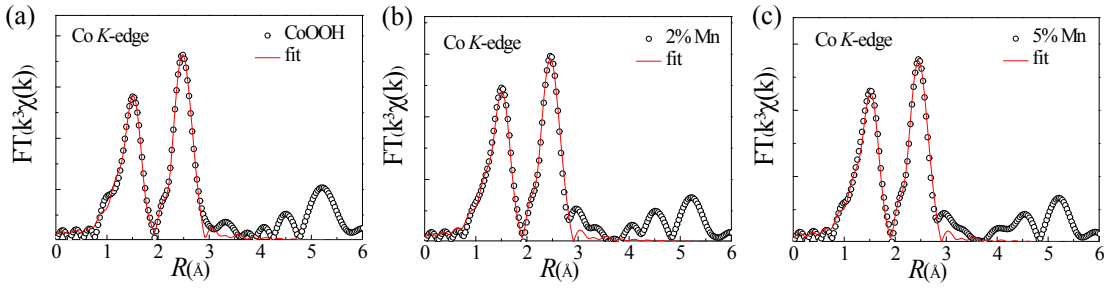

Figure S2. Co *K*-edge EXAFS fitting results for (a) pure CoOOH, (b) 2% Mn-CoOOH and (c) 5% Mn-CoOOH.

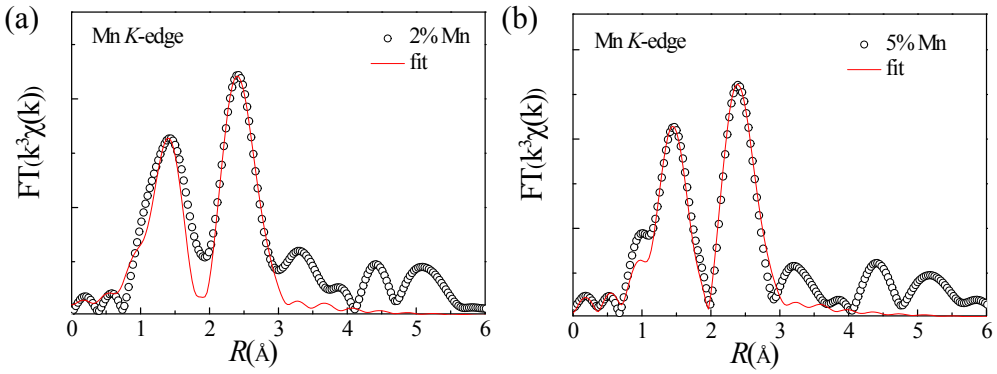

Figure S3. Mn *K*-edge EXAFS fitting results for (a) 2% Mn-CoOOH and (b) 5% Mn-CoOOH.

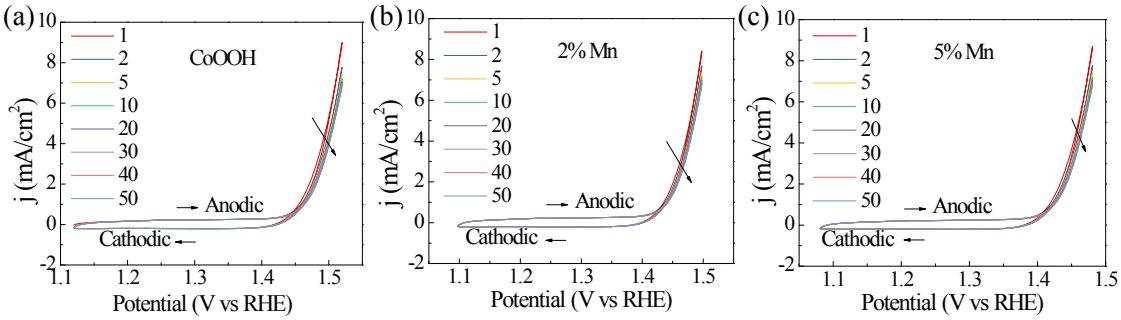

Figure S4. CVs before OER measurements for (a) 2%Mn-CoOOH and (b) 5%Mn-CoOOH.

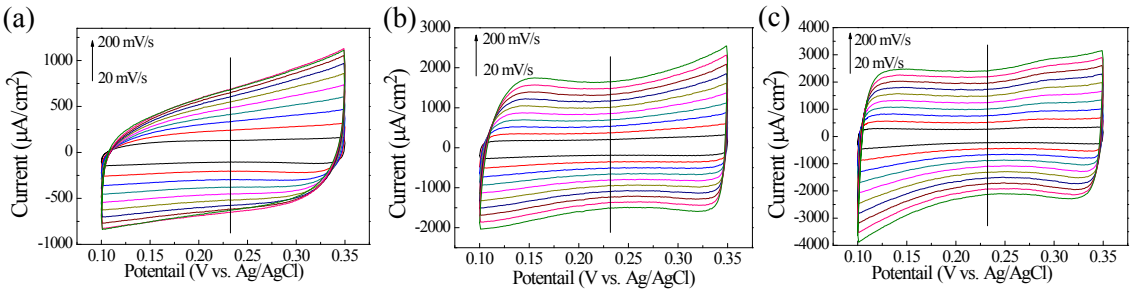

Figure S5. CVs towards double-layer capacitance calculations for (a) CoOOH, (b) 2%Mn-CoOOH, and (c) 5%Mn-CoOOH.

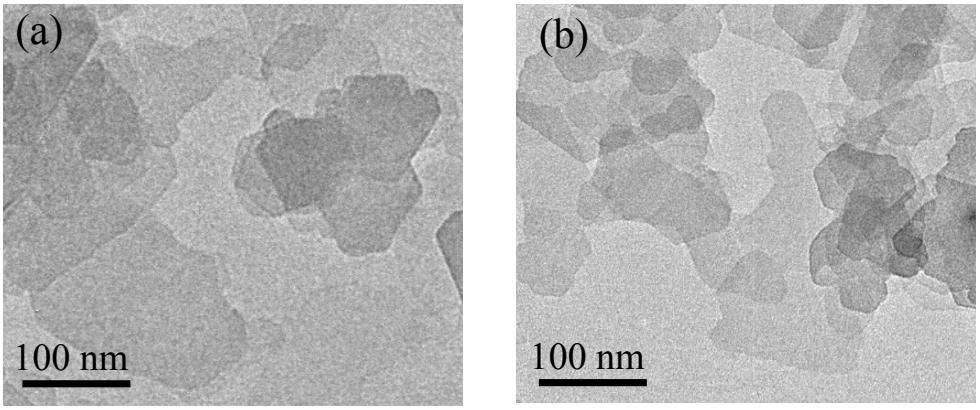

Figure S6. TEM images of (a) 2% and (b) 5% Mn- CoOOH after OER measurements.

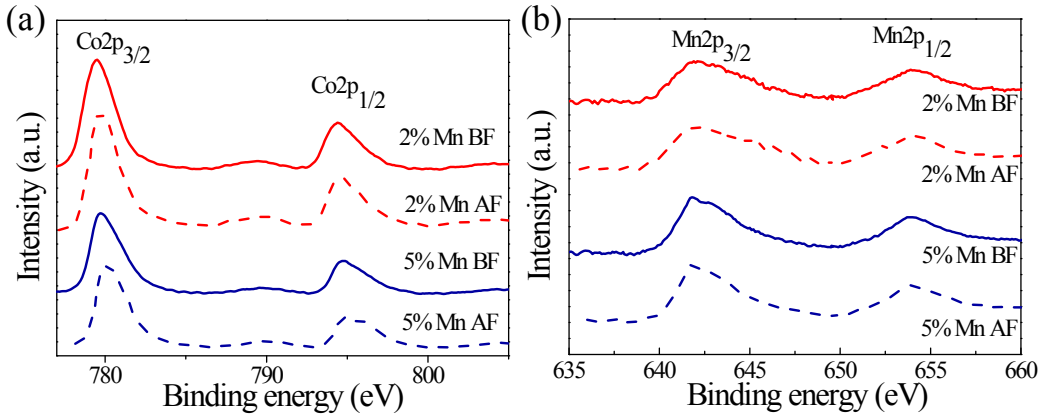

Figure S7. (a) Co 2*p* and (b) Mn 2*p* XPS spectra for Mn-CoOOH before (BF) and after (AF) OER tests.

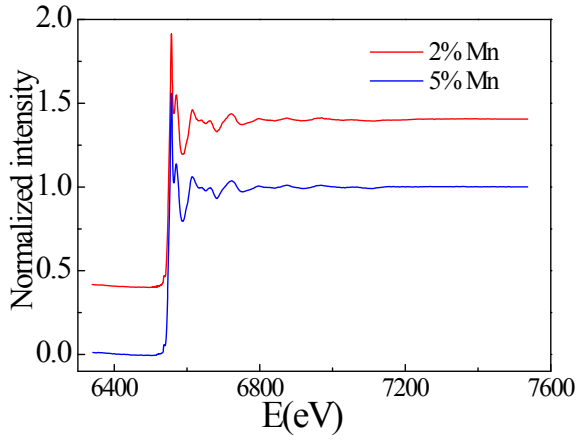

Figure S8. Mn K-edge EXFAS spectra of 2% and 5% Mn-doped CoOOH nanosheets.

Table S1. Summary of OER performance of cobalt-based electrocatalysts.

Catalysts	Over-potential @10mA/cm^2 (mV)	Tafel slope (mV/dec)	Electrolyte	Substrate	Reference
Mn-CoOOH nanosheets	255	38	1M NaOH	Glassy carbon	This work
CoOOH nanosheets	300	38	1M KOH	Glassy carbon	[1]
Ni-CoOOH nanowires	285	36	0.1M KOH	Stainless steel	[2]
Mn-CoOOH nanowires	315	52	0.1M KOH	Stainless steel	[2]
CoO*x*/B,N-graphene	295	57	0.1M KOH	Glassy carbon	[3]
$NiCo_2S_4$	210	40	1M KOH	3D Ni foam	[4]
Co_3O_4	300	68	0.1M KOH	Ti foil	[5]
CoNi(OH)x	280	77	1M KOH	Cu foil	[6]
Co_3O_4/C	290	70	0.1M KOH	Cu foil	[7]

References

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