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Support information

Mn-doped $CoSe_2$ nanosheets as high-efficiency catalysts for oxygen evolution reaction

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Experimental Details

Preparation of Co-MOF/NF

In a typical synthesis, 2.01 g of 2-methylimidazole ($C_4H_6N_2$) was dissolved in 60 mL deionized water to form a homogenous solution, which subsequently was mixed with an aqueous solution containing 0.886 g of cobalt nitrate hexahydrate ($Co(NO_3)_2$•$6H_2O$) and 60 ml deionized water. And then, a piece of pretreated Ni foam (NF) was immersed into the above mixture solution. After reaction for 4 h at room temperature, the Co-MOF/NF was taken out and washed with deionized water carefully, then dried at 60 °C for 8 h.

Preparation of Mn-$CoSe_2$/NF

The as-prepared Co-MOF/NF was placed into a 100 mL ethanol solution containing 2 mL manganese nitrate ($Mn(NO_3)_2$•$4H_2O$, 50 wt.%). After stirring slowly for 15 min, the MnCo LDH/NF was washed with ethanol for three times and dried at 60 °C, followed by selenylation with 0.5 g of Se powder in a Ar atmosphere at 400 °C for 2 h under a heating ramp of 2 °C min^{-1} to get the Mn-$CoSe_2$/NF product. Pure $CoSe_2$/NF was also obtained under the same conditions for comparison. Each electrode has the same mass-loading of 1.1 mg cm^{-2}.

Material Characterization

Scanning electron microscopy (SEM, ZEISS Sigma), transmission electron microscopy (TEM, Tecnai F30), X-ray diffraction (XRD, Rigaku Ultima IV) and X-ray photoelectron spectroscopy (XPS, PHI Quantum-2000) were employed to investigate the morphologies, phase structure and chemical valence state of the samples. For inductively coupled plasma-mass spectrometry (ICP-MS) analysis, the Mn-$CoSe_2$ powders were scraped from Mn-$CoSe_2$/NF with a knife and then acidified in HNO_3/HCl solution with a desired concentration for injection into the ICP-MS analyzer (Thermo Fisher).

Electrochemical measurements

The catalytic activities were examined on an electrochemical workstation (CHI 660E, CH Instruments) using a typical three-electrode setup in 1 M KOH with the as-synthesized catalysts as the working electrode, a platinum plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All the polarization curves were calibrated for iR compensated no otherwise stated using $E_{\mathrm{corrected}} = E_{\mathrm{uncorrected}} - iR_s$, where R_s (equivalent series resistance) was determined by fitting the EIS spectra with the ZSimpWin software. Additionally, all the potentials vs SCE in this work were transformed into reversible hydrogen electrode (RHE) based on the Nernst equation: $E_{\mathrm{RHE}} = E_{\mathrm{SCE}} + 0.059 \times \mathrm{pH} + 0.241$ V.

Additional Figures and Data

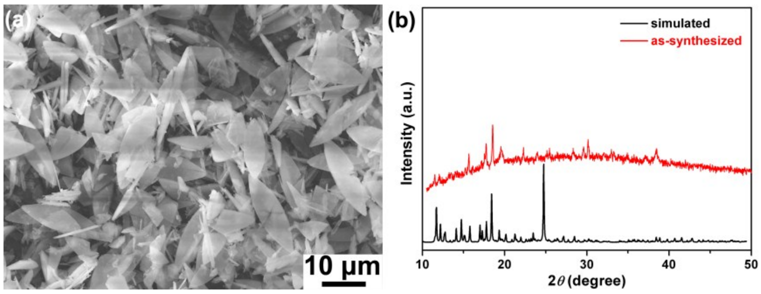

Fig. S1 (a) SEM images of pure MOF and (b) XRD patterns of Co-MOF.

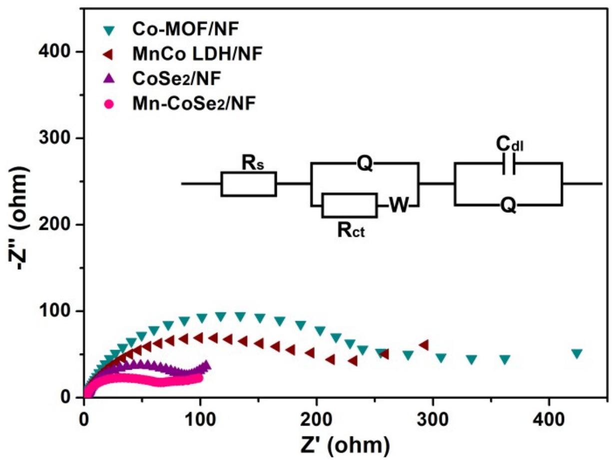

Fig. S2 Nyquist plots of Co-MOF, MnCo LDH, $CoSe_2$ and Mn-$CoSe_2$/NF catalysts (inset: equivalent circuit model).

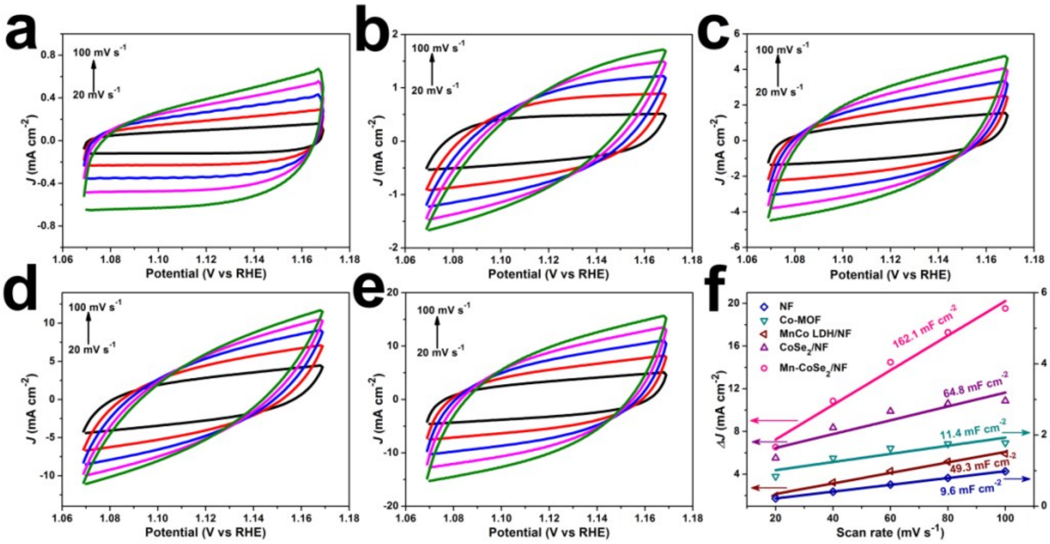

Fig. S3 Cyclic voltammetry curves at different scan rates for (a) NF, (b) Co-MOF/NF, (c) MnCo LDH/NF, (d) $CoSe_2$/NF and (e) Mn-$CoSe_2$/NF catalysts. (f) Corresponding linear relationship between current density differences and scan rate.

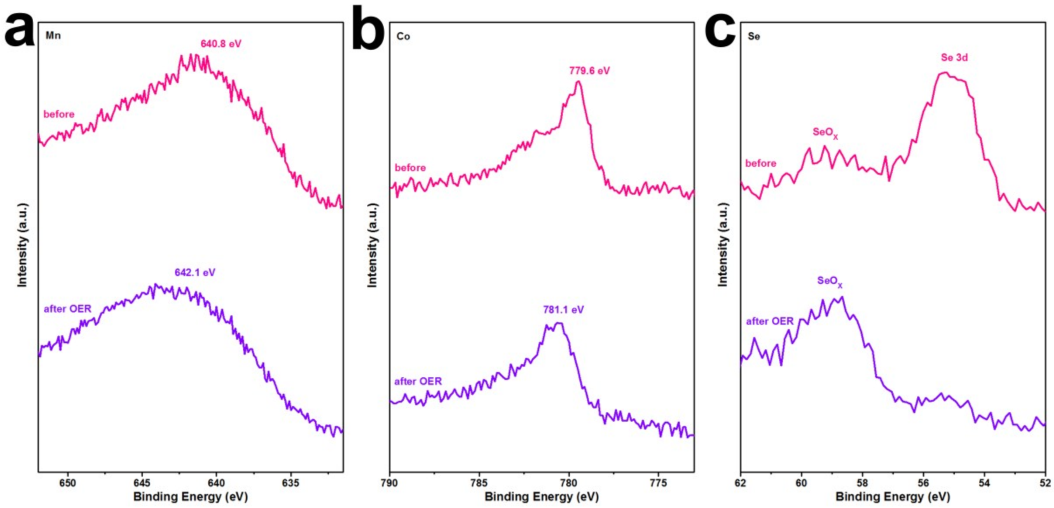

Fig. S4 High resolution XPS spectra of (a) Mn $2p_{3/2}$, (b) Co $2p_{3/2}$ and (c) Se 3d of as-prepared and post-OER Mn-$CoSe_2$/NF catalysts.

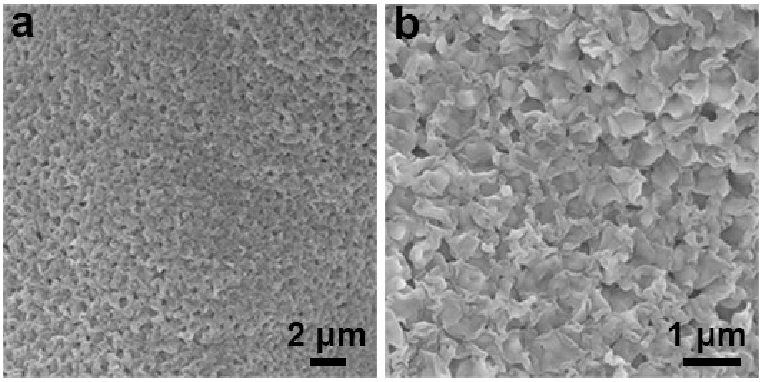

Fig. S5 SEM images of post-OER Mn-$CoSe_2$/NF catalysts.

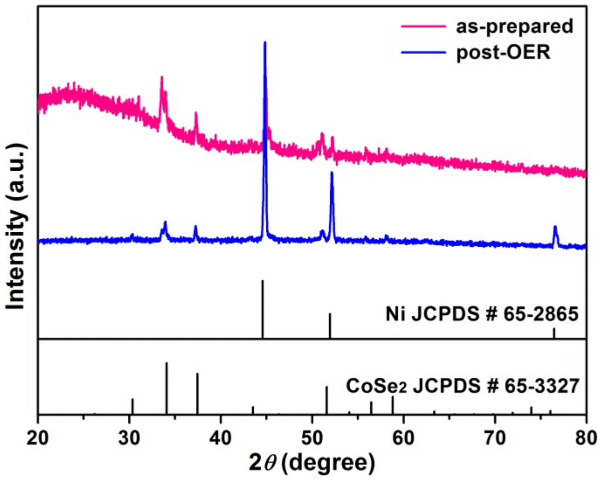

Fig. S6 XRD patterns of as-prepared and post-OER Mn-$CoSe_2$/NF catalysts.

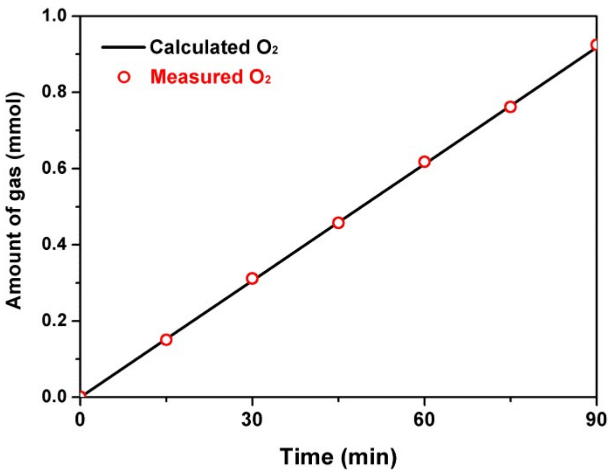

Fig. S7 O_2 production amount of the theoretically calculated and experimentally measured versus time for Mn-$CoSe_2$ catalysts at 60 mA cm^{-2}.

The amount of O_2 gas detected by a water-gas displacing method is consistent with the theoretically calculated value, corresponding to almost 100% Faradic efficiency.

Table S1 Comparison of OER activities of Mn-$CoSe_2$/NF with other Co-based catalysts in alkaline electrolyte

Catalysts	***J*** **($mA\ cm^{-2}$)**	***η*** **(mV vs RHE)**	**Tafel slope ($mV\ dec^{-1}$)**	**Reference**
Mn-$CoSe_2$/NF	60 100	274 296	82	This work
$CoSe_2$	10	430	50	*ACS Appl. Mater. Interfaces 8 (2016) 5327-5334.*
$CoSe_2$	10	468	66	*Small 11 (2015) 182-188.*
Ni-CoS_2 NN	50	286	55	*Catalysts 7 (2017) 366.*
Ni-CoS_2	10	156	52	*Electrochim. Acta 228 (2017) 428-435.*
Mn-CoN	10	285	64	*Chem. Commun. 53 (2017) 13237-13240.*
Mn-CoP	10	290	76	*Dalton Trans. 47 (2018) 14679-14685*
$MnCo_2O_4$	10	400	80	*Dalton Trans. 46 (2017) 14382-14392.*
Ni-Co-P HNBs	10	270	76	*Energy Environ. Sci. 11 (2018) 872-880.*
$MnCo_2S_4$ NA/TM	50	325	115	*J. Mater. Chem. A 5 (2017) 17211-17215*
Mn-Co-P@$MnCo_2O_4$/Ti	10	269	102	*Chem. Commun. 54 (2018) 1077-1080.*
$MnCo_xO_4$/NCNT	10	479	75	*Int. J. Hydrogen Energy 43 (2018) 19451-19459.*
CoO/$CoSe_2$	10	510	137	*Adv. Sci. 3 (2016) 1500426*