Supporting information

In situ composite of NiCo-LDH or MnCo-LDH nanosheet with ZIF-9 as efficient bifunctional electrocatalysts for water splitting

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Experimental

Materials and characterization

All of the reagents employed in this study are commercially available analytical-grade and used as received without further purification. Infrared spectra were recorded on a Nicolet iS50 FT-IR spectrometer using KBr pellet technique. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were taken using a Gemini 500 field emission scanning electron microscope. Inductively coupled plasma-mass spectrometry (ICP-AES) were conducted using ICAP PRO XP. Before the analysis, the materials were digested by aqua regia. Powder X-ray diffraction data (PXRD) were collected on a Bruker D8 Advance with graphite-filtered Cu Kα radiation source (λ = 0.15418 nm). Thermogravimetric analyses (TGA) were performed under N_2 atmosphere at a heating rate of 10 K min^{-1} with a Mettler-Toledo TGA/DSC 3+/1600 HT. X-ray photoelectron spectroscopy (XPS) was tested by Thermo Scientific™ K-Alpha™+ spectrometer. Adsorption measurements were performed using a Quantachrome Autosorb-iQ2 analyzer. Raman spectroscopy was conducted by VIS-

NIR Confocal Raman Microscope System at 532nm. The electrochemical measurements were conducted on Biologic VMP3 electrochemical workstation using a conventional three electrode undivided cell with the graphite rod electrode, Ag/AgCl electrode in a 3 M KCl aqueous solution and glassy carbon electrode (GCE) as the counter, reference and working electrodes, respectively.

Synthesis of ZIF-9/MCo-LDH[1], Pure MnCo-LDH and NiCo-LDH

$Co(NO_3)_2$ $6H_2O$ (0.35 g, 1.2 mmol) and benzimidazole (0.1 g, 0.8 mmol) was dissolved with 30 mL DMF in a Teflon-lined autoclave and heated for 2 d at 130 °C. After cooled down to RT, the mixture was filtered off and washed with EtOH and dried in vacuum to obtain the ZIF-9.

The metal nitrates were mixed with ZIF-9 in 30 mL EtOH/H_2O (volume ratio=2:1) and heated for 1 d at 130 °C. After cooled down to RT, the mixture was filtered off and washed with EtOH and dried in vacuum to obtain the ZIF-9/MCo-LDH. The dosage of various metal nitrates was shown in the Table S1-S3. Pure MnCo-LDH and NiCo-LDH were obtained by changing the temperature from 130 to 200 ºC。

Theoretical calculation

All the DFT calculations were conducted based on the Vienna Ab-inito Simulation Package (VASP).[2, 3] The exchange-correlation effects were described by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) method.[4, 5] The core-valence interactions were accounted by the projected augmented wave (PAW) method.[6] The energy cutoff for plane wave expansions was set to 480 eV, and the 3×3×1 Monkhorst-Pack grid k-points were selected to sample the Brillouin zone integration. The vacuum space is adopted 15 Å above the surfaces to avoid periodic interactions. The structural optimization was completed for energy and force convergence set at 1.0×10-4 eV and 0.02 eV Å-1, respectively. The Gibbs free energy change (ΔG) of each step is calculated using the following formula:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

where ΔE is the electronic energy difference directly obtained from DFT calculations, ΔZPE is the zero point energy difference, T is the room temperature (298.15 K) and ΔS is the entropy change.

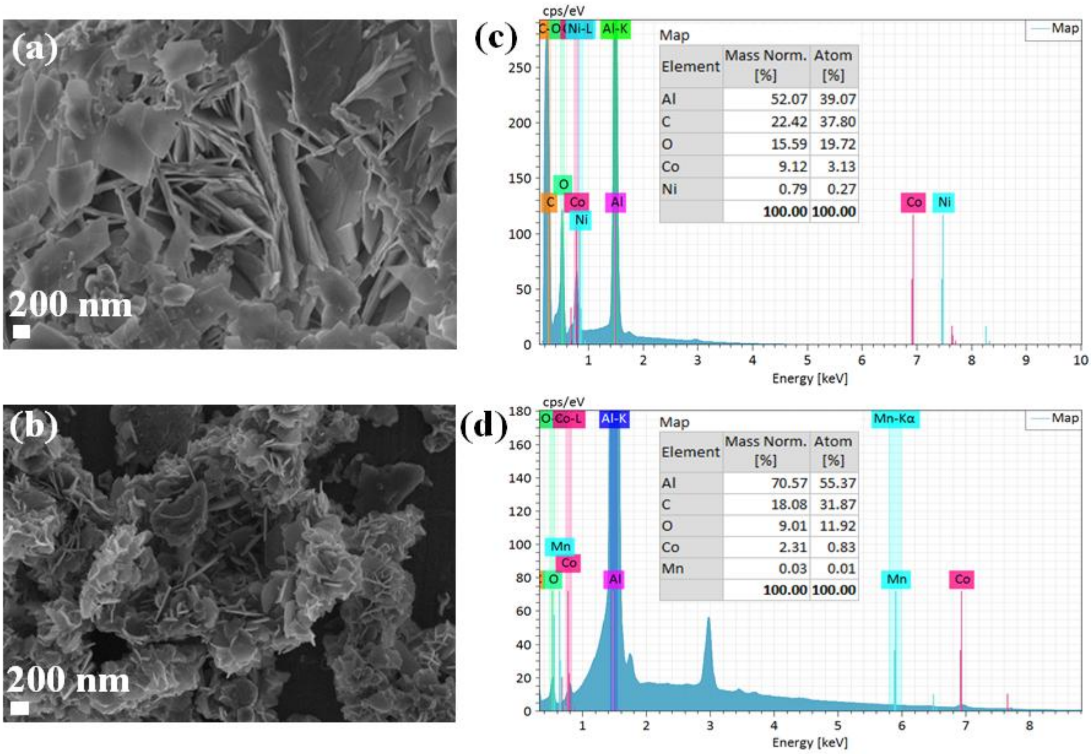

Fig. S1 SEM images of (a) ZIF-9/NiCo-LDH and (b) ZIF-9/MnCo-LDH (200 nm). EDX spectra of (c) ZIF-9/NiCo-LDH and (d) ZIF-9/MnCo-LDH. The Al content shown on EDX spectra is due to the use of Al specimen holder and Al foil during sample preparation.

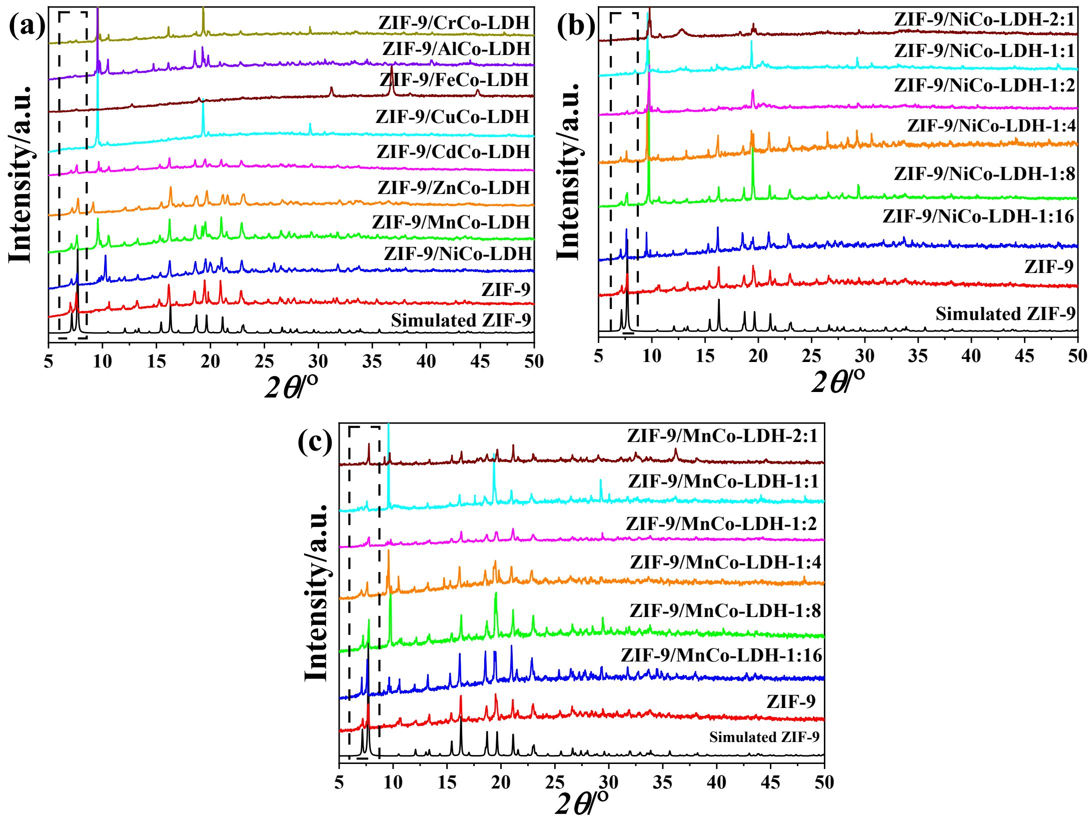

Fig. S2 PXRD patterns of (a) various metal nitrates composited with ZIF-9. (b) ZIF-9/NiCo-LDH and (c) ZIF-9/MnCo-LDH composites with different molar ratio of metal nitrates to ZIF-9

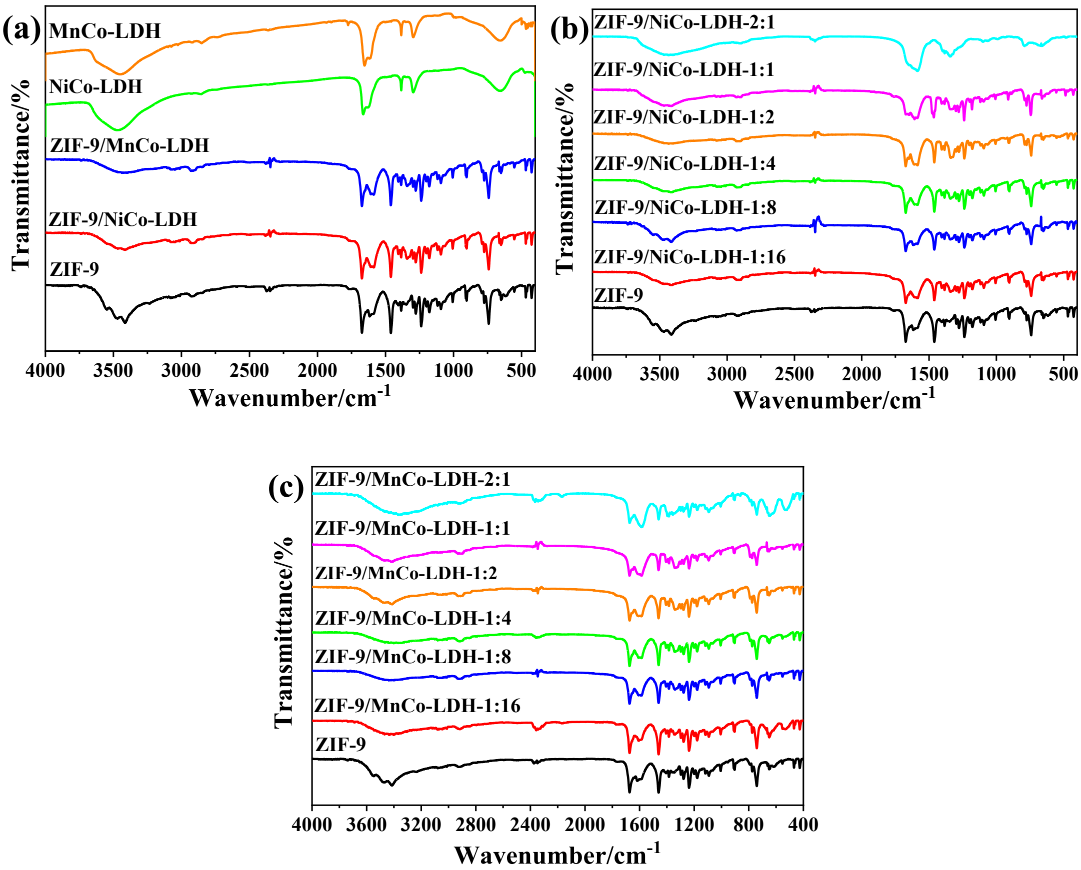

Fig. S3 FTIR spectra of (a) ZIF-9/NiCo-LDH, (b) ZIF-9/MnCo-LDH composites with different molar ratio of metal nitrates to ZIF-9.

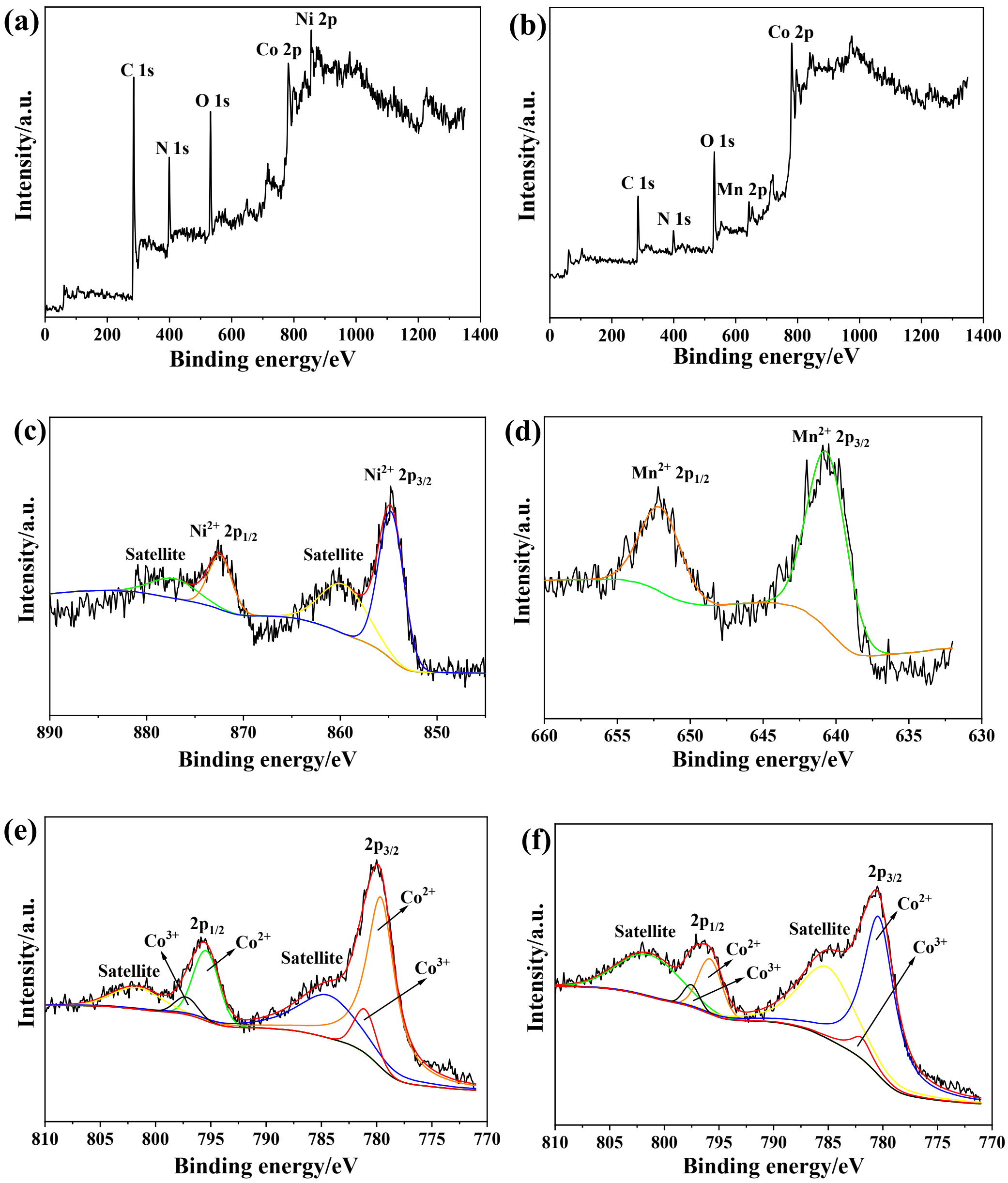

Fig. S4 XPS survey spectra of (a) ZIF-9/NiCo-LDH, (b) ZIF-9/MnCo-LDH. XPS spectra of (c) Ni 2p for ZIF-9/NiCo-LDH and (d) Mn 2p for ZIF-9/MnCo-LDH. Co 2p for (e) ZIF-9/NiCo-LDH and (f) ZIF-9/MnCo-LDH

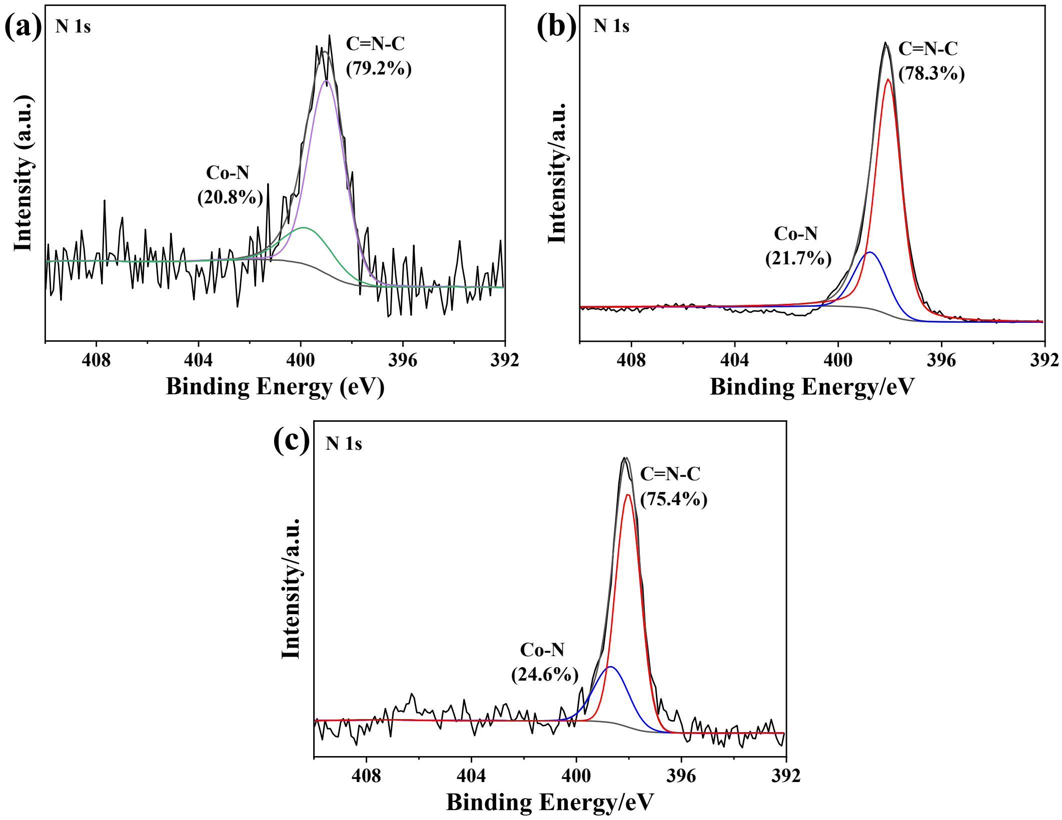

Fig. S5 XPS spectra ofN 1s for (a) ZIF-9/NiCo-LDH, (b) ZIF-9/MnCo-LDH and (c) ZIF-9

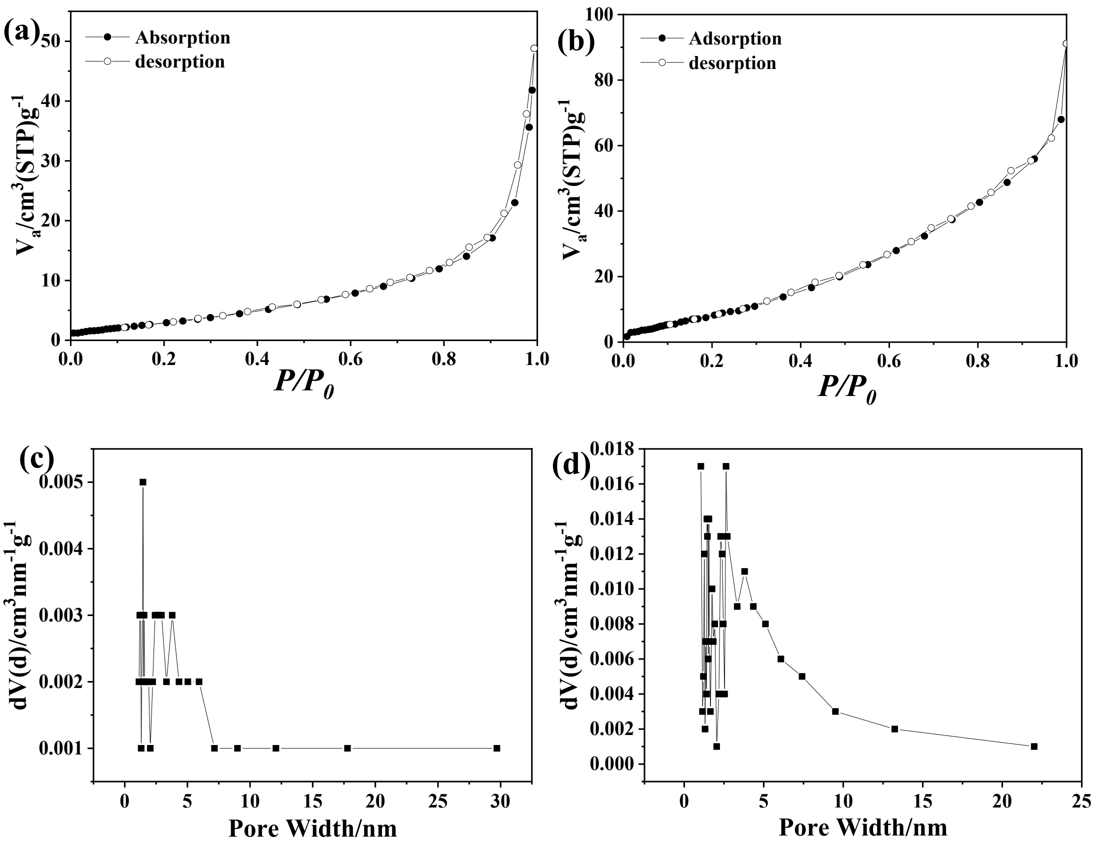

Fig. S6 N_2 adsorption (closed symbols)/desorption (open symbols) isotherms of (a) ZIF-9/NiCo-LDH and (b) ZIF-9/MnCo-LDH at 77K. DFT method of (c) ZIF-9/NiCo-LDH and (d) ZIF-9/MnCo-LDH. Calc. Model: N_2 at 77 K on carbon (slit pores, NLDFT adsorption branch)

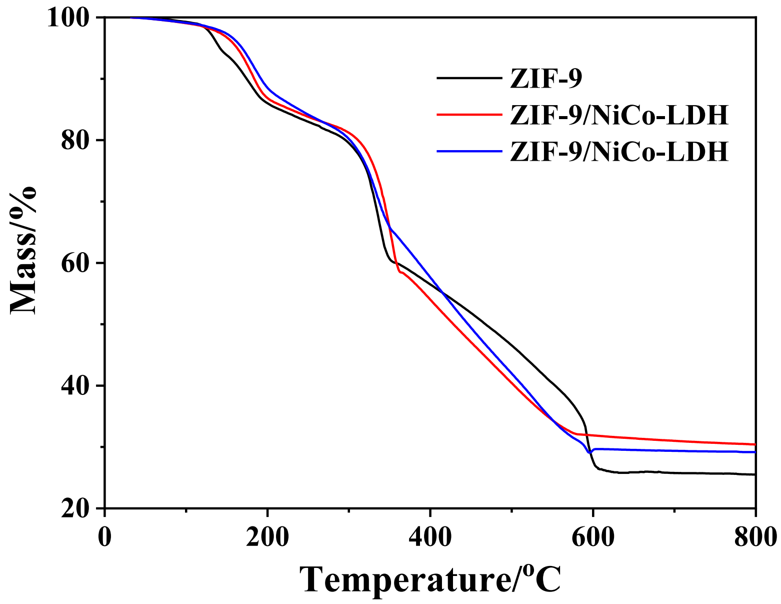

Fig. S7 TGA profiles of the ZIF-9/NiCo-LDH, (b) ZIF-9/MnCo-LDH and ZIF-9

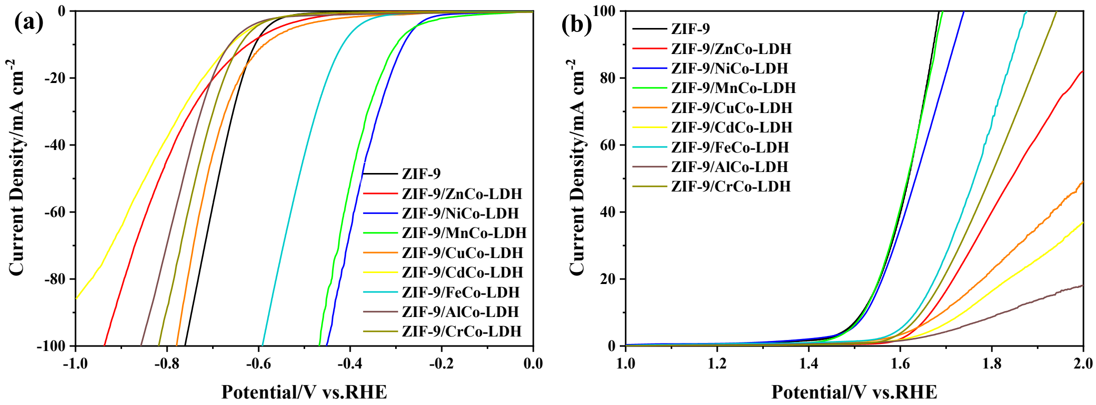

Fig. S8 Linear scanning voltammetry (LSV) curves of ZIF-9/MCo-LDH (M=Zn, Ni, Mn, Cu, Cd, Fe, Al, Cr) on glassy carbon electrode (GCE) in 1.0 M KOH solution for (a) HER and (b) OER at 0.1 V s^{-1}

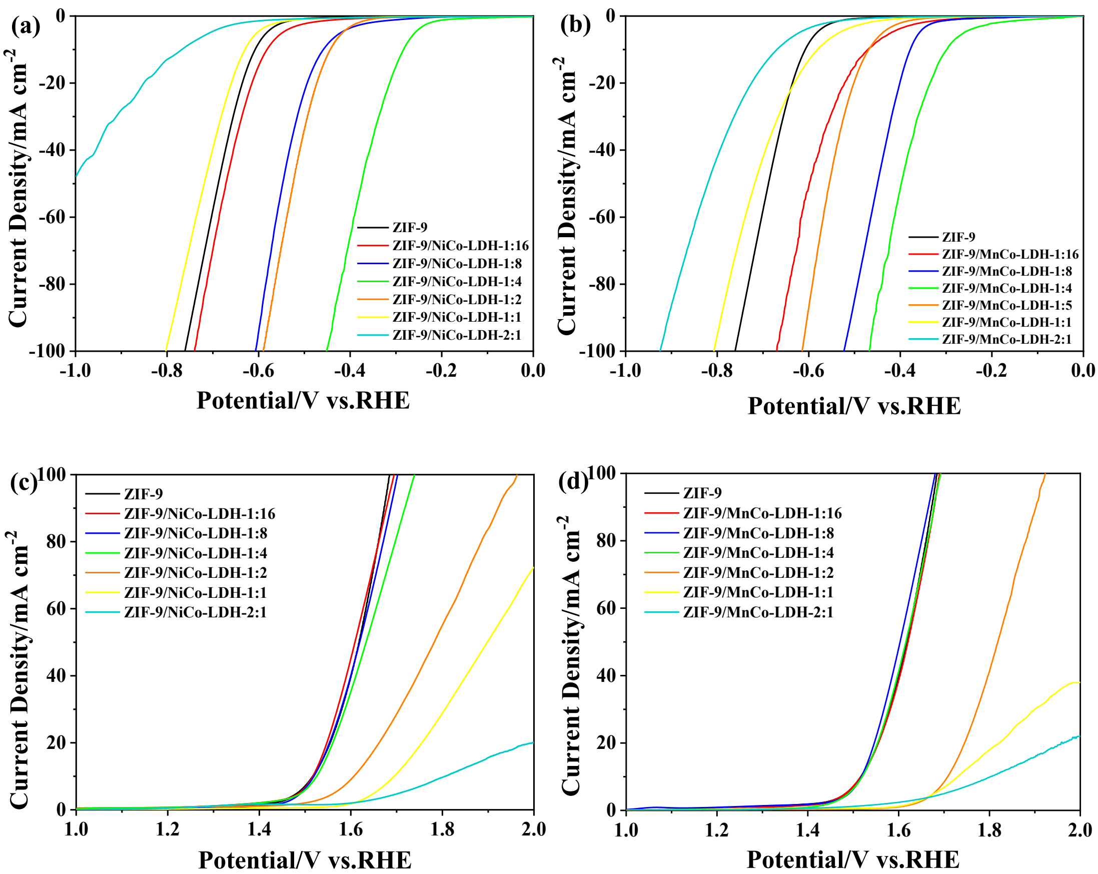

Fig. S9 LSV curves of ZIF-9/NiCo-LDH for (a) HER, (b) OER and ZIF-9/MnCo-LDH for (c) HER, (d) OER with different molar ratio of metal nitrates to ZIF-9 in 1.0 M KOH at 0.1 V s^{-1}

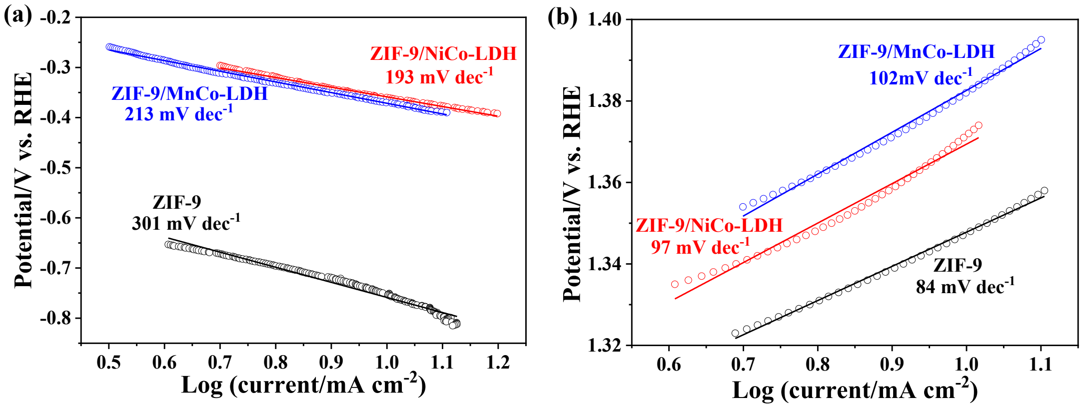

Fig. S10 Tafel slope of ZIF-9/NiCo-LDH, ZIF-9/MnCo-LDH, ZIF-9 for (c) HER and (d) OER in 1.0 M KOH.

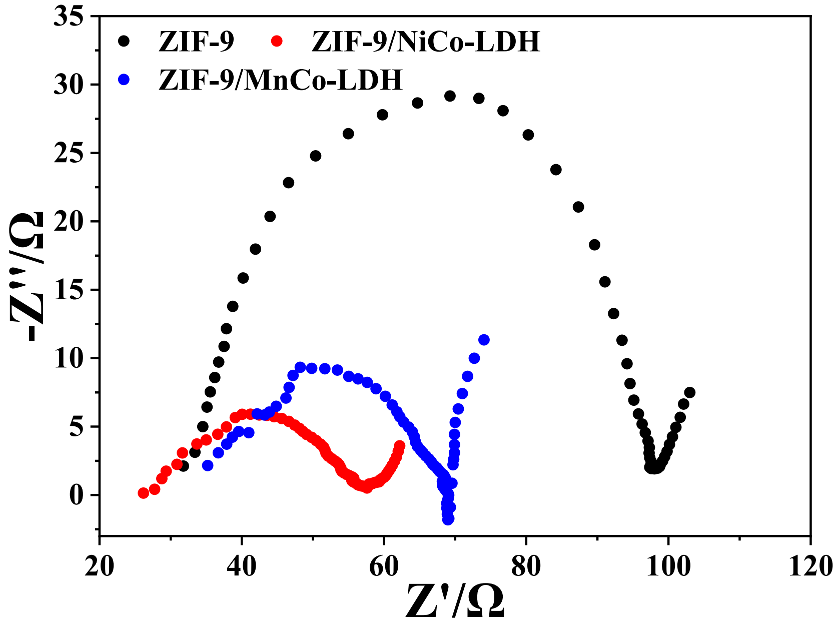

Fig. S11 Electrochemical impedance spectroscopy (EIS) of ZIF-9/NiCo-LDH, ZIF-9/MnCo-LDH, ZIF-9 in 1.0 M KOH

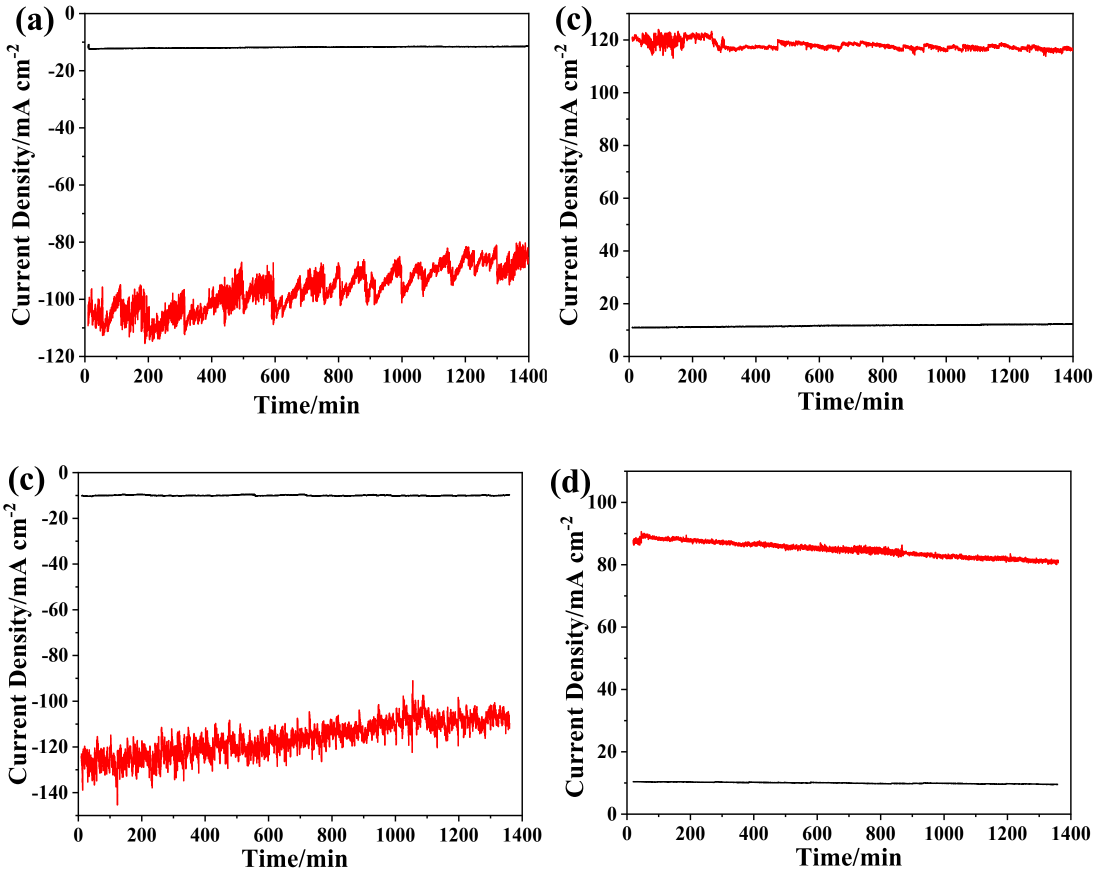

Fig. S12 Chronoamperometric response of ZIF-9/NiCo-LDH for (a) HER, (b) OER and ZIF-9/NiCo-LDH for (c) HER, (d) OER at about 10 mA cm^{-1} (black line) and 100 mA cm^{-1} (red line)

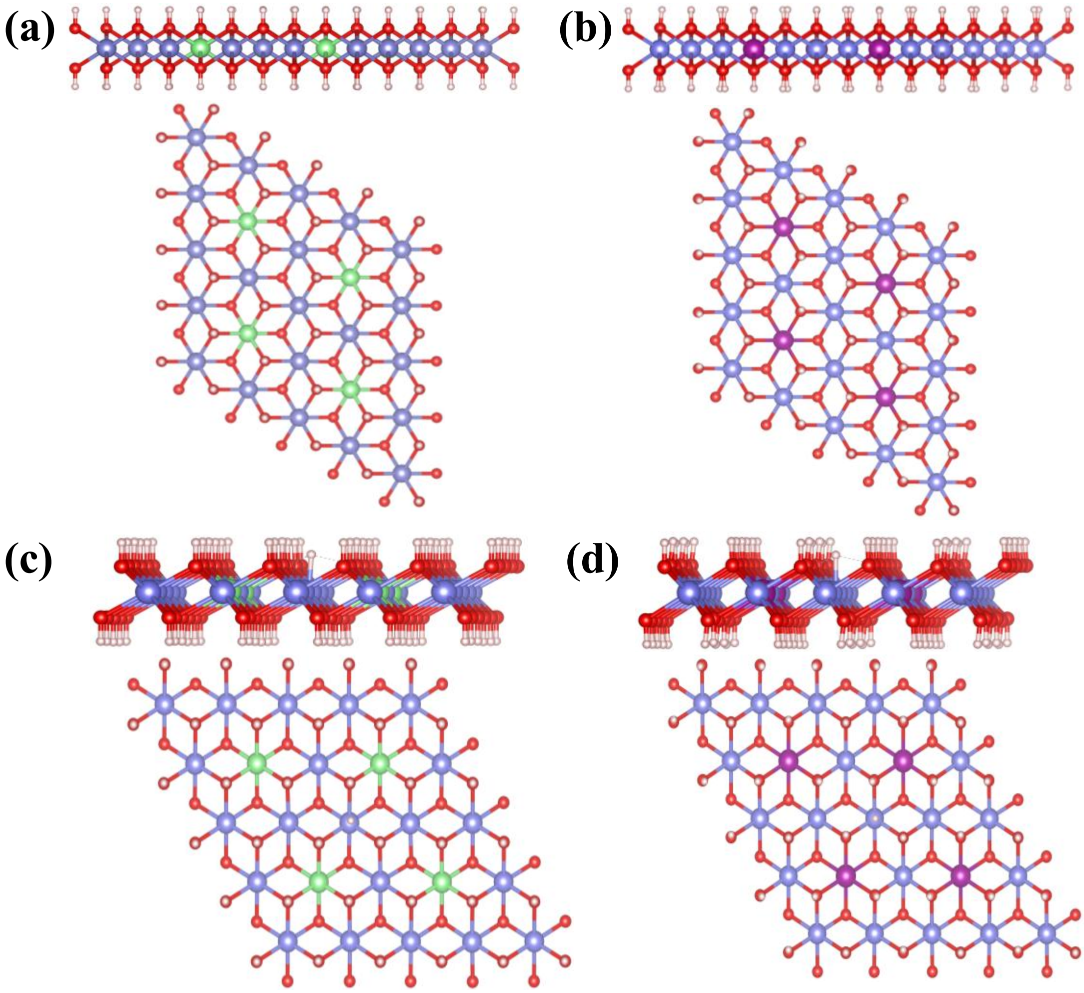

Fig. S13 The side (up) and top (down) view of the models of (a) NiCo-LDH and (b) MnCo-LDH. The side (up) and top (down) view of optimized configuration of the HER processes on the (c) Co site on NiCo-LDH and MnCo-LDH.

Table S1 The addition of reactants of ZIF-9/NiCo-LDH with different molar ratio of $Ni(NO_3)_2$ $6H_2O$ to ZIF-9

Simples	The dosage of the $Ni(NO_3)_2$ $6H_2O$ /mmoL	The dosage of ZIF-9 /mmoL
ZIF-9/NiCo-LDH-1:16	0.063 mmoL	1.0 mmoL
ZIF-9/NiCo-LDH-1:8	0.13 mmoL	1.0 mmoL
ZIF-9/NiCo-LDH-1:4	0.25 mmoL	1.0 mmoL
ZIF-9/NiCo-LDH-1:2	0.50 mmoL	1.0 mmoL
ZIF-9/NiCo-LDH-1:1	1.0 mmoL	1.0 mmoL
ZIF-9/NiCo-LDH-2:1	2.0 mmoL	1.0 mmoL

Table S2 The addition of reactants of ZIF-9/MnCo-LDH with different molar ratio of $Mn(NO_3)_2$ $4H_2O$ to ZIF-9

Simples	The dosage of the $Mn(NO_3)_2$ $4H_2O$ /mmoL	The dosage of ZIF-9 /mmoL
ZIF-9/MnCo-LDH-9-1:16	0.063 mmoL	1.0 mmoL
ZIF-9/MnCo-LDH-1:8	0.12 mmoL	1.0 mmoL
ZIF-9/MnCo-LDH-1:4	0.25 mmoL	1.0 mmoL
ZIF-9/MnCo-LDH-1:2	0.50 mmoL	1.0 mmoL
ZIF-9/MnCo-LDH-1:1	1.0 mmoL	1.0 mmoL
ZIF-9/MnCo-LDH-2:1	2.0 mmoL	1.0 mmoL

Table S3 The addition of various metallic nitrate for synthesizing the ZIF-9/MCo-LDH (the molar ratio of Metal nitrates to ZIF-9 was 1:4)

Simples	Metal nitrates	The dosage of the Metal nitrates /mmoL	The dosage of ZIF-9 /mmoL
ZIF-9/ZnCo-LDH	$Zn(NO_3)_2$ $6H_2O$	0.25	1.0
ZIF-9/CdCo-LDH	$Cd(NO_3)_2$ $4H_2O$	0.25	1.0
ZIF-9/CuCo-LDH	$Cu(NO_3)_2$ $3H_2O$	0.25	1.0
ZIF-9/FeCo-LDH	$Fe(NO_3)_2$ $9H_2O$	0.25	1.0
ZIF-9/AlCo-LDH	$Al(NO_3)_2$ $9H_2O$	0.25	1.0
ZIF-9/CrCo-LDH	$Cr(NO_3)_2$ $9H_2O$	0.25	1.0

Reference

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