Supporting Information

Manganese-cobalt hydroxide nanosheets anchored on hollow sulfur-doped bimetallic MOF for high-performance supercapacitors and hydrogen evolution reaction in alkaline

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1. Experimental Section

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1. Experimental Section

Materials

Manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$), Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), urea, Ammonium fluoride (NH_4F), 2, 5, - Dihydroxyterephthalic acid, N, N-Dimethylformamide (DMF), activated carbon (AC) were purchased from Aladdin Reagents Company. Nickel-foam (NF) is purchased in Hefei Kejing Company and washed with HCl, deionized water and acetone before use. AR grade chemicals without further purification were employed in this work including deionized water.

Materials characterization

The structure was characterized by X-ray diffraction (XRD, BRUKER-AXS D8). The detailed morphology was acquired on a field emission scanning electron microscope (SEM, S4-3400) The chemical compositions were measured on an X-ray photoelectron spectroscope (XPS, AMATAB-MKII) with Mg Kα X-ray radiation as the X-ray source for excitation. The detailed morphology was acquired on a field emission scanning electron microscope (SEM, S4-3400), transmission electron microscope (TEM, Talos F200 FEI).

Electrochemical Supercapacitor Measurement

The electrochemical testing was carried out in the three-electrode mode, where NF, platinum wire, and Hg/HgO were used as the working, counter and a reference electrode, respectively. All the electrochemical measurements were carried out in 6 M KOH electrolyte using the CHI760E electrochemical workstation at room temperature.

Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 0.01Hz to 100 kHz at a fixed perturbation amplitude of 10 mV.

The specific capacitance of each sample was calculated from galvanostatic charge-discharge curves as follows:

$$C_m = I \times \Delta t / (\Delta V \times m)$$

here C_m (F g^{-1}) indicate the specific capacitance of the electrode base on different unit of measurements; I is the discharge current; Δt (s) is the discharge time; ΔV (V) corresponds to the voltage change after a full charge or discharge process; m (g) indicates the mass of active composite material loaded on the NF.

In the two-electrode system, S-MnCo-MOF-74@MnCo LDH/NF//AC was assembled by employing the S-MnCo-MOF-74@MnCo LDH/NF and AC as positive electrode and negative electrode respectively, and a piece of polypropylene fiber was put between the positive and negative electrodes to separate each other. The optimal mass ratio of positive electrode and negative electrode was followed the equation：

$$m_+/m_- = C_- \times \Delta V_- / C_+ \times \Delta V_+$$

where m, C and ΔV are the mass, specific capacity and potential of electrode respectively.

The property of the devices was conducted at room temperature in 6 M KOH. The energy density (E) and power density (P) were calculated by the following equations:

$$E = (C \times \Delta V^2)/7.2$$

$$P = E \times 3600/(\Delta t)$$

where E (Wh kg^{-1}) is the energy density, P (W kg^{-1}) is the power density, C (F g^{-}

[1]) is the capacitance value, ΔV (V) is the voltage window, and Δt (s) is the discharge time.

Electrochemical hydrogen evolution reaction Measurement

The electrochemical testing was carried out in the three-electrode mode, where NF, graphite rod, and Hg/HgO were used as the working, counter and a reference electrode, respectively. All the electrochemical measurements were carried out in 1M KOH electrolyte using the CHI760E electrochemical workstation at room temperature. All the applied potentials were converted with respect to the reversible hydrogen potential electrode (RHE) using the equation $E_{RHE} = E_{Hg/HgO} + 0.059 \times pH + 0.098$.

2. Supplementary Figures and tables

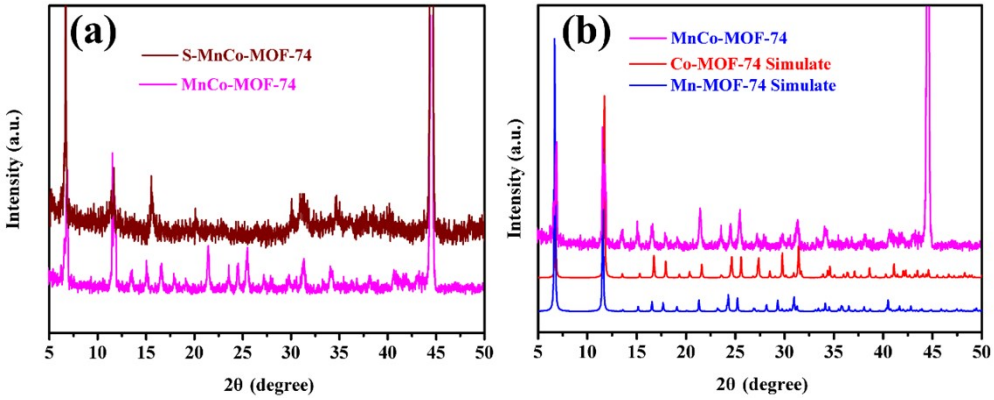

Fig.S1 XRD patterns of MnCo-MOF-74, S-MnCo-MOF-74 (a) and MnCo-MOF-74 (b)

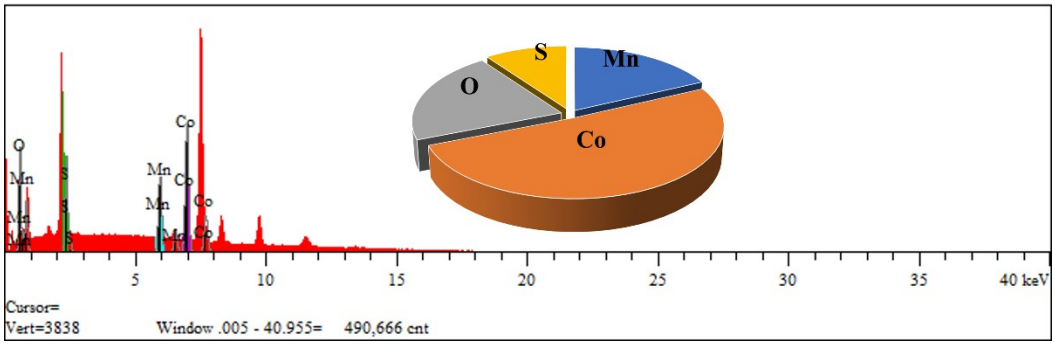

Fig. S2 EDS analysis of S-MnCo-MOF-74@MnCo LDH.

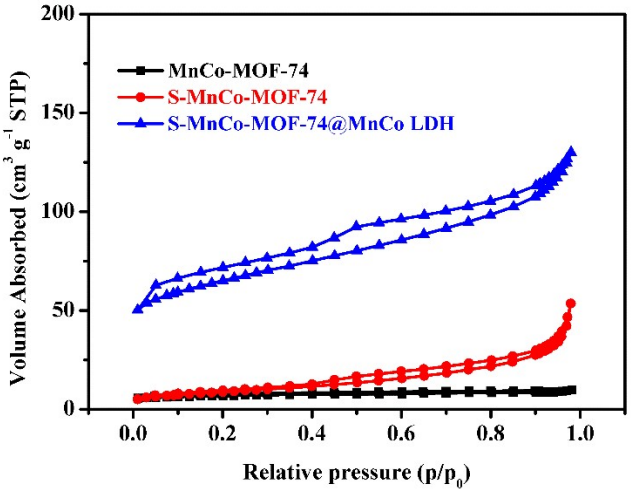

Fig. S3 Nitrogen adsorption/desorption isotherms of MnCo-MOF-74/NF, S-MnCo-MOF-74, and S-MnCo-MOF-74@MnCo LDH.

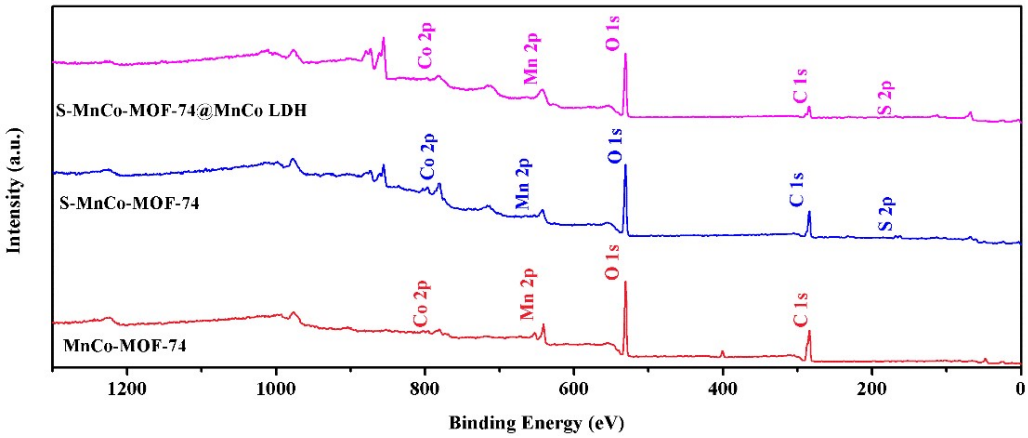

Fig. S4 XPS survey spectrum of MnCo-MOF-74, S-MnCo-MOF-74, and S-MnCo-MOF-74@MnCo LDH.

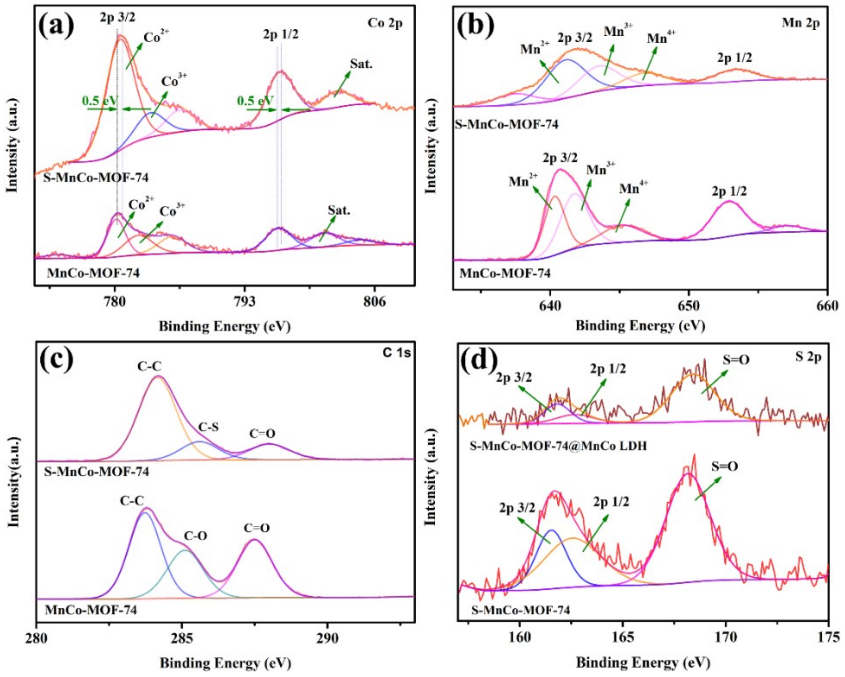

Fig. S5 XPS of (a)Co 2p, (b) Mn 2p, (C) C1s in MnCo-MOF-74 and S-MnCo-MOF-74, (d) XPS of S 2p in S-MnCo-MOF-74 and S-MnCo-MOF-74@MnCo LDH.

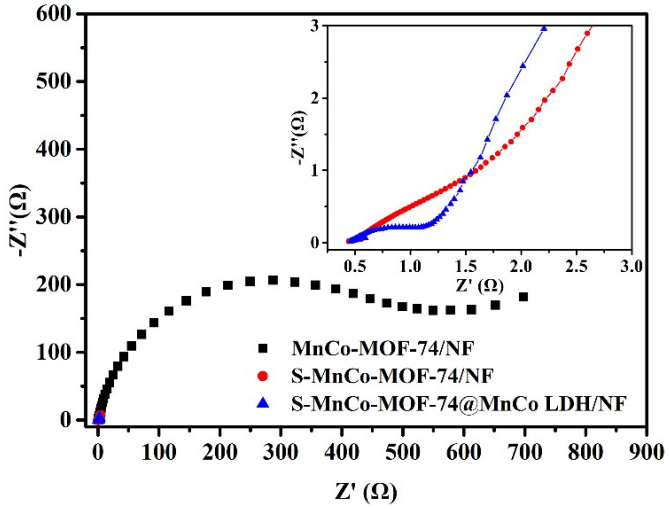

Fig. S6 EIS of MnCo-MOF-74, S-MnCo-MOF-74 and S-MnCo-MOF-74@MnCo LDH.

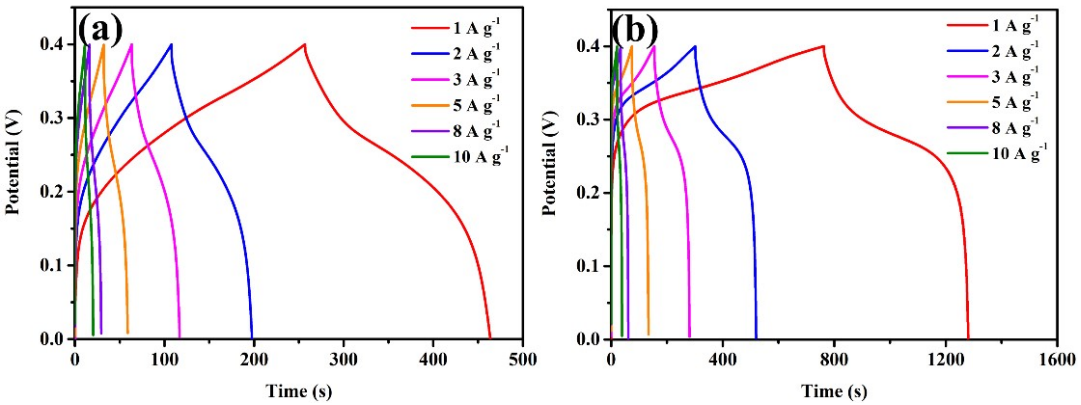

Fig. S7 GCD curves of MnCo-MOF-74 (a) and S-MnCo-MOF-74 (b) at different current densities.

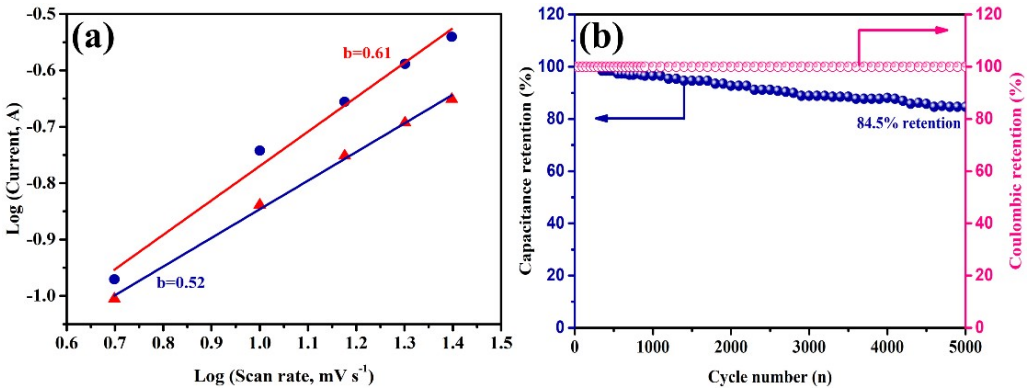

Fig. S8 (a) The plots of log (i_p) vs. log (v), (b) capacitance retention and coulombic retention of S-MnCo-MOF-74@MnCo LDH/NF after 5000 cycles.

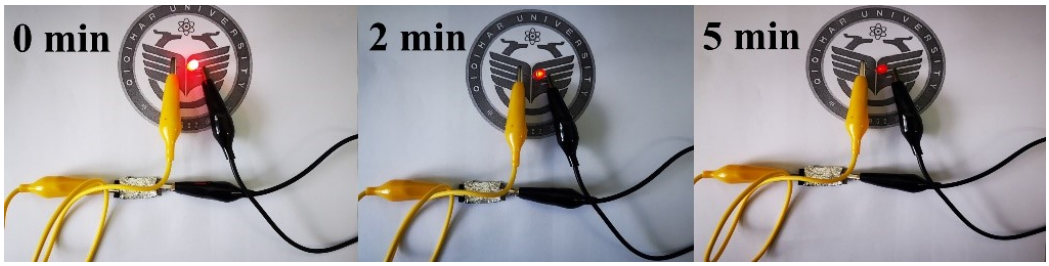

Fig. S9 Glowing LED at a different time interval after charging.

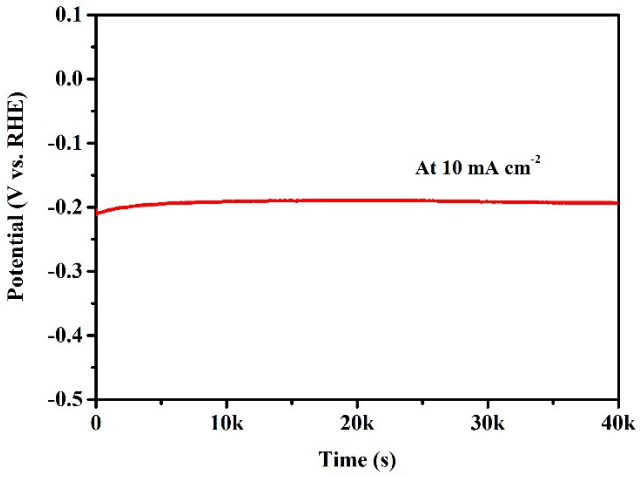

Fig. S10 Chronopotentiometric curve of S-MnCo-MOF-74@MnCo LDH at 10 mA cm^{-2} up to 10h.

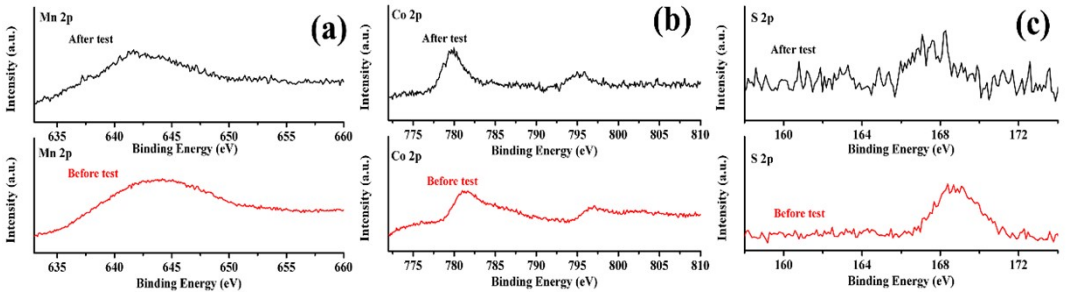

Fig. S11 The XPS spectrum of S-MnCo-MOF-74@MnCo LDH/NF before and after test: (a) Mn 2p, (b) Co 2p, (c) S 2p

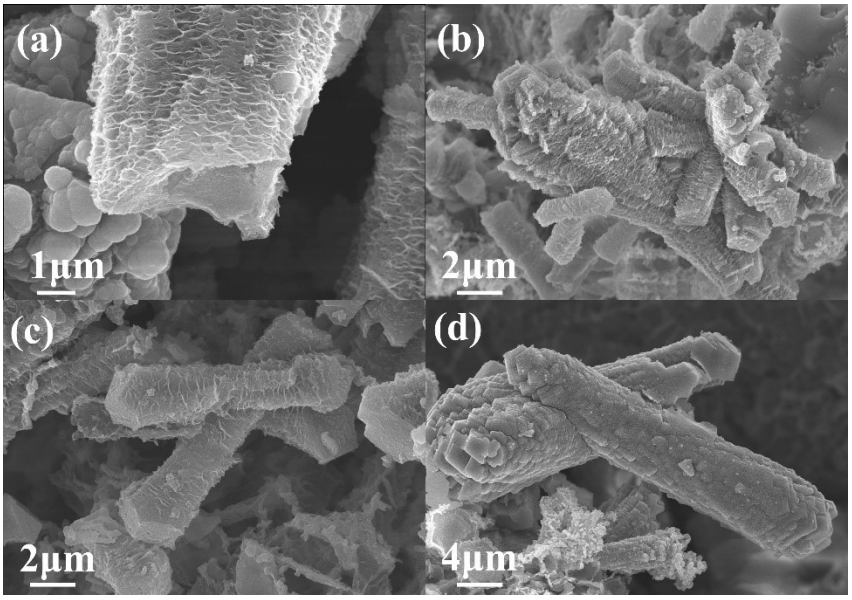

Fig. S12 The SEM image of S-MnCo-MOF-74@MnCo LDH/NF after stability test

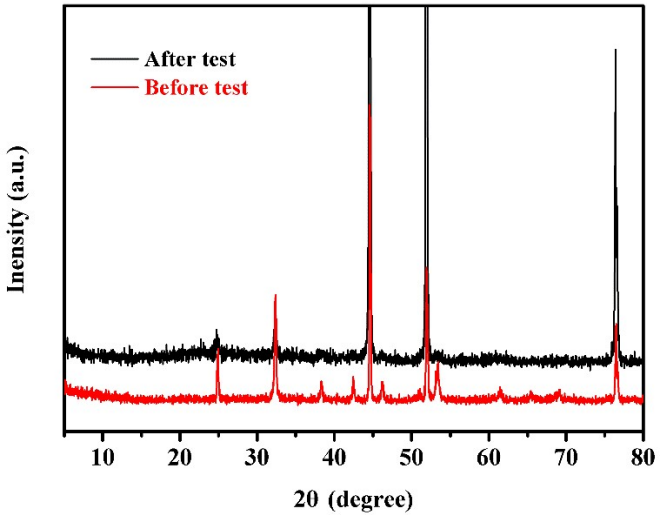

Fig. S13 XRD patterns of S-MnCo-MOF-74@MnCo LDH/NF before and after stability test.

Table S1. Comparison HER performance of S-MnCo-MOF-74@MnCo LDH with other electrocatalysts at 1M KOH solution.

Catalyst	Overpotential (η/mV) Vs. 10mA cm^{-2}	Tafel slope (mV dec^{-1})	Electrolyte	Reference
S-MnCo-MOF-74@MnCo LDH/NF	197	128.9	1 M KOH	This work
Cr-CoFe LDH	205	101	1 M KOH	*Nanomaterials 2022, 12, 1227*
NiFe-LDH/NF	210	59	1 M KOH	*Science, 2014, 345, 1593–1596*
$Zn_{1-x}Fe_x$–LDH/NF	221	110	1 M KOH	*Small, 2018, 14, 1803638.*
EG/$Co_{0.85}$Se/NiFe-LDH	265	160	1 M KOH	*Energy Environ. Sci., 2016, 9, 478-483.*
NiFe LDH NS@DG10	300	110	1 M KOH	*Adv. Mater.*, *2017*, *29*, 1700017
CoFe@ NiFe LDH	240	84	1 M KOH	*Appl. Catal. B-Enviro.*2019,*253,131*

Table S2. Comparison of capacitances between the present electrode S-MnCo-MOF-74@MnCo LDH with other composites

Materials	Specific capacitance (F/g)	Electrolyte	Ref.
S-MnCo-MOF-74@MnCo LDH/NF	1875.4 F g^{-1} at 1 A g^{-1}	6M KOH	This work
NiCoP/S NCs	2229.9 F g^{-1} at 1 A g^{-1}	1M KOH	Ref.64
Co_3O_4@$CoNi_2S_4$-20/CC	1798 F g^{-1} at 1 A g^{-1}	1M KOH	Ref.65
MoS_2@Mo_2C	1040 F g^{-1} at 0.5 A g^{-1}	1M KOH	Ref.66
NiCo-sulfide@CC	1801.13 F g^{-1} at 1 A g^{-1}	6M KOH	Ref.67
CoNi-SDS-LDH	1018.4 F g^{-1} at 1 A g^{-1}	1M KOH	Ref.68
HS-NCS@MXene	2637 F g^{-1} at 2.5 A g^{-1}	2M KOH	Ref.69