Three-dimensional flower-like Ni-S/Co-MOF grown on Ni foam as bifunctional electrocatalyst for efficient overall water splitting

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Materials and Reagents

The cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and sodium carbonate ($NaNO_3$) were obtained from Sinopharm Chemical Reagent Co. Ltd. The 2-aminoterephthalic acid (2-NH_2-BDC) and thiourea (H_2NCSNH_2) were purchased from Sigma-Aldrich Co. ltd. The potassium hydroxide (KOH) and N,N dimethylformamide (DMF) were purchased from Shanghai Maclean Biochemical Technology Co., ltd. Besides, ultrapure water (18.2 MΩ) was utilized throughout the whole experiment. The purity of all reagents more than 99%.

Materials characterization

The morphologies and microstructures of the prepared products were tested by scanning electron microscope (SEM, JSM-6360LA, Japan) and transmission electron microscopy (TEM, JEM-2010, Japan). The X-ray diffraction (XRD) was used to identify the crystal phases of products on the Max-2000 (Rigaku Co., Ltd., Japan) and X-ray photoelectron spectroscopy (XPS) can be used to analyze the elemental chemical states of the catalyst materials on the AXIS-Ultra DLD (Shimazu, Japan).

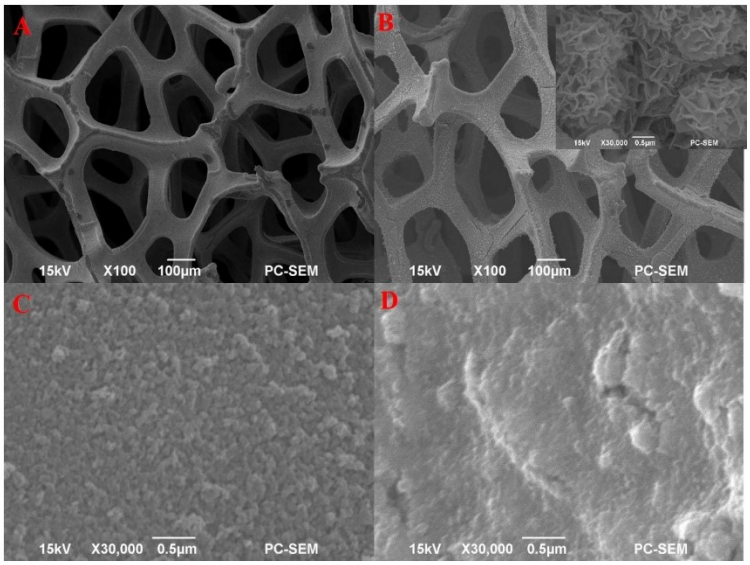

Fig. S1. The SEM images of the bare NF (A) and the Ni-S/Co-MOF/NF (B), Ni/NF (C), Ni-S/NF (D).

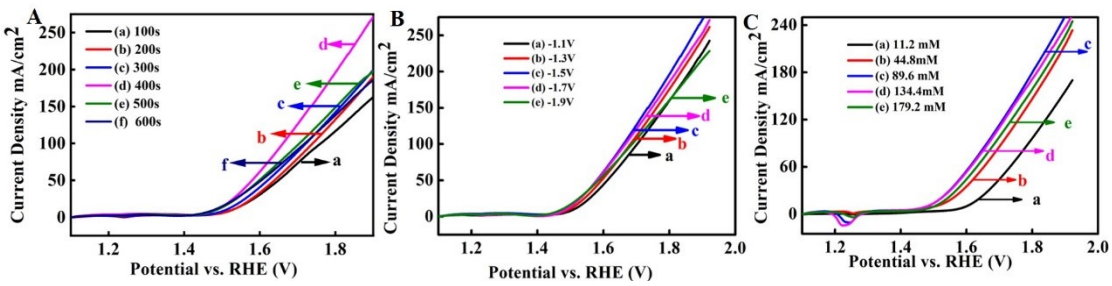

Fig. S2. Polarization curves of Co-MOF/NF with various deposition time (A), applied potential (B) and the concentration of Co^{2+} in 1 M KOH.

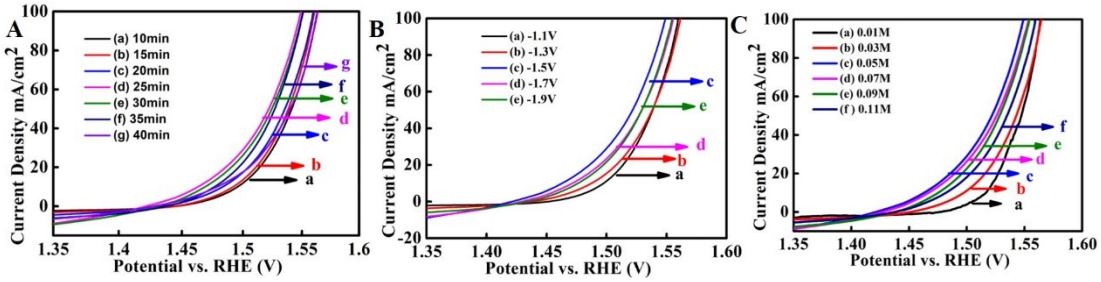

Fig. S3. Polarization curves of Ni-S/Co-MOF/NF with various deposition time (A), applied potential (B) and the concentration of Ni^{2+} in 1 M KOH.

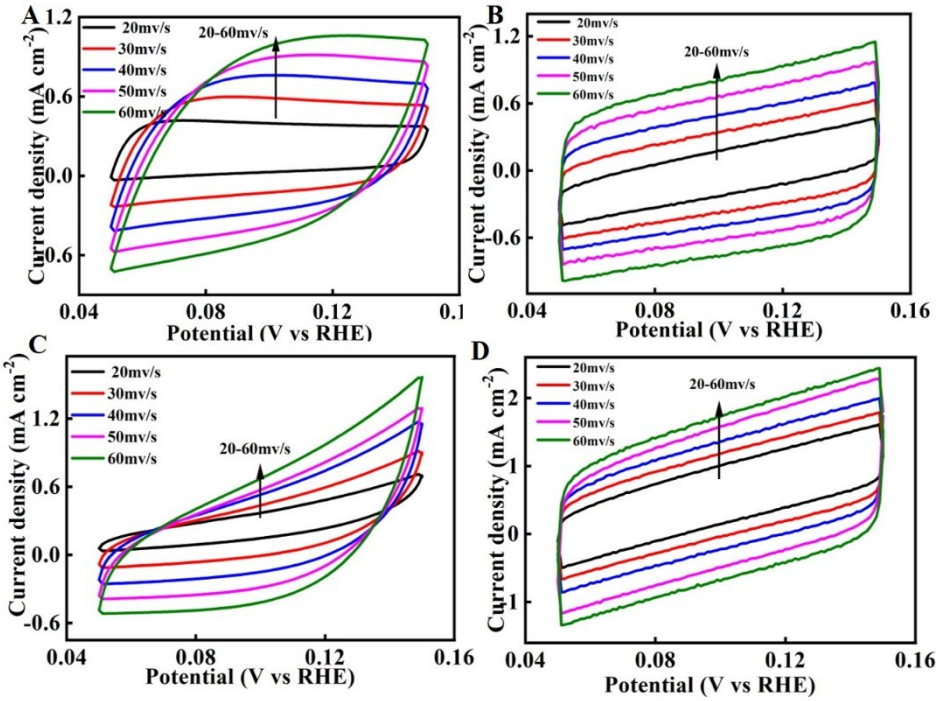

Fig. S4. CV curves of various electrodes in the potential window from 0.05 to 0.15 V (vs. RHE) at 20, 30, 40, 50, and 60 mV s^{-1}: (A) Co-MOF/NF, (B) Ni/NF, (C) Ni-S/NF and (D) Ni-S/Co-MOF/NF.

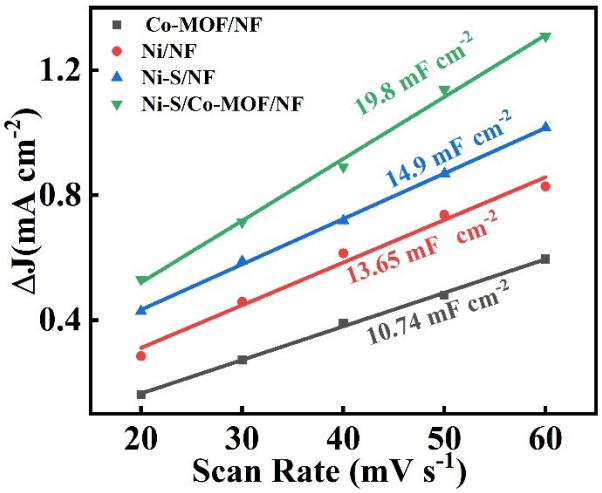

Fig. S5. Double-layer capacitances (C_{dl}) of the four samples derived from the cyclic voltammograms.

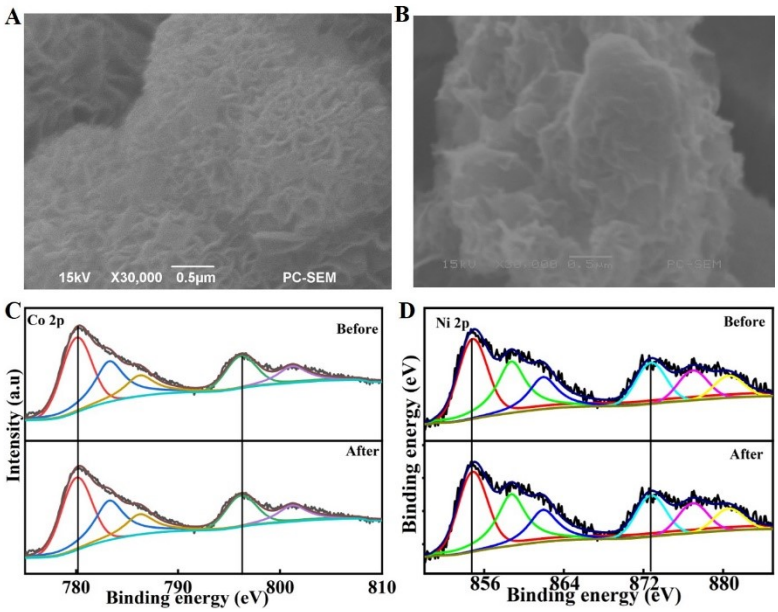

Fig. S6. (A, B) SEM images of Ni-S/Co-MOF/NF before and after 16 h of stability test at a constant current density for HER and OER, respectively. (C,D) High resolution XPS spectra of Ni-S/Co-MOF/NF after stability test for HER.

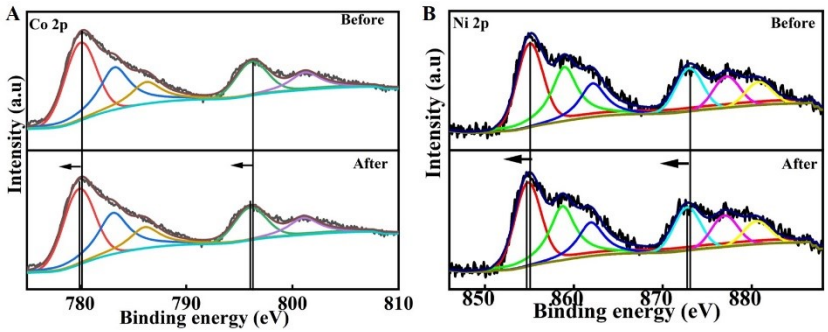

Fig. S7. High resolution XPS spectra of Ni-S/Co-MOF/NF after stability test for OER.

Table S1. Comparison of OER activity at 10 mA cm^{-2} and stability of various Co-based MOFs catalysts.

Catalyst	η_{10}/mV	Tafel slope/ mV dec^{-1}	Electrolyte	Reference
Ni-S/Co-MOF/NF	**248**	**29.1**	**1M KOH**	**This work**
CoFe-MOF	265	44	1M KOH	[1]
NiCo-MOF@Fe-MOF	275	54	1M KOH	[2]
CoPS@NPS-C	320	45	1M KOH	[3]
Hollow CoS_2–MoS_2	266	104	1M KOH	[4]
Ni–S/MIL-53(Fe)	256	39	1M KOH	[5]
Fe-Co-Ni MOF	254	51.3	1M KOH	[6]
$(Ni_2Co_1)_{0.925}Fe_{0.075}$-MOF	257	41.3	1M KOH	[7]
Co-BPDC/Co-BDC-3	335	72.1	1M KOH	[8]
Co-Ni@HPA-MOF	320	58	1M KOH	[9]
$CoWO_4$−$Co(OH)_2$	280	70.6	1M KOH	[10]

Table S2. Comparison of HER activity at 10 mA cm^{-2} and stability of various Co-based MOFs catalysts.

Catalyst	η_{10}/mV	Tafel slope/ mV dec^{-1}	Electrolyte	Reference
Ni-S/Co-MOF/NF	**127**	**32.25**	**1M KOH**	**This work**
CoPS@NPS-C	320	45	1M KOH	[3]
CoNC@MoS_2/CNFs	143	68	1M KOH	[11]
BP/MOF-Fe/Co	180	67	1M KOH	[12]
CoCoO/$ZnFe_2O_4$@CNWs	226	138	1M KOH	[13]
NiCo-MOF-P	195	105	1M KOH	[14]
Ni−Co-Se/CFP	162	54	1M KOH	[15]

Table S3. Comparison of overall water splitting at 10 mA cm^{-2} and stability of various Co-based MOFs catalysts.

Catalyst	Volatage/ V	Electrolyte	Reference
Ni-S/Co-MOF/NF	**1.59**	**1M KOH**	**This work**
BP/MOF-Fe/Co	1.63	1M KOH	[3]
Fe-Co-Ni-MOF	1.60	1M KOH	[6]
CoNC@MoS_2/CNF	1.62	1M KOH	[11]
CoNiP/NF	1.62	1M KOH	[16]
FeCoMnNi-MOF-74/NF	1.62	1M KOH	[17]
Co,Fe-MOF-74/Co/CC	1.65	1M KOH	[18]

Notes and references

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