Electronic Supplementary Information for

Monolithic-structured ternary hydroxides as freestanding bifunctional electrocatalysts for overall water splitting

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1. Supplementary Figures

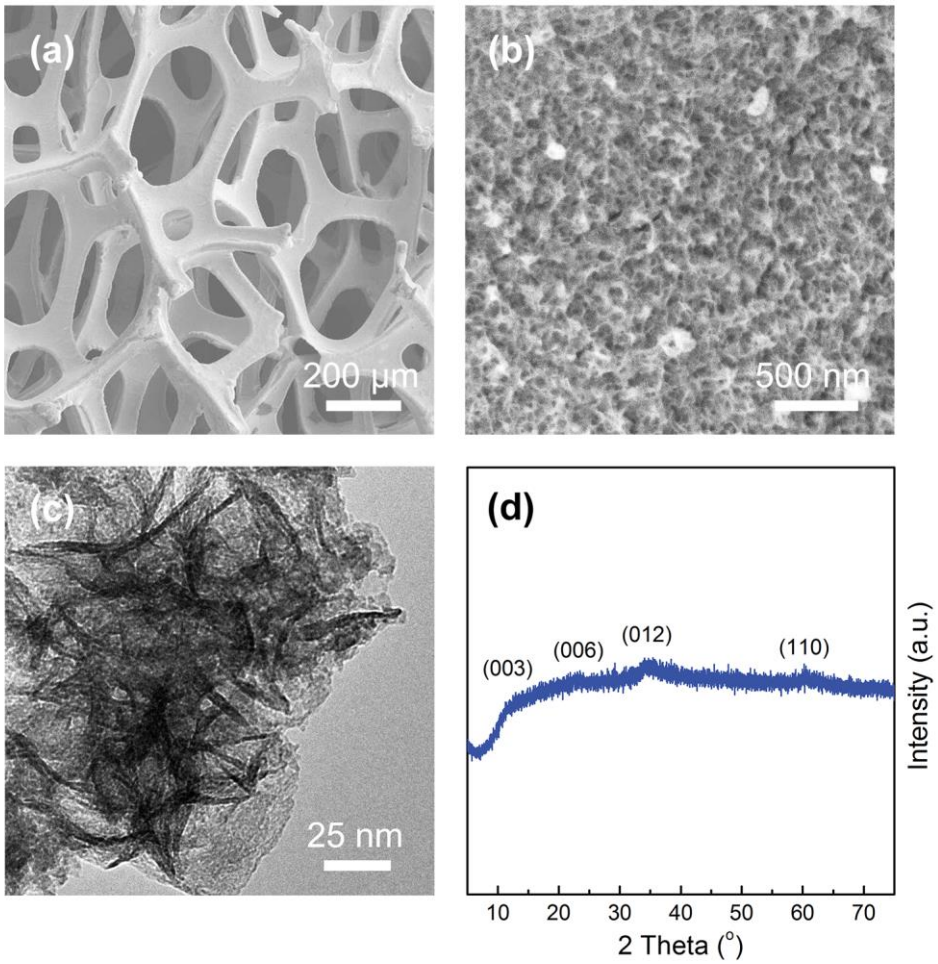

Fig. S1 Morphology and structure characterizations of NiFe/NF electrode. (a,b) SEM images of the NiFe/NF electrode. (c) TEM image of the electrodeposited NiFe LDHs. (d) XRD pattern of NiFe LDHs.

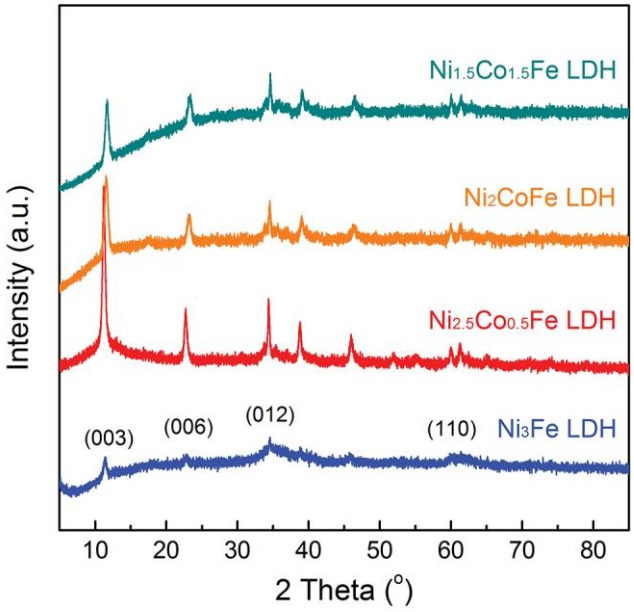

Fig. S2 XRD patterns of NiCoFe LDH samples with different compositions prepared by hydrothermal method.

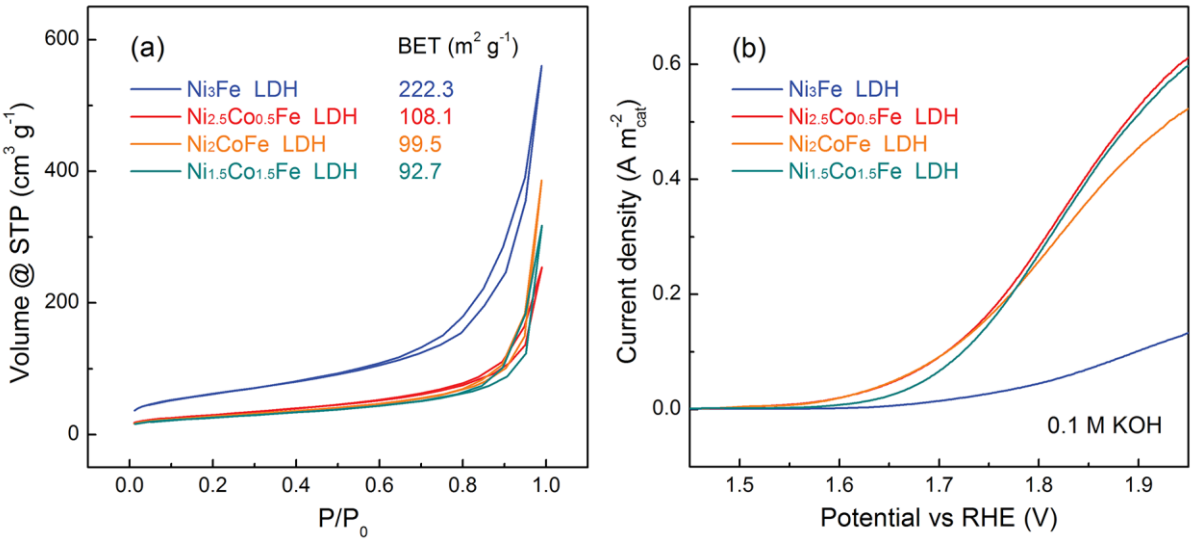

Fig. S3 (a) N_2 adsorption-desorption isotherms and BET specific surface areas of NiCoFe LDHs with different compositions. (b) OER activity respect to catalyst surface area in 0.10 M KOH electrolyte.

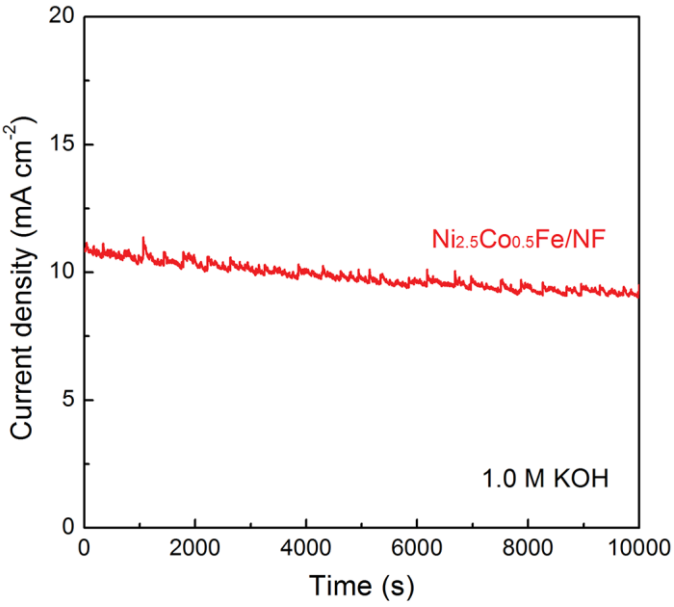

Fig. S4 Stability of $Ni_{2.5}Co_{0.5}Fe$/NF electrodes for overall water splitting at an initial current density around 10 mA cm^{-2}.

2. Supplementary Tables

Table S1. Summary of OER performance of NiFe-based electrocatalysts in 0.10 M KOH electrolyte.

Samples	η_{10} (mV)	Current density@400 mV overpotential (mA cm^{-2})	Tafel slope (mV dec^{-1})	Reference
$Ni_{2.5}Co_{0.5}Fe$/NF	275	62	105	
Ni_2CoFe/NF	310	55	82	This work
Ni_3Fe/NF	305	57	92	
NiFe-LDH/CNT	309	-	35	S1
CQD/NiFe-LDH	305	-	35	S2
n-NiFe LDH/NGF	337	30	45	S3
NiFe LDH/oGSH	350	21	54	S4
m-NiFe/CNx	360	13	59	S5
3D NiFe-LDH	250	-	50	S6
O-NiCoFe-LDH	420	9	93	S7
a-$Fe_{40}Ni_{60}O_x$	-	6	34 ± 8	S8
Ni-Fe film [40% Fe]	420	-	40	S9

Table S2. Elemental compositions of various NiCoFe LDH samples as determined by EDS measurement.

Sample	Relative amounts of different elements (at.%)				Atomic ratio of Ni:Co:Fe
	Ni	Co	Fe	O	
Electrodeposited					
Ni_3Fe LDH	28.24	-	13.01	58.75	2.17: - :1.00
$Ni_{2.5}Co_{0.5}Fe$ LDH	23.48	7.63	12.34	56.55	1.90:0.62:1.00
Hydrothermally synthesized					
Ni_3Fe LDH	29.55	-	11.29	59.16	2.62: - :1.00
$Ni_{2.5}Co_{0.5}Fe$ LDH	25.28	5.94	11.88	56.90	2.13:0.50:1.00
Ni_2CoFe LDH	21.69	11.45	12.42	54.44	1.75:0.92:1.00
$Ni_{1.5}Co_{1.5}Fe$ LDH	18.78	14.51	12.98	53.73	1.45:1.12:1.00

Table S3. OER activation energy correlating parameters of $Ni_{2.5}Co_{0.5}Fe$ LDH and Ni_3Fe LDH obtained at various temperatures in 0.10 M KOH solution.

Samples	Temperature (^oC)	Tafel slope ($mV\ dec^{-1}$)	Exchange current density J_0 ($mA\ cm^{-2}$)
$Ni_{2.5}Co_{0.5}Fe$ LDH [21.0 $kJ\ mol^{-1}$]	11.5	191	236
	15.9	183	248
	20.1	175	254
	25.1	164	290
	30.1	151	356
	35.0	141	402
	40.3	122	612
	44.9	118	599
	50.0	113	532
Ni_3Fe LDH [52.3 $kJ\ mol^{-1}$]	11.7	246	112
	15.0	239	107
	20.1	217	128
	25.5	191	176
	30.0	165	284
	35.2	139	516
	40.3	123	730
	45.3	109	981
	50.3	100	1057

Table S4. Summary of overall water splitting performance of the recently reported bifunctional electrocatalysts in 1.0 M KOH electrolyte.

Samples	Mass loading (mg cm^{-2})	Voltage@10 mA cm^{-2} (V)	Reference
$Ni_{2.5}Co_{0.5}Fe$/NF	0.3	1.62	This work
NiFe LDH/NF	-	1.70	S10
$Ni(OH)_2$/NF	-	1.82	S10
$NiFeO_x$/CFP	1.6	1.55	S11
Ni_2P/NF	5.0	1.63	S12
Ni_5P_4/Ni foil	3.5	1.70	S13
Ni-P/Cu foam	5.0	1.68	S14
NiSe/NF	2.8	1.63	S15
Ni_3Se_2/Cu foam	3.0	1.65	S16
Co-P/Cu foil	2.6	1.64	S17
CoO_x@CN on NF	2.1	1.60	S18
CoMnO@CN on NF	2.0	1.50	S19
Co_3O_4 NCs/CFP	0.35	1.91	S20

3. Supplementary Movies

Movie S1. Overall water splitting at different cell voltages on a two-electrode configuration using $Ni_{2.5}Co_{0.5}Fe$/NF for both OER and HER in 1.0 M KOH, indicating that plentiful O_2 and H_2 bubbles were released during water electrolysis.

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