Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information (ESI)

Zr-doped heterostructure interface to tune the electronic structure of bi-functional electrocatalysts for water splitting

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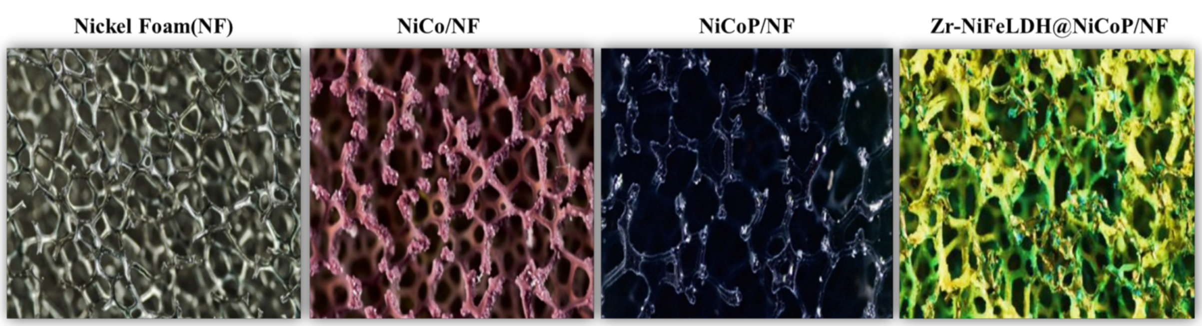

Fig. S1. The microscopic images of (a) Nickel Foam (NF), (b) NiCo/NF, (c) NiCoP/NF, (d) Zr-NiFeLDH@NiCoP/NF.

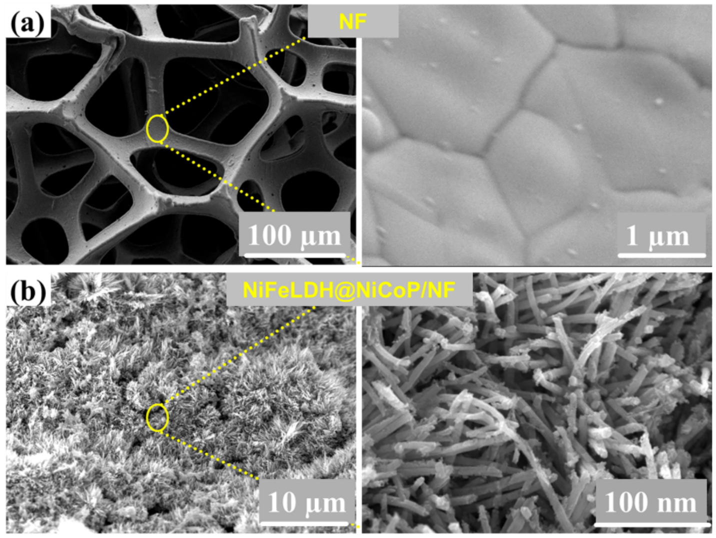

Fig. S2. The SEM images of (a) NF and (b) NiFe LDH@NiCoP/NF.

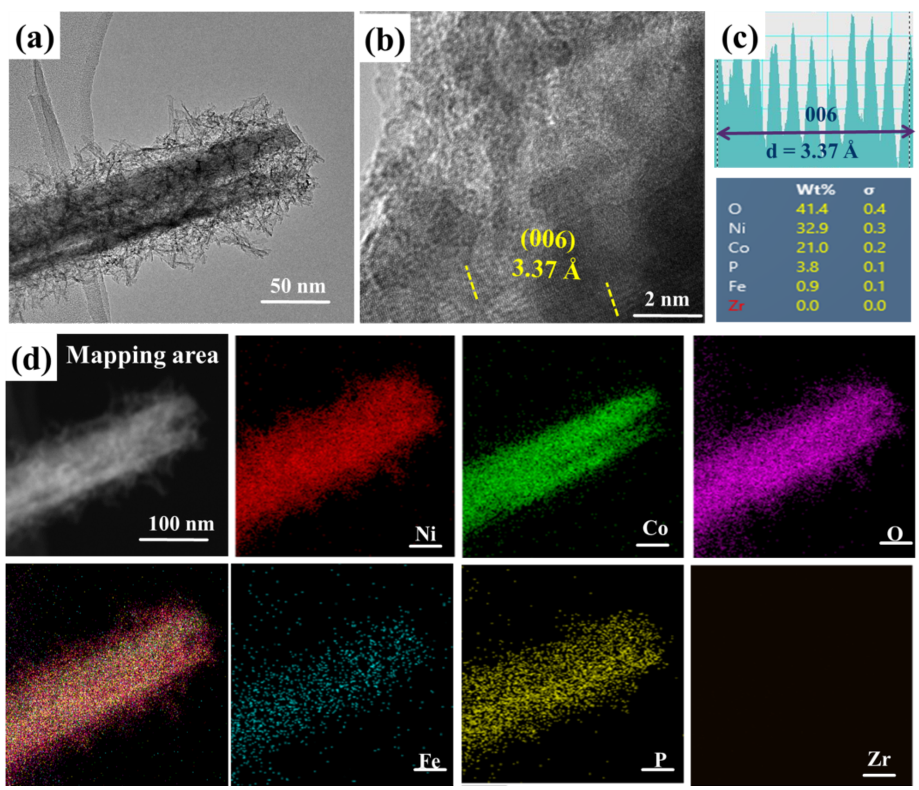

Fig. S3. TEM images of NiFeLDH@NiCoP/NF with EDX elemental mapping. (a) TEM image of the NiFeLDH@NiCoP/NF, (b) HRTEM image of the NiFeLDH@NiCoP/NF, (c) Corresponding intensity line profile of interplanar crystal spacing, (e) EDX elemental mapping images of the NiFeLDH@NiCoP/NF.

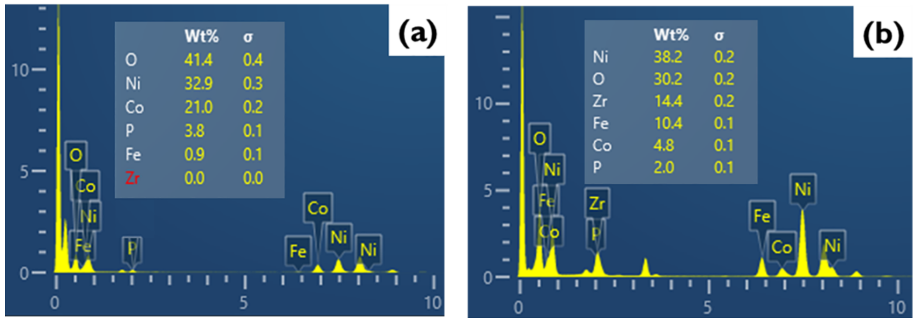

Fig. S4. EDX spectrum of the as prepared (a) NiFeLDH@NiCoP/NF and (b) Zr-NiFeLDH@NiCoP/NF.

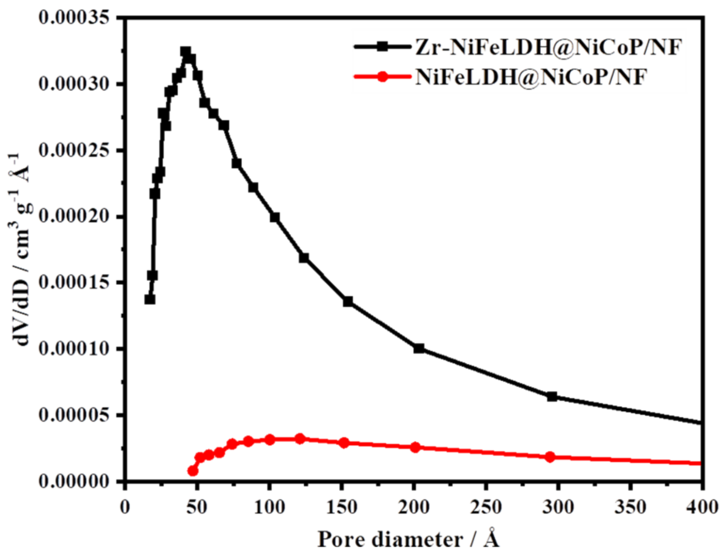

Fig. S5. Pore size distribution of Zr-NiFeLD@NiCoP/NF and NiFeLD@NiCoP/NF.

Table S1. Elemental analysis of all present metals by ICP-OES.

Sample	Co (mg)	P (mg)	Zr (μg)	Fe (μg)
NiFeLDH@NiCoP/NF	22.745	1.102	-	88.988
Zr-NiFeLDH@NiCoP/NF	24.828	1.753	2.042	68.631

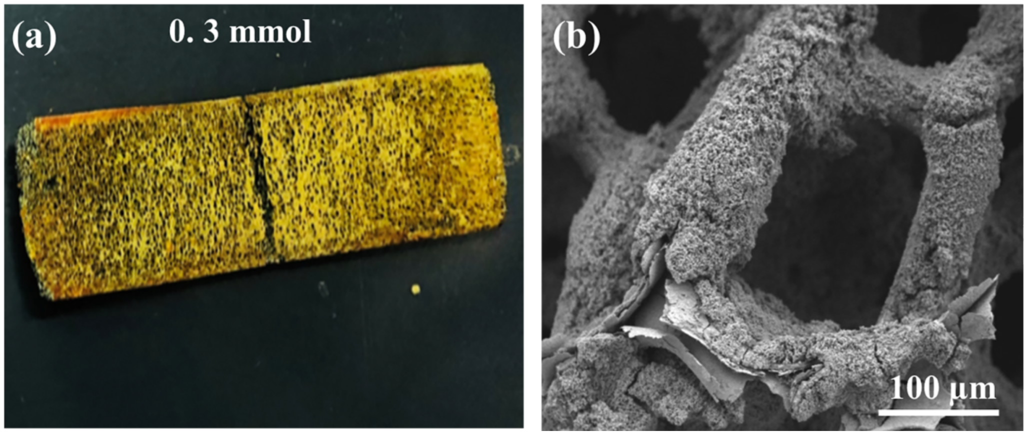

Fig. S6. Electrocatalysts with high concentrations of $ZrCl_4$ decrease mechanical strength, (a) digital image and (b) SEM image.

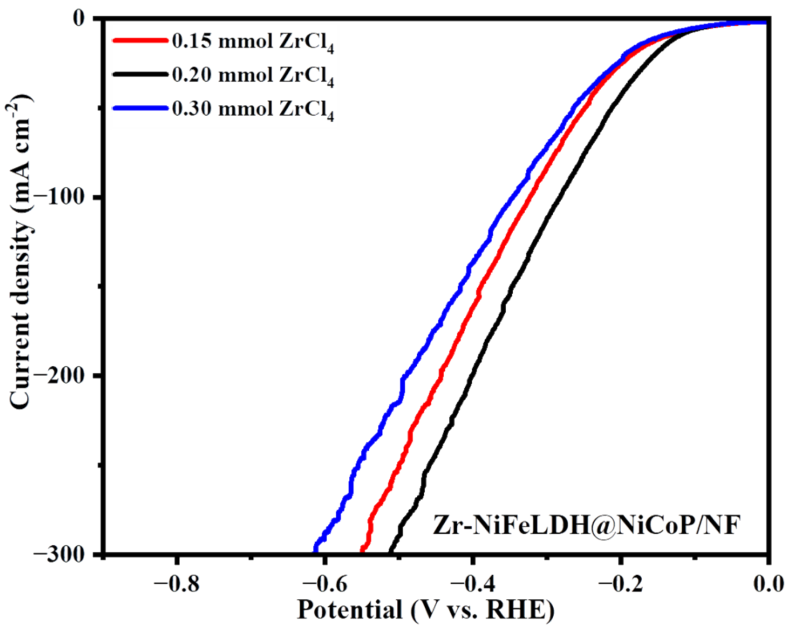

Fig. S7. The HER LSV curves of Zr-NiFeLD@NiCoP/NF with various ratios.

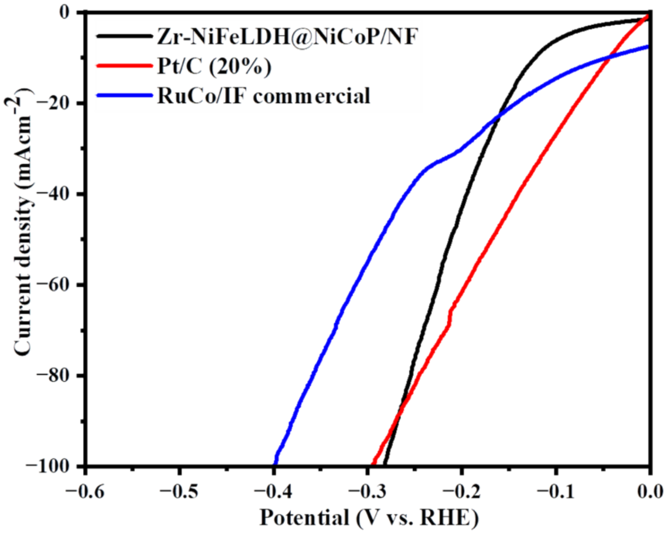

Fig. S8. The HER polarization curves of the Zr-NiFeLD@NiCoP/NF, Pt/C (20%) and RuCo/IF.

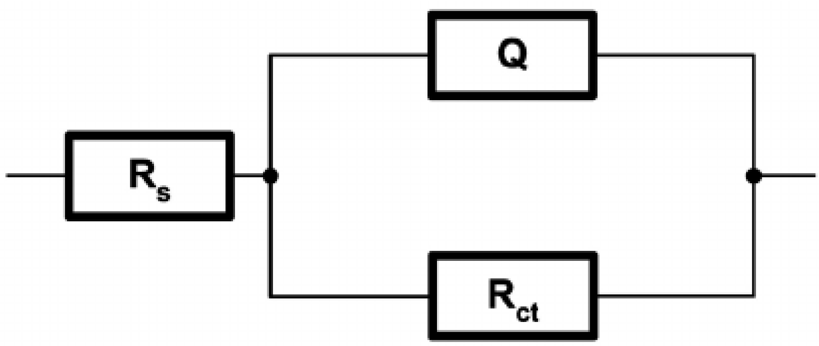

Fig. S9. The equivalent circuit diagram used for analysis of the EIS curves measured for the HER and the OER.

Table S2. Summary of the EIS results fitted to the equivalent circuit board as shown in Figure S9.

Sample	**Reaction**	**$R_{ct}(\Omega)$**
This work	HER & OER	0.496 & 0.32
NiFeLDH@NiCoP/NF	HER & OER	2.77 & 0.41
IrFe@Fe_3O_4@NiFeLDH/IF	HER & OER	2.34 & 2.44
$Zr_{0.1}Ni_{1.9}P$/NF	HER & OER	5 & 8
NiFexP@NiCo-LDH/CC	OER	3
NiSe@NiFe-LDH/NF	OER	0.31
RuO_2/NiFeLDH/NF	HER &OER	6.25 & 1.55
$FeNi_3/NiFeO_x$	HER	2

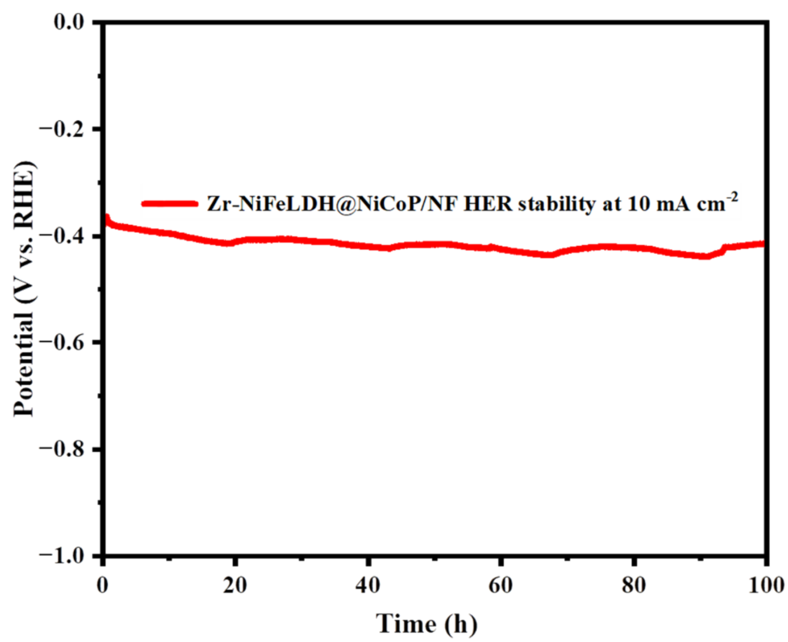

Fig. S10. The Zr-NiFeLDH@NiCoP/NF HER potential stability test at 10 mA cm^{-2} for 100 h.

Table S3. Comparison of HER performance for Zr-NiFeLDH@NiCoP/NF with other reported electrocatalysts in the alkaline media.

Catalyst	Electrolyte	η_{10}(mV)	Tafel Slope (mV/dec)	Stability (h)	Ref.
Zr-NiFeLDH@NiCoP/NF	**1M KOH**	**122**	**102.2**	**100($j_{10\ and}\ j_{500}$)**	**This work**
3DOM-Ni_2P/FexP	1M KOH	106	81	16(j_{10})	S[1]
CoMnP/Ni_2P/NiFe	1M KOH	87	95	-	S[2]
$Zr_{0.1}Ni_{1.9}P$/NF	1M KOH	68	79	100($j_{10}$and j_{100})	S[3]
Ni_2P/$NiMoP_2$/CC	1M KOH	102	84	28(j_{10})	S[4]
Zr-NiCoLDH/NF	1M KOH	159	132.7	35(j_{10})	S[5]
$NiFe_XP$@NiCo-LDH/CC	1M KOH	100	116	-	S[6]
Co_4S_3-NiCo LDH/CC	1M KOH	124	107	20(j_{10})	S[7]
W-$FeNi_2S_4$/Ni_3S_2/NF	1M KOH	93	109.7	-	S[8]
NiFeZn LDH	1M KOH	154	103.5	10(j_{10})	S[9]
Ni_2P@$FePO_x$	1 M KOH	75	67	25(j_{10})	S[10]
RuO_2/NiFeLDH/NF	1 M KOH	99	154.2	12($j_{10\ \&\ 50}$)	S[11]
NiFe-LDH/MoS_2–Ni_3S_2/NF	1 M KOH	79	62.4	24(j_{10})	S[12]
$FeNi_3$/$NiFeO_x$	1 M KOH	99	45	4 (j_{25})	S[13]
NiFe LDH/$NiCo_2O_4$/NF	1 M KOH	192	59	10(j_{45})	S[14]
$Co_{0.4}Fe_{0.6}$LDH/g-CN_x	1 M KOH	270	79	24(j_{10})	S[15]
Cu@CoFe LDH	1 M KOH	171	36.4	30(j_{20})	S[16]

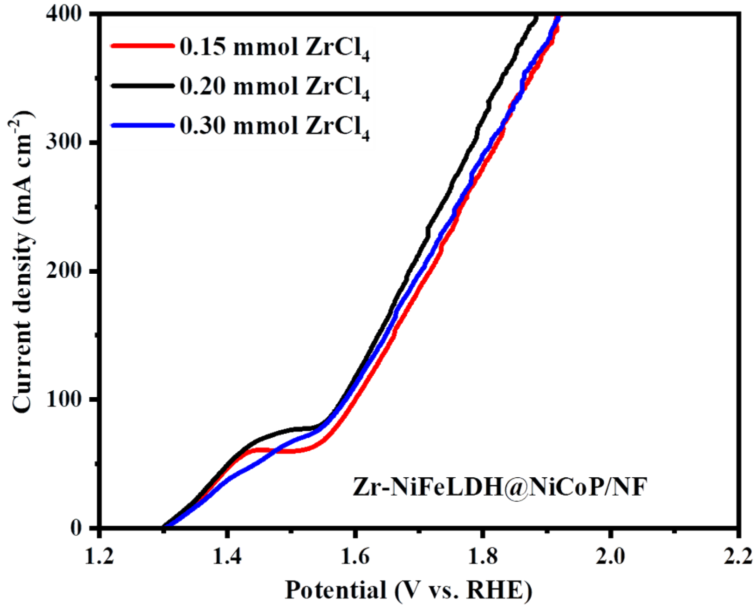

Fig. S11. OER LSV curves of Zr-NiFeLD@NiCoP/NF with various ratios.

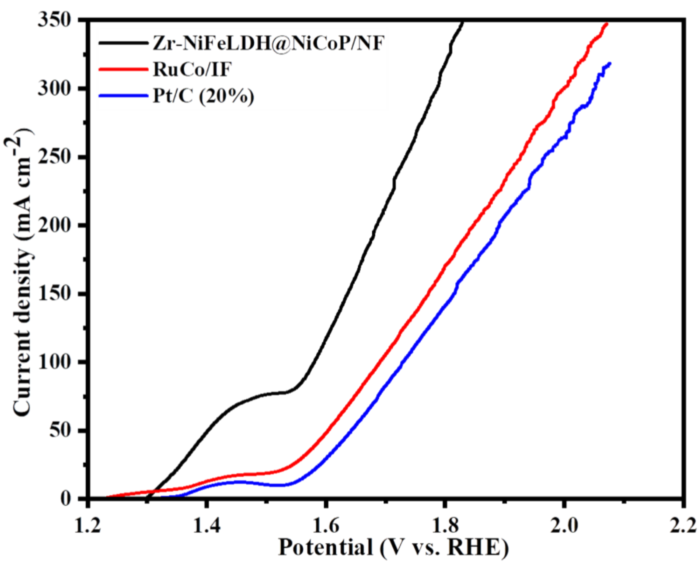

Fig. S12. The OER polarization curves of the Zr-NiFeLD@NiCoP/NF, RuCo/IF and Pt/C (20%).

Table S4. Calculated double layer capacitance (C_{dl}), roughness factor (σ) and normalized current density at overpotentials (η) of 0 and 100 mV. The unit for capacitance and normalized current densities are mF cm^{-2} and mA cm^{-2}, respectively.

Catalysts	C_{dl}	σ	j/σ at η = 0 mV	j/σ at η = 100 mV
Zr-NiFeLDH@NiCoP/NF	**12.25**	**281.25**	**0.00218**	**0.0539**
NiFeLDH@NiCoP/NF	6.53	163.25	0.00018	0.0469
NF	3.72	93	0.00008	0.00658

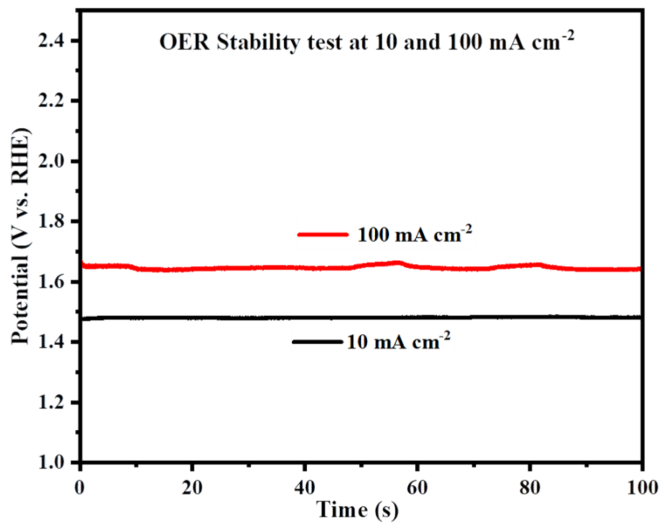

Fig. S13. The Zr-NiFeLDH@NiCoP/NF sample OER potential stability test at 10 and 100 mA cm^{-2} current density for 100 h.

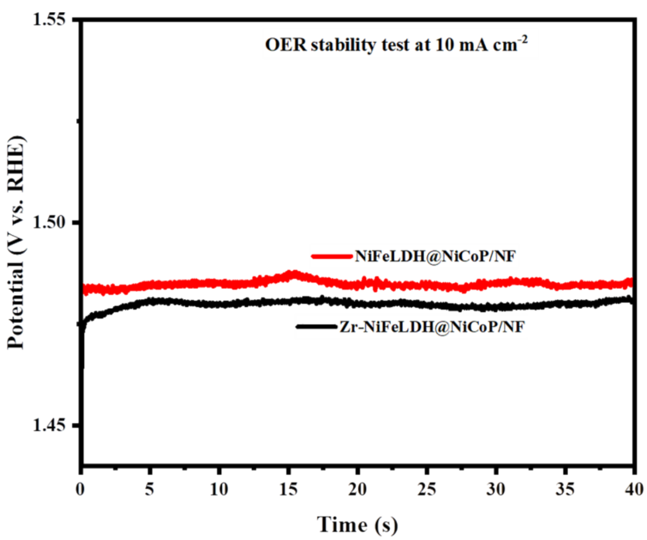

Fig. S14. OER stability test comparison at 10 mA cm^{-2} for Zr-NiFeLDH@NiCoP/NF and NiFeLDH@NiCoP/NF.

Table S5. Comparison of OER performance for Zr-NiFeLDH@NiCoP/NF with other reported electrocatalysts in the alkaline media.

Catalyst	**Electrolyte (KOH)**	**η_{10}(mV)**	**Tafel Slope (mV/dec)**	**Stability (h)**	**Ref.**
Zr-NiFeLDH@NiCoP/NF	**1M KOH**	**92**	**45.6**	**100($j_{10}$and j_{500})**	**This Work**
$Zr_{0.1}Ni_{1.9}P$/NF	1M KOH	239	74	100($j_{10}$and j_{100})	S[3]
$Ni_2P/NiMoP_2$/CC	1M KOH	230	138	28(j_{10})	S[4]
$NiFe_XP$@NiCo-LDH/CC	1M KOH	140	97	10(j_{38})	S[6]
Zr-NiFe$(OH)_X$/NFF	1M KOH	211	45.12	40h(j_{10})	S[17]
$Ni_{0.83}Co_{0.17}P$	1M KOH	295	45	25(j_{10})	S[18]
Zr-NiCoLDH/NF	1M KOH	233	40.9	25(j_{100})	S[5]
NiFe LDH@NiFe	1M KOH	201	48.52	25(j_{10})	S[19]
Fe-Ni_2P/N-GO	1M KOH	269	72	7(j_{100})	S[20]
(Ru-Co)O_x-350	1M KOH	265	60	20(j_{10})	S[21]
NiSe@NiFe-LDH/NF	1M KOH	194	58.2	100(j_{100})	S[22]
Ni_2Fe_1-LDH/NF	1 M KOH	239(j_{50})	64.1	24(j_{10})	S[23]
RuO_2/NiFeLDH/NF	1 M KOH	226	77.4	12($j_{10\ \&\ 50}$)	S[11]
NiFe-LDH/MoS_2–Ni_3S_2/NF	1 M KOH	220(j_{50})	108	24(j_{10})	S[12]
NiFeLDH@NiCoP/NF	1 M KOH	220	48.6	100(j_{10})	S[24]

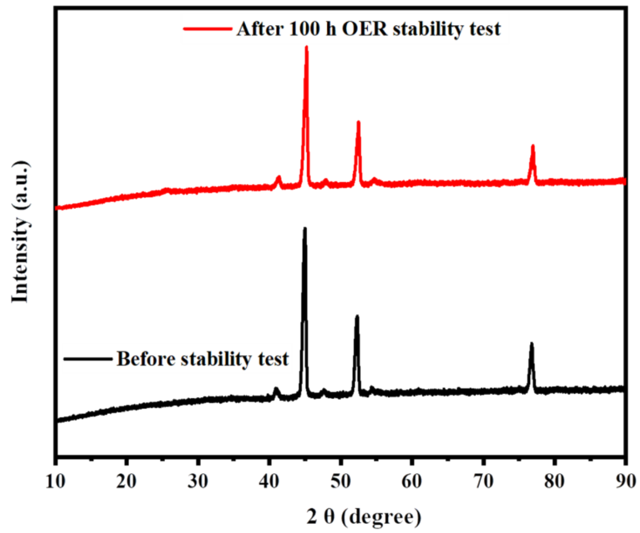

Fig. S15. XRD pattern comparison of the Zr-NiFeLDH@NiCoP/NF (a) before stability and (b) after OER stability for 100 h at 10 mA cm^{-2}.

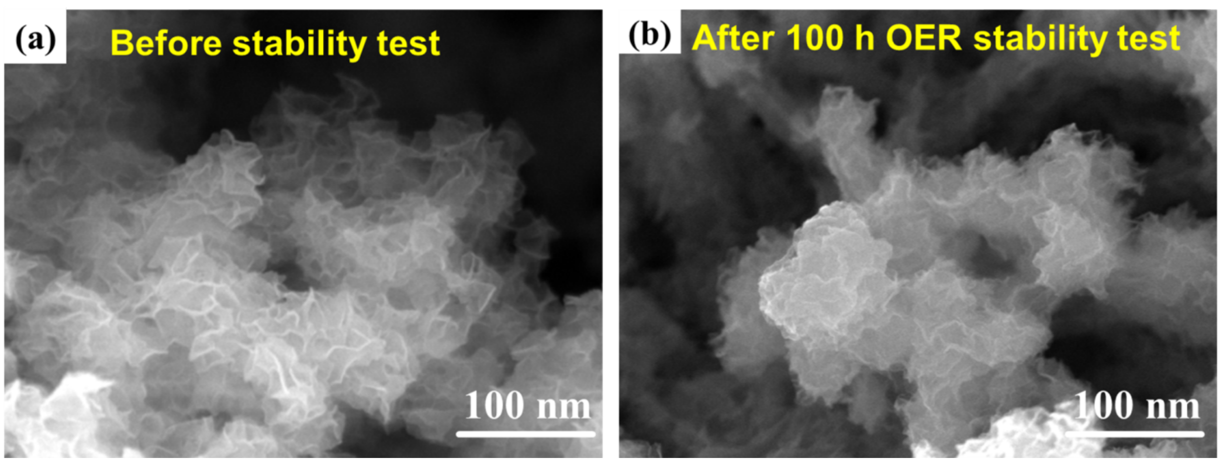

Fig. S16. SEM images of the Zr-NiFeLDH@NiCoP/NF (a) before stability and (b) after 100 h OER stability at current density of 10 mA cm^{-2}.

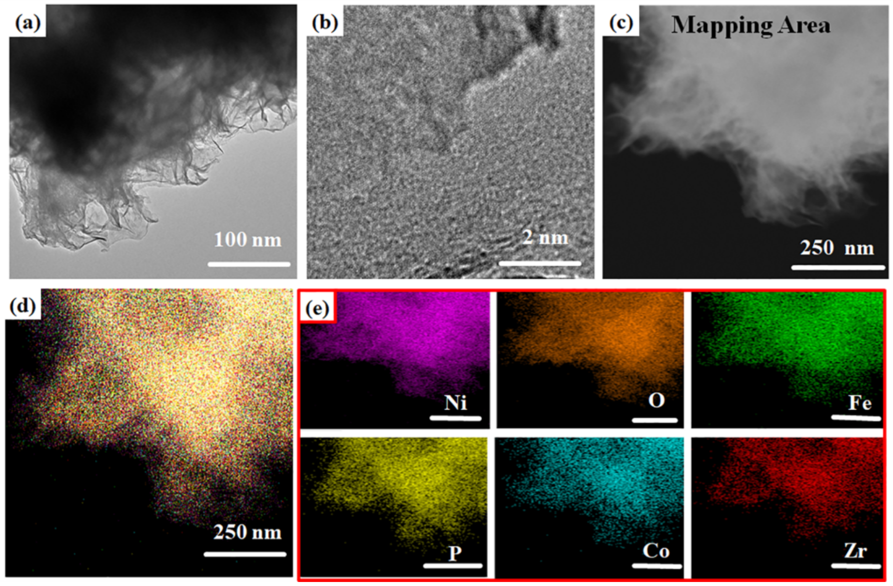

Fig. S17. The TEM analysis after OER stability tests under constant current density of 10 mA cm^{-2} for over 100 h.

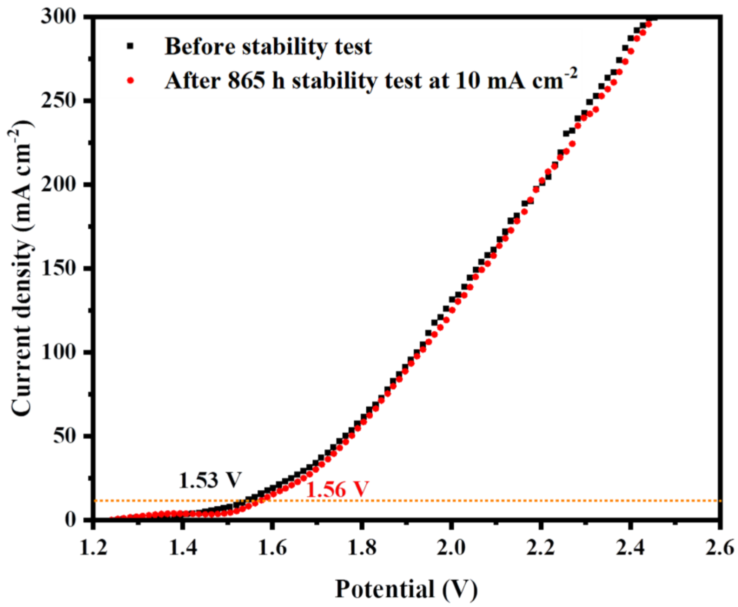

Fig. S18. The polarization curves of the electrode before and after 865 h stability test for overall water splitting at 10 mA cm^{-2}.

Table S6. Comparison of overall water splitting for Zr-NiFeLDH@NiCoP/NF with other reported electrocatalysts in the alkaline media.

Catalyst	Electrolyte (KOH)	Cell Voltage j_{10} (V)	Stability (h)	Ref.
Zr-NiFeLDH@NiCoP/NF	**1 M KOH**	**1.53**	**865(j_{10})**	**This Work**
3DOM-Ni_2P/Fe_xP	1 M KOH	1.54	30(j_{10})	S[1]
$Zr_{0.06}Co_{0.9}P$/CC	1M KOH	1.53	24(j_{10})	S[25]
CoFeZr oxides/NF	1M KOH	1.63	12(j_{10})	S[26]
$Ru_{SA}CoFe_2$/G	1 M KOH	1.48	100 (j_{100})	S[27]
$Zr_{0.1}Ni_{1.9}P$/NF	1M KOH	1.5	50(j_{10})	S[3]
$Ni_2P/NiMoP_2$/CC	1M KOH	1.59	28(j_{10})	S[4]
NiFeLDH@NiCoP/NF	1M KOH	1.57	100(j_{10})	S[24]
Ni_3S_2/NF	1 M KOH	~1.76	150(j_{13})	S[28]
Ru-NiFeP/NF	1 M KOH	1.47	120(j_{10})	S[29]
$Ni_{0.83}Co_{0.17}P$	1 M KOH	1.60	25(j_{10})	S[18]
CoFeZr/NF	1M KOH	1.66	20(j_{15})	S[5]
(Ru-Co)O_x-350	1 M KOH	1.57	20(j_{10})	S[21]
W-$FeNi_2S_4/Ni_3S_2$/NF	1 M KOH	1.52	24(j_{10})	S[8]
$Ni_2P@FePO_x$	1 M KOH	1.51	100(j_{10})	S[10]
RuO_2/NiFeLDH/NF	1 M KOH	1.52	100h(j_{10})	S[11]
NiFe-LDH/MoS_2–Ni_3S_2/NF	1 M KOH	1.50	50($j_{10\ to\ 50}$)	S[12]

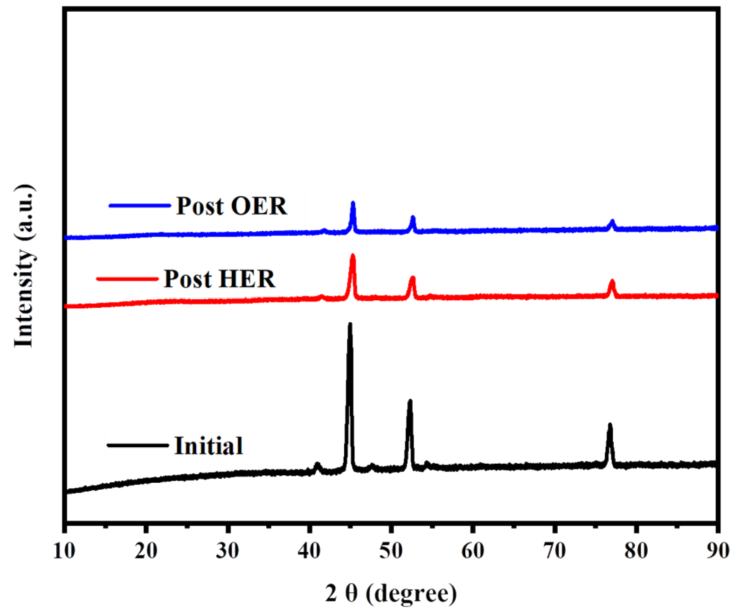

Fig.S19. XRD pattern comparison of the Zr-NiFeLDH@NiCoP/NF as a cathode (HER) and anode (OER) for 865 h overall water splitting at 10 mA cm^{-2}.

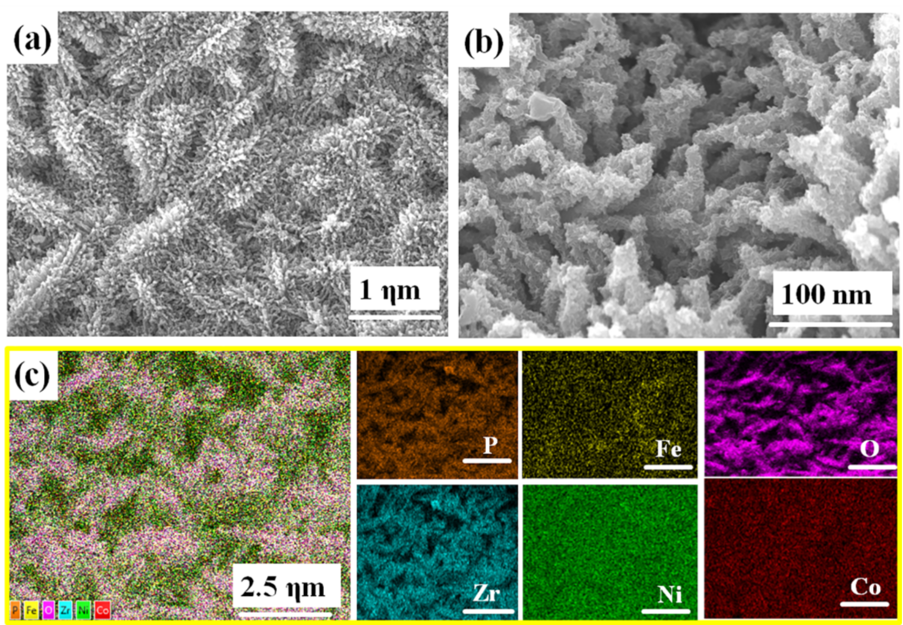

Fig.S20. SEM images of the Zr-NiFeLDH@NiCoP/NF after 865 h overall water splitting as a cathode. (a-b) the corresponding high-resolution SEM images, (c) EDX mapping area and elemental mapping images.

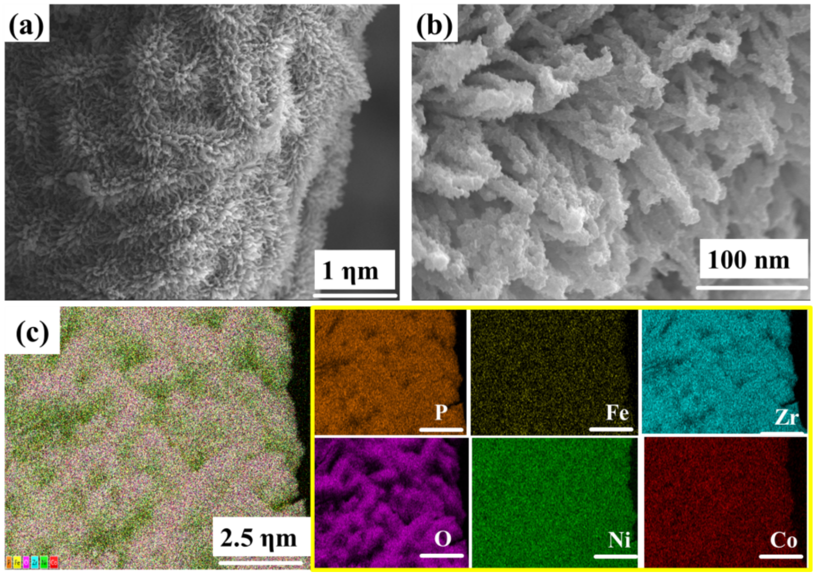

Fig.S21. SEM images of the Zr-NiFeLDH@NiCoP/NF after overall water splitting as an anode (OER). (a-b) the corresponding high-resolution SEM images, (c-e) EDX mapping area and elemental mapping images.

Table S7. The elements contents of different electrocatalysts from XPS analysis.

Sample/Elements	Ni 2p	Fe 2p	Co 2p	P 2p	Zr3d
Zr-NiFeLDH@NiCoP/NF (Before stability)	856.37/874.14	709.89/714.44	781.17/797.10	129.64/133.25	182.24/184.49
Zr-NiFeLDH@NiCoP/NF (After 865 h HER stability at 10 mA cm^{-2})	856.11/873.87	710.73/715.34	780.84/796.00	129.07/134.99	181.72/184.39
Zr-NiFeLDH@NiCoP/NF (After 865 h OER stability at 10 mA cm^{-2})	855.22/873.82	709.83/714.41	779.81/794.98	128.65/132.40	181.61/184.20

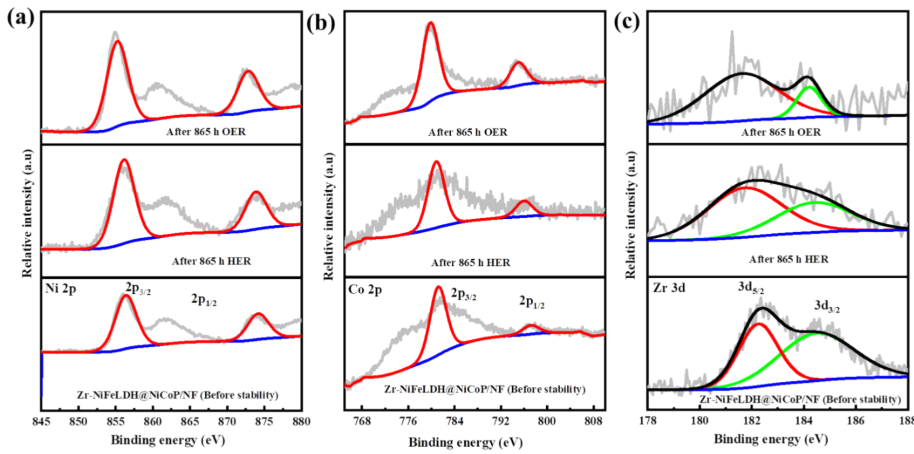

Fig. S22. The high-resolution XPS spectra of Zr-NiFeLDH@NiCoP/NF after 865 h stability test. (a) Ni 2p, (b) Co 2p (c) Zr 3d.

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