Supplementary Information

Modulating the Oxidation States in Nickel–Iron Layered Double Hydroxides by Natural Cooling for Enhanced Oxygen Evolution Activity

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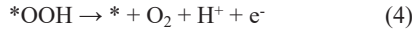

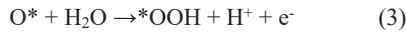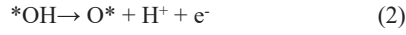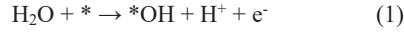Email: pengyu@cqnu.edu.cn (P. Yu);

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Experimental Section

1. Computational detail

Spin-plorazed density functional theory (DFT) calculations were performed by utilizing the Vienna Ab-Initio Simulation Package (VASP) code [1] in this work. The projector augmented wave (PAW) [2] method was used to describe the ionic cores. And the electron exchange-correlation was modelled by Perdew-Burke- Ernzerhof (PBE) function within generalized gradient approximation (GGA) [3]. The Hubbared-U calculations were included with the value of U_{Ni}=6.5, U_{Fe}=5.3 [4, 5]. A cutoff energy of 450 eV was used for the plane-wave basis set. The convergence criterion was 10^{-4} eV for energy and 0.05eV/Å for force. And the Γ-centered 3*3*1 k-point mesh were set for Brillouin Zone. The NiFe LDH surface was minimic by cleaving the $Fe(OH)_2$ (010) surface from $Fe(OH)_2$ bulk cell and replace partial Fe atoms with Ni **atoms of the relaxed** $Fe(OH)_2$ (010) surface. Further, the surface H atoms of NiFe LDH were partially removed and the final structure was relaxed to represent the o-NiFe LDH surface. For all the surface structures, a 15 Å thick vacuum along the vertical direction was added to separate adjacent periodic images. During the geometry optimization, the bottom two six atomic layers of the structure were fixed and other atoms were allowed to relax.

The key OER steps include [6-8]:

$$H_2O + * \rightarrow *OH + H^+ + e^- \qquad (1)$$

$$*OH \rightarrow O* + H^+ + e^- \qquad (2)$$

$$O* + H_2O \rightarrow *OOH + H^+ + e^- \qquad (3)$$

$$*OOH \rightarrow * + O_2 + H^+ + e^- \qquad (4)$$

The adsorption free energy of intermidiates were calculated using the equations:

$$\Delta G_{*OH} = G_{*OH} + \frac{1}{2}G_{H_2} - G_* - G_{*H_2O} - (eU)$$

$$\Delta G_{*O} = G_{*O} + G_{H_2} - G_* - G_{*H_2O} - (2eU)$$

$$\Delta G_{*OOH} = G_{*OOH} + \frac{3}{2}G_{H_2} - G_* - 2G_{*H_2O} - (3eU)$$

$$\Delta G_{*O_2} = G_{*O_2} + 2G_{H_2} - G_* - 2G_{*H_2O} - (4eU)$$

The Gibbs free energy G was calculated as follow:

$$G = E + ZPE - TS$$

where G, E, ZPE and TS are the free energy, total energy from DFT calculations, zero point energy and entropic contributions (T was set to be 300K), respectively. ZPE could be derived after frequency calculation by:

$$ZPE = \frac{1}{2}\sum h v_i$$

And the TS is entropic contributions (T was set to be 300K) values of adsorbed species are calculated after obtaining the vibrational frequencies

$$TS = k_B T[\sum \ln\left(\frac{1}{1 - e^{-hv_i/k_B T}}\right) + \sum \frac{hv}{k_B T}\frac{1}{(e^{hv_i/k_B T} - 1)} + 1]$$

2. Faraday efficiency

The Faraday efficiency (FE) of NiFe LDH/NF-36 h in OER was tested with a rotating ring-disk electrode (RRDE) method. with a glassy carbon disk (5.0 mm diameter) and Pt ring (5.0 mm ID/7.0 working electrode using mm OD). 15 µL of NiFe LDH/NF-36 h was dispersed on the membrane 1 M KOH was used as the electrolyte. When a constant oxygen precipitation current is applied on the disc electrode, the oxygen generated at the disc electrode is dissolved in the electrolyte and then partially detected by the Pt ring electrode. At the same time, the Pt ring is set at a constant potential of 0.4 V (vs. RHE) for oxygen evolution reaction Prior to the measurement, the electrolyte will be saturated with an argon gas to completely remove the dissolved oxygen, and the rotation rate is kept at 1600 rpm during the test. The FE of NiFe LDH/NF-36 h is calculated as follows: $FE = I_{ring} / (C_e * I_{disk})$ where I_{ring} and I_{disk} denote the ring current and disk current, respectively [9]; Ce is the oxygen collection coefficient (0.37) for this type of electrode configuration.

3. ECSA corrected LSV

The specific activity was obtained using the method of normalizing the current to the electrochemically active surface area (ECSA). That is, the capacitance value in terms of area in various methods of estimating ECSA, the specific capacitance can be further converted to ECSA real surface area, ESCA can be calculated by the following equation: $A_{ESCA} = C_{dl}/C_s$ [10]. The value of C_s was previously presented and discussed by Lyons and Brandon. where the specific capacitance per unit area (C_s) obtained from a smooth $Ni(OH)_2$ surface by Watzele and Bandarenka was 0.3 mF cm^{-2} [11], converting the C_s capacitance to the real surface area. Fabio Dionigi et al. concluded that the crystal structures of NiFe LDH catalysts and $Ni(OH)_2$ are similar and their specific capacitance is expected to deviations are small. Therefore, the Cs values of $Ni(OH)_2$ were used for all NiFe LDH catalysts [11]. Under this assumption, the method solves and overcomes the ECSA of NiFe LDH electrocatalysts.
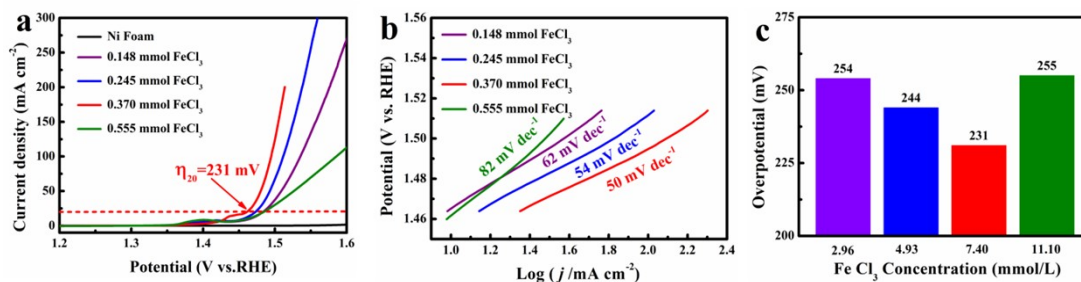
Fig. S1 (a) The LSV of NiFe LDH with different FeCl$_3$ concentration as precursors, (b) the corresponding Tafel plots of the NiFe LDH with different FeCl$_3$ concentration, (c) the correlation between different FeCl$_3$ concentration and overpotential.
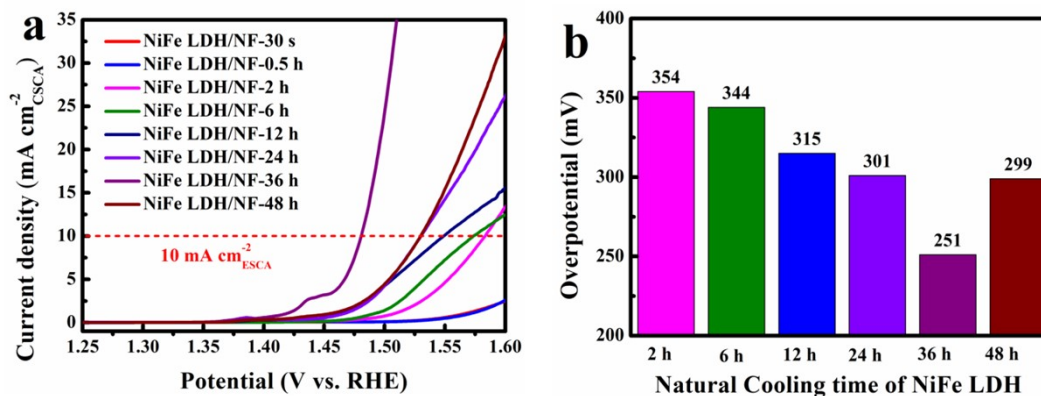

Fig. S2 (a) Linear sweep voltammetry curves recorded the current densities normalized by the ECSA values (c). Dashed horizontal and vertical lines show the values of 10 mA cm$^{-2}_{ECSA}$.
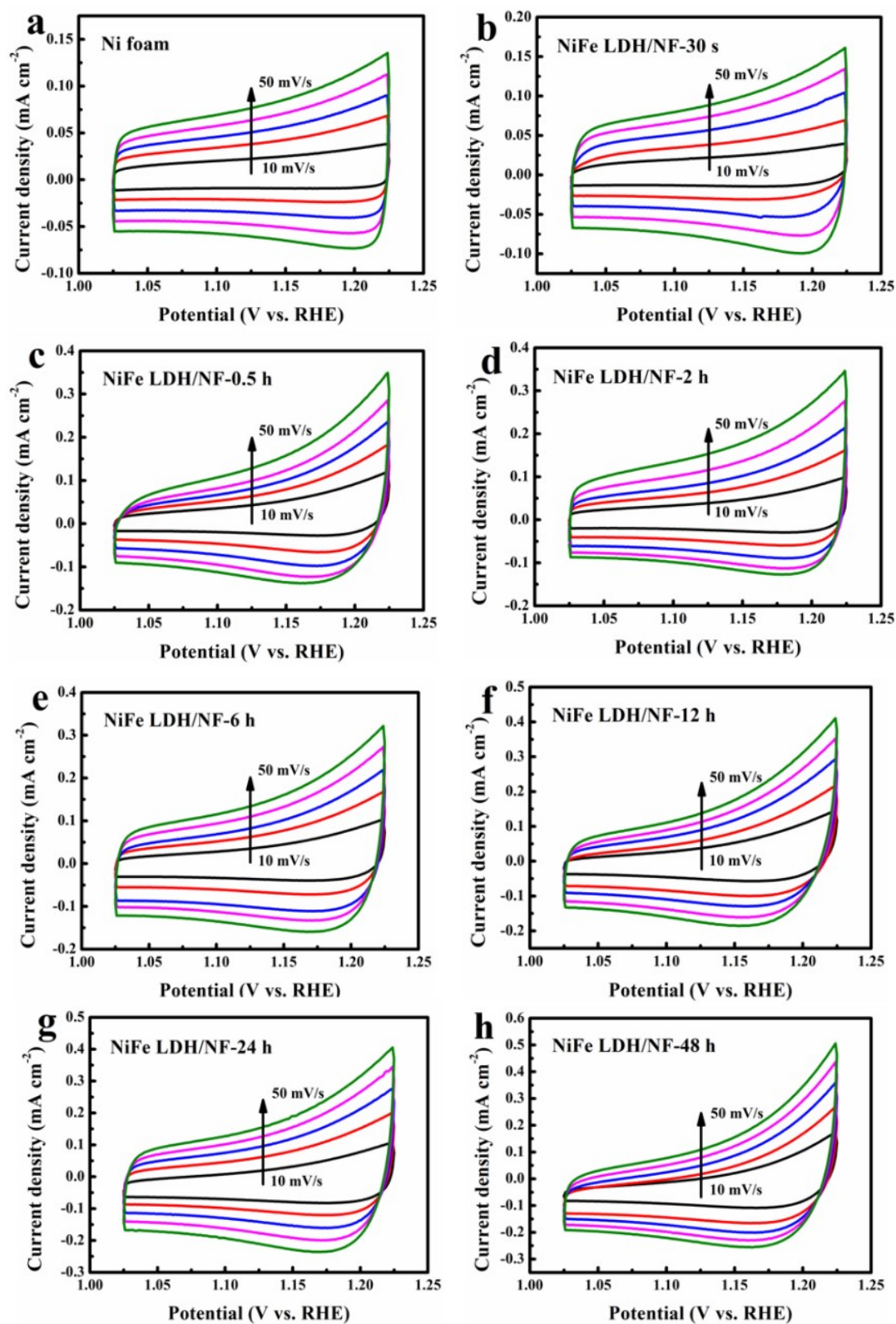
Fig. S3 Depicts typical cyclic voltammetry (CV) curves of (a) Ni foam, (b) NiFe LDH/NF-30 s, (c) NiFe LDH/NF-0.5 h, (d) NiFe LDH/NF-2 h, (e) NiFe LDH/NF-6 h, (f) NiFe LDH/NF-12 h, (g) NiFe LDH/NF-24 h, (h) NiFe LDH/NF-48 h, respectively.
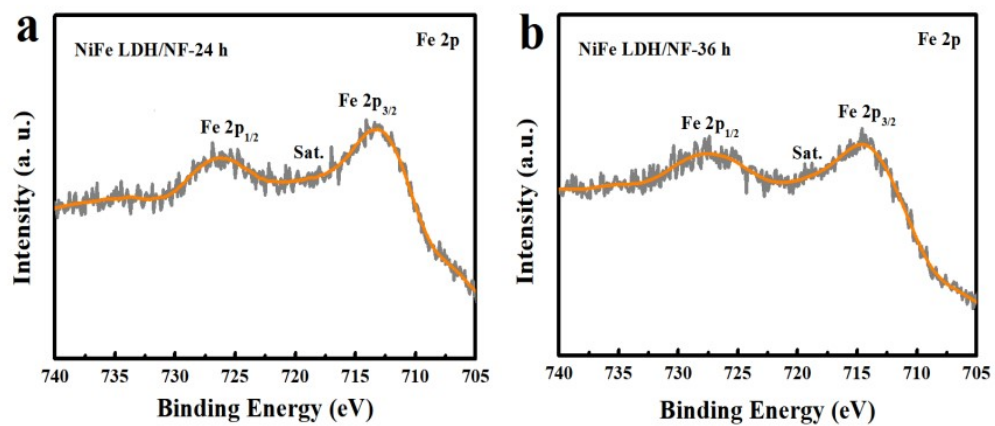
Fig. S4 XPS spectra of NiFe LDH: (a) Ni 2p, (b) Fe 2p.
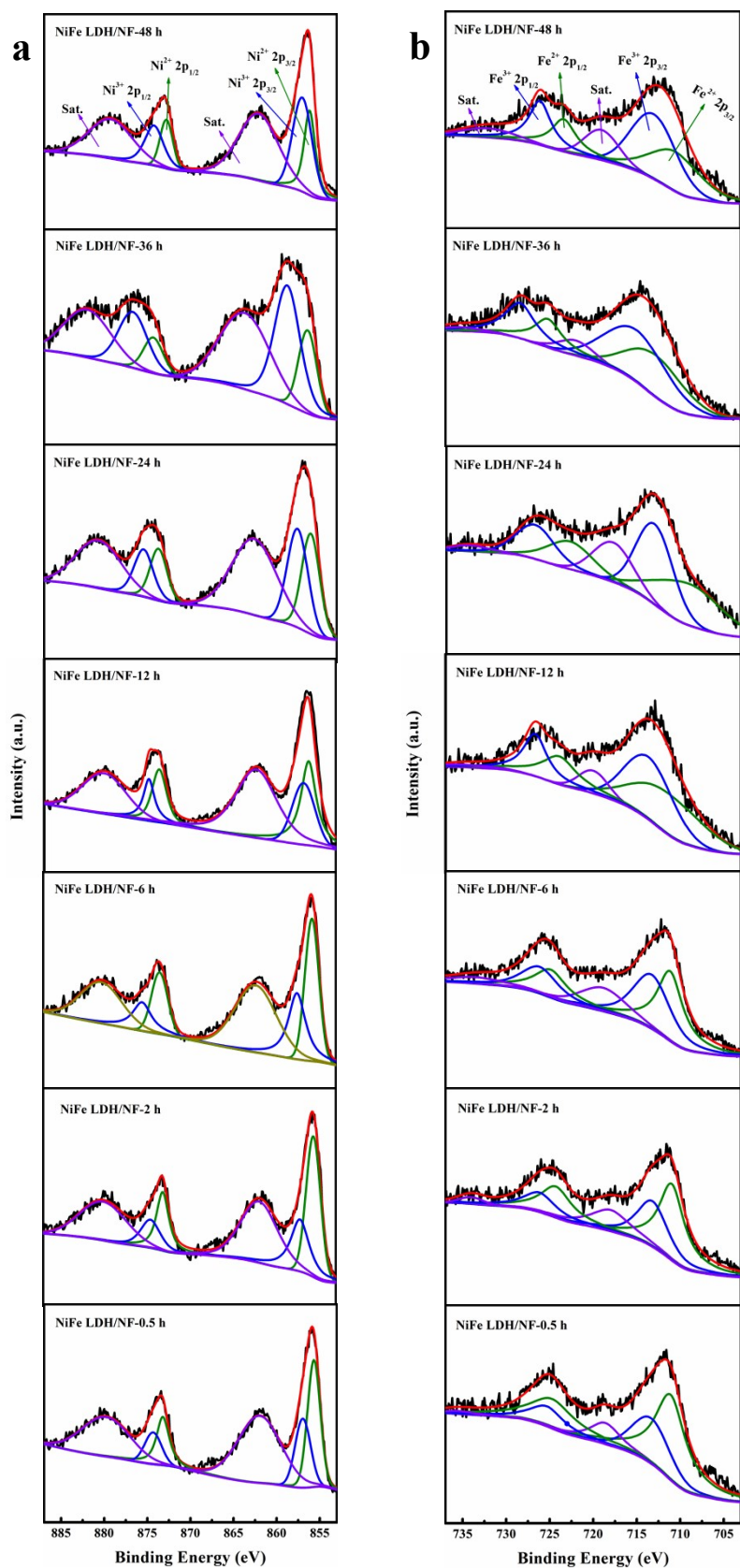
Fig. S5 XPS of NiFe LDH/NF-0.5 h, NiFe LDH/NF-2 h, NiFe LDH/NF-6 h, NiFe LDH/NF-12 h, NiFe LDH/NF-24 h, NiFe LDH/NF-36 h, NiFe LDH/NF-48 h, respectively. (a) Ni 2p spectra. (b) Fe 2p spectra.
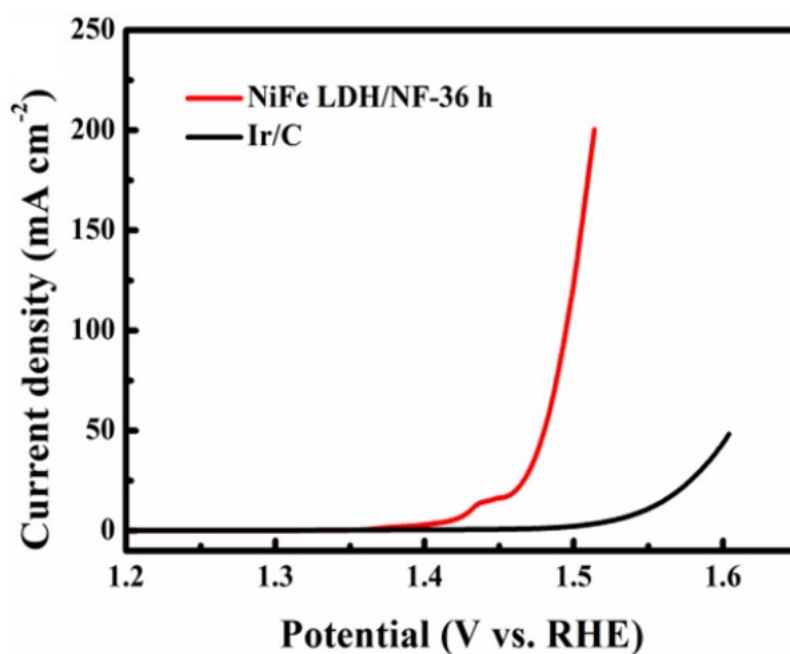
Fig. S6 OER polarization curves of NiFe LDH/N-36 h and Ir/C.
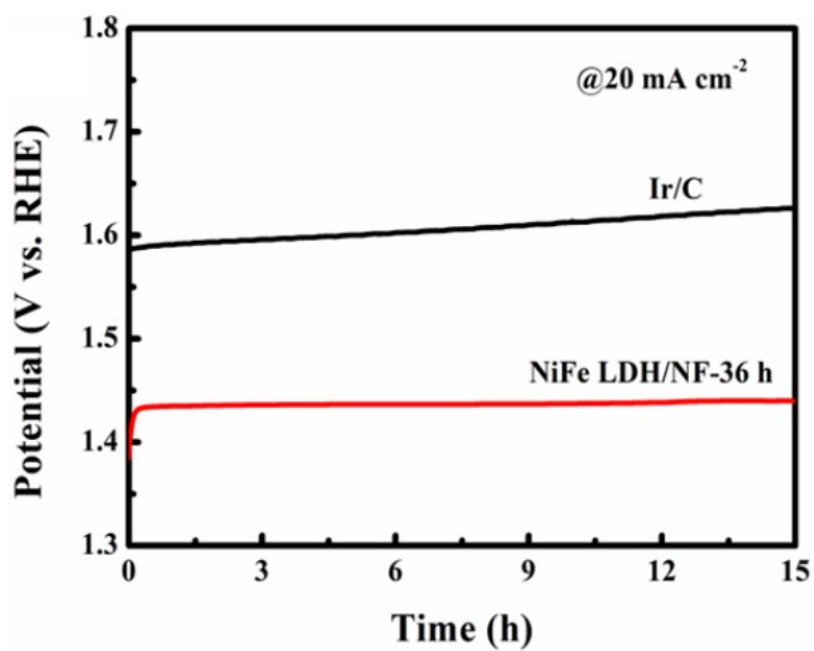
Fig. S7 Long-term stability of NiFe LDH/N-36 h and Ir/C at constant current density of 20 mA·cm^{-2} for 15 h, respectively.
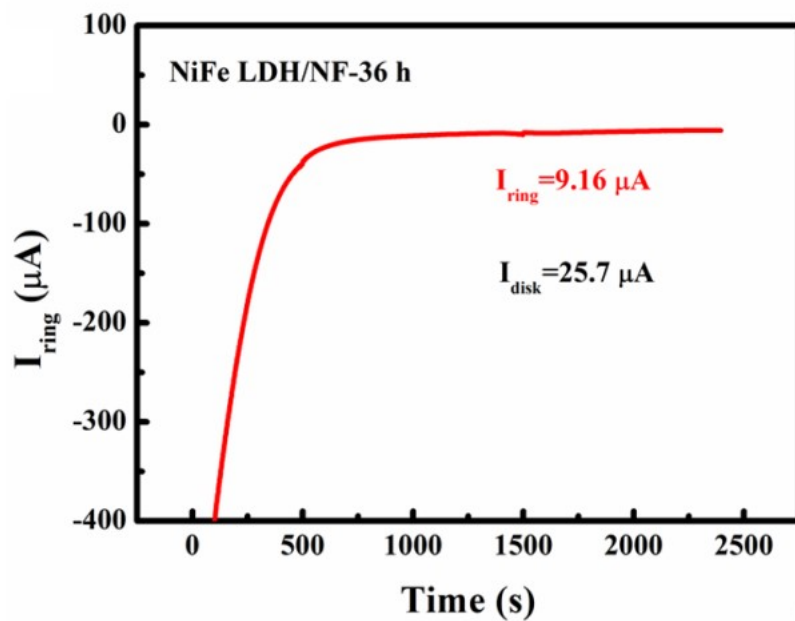
Fig. S8 The Faraday efficiency (FE) of NiFe LDH/NF-36 h during OER.
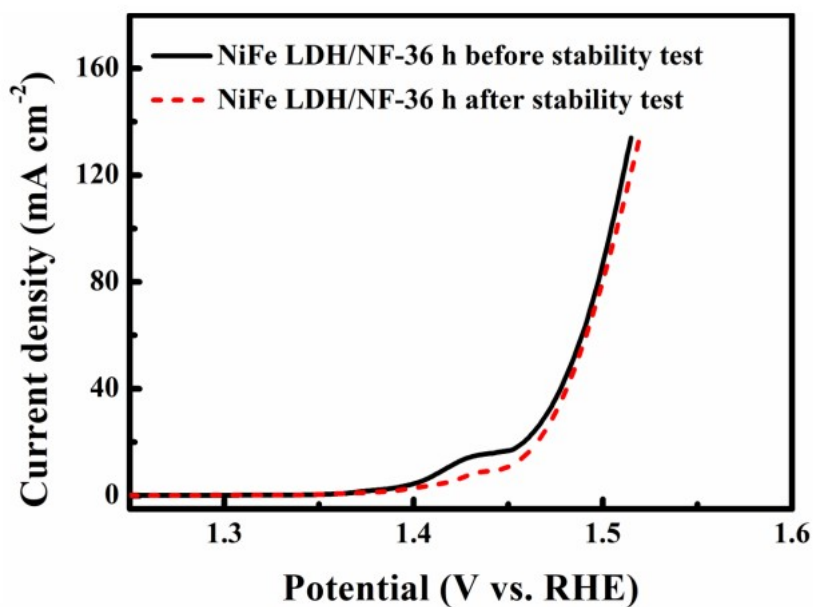
Fig S9. LSV of NiFe LDH/NF- 36h sample long-term stability test after.
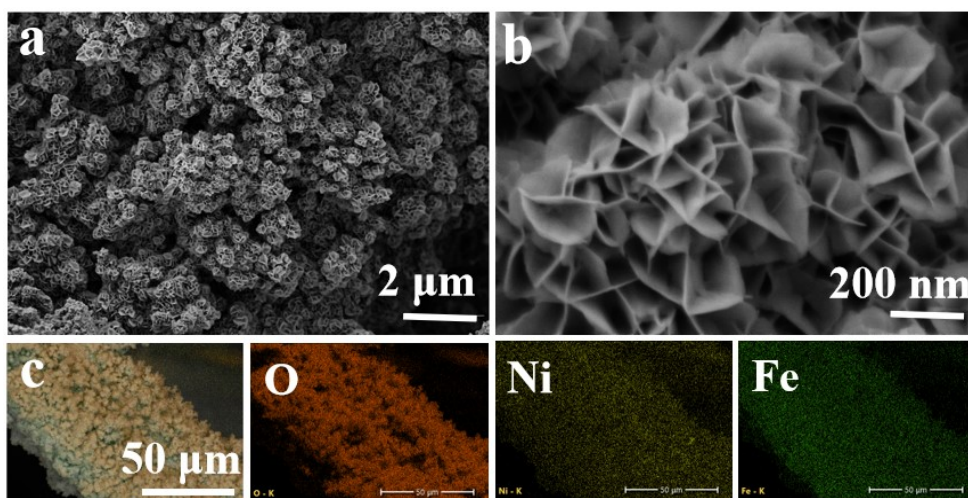
Fig. S10 NiFe LDH/NF- 36h sample long-term stability test after. (a) and (b) SEM images, (c) the corresponding elemental mappings of Ni, Fe and O.
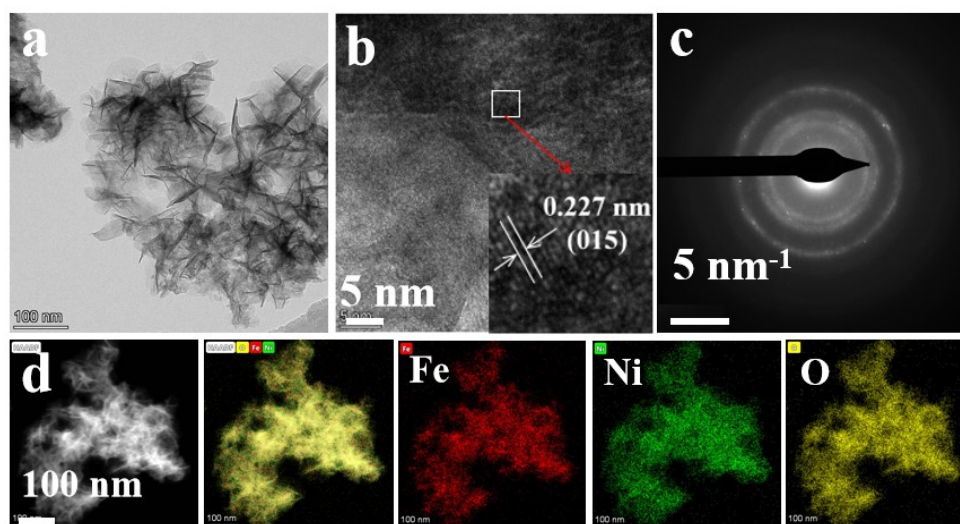
Fig. S11 NiFe LDH/NF- 36h sample long-term stability test after: (a) TEM image, (b) HRTEM image, (c) SEAD image, (d) the corresponding elemental mappings of Ni, Fe and O.
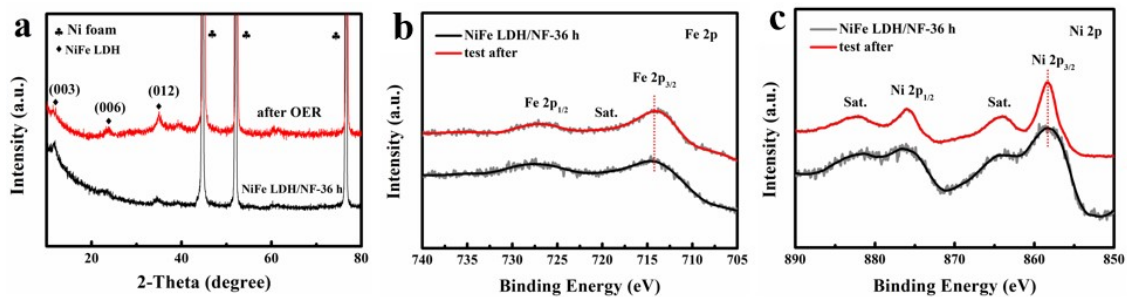
Fig. S12 NiFe LDH/NF- 36h sample long-term stability test after. (a) XRD pattern, (b) Ramma spectrum, (c) XPS spectra of Fe 2p, (d) XPS spectra of Ni 2p.

Table S1 Loading mass of NiFe LDH with different natural cooling time.

Natural cooling time	Loading mas (mg/cm^2)
NiFe LDH-2 h	0.08
NiFe LDH-6 h	0.19
NiFe LDH-12 h	0.28
NiFe LDH-24 h	0.34
NiFe LDH-36 h	0.41
NiFe LDH-48 h	0.36

Table S2. The atom ratio of Ni^{3+}/Ni^{2+} and Fe^{3+}/Fe^{2+} can be calculated by XPS.

Natural cooling time	Ni^{3+}/Ni^{2+}	Fe^{3+}/Fe^{2+}
NiFe LDH-0.5 h	0.581	0.537
NiFe LDH-2 h	0.721	0.782
NiFe LDH-6 h	0.782	0.950
NiFe LDH-12 h	0.975	1.000
NiFe LDH-24 h	1.105	1.055
NiFe LDH-36 h	2.282	1.325
NiFe LDH-48 h	1.481	1.220

Table S3. Comparison of OER activity of NiFe LDH (this work) with recently reported electrocatalysts in alkaline media. The overpotential was measured at the corresponding current density (10 mA cm^{-2}).

Catalyst	Substrate	Medium	j (mA·cm^{-2})	η (mV)	Tafel slope (mV dec^{-1})	Reference
NiFe LDH	Ni foam	1 M KOH	20	231	50	**This work**
NiFe LDH	GC RDE	0.1 M KOH	10	348	–	S[12]
NiFe LDH	RDE	1 M KOH	10	243	50	S[13]
NiFe LDH	Carbon paper	1 M KOH	10	247	37	S[14]
Ni-Fe LDH	Carbon paper	1 M KOH	20	246	71	S[15]
NiFeTiOOH	GC RDE	0.1 M KOH	10	400	–	S[16]
NiCoFe–LDH	CFP	1 M NaOH	10 20	288 330	92	S[17]
Ni–Fe–Ce–LDH	GCE	1 M KOH	10	242	34	S[18]
Ni$_{60}$Fe$_{40}$	Ti foil	1 M NaOH	10	300	38	S[19]
Ni$_{65}$Fe$_{35}$(OOH)	Glass rod	0.1 M CsOH	10	295	38	S[20]
NiFe–MOFs	GCE	1 M KOH	10	230	86.6	S[21]
NiFeCr	Ni foam	1 M KOH	10	265	41	S[22]
FeNi–HDNAs	Ni foam	1 M KOH	10	260	91.66	S[23]
FeNi–Mo$_2$C	GCE	1 M KOH	10	288	38.8	S[24]
FeNiCoCrMn-HEG	Ni foam	1 M KOH	10	229	40	S[25]
FeNi-SAs@NC	Carbon paper	1 M KOH	10	298	74.6	S[26]
NiCoFe–P–NP@ NiCoFe–PBA	GCE	1 M KOH	10	233	78	S[27]
Fe$_{0.63}$Co$_{0.19}$Ni$_{0.18}$O$_x$	FTO	1 M KOH	10	247	38.23	S[28]
Ni-MoO$_2$/NF–IH	Ni foam	1 M KOH	10	246	75	S[29]
Fe–doped–Ni$_2$B	Ni foam	1 M KOH	10	257	110	S[30]
FeNi$_2$S$_4$ NPs	RDE	1 M KOH	10	250	62	S[31]
Ni–CoP	GCE	1 M KOH	10	290	41	S[32]

NiFe–Se	CFP	1 M KOH	10	280	40.93	S[33]
NiFeB	GCE	1 M KOH	10	242	24	S[34]
FeCo/Se–CNT	GCE	0.1 M KOH	10	340	60.9	S[35]
Ir_{16}–PdCu/C	RDE	0.1 M KOH	10	284	48.9	S[36]
Co-C@NiFe LDH	GCE	1 M KOH	10	249	57.9	S[37]
CoOOH HNSs	GCE	1 M KOH	10	305	63	S[38]
PHI–Co	RDE	1 M KOH	10	324	44	S[39]
V_O–$MnCo_2O_4$	GCE	0.1 M KOH	10	400	87	S[40]
CoFeNiMnMoPi	GC	1 M KOH	10	270	74	S[41]
LiNiFe-BPO	Ni foam	1 M KOH	10	215	37	S[42]
$Fe_1(OH)_x$/P–C	GCE	1 M KOH	10	320	41	S[43]
$Ni_{1.5}$Sn@triMPO$_4$	CC	1 M KOH	10	240	45.2	S[44]
MoS_x–sulphate	GCE	1 M KOH	10	260	47	S[45]
CoFe–cyanide	GCE	1 M KOH	10	293	57	S[46]
LC–CoOOH NAs	CFC	1 M KOH	10 / 20	294 / 310	70.73	S[47]
Ir–Ni(OH)$_2$	GC	1 M KOH	10	270	45.2	S[48]
NiCo-LDH@MOF	Carbon cloth	1 M KOH	10	289	55.2	S[49]
Fe-CoP/Ni(OH)$_2$	Ni foam	1 M KOH	10	206	32	S[50]
La(CrMnFeCo$_2$Ni)O$_3$	Ni foam	1 M KOH	10	325	51.2	S[51]
LDH-Bir	Ni foam	1 M KOH	10	258	43	S[52]
OLC/Co-N-C	RDE GCE	0.1 M KOH	10	344	57.8	S[53]
Co$_{0.85}$Se$_{1-x}$@C	GCE	1 M KOH	10	231	57	S[54]
PdNi/Ni@N-C	RRDE	0.1 M KOH	10	360	121	S[55]
Co/Ni-CW	Wood chip	0.1 M KOH	10	330	68	S[56]
NF-Na-Fe-P	Ni foam	1 M KOH	10	261	39.68	S[57]

Note: glassy carbon (GC), Current density (*j*), glassy carbon electrode (GCE), carbon fiber cloth (CFC), Carbon Fiber Paper (CFP), rotating disk electrode (RDE).

Table S4 Ni/Fe ratios in the NiFe LDHs under different feeding FeCl$_3$ concentration.

FeCl$_3$ concentration（mmol/L）	Ni/Fe ratios
2.96	3.63
4.93	1.91
7.40	1.32
11.10	0.80

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