

Electronic Supplementary Material (ESI)

Coupling Thulium 4f Orbitals with Ni₃Fe LDH to Form Electronic Buffer Band with Loaded Pt and Catalyzing Alkaline Overall Water Splitting

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Extra experimental details

Synthesis of Ni₃Fe LDH

The amount of 3.0 mmol NiCl₂·6H₂O, 1.0 mmol FeCl₃·6H₂O were dissolved in 30.0 mL deionized water and stirred for 30 min, then the solutions was added by 20.0 mL aqueous solution containing 1.0 g C₁₉H₄₂BrN dropwise. Afterwards, the solution was homogeneously added by a fresh-prepared solution (20.0 mL) containing 200.0 mg NaBH₄ under stirring. For about 10.0 min the bubbles disappeared, and the solution

was further stirred for another 2.0 h. The precipitation was removed via centrifugation, and washed alternatively with deionized water and anhydrous ethanol for three runs. The sample was dried in vacuum at 60°C overnight to get Ni₃Fe LDH powders.

Synthesis of Ni₃Fe LDH-Tm

The preparative procedure of Ni₃Fe LDH-Tm was similar to that of Ni₃Fe LDH, except different moles of Tm(NO₃)₃·5H₂O being added to the precursor solution. Samples obtained were named as the molar ratio of Tm to the sum of Ni and Fe. Samples were named Ni₃Fe LDH-Tm0.01, Ni₃Fe LDH-Tm0.03, Ni₃Fe LDH-Tm0.05 and Ni₃Fe LDH-Tm0.07, which means the content of Tm was 0.04 mmol, 0.12 mmol, 0.2 mmol and 0.28 mmol, respectively.

Synthesis of Ni₃Fe LDH-Tb

Terbium at various concentrations were selected for control experiments, and the rest of experimental conditions were the same, except that, for example, 0.03 mmol of Tb(NO₃)₃·5H₂O was replaced by 0.03 mmol Tb(NO₃)₃·5H₂O. The amount of 3.0 mmol NiCl₂·6H₂O, 1.0 mmol FeCl₃·6H₂O were dissolved in the 30 mL deionized water and stirred for 30.0 min until clarified, and then 20.0 mL solution containing 1.0 g C₁₉H₄₂BrN was added dropwise under stirring. After the solution was homogeneous 200.0 mg NaBH₄ was add to the 20.0 mL solution. When the bubbles were disappeared, the solution was stirred for another 2.0 h. The sample was collected via centrifugation and washed three times with anhydrous ethanol and deionized water, respectively. The samples were dried in a vacuum oven at 60°C overnight and were named as Ni₃Fe LDH-Tb. Similar procedures were used in preparing Yb-doped LDH

samples.

Methods for electrochemical analyses

All potentials to reversible hydrogen electrodes (RHE) were converted according to the following equation:

$$E_{RHE} = E_{Hg/HgO} + 0.098 + 0.059 \times PH... (S1)$$

The overpotentials were obtained as:

$$\eta_{OER} = E_{RHE} - 1.23... (S2)$$

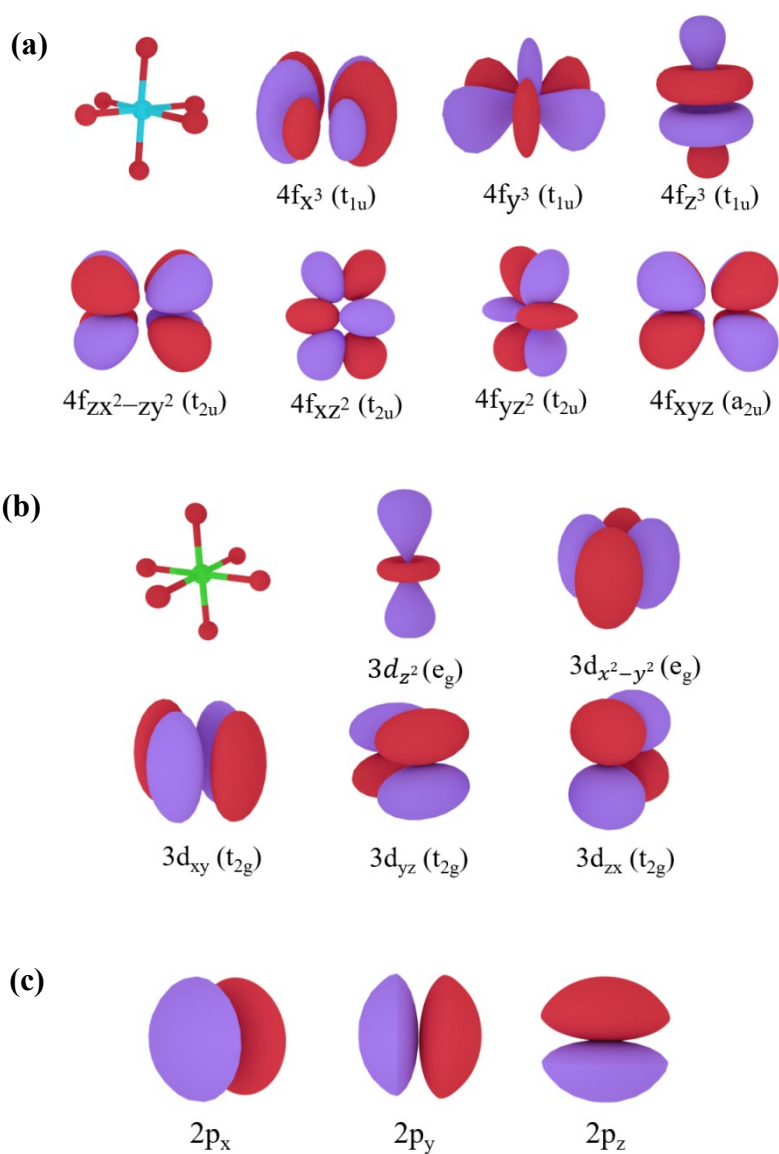
The formula for Tafel's slope, and the slop b was obtained as followed:

$$\eta = b \log j + a... (S3)$$

Mott-Hubbard splitting

Based on Mott-Hubbard splitting, the orbital coupling of 4f, 3d, 2p orbitals of Tm were provide as followed showing the electronic configurations. The coordination of O atoms with Tm via sp-mixing orbitals to produce metal-oxygen (M-O) consisting with bonding of a_{1g} , t_{1u} , e_g , and t_{2g} and antibonding (M-O)* of a_{1g}^* , t_{1u}^* , e_g^* , and t_{2g}^* .

The configuration was listed as followed (Fig. S1).



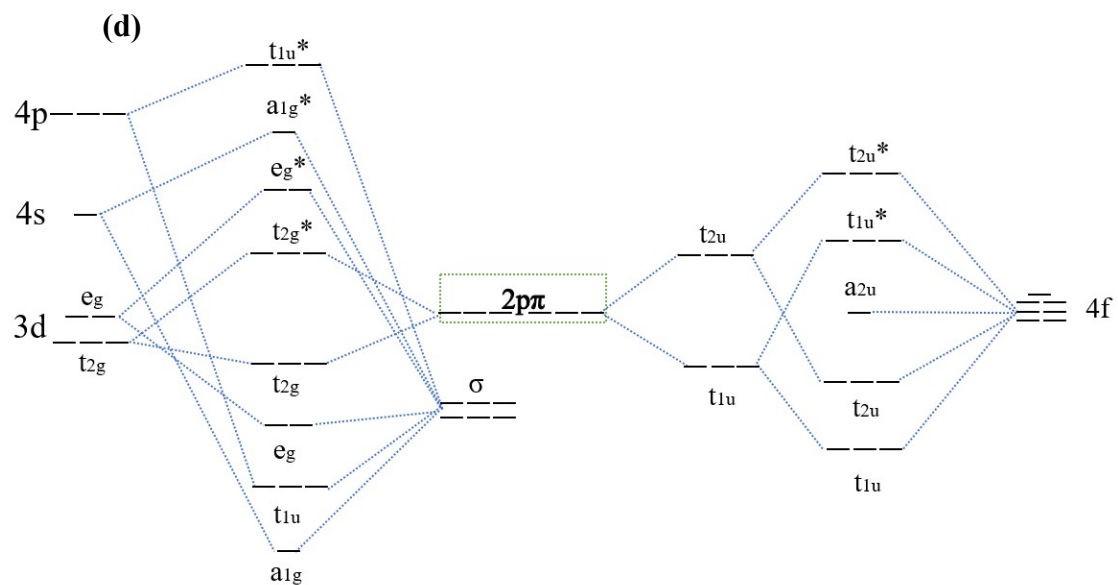


Fig. S1 Orbital configuration diagram of (a) 4f orbital diagram; (b) 3d orbital diagram; and (c) 2p orbital diagram of O; (d) The qualitative molecular orbital diagram with an O_h symmetry.

Series characterizations on Tm-doped samples including XRD, SEM, TEM, XPS, N_2 adsorption-desorption and electrochemical analyses (results shown as Fig. S2~Fig. S17, Table S1 and S2 provided OER performance and EIS parameters).

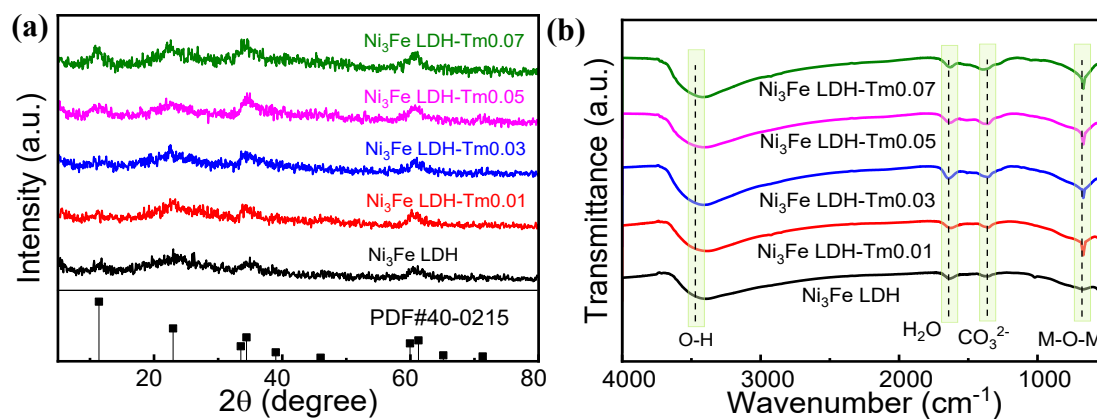
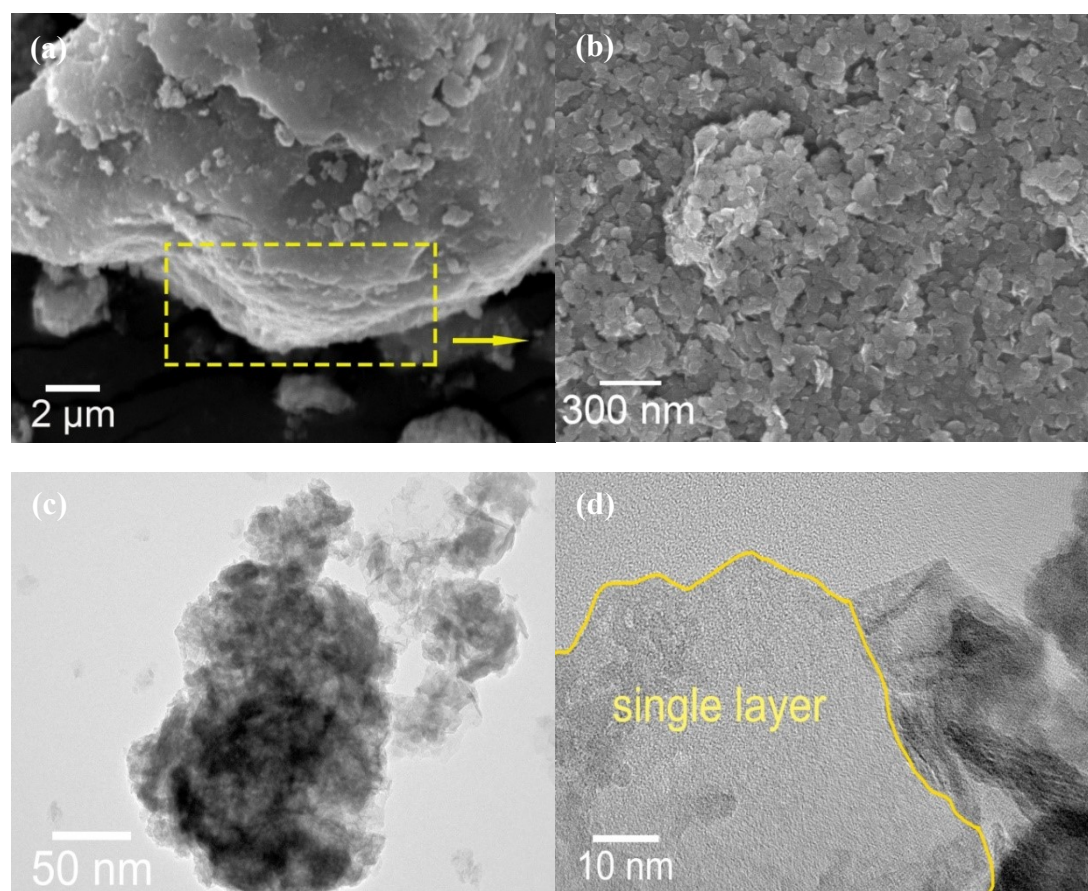


Fig. S2 (a) XRD patterns and (b) FT-IR spectra of Ni₃Fe LDH, Ni₃Fe LDH-Tm0.01, Ni₃Fe LDH-Tm0.03, Ni₃Fe LDH-Tm0.05 and Ni₃Fe LDH-Tm0.07.



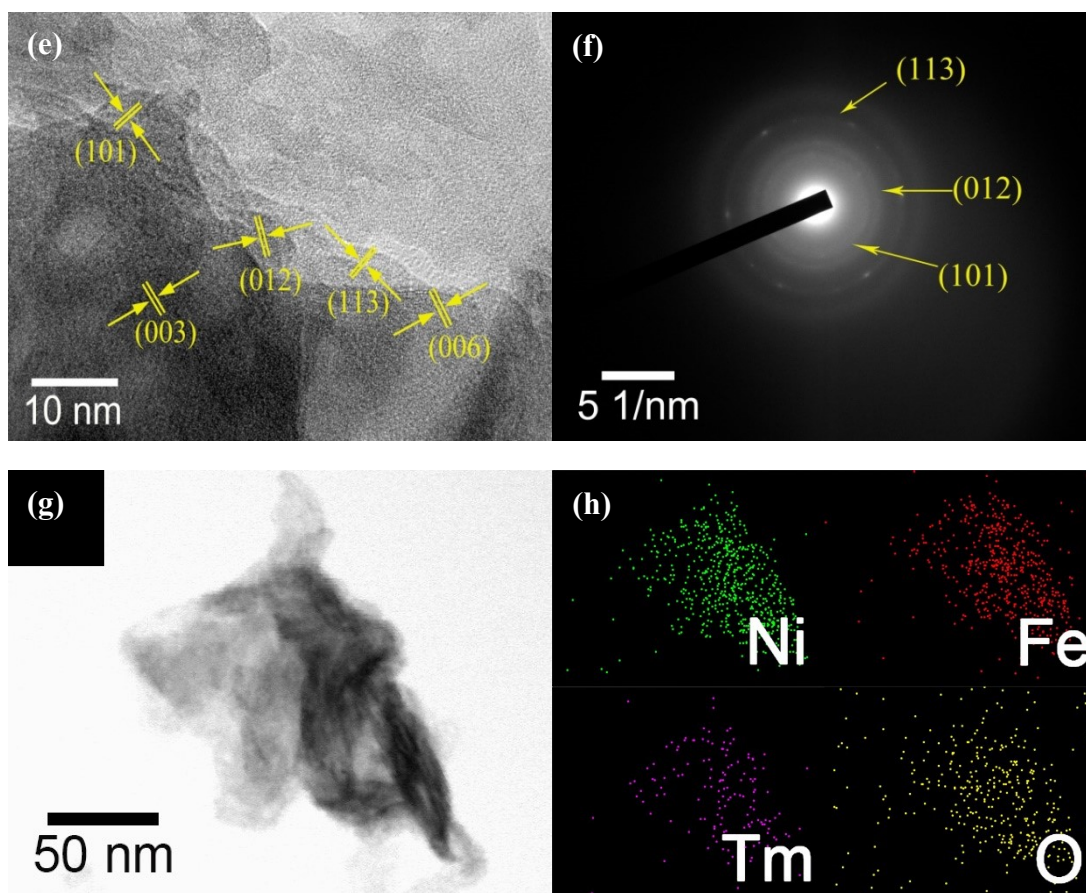
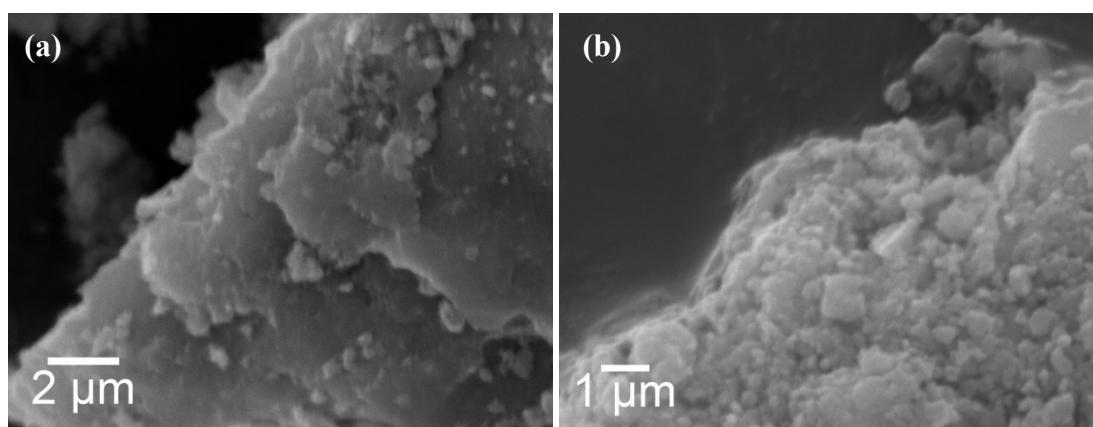


Fig. S3 Morphological and structural characterizations on samples including: (a, b) SEM image, (c) TEM image, (d, e) HRTEM image with enlarged lattice structure, (f) SAED pattern and (g, h) corresponding EDS elemental mapping images of Ni_3Fe LDH-Tm0.03.



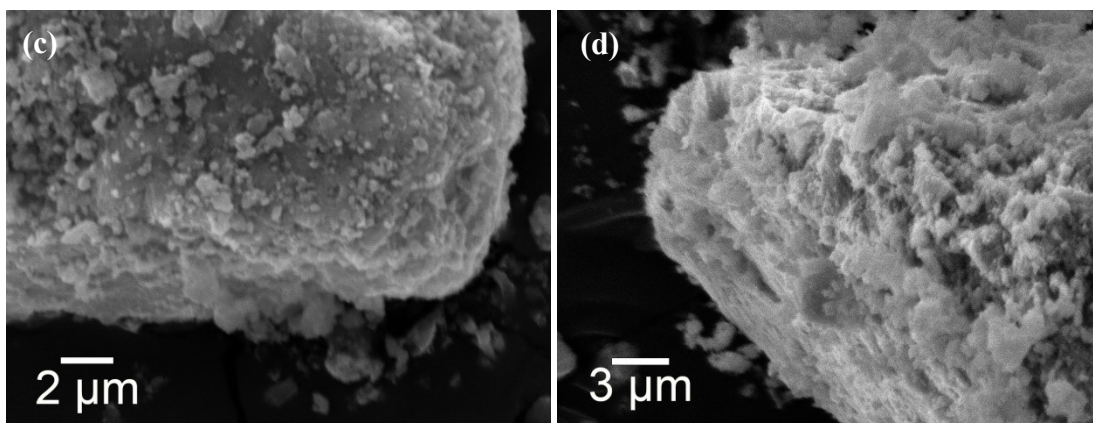


Fig. S4 SEM image of (a) Ni₃Fe LDH, (b) Ni₃Fe LDH-Tm0.01, (c) Ni₃Fe LDH-Tm0.05 and (d) Ni₃Fe LDH-Tm0.07.

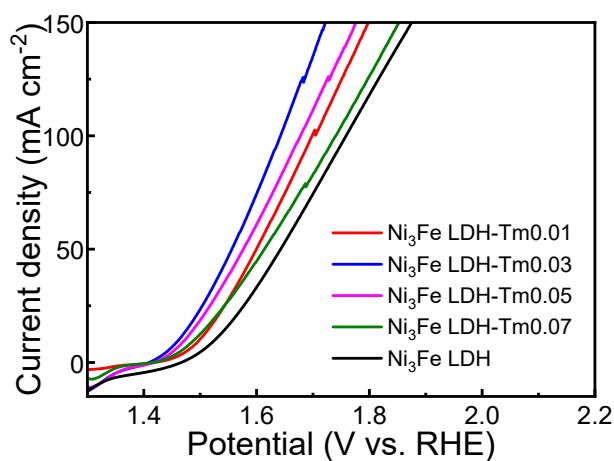


Fig. S5 LSV curves of Ni₃Fe LDH, Ni₃Fe LDH-Tm0.01, Ni₃Fe LDH-Tm0.03, Ni₃Fe LDH-Tm0.05 and Ni₃Fe LDH-Tm0.07 conducted for OER in alkaline system.

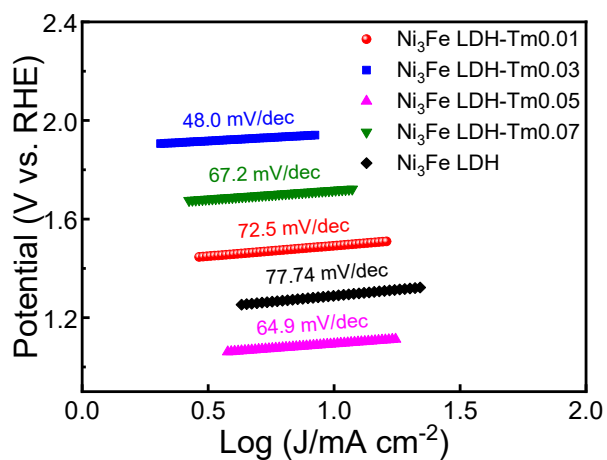


Fig. S6 Tafel curves of Ni₃Fe LDH, Ni₃Fe LDH-Tm0.01, Ni₃Fe LDH-Tm0.03, Ni₃Fe LDH-Tm0.05 and Ni₃Fe LDH-Tm0.07 conducted for OER in alkaline system.

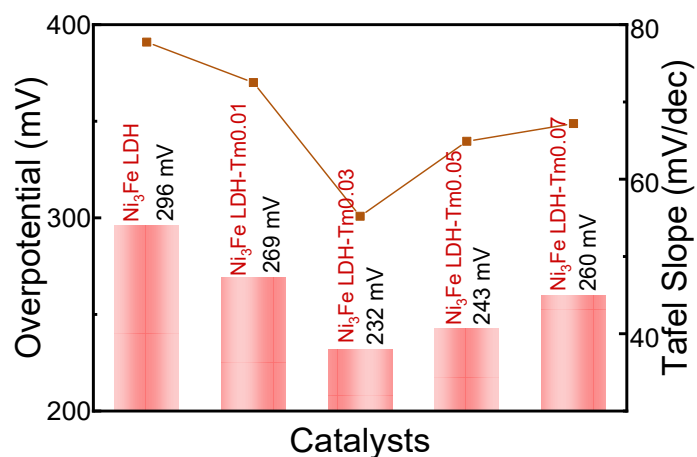
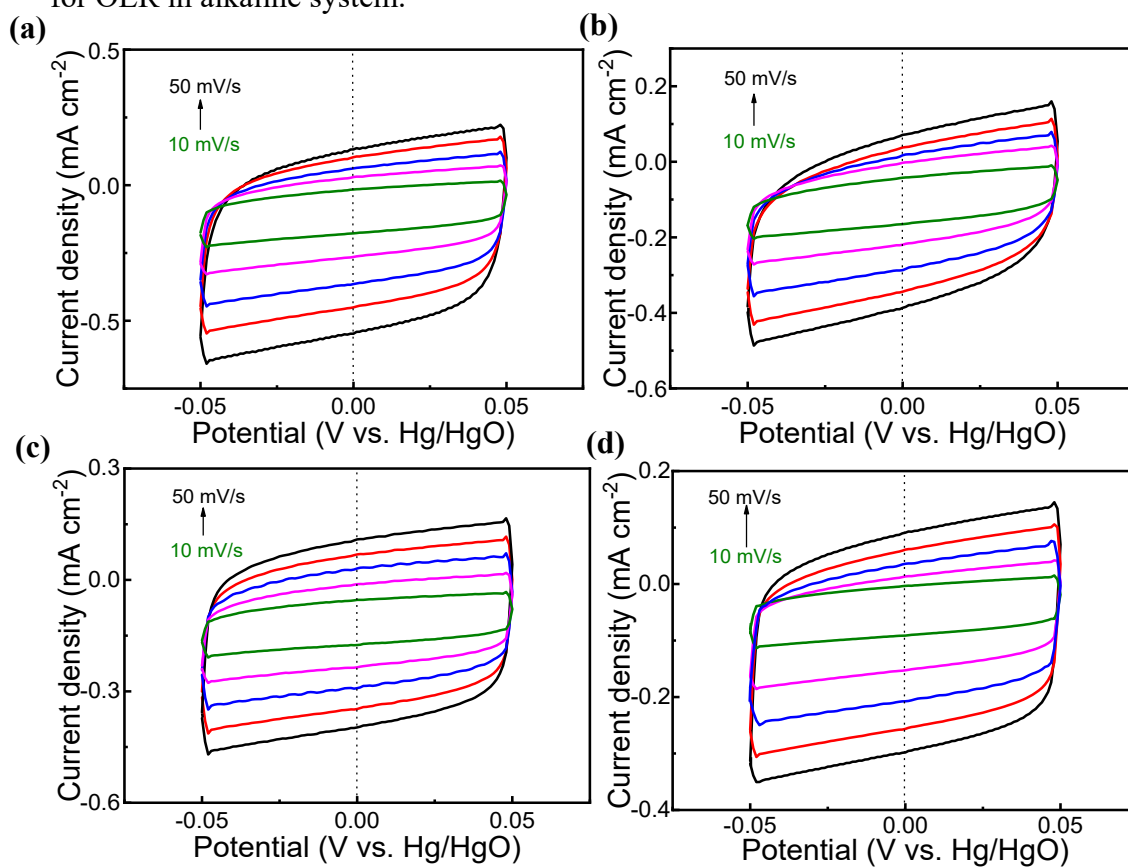


Fig. S7 Comparative diagram of the overpotential and Tafel slope values conducted for OER in alkaline system.



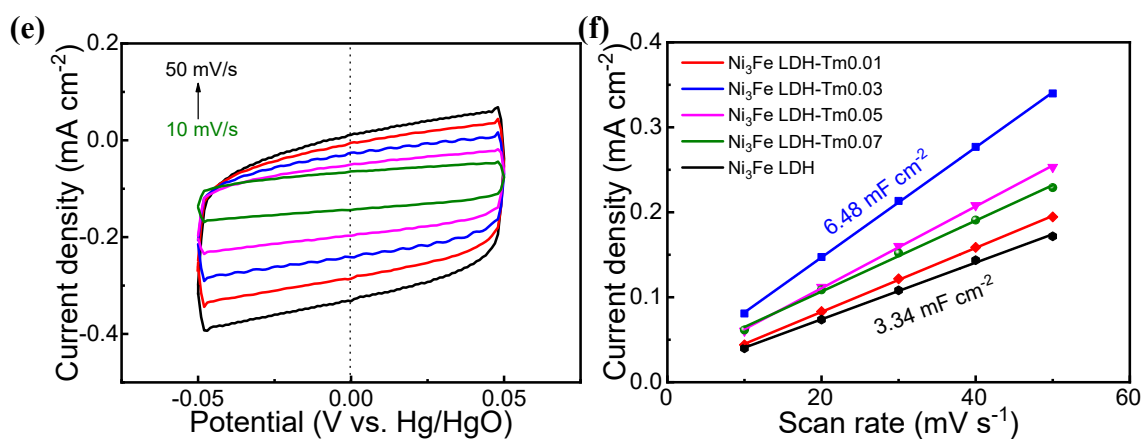


Fig. S8 Cyclic voltammetry curves in the -0.05 V~0.05 V voltage range of (a) Ni₃Fe LDH, (b) Ni₃Fe LDH-Tm0.01, (c) Ni₃Fe LDH-Tm0.03, (d) Ni₃Fe LDH-Tm0.05 and (e) Ni₃Fe LDH-Tm0.07 and (f) C_{dl} values of different samples.

C_{dl} was estimated by plotting the scan rates against current density (Fig. S8b):

$$C_{dl} = \frac{(j_a - j_c)}{2} \dots (S4)$$

while ECSA was calculated by the following equation:

$$ECSA = \frac{C_{dl}}{C_s} \dots (S5)$$

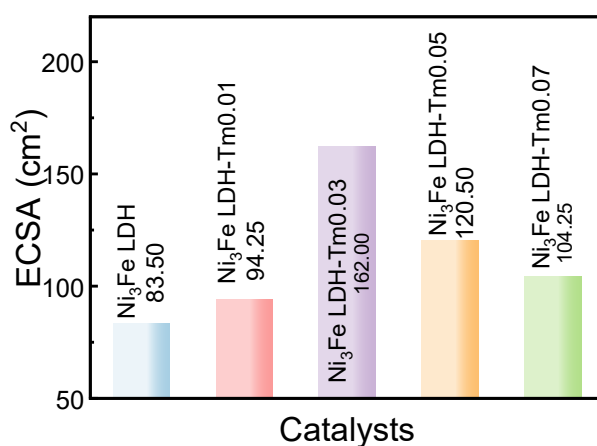


Fig. S9 Comparison of ECSA values of different samples.

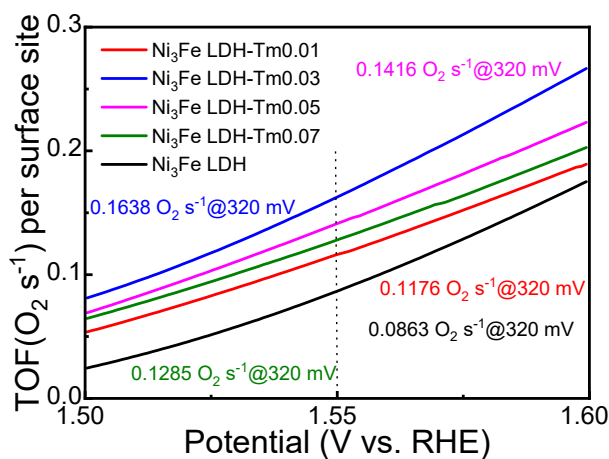


Fig. S10 TOF curves of different samples conducted for OER in alkaline system.

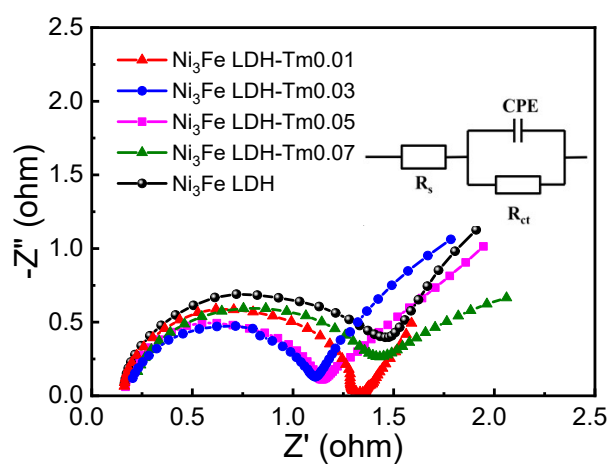


Fig. S11 Nyquist plots of above samples (the equivalent circuit image was displayed in the inset) conducted for OER in alkaline system.

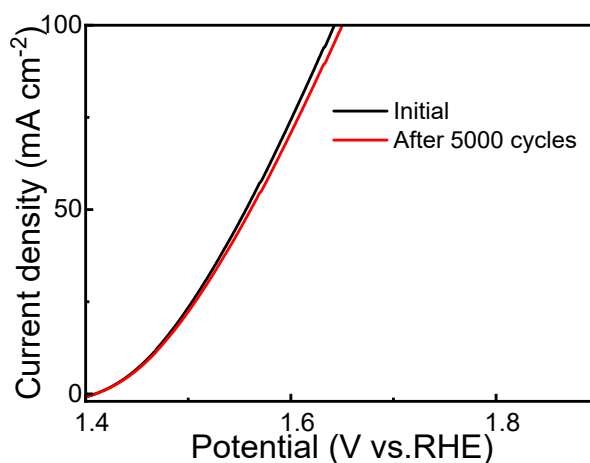


Fig. S12 The polarization curves of Ni₃Fe LDH-Tm0.03 before and after 5000 CV cycles in 1.0 M KOH solution.

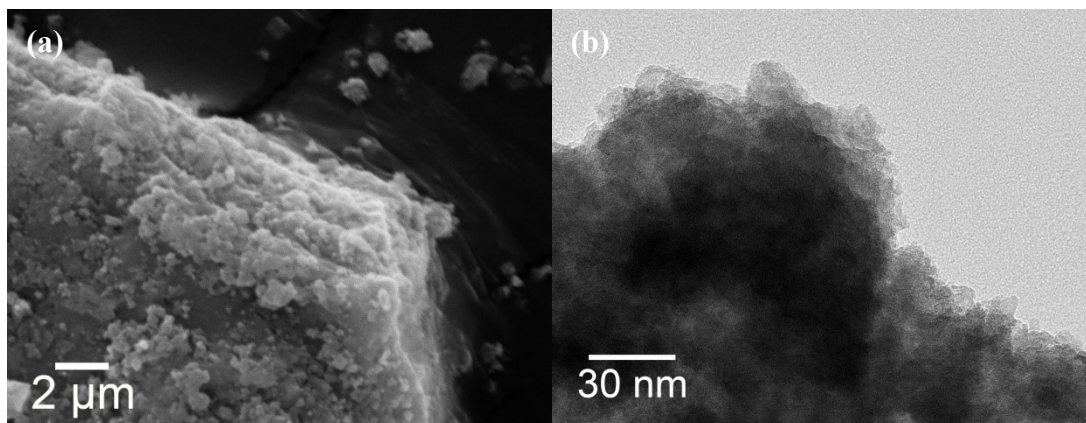


Fig. S13 SEM image (a) and TEM image (b) of Ni₃Fe LDH-Tm after OER testing.

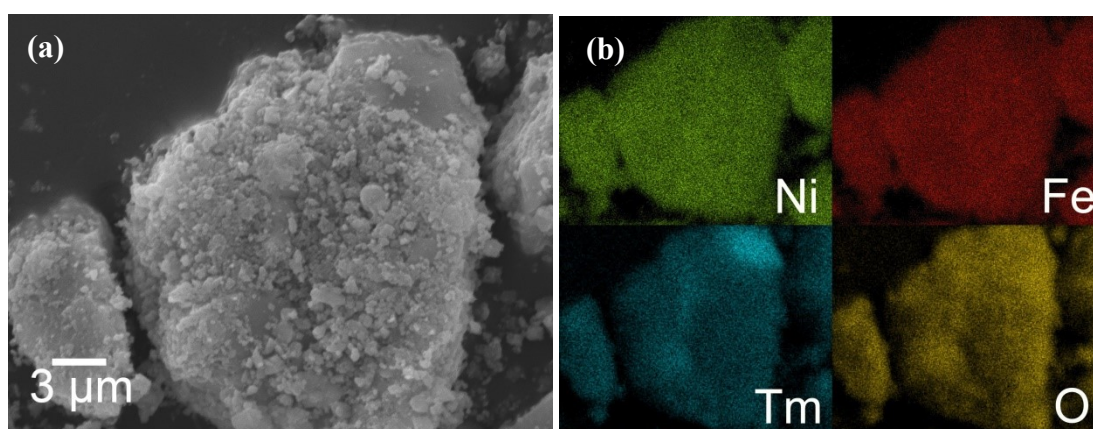


Fig. S14 SEM image of Ni₃Fe LDH-Tm (a) and the corresponding EDS elemental mapping images (b) after OER testing.

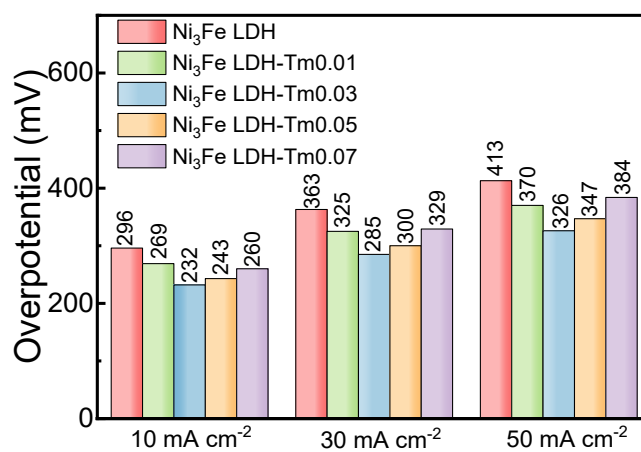


Fig. S15 Comparison of overpotentials at different current densities.

Following formula was used to calculate the theoretical oxygen production:

$$n_{(O_2)} = \frac{i \times t}{4 \times e \times N_A} \dots (S6)$$

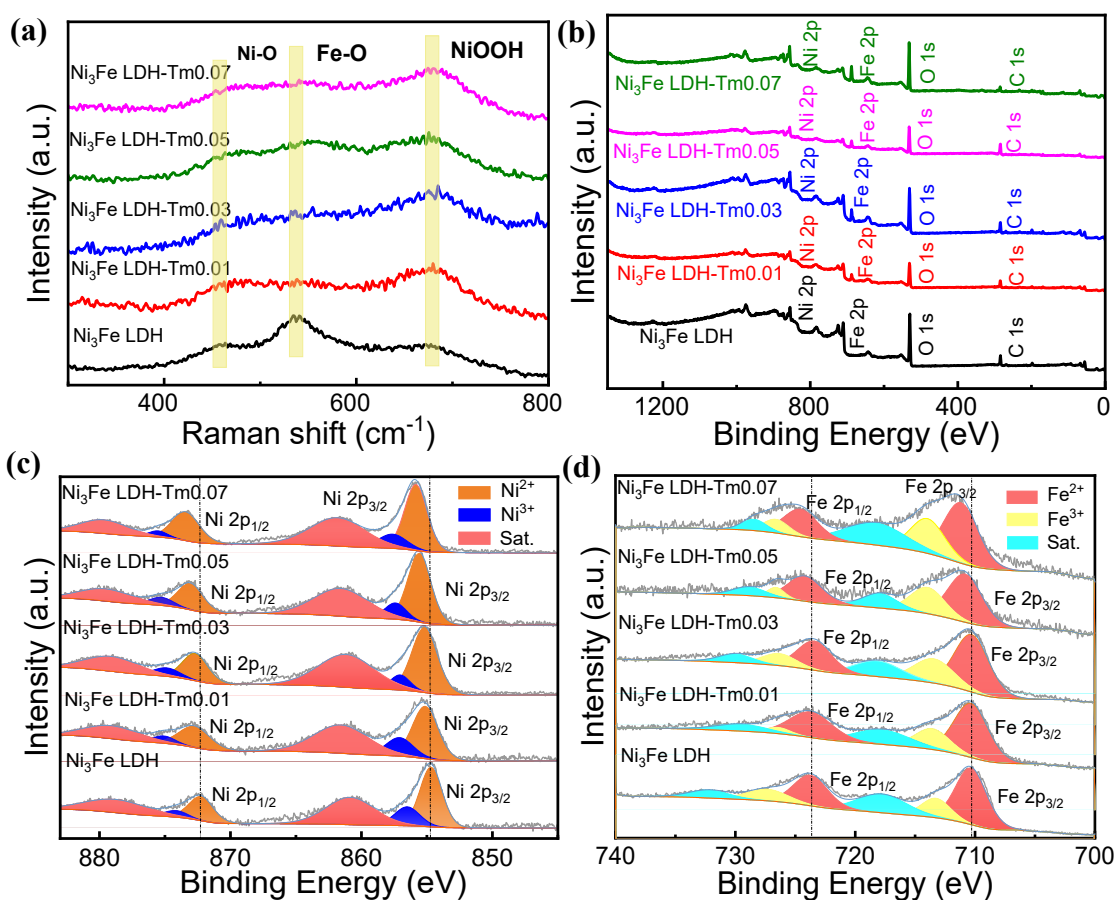
where the “i” is the current density, $i=50 \text{ mA cm}^{-2}$, “t” is time and “e” is the elementary charge.

Table S1 Comparison of OER performances of the as-prepared electrodes with that of other reported NiFe-based electrocatalysts evaluated.

Electrocatalyst	Electrolyte	Tafel slope (mV dec ⁻¹)	η /mV (at 10 mA cm ⁻²)	Ref.
Ni ₃ Fe LDH-Tm0.03	1 M KOH	48	230	This work
La-NiFe LDH	1 M KOH	77	340	1
NiFe-LDH Sn _{0.015}	1 M KOH	66	250	2
LaNi _{1-x} Fe _x O ₃	1 M KOH	52	340	3
ZnO/NiFe-LDH	1 M KOH	67	320	4
NiFe LDH/C	0.1 M KOH	51	360	5
NiFe LDH-Bir	1 M KOH	55	260	6
Ni _x Fe _{3-x} O ₄	1 M KOH	53	402	7
Ni-Fe-Ce-LDH	1 M KOH	54	246	8
Co ²⁺ /NiFe LDH	1 M KOH	59.4	264	9
S-NiFe-LDH/rGO	1 M KOH	55	265	10
Ru-NiFe LDH	1 M KOH	67.2	246	11
NiFe-LDH/Co-NC	1 M KOH	64	282	12
NiFeCo LDH	1 M KOH	57	270	13
NiFe-LDH@CNT	1 M KOH	51.4	255	14

Table S2 EIS parameters of samples.

	R_{ct}	CPE	R_s
Ni ₃ Fe LDH	2.446	0.001577	4.694
Ni ₃ Fe LDH-Tm0.01	1.814	0.001099	2.987
Ni ₃ Fe LDH-Tm0.03	0.9738	0.005289	0.854
Ni ₃ Fe LDH-Tm0.05	1.06	0.003186	1.583
Ni ₃ Fe LDH-Tm0.07	1.238	0.002495	1.846
Ni ₃ Fe LDH-Tb	1.785	0.006579	3.853
Ni ₃ Fe LDH-Yb	1.699	0.001891	4.024



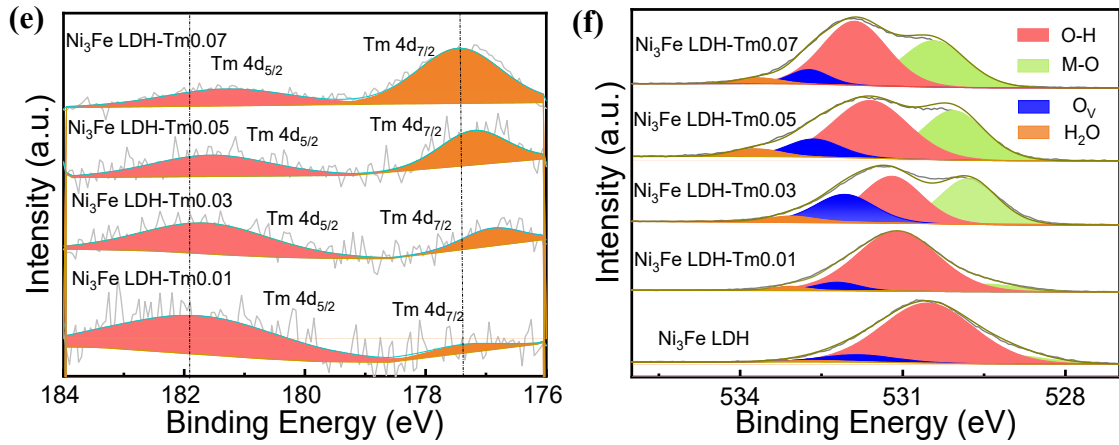


Fig. S16 (a) Raman spectra, (b) XPS survey spectra of the samples and High resolution: (c) Ni 2p, (d) Fe 2p, (e) Tm 4d and (f) O 1s.

The percentage of Ni^{3+} was calculated by the following equation:

$$C_{(Ni^{3+})} = \frac{Area(Ni^{3+})}{Area(Ni^{2+}) + Area(Ni^{3+})} \times 100\% \dots (S7)$$

The optical band gap of all samples is determined by using the equation:

$$(ahv)^n = k(hv - E_g) \dots (S8)$$

$$hv = \frac{1240}{Wavelength} \dots (S9)$$

$$(ahv)^n = (2.303 \times Absorbance \times Energy)^n \dots (S10)$$

where α is the absorbance coefficient and $n=2$ for direct transition and $n=0.5$ for indirect transition.

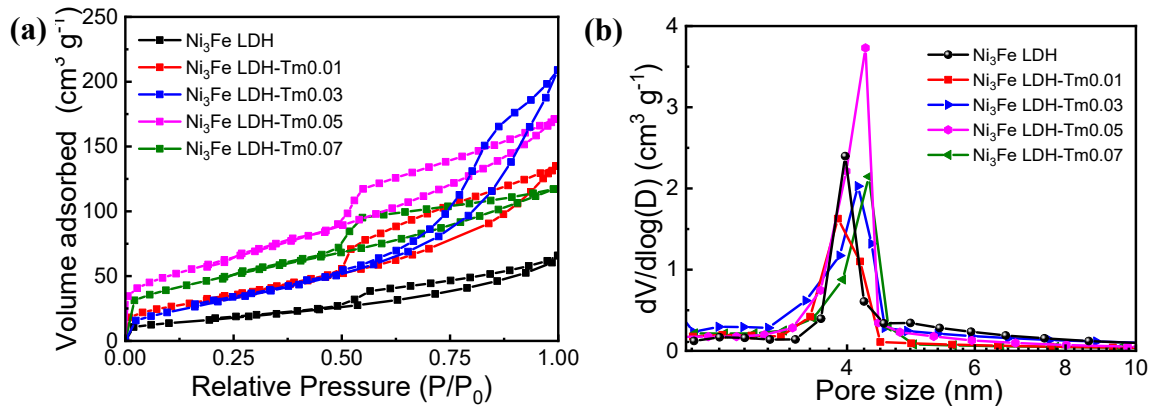


Fig. S17 (a) Nitrogen adsorption-desorption isotherms and (b) BJH pore size

distribution curves of the samples.

Series characterizations on REE (Tm, Tb, and Yb)-doped samples for comparison study, which included the XRD, SEM, TEM, XPS, electrochemical analyses, contact angle measurements, and N_2 adsorption-desorption isotherms (Fig. S18~Fig. S36).

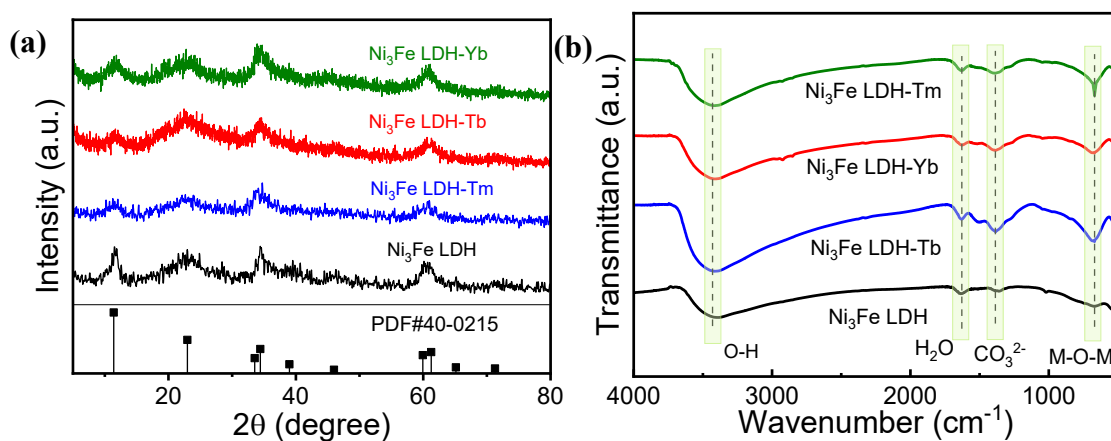


Fig. S18 (a) XRD patterns and (b) FT-IR spectra of Ni_3Fe LDH, Ni_3Fe LDH-Tb, Ni_3Fe LDH-Tm and Ni_3Fe LDH-Yb.

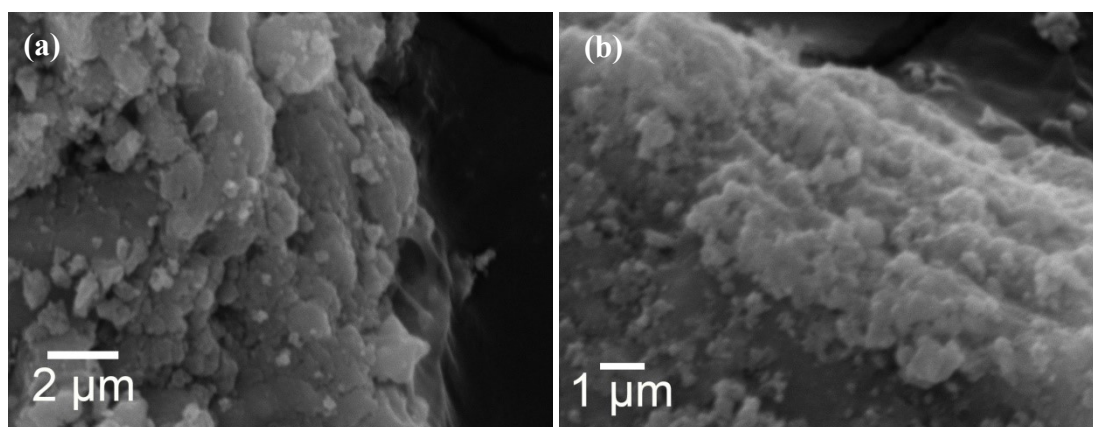


Fig. S19 SEM image of (a) Ni_3Fe LDH-Tb and (b) Ni_3Fe LDH-Yb.

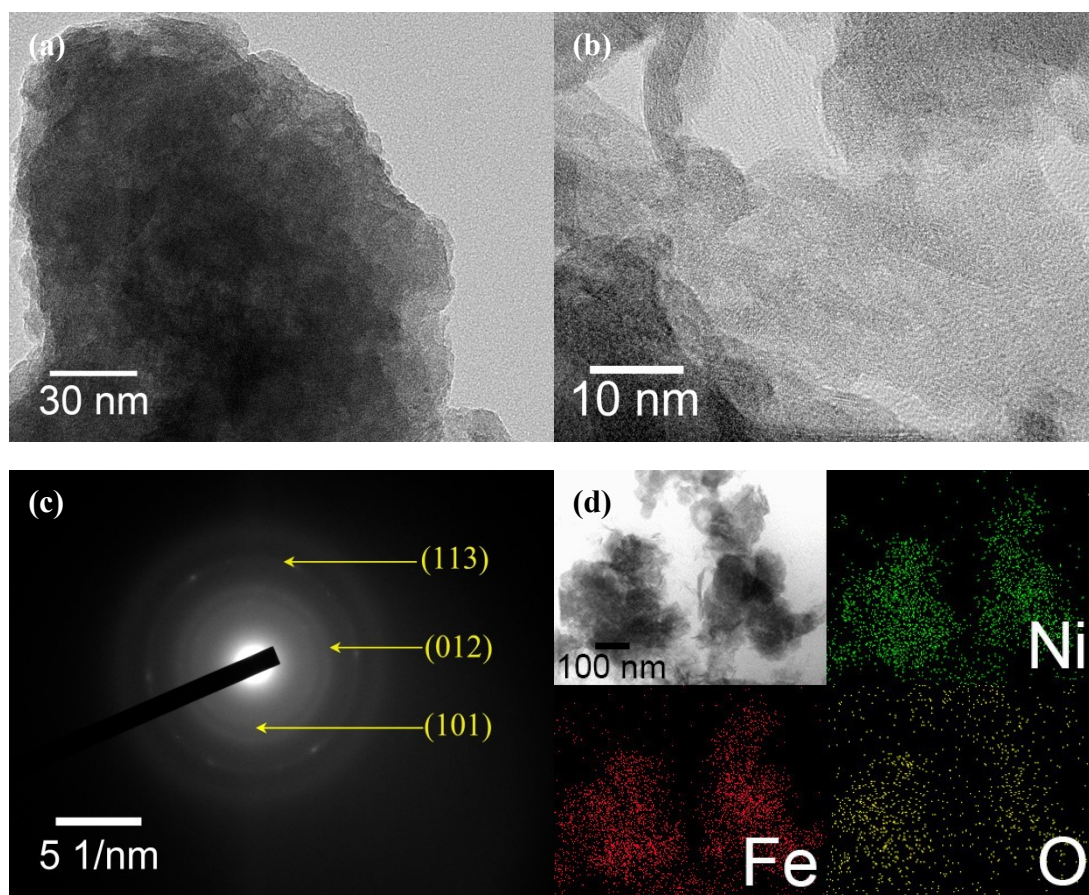


Fig. S20 (a) TEM, (b) HRTEM image, (c) SAED pattern and (d) EDS elemental mapping images of Ni_3Fe LDH.

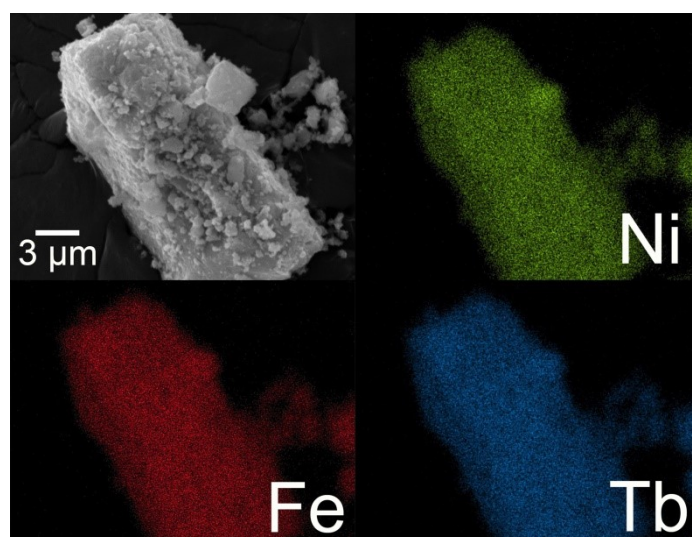


Fig. S21 EDS elemental mapping images of Ni_3Fe LDH-Tb.

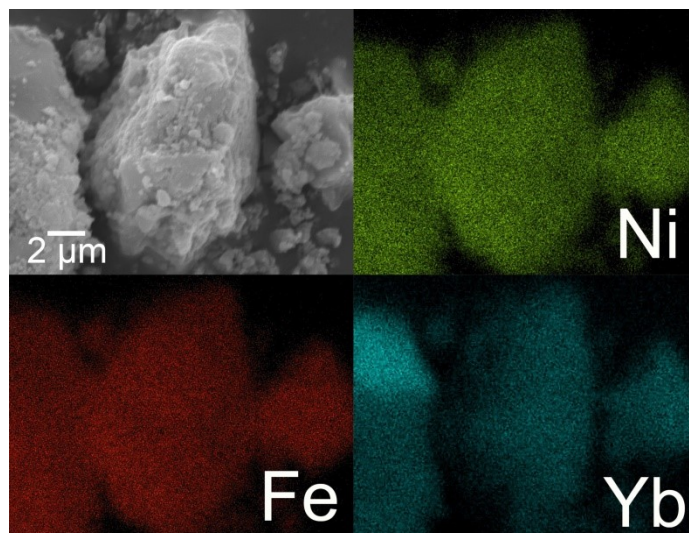


Fig. S22 EDS elemental mapping images of Ni₃Fe LDH-Yb.

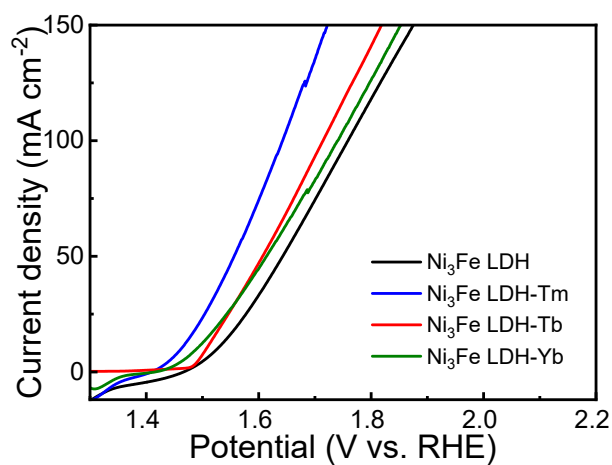


Fig. S23 LSV curves of Ni₃Fe LDH, Ni₃Fe LDH-Tb, Ni₃Fe LDH-Tm and Ni₃Fe LDH-Yb for OER.

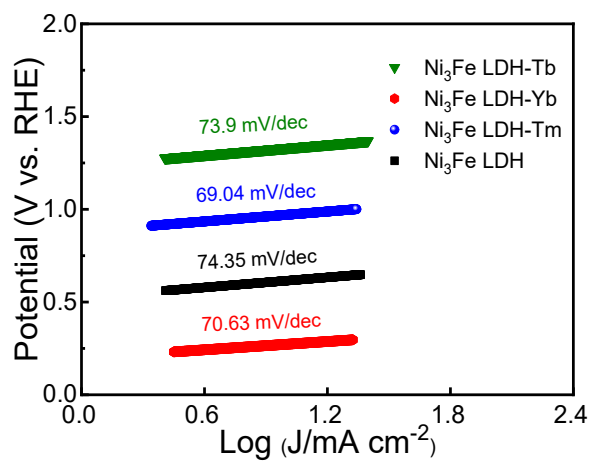


Fig. S24 Tafel plots of Ni₃Fe LDH, Ni₃Fe LDH-Tb, Ni₃Fe LDH-Tm and Ni₃Fe LDH-Yb.

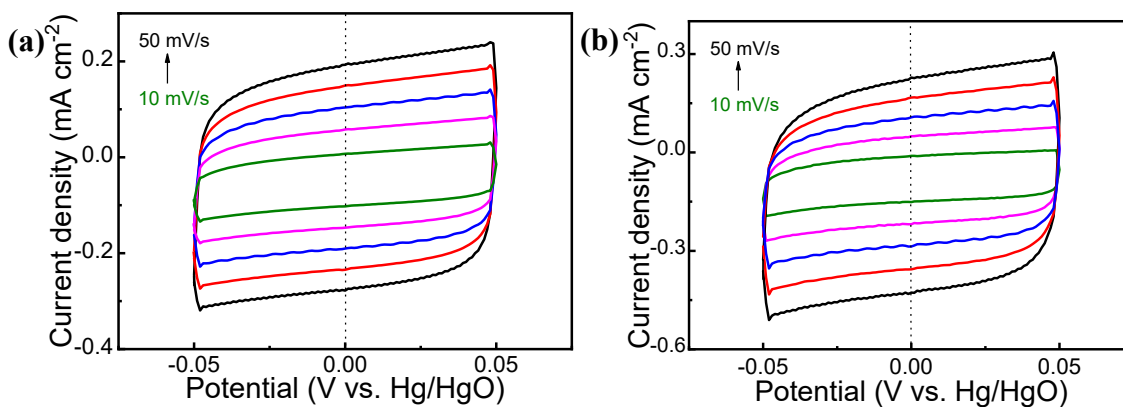


Fig. S25 Cyclic voltammetry curves in the -0.05 V~0.05 V voltage range of (a) Ni₃Fe LDH-Tb and (b) Ni₃Fe LDH-Yb.

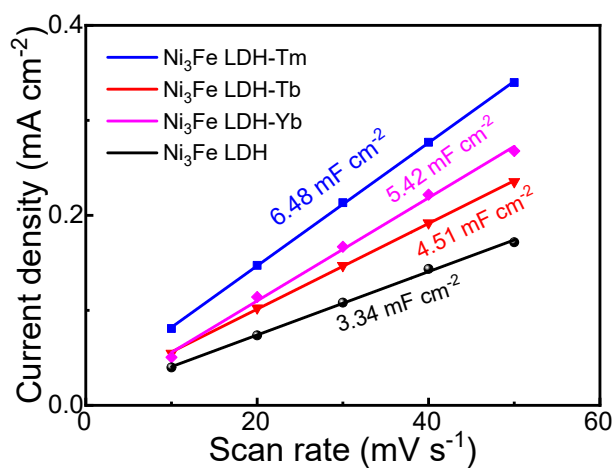


Fig. S26 C_{dl} values of different samples.

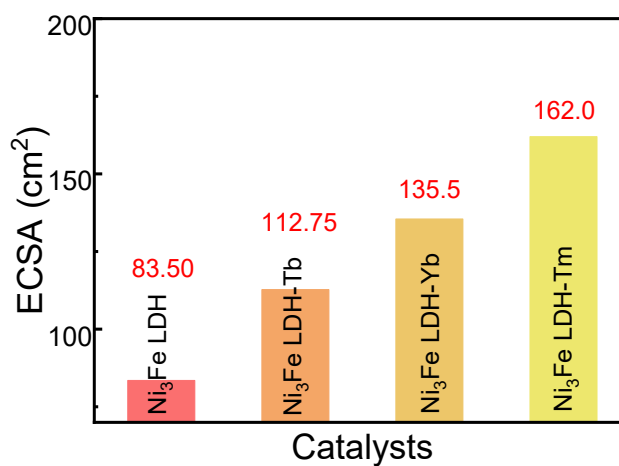


Fig. S27 Comparison of ECSA values of different samples.

$$TOF_{per\ site} = \frac{\text{total hydrogen turnover/cm}^2 \text{ geometric area}}{\text{surface sites of catalyst/cm}^2 \text{ geometric area}} \dots \text{(S11)}$$

$$\begin{aligned} & \text{total hydrogen turnover/cm}^2 \text{ geometric area (OER)} \\ &= \frac{6.02 \times 10^{23}}{1 \text{ mol } O_2} \times \frac{1 \text{ mol } O_2}{4 \text{ mol } e^-} \times \frac{1 \text{ mol } e^-}{96485 \text{ C}} \times \frac{1 \text{ C s}^{-1}}{1000 \text{ mA}} \times j_{OER} \frac{\text{mA}}{\text{cm}^2} \end{aligned}$$

$$\begin{aligned} & \text{surface sites of catalyst/cm}^2 \text{ geometric area} \\ &= ECSA \times \frac{\text{total number of atoms}}{\text{cm}^2 \text{ unit cell}} \end{aligned}$$

Lattice parameters: $a=b=3.079 \text{ \AA}$, $c=22.790 \text{ \AA}$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$. Volume of the hexagonal cell = 187.11 \AA^3 .

$$\begin{aligned} & \text{surface sites of catalyst/cm}^2 \text{ geometric area} \\ &= ECSA \times \left(\frac{39 \text{ atoms per unit cell}}{187.11 \text{ \AA}^3} \right)^{\frac{2}{3}} \end{aligned}$$

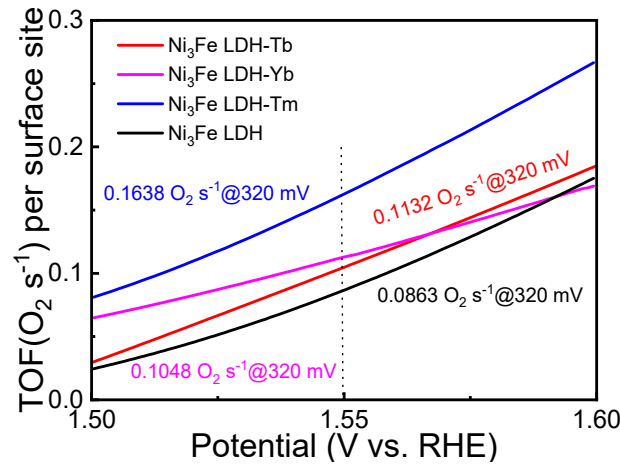


Fig. S28 TOF curves of different samples.

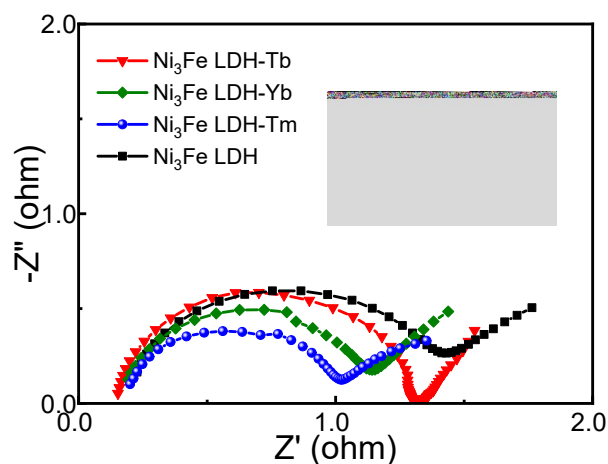
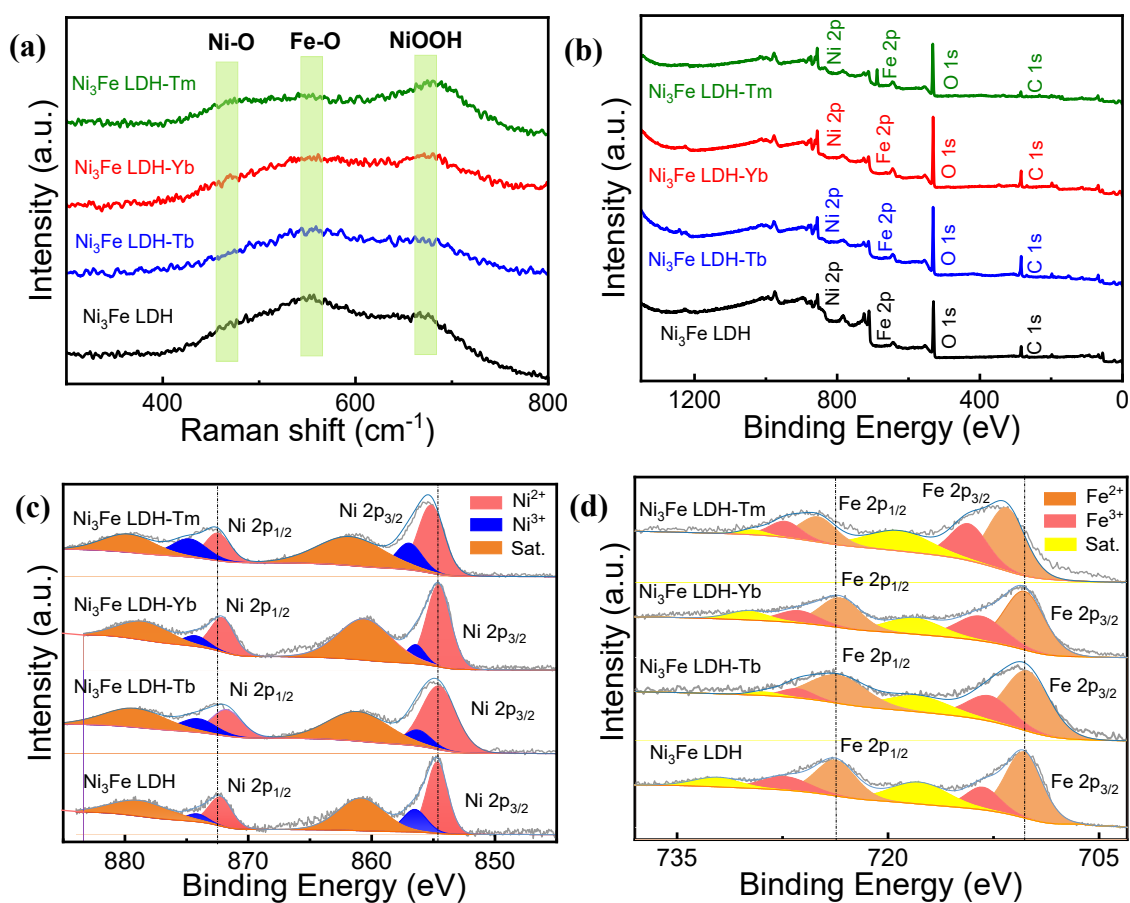


Fig. S29 Nyquist plots of above samples (the equivalent circuit image is displayed in the inset).



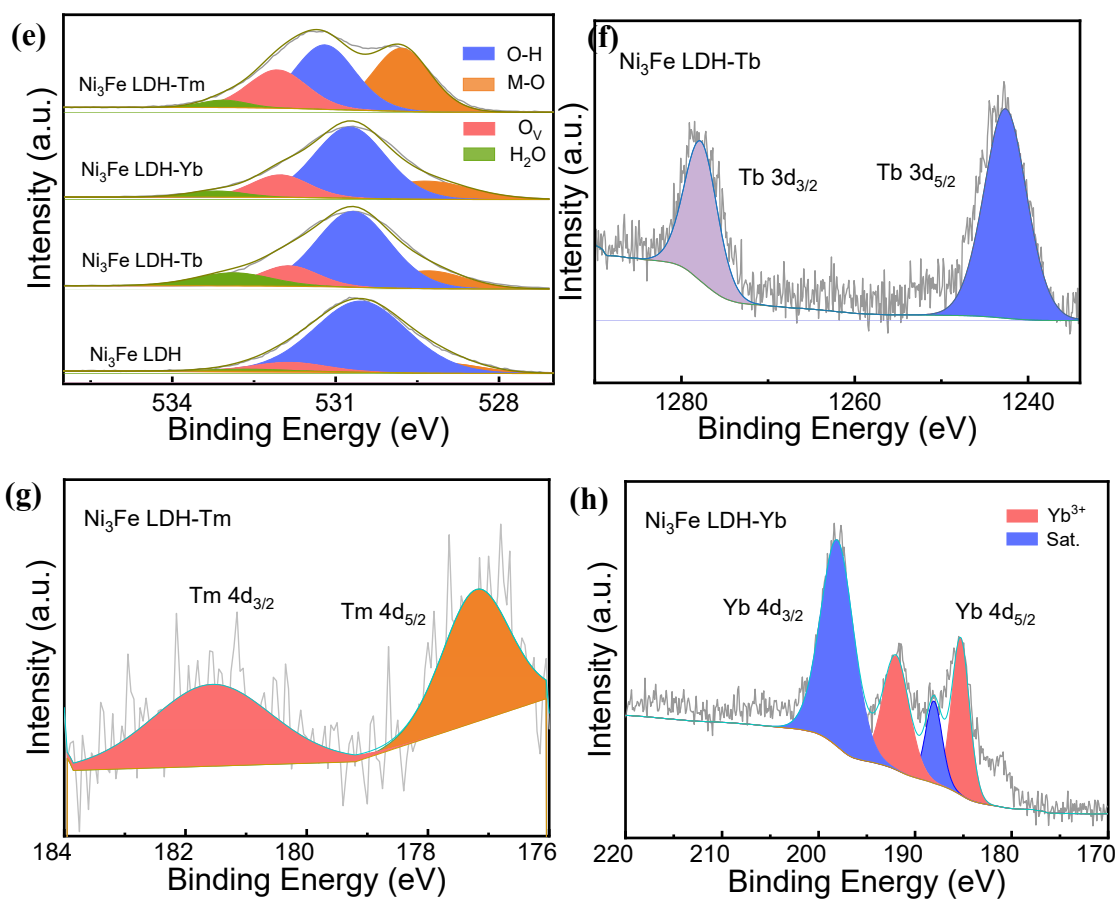


Fig. S30 (a) Raman spectra, (b) XPS survey spectra of the samples and high resolution: (c) Ni 2p, (d) Fe 2p, (e) O 1s, (f) Tb 3d, (g) Tm 4d and (h) Yb 4d.

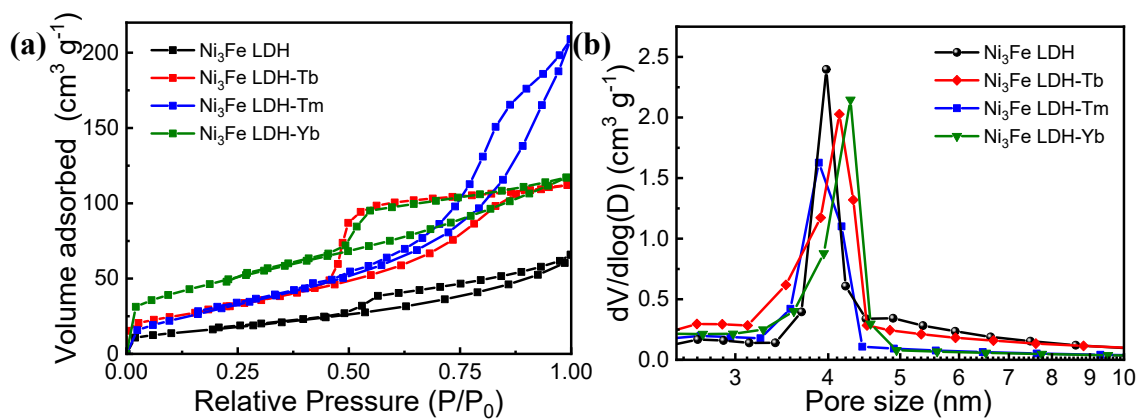


Fig. S31 (a) Nitrogen adsorption-desorption isotherms and (b) BJH pore size distribution curves of the samples.

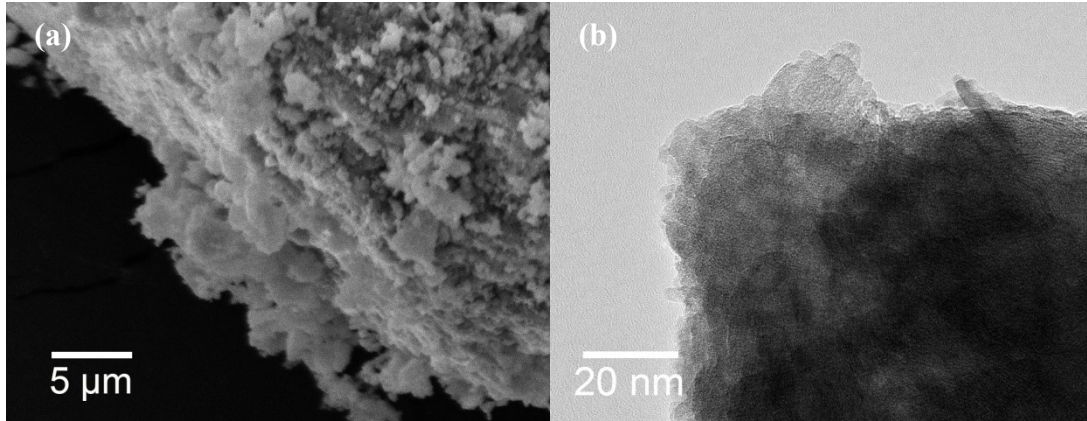


Fig. S32 (a) SEM image and (b) TEM image of Ni₃Fe LDH/NiFe₂O₄/Pt.

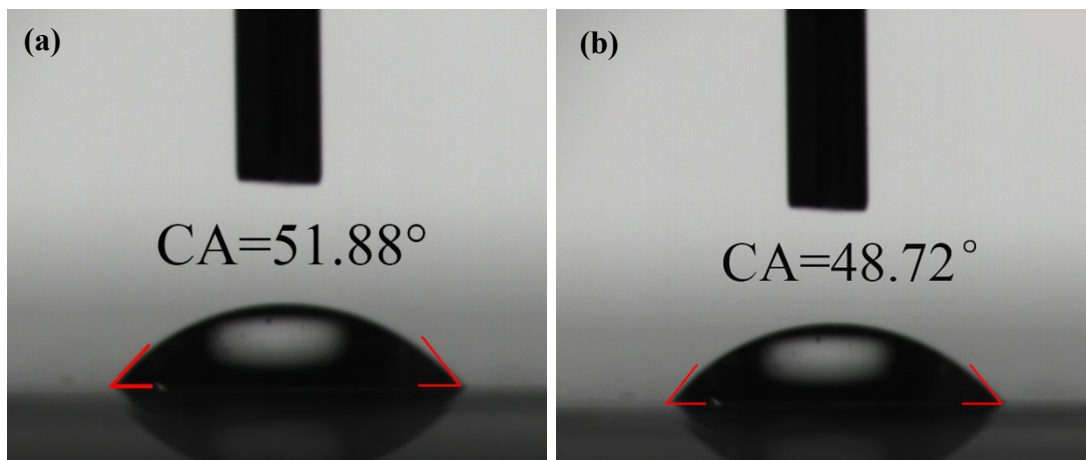


Fig. S33 The contact angle of Ni₃Fe LDH and Ni₃Fe LDH/NiFe₂O₄/Pt-Tm.

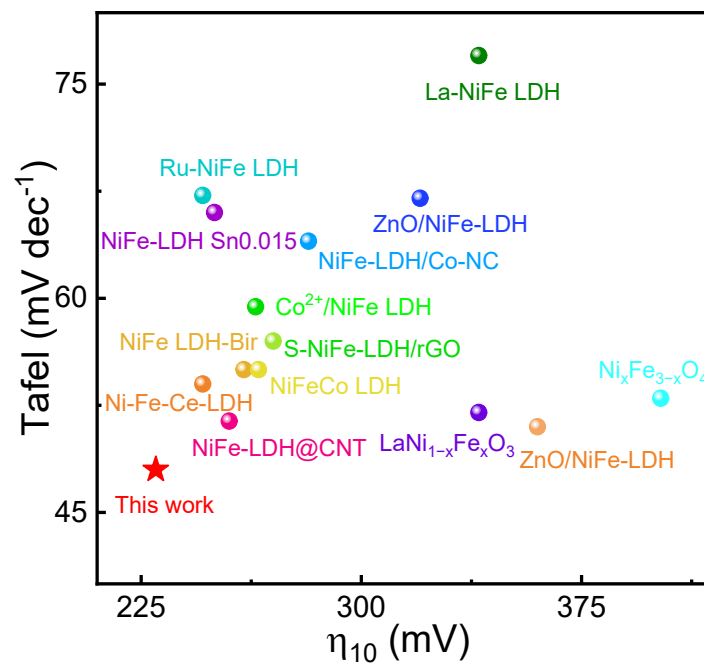


Fig. S34 Comparison of the overpotentials and Tafel plots for various NiFe-based

catalysts reported.

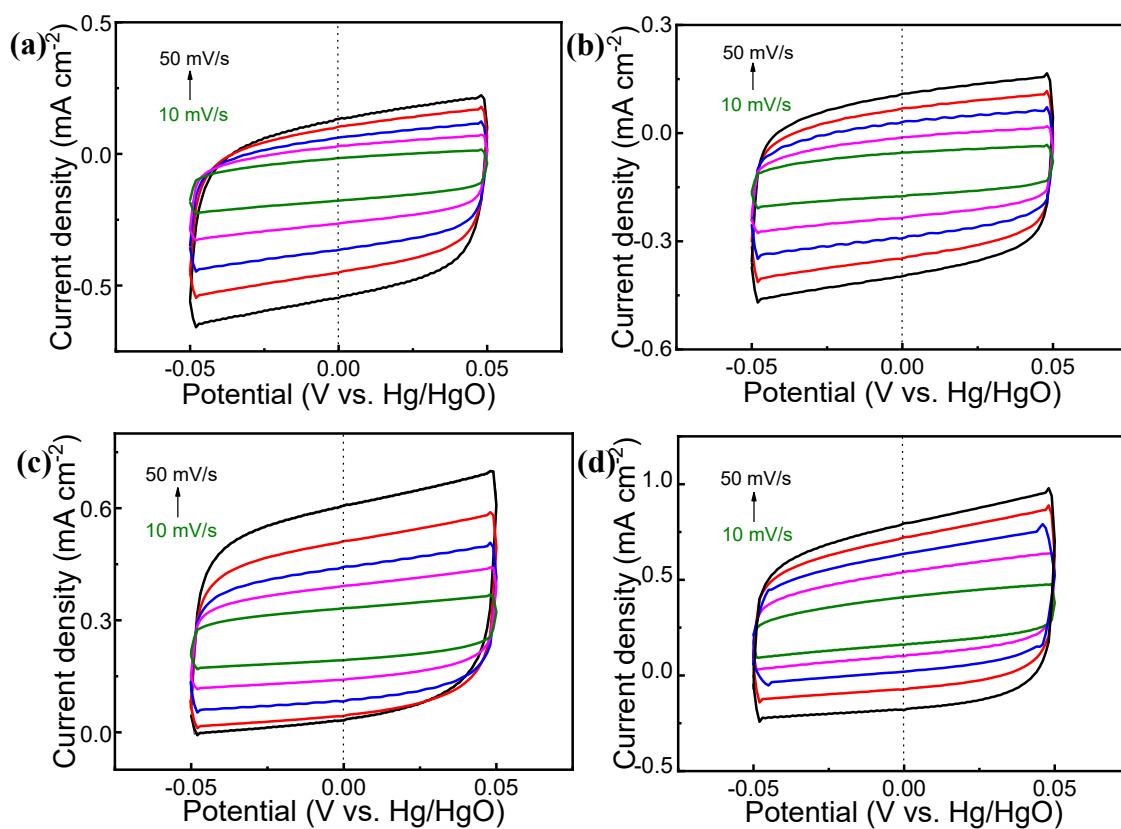


Fig. S35 Cyclic voltammety curves in the -0.05 V~0.05 V voltage range of (a) Ni₃Fe LDH, (b) Ni₃Fe LDH-Tm, (c) Ni₃Fe LDH/NiFe₂O₄/Pt and (d) Ni₃Fe LDH/NiFe₂O₄/Pt-Tm.

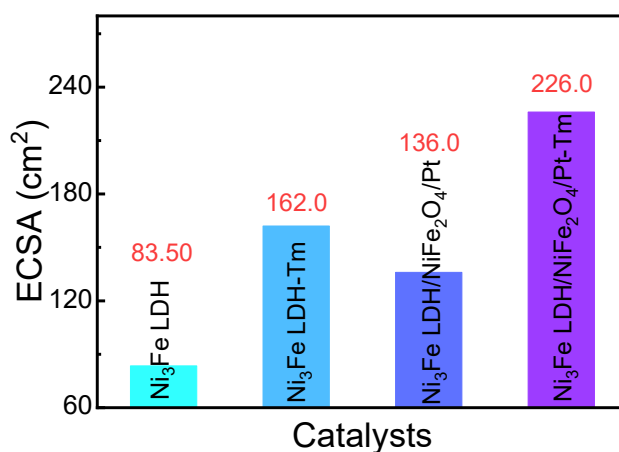


Fig. S36 Comparison of ECSA values of different samples.

Electrochemical measurements on overall water splitting catalyzed by the Ni₃Fe LDH/NiFe₂O₄/Pt-Tm (Fig. S37~Fig. S41, and Table S3 provided comparison with reported data on OER and HER performances)

$$TOF_{per\ site} = \frac{\text{total hydrogen turnover/cm}^2 \text{ geometric area}}{\text{surface sites of catalyst/cm}^2 \text{ geometric area}} \dots \text{(S12)}$$

$$\begin{aligned} & \text{total hydrogen turnover/cm}^2 \text{ geometric area (HER)} \\ &= \frac{6.02 \times 10^{23}}{1 \text{ mol H}_2} \times \frac{1 \text{ mol H}_2}{2 \text{ mol e}^-} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ C s}^{-1}}{1000 \text{ mA}} \times |j_{HER}| \frac{\text{mA}}{\text{cm}^2} \end{aligned}$$

$$\begin{aligned} & \text{surface sites of catalyst/cm}^2 \text{ geometric area} \\ &= ECSA \times \frac{\text{total number of atoms}}{\text{cm}^2 \text{ unit cell}} \end{aligned}$$

Lattice parameters: a=b=3.079 Å, c=22.790 Å, α=β=90°, γ=120°. Volume of the hexagonal cell = 187.11 Å³.

$$\begin{aligned} & \text{surface sites of catalyst/cm}^2 \text{ geometric area} \\ &= ECSA \times \left(\frac{39 \text{ atoms per unit cell}}{187.11 \text{ Å}^3} \right)^{\frac{2}{3}} \end{aligned}$$

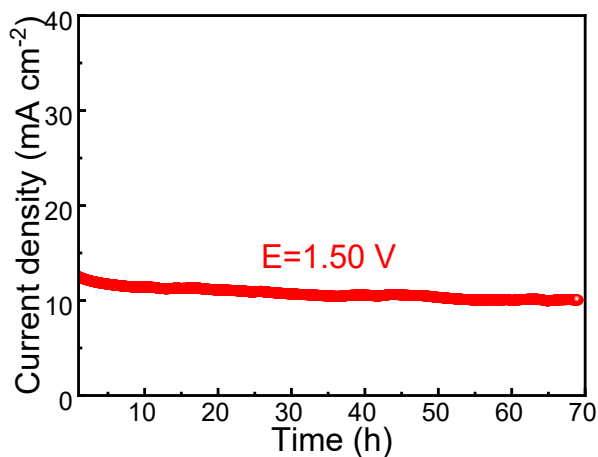


Fig. S37 Chronoamperometric response at a constant overpotential of 1.50 V.

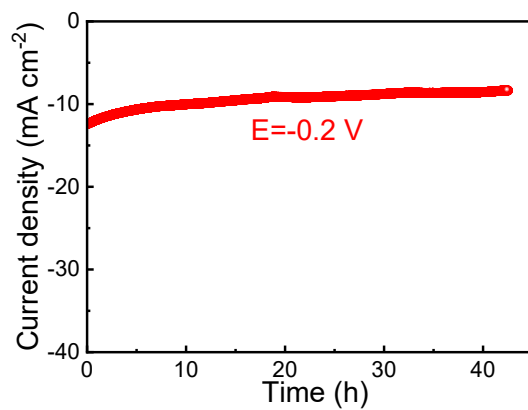


Fig. S38 Chronoamperometric response at a constant overpotential of -0.2 V.

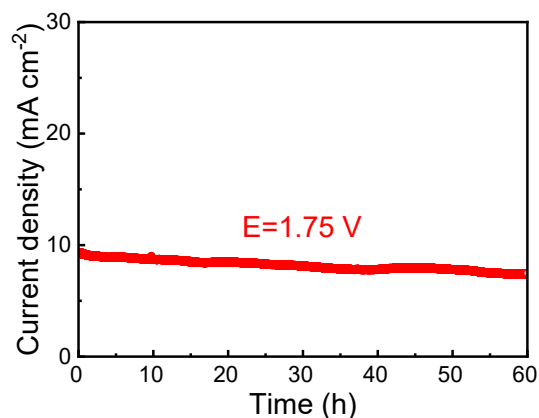


Fig. S39 Chronoamperometric response at a constant overpotential of 1.75 V.



Fig. S40 The Hoffmann electrolytic device for overall water splitting.

We calculated the energy efficiency of overall water electrolysis at the current density of 10 mA cm^{-2} as follows. The specific energy for producing 1.0 kg of hydrogen is thermodynamically given as 143 MJ kg^{-1} or 39.4 kWh kg^{-1} . Since the

electrolysis cell operates near 1.690 V at 10 mA cm⁻², the energy required for producing 1.0 kg H₂ can be calculated as follows. The current density of 10 mA cm⁻² can be expressed as 0.01 C s⁻¹ cm⁻² (∵ 1 A = 1 C s⁻¹). Then, the transferred amount of electron can be calculated as 1.036×10⁻⁶ mol s⁻¹ cm⁻² (∵ F = 96500 C mol⁻¹ e⁻), and H₂ generation rate is calculated as 5.181 ×10⁻⁷ mol H₂ s⁻¹ cm⁻², which is equivalent to 3.731×10⁻⁴ g H₂ h⁻¹ cm⁻². For producing 1 kg of H₂, the multiplication constant can be calculated as 2.681×10⁶ h cm². Since the electrolysis cell operates at 0.169 W cm⁻², the energy required for producing 1 kg H₂ is calculated as 45.31 kWh. The energy efficiency can be calculated by dividing the theoretical specific energy for 1 kg H₂ production, i.e., 39.4 kWh. Then, the energy efficiency turns out to be 87.0%. Considering the energy efficiency for conventional alkaline electrolysis is less than 70% with the use of platinum electrode, the proposed catalyst can be considered as highly efficient for the water electrolysis.

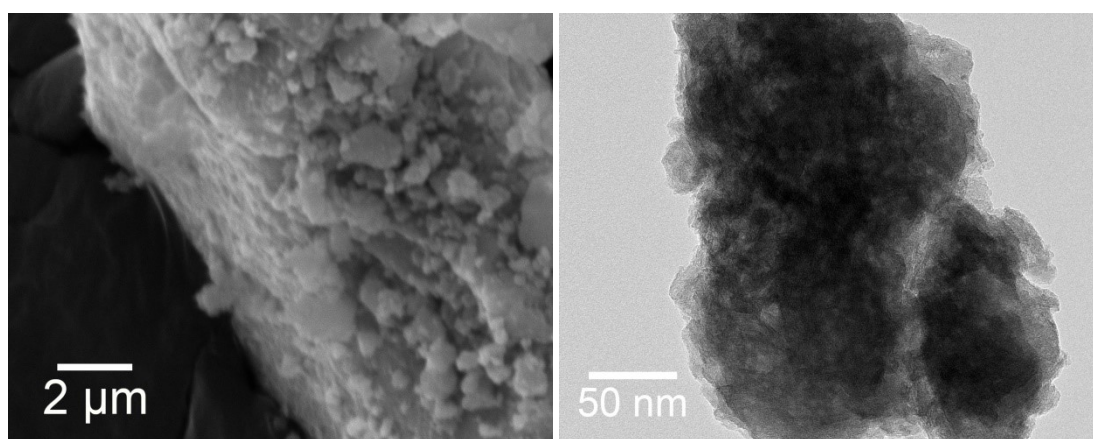


Fig. S41 (a) SEM image and (b) TEM image of Ni₃Fe LDH/NiFe₂O₄/Pt-Tm after OER testing.

Table S3 Comparison of OER and HER performances of the as-prepared electrodes with that of other reported LDH-based electrocatalysts evaluated in 1.0 M KOH alkaline solution.

Electrocatalyst	$\eta_{\text{OER}}/\text{mV}$ (at 10 mA cm ⁻²)	$\eta_{\text{HER}}/\text{mV}$ (at 10 mA cm ⁻²)	Ref.
Ni ₃ Fe LDH/NiFe ₂ O ₄ /Pt-Tm	224	125	This work
NiCo-LDH-OH	317	180	15
CeCO ₃ OH/Ce-CoFe LDH	216	165	16
CoMo-LDH	290	115	17
NiFe-LDH/FeCoS ₂ /CFC	190	308	18
CoFeZr/NF	233	159	19
H-CoS _x @NiFe LDH/NF	250	95	20
NiCo LDH	227	195	21
Pd-NiAl-LDH	264	189	22
Mo-CoP	317	118	23
Zn _{1-x} Fe _x -oxyselenide/NF	256	202	24
NiFe LDH/NiS ₂ /VS ₂	286	76	25
Co _{0.4} Fe _{0.6} LDH/g-CN _x	280	125	26
Co _{0.25} Fe _{0.75} -LDH	270	365	27

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