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

Supporting Information

Enhancing hydrogen evolution reaction through modulating electronic structure of self-supported NiFe LDH

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1. EXPERIMENTAL SECTION

1.1 Materials.

All the chemicals were of analytical grade and used directly without any further purification after purchasing. Chemicals including Iron nitrate nonahydrate Fe $(NO_3)_3 \cdot 9H_2O$, Urea ($CO(NH_2)_2$) hydrochloric acid (HCl) and potassium hydroxide (KOH) were purchased from Tianjin Damao Chemical Reagent Factory in China. Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot 3H_2O$) was purchased from Sigma Aldrich. The purchased chloroauric acid is formulated into a solution of 2.538 M, which was from Aladdin (Shanghai, China). The 20 wt% Pt/C, IrO_2 and Nafion solution (5 wt%) was obtained from Aladdin (Shanghai, China). Deionized water with a resistivity $\geq$ 18 MΩ was used to prepare all aqueous solutions.

1.2 Synthesis of catalysts

1.2.1 Synthesis of NiFe LDH.

NiFe LDH on Nickel foam was synthesized by one-step hydrothermal method. First, the Ni foam was successively washed with 3M HCl aqueous solution, ethanol and deionized water. In a typical synthesis procedure, using Nickel foam as the source of Ni, Fe $(NO_3)_3 \cdot 9H_2O$ (0.0125 M) and $CO(NH_2)_2$ (0.1 M) were dissolved in 100 mL of distilled water and stirred to form a clear solution. Nickel foam (NF, 1 cm × 3 cm) was cleaned thoroughly with about 3 M HCl, ethanol, and water in sequence under sonication for 10 min each time in order to remove the possible surface oxide layer. The solution and the Nickel foam were transferred to a 20 mL Teflon-lined stainless-steel autoclave and sealed, maintained at 100 °C for 14 h, and then allowed to cool to room temperature naturally. A brown metal substrate was formed and subsequently rinsed with deionized water for 5 min with the assistance of ultrasonication, and dried in an oven at 60 °C for 10 h.

1.2.2 Synthesis of NiFeAu LDH.

Adding $HAuCl_4$ with Nickel foam (NF, 1 cm × 3 cm), Fe $(NO_3)_3 \cdot 9H_2O$ (0.0125 M) and $CO(NH_2)_2$ (0.25 M) material, the following steps are consistent with the preparation of NiFe LDH. The $HAuCl_4$ is solution is 2.538 mM and added at various capacity (0.1 mL, 0.2 mL, 0.3 mL, 0.4 mL, 0.5 mL).

1.3 Characterizations

The morphological and lattice structural of as-synthesized samples were revealed with field emission scanning electron microscopy (FE-SEM, JSM-7600F) and transmission electron microscopy (TEM, JEOL 2100F). The phase composition of the catalysts was analyzed by X-ray diffraction (XRD) at 40 kV and 120 mA with Cu Kα radiation (λ = 1.5418 Å) in 2θ angular range of 5−80°. The Raman spectra were recorded on the Lab RAM Aramis Raman spectrometer (HORIBA JobinYvon) with 514 nm laser as the excitation source. AFM characterization was carried out with Bruker edge (Digital Instruments). X-ray Photoelectron Spectroscopy (XPS), which model was PHI, PHI5300 system with coupled with a Kratos Axis Ultra DLD electron spectrometer, was carry out to gain detailed chemical composition of samples.

1.4 Electrochemical measurements

4.4.1 Electrode preparation.

All of the electrochemical measurements are performed with Princeton Applied Research electrochemical workstation, under identical conditions with a typical standard three-electrode system. The as-prepared catalyst is directly used as the working electrode. A carbon rod serves as the counter electrode, and the saturated calomel electrode (SCE) acts as the reference electrode. The 2 mg 20 wt% Pt/C/NF and IrO_2/NF were first ultrasonically dispersed in the mixture of DI water, ethanol and Nafion® solution (5.0 wt%). Then, the catalyst dispersion (2 mg mL^{-1}) is transferred onto the Ni foam (1×1 cm^2), then drying overnight in room temperature. The resulting electrode serves as the working electrode. The overall water splitting electrode is used as both cathode and anode by the prepared NiFeAu LDH.

1.4.2 Electrocatalytic hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) testing.

The electrochemical properties of the as-prepared samples are investigated. After 20 cyclic voltammetry scans, the linear scanning voltammetry (LSV) was used to collect polarization data at a scanning rate of 5 mV s^{-1} to reduce the capacitive current. After CV test, Electrochemical impedance spectroscopy (EIS) profiles were immediately recorded under

1.47 V (vs. RHE) for OER and -0.18 V (vs RHE) for HER in a frequency range from 0.01 to 100 KHz with an amplitude of 5 mV. ECSA data were derived from cyclic voltammetry (CV) measurements are conducted by sweeping the potential across the non-Faradaic region with different scan rates (10 mV s^{-1} to 50 mV s^{-1}) from 1.17 V to 1.27 V vs. RHE. The relationship between current density and voltage form a straight line with a slope equal to C_{dl}. The electrochemically active surface areas (ECSA) were studied based on the electrochemical double-layer capacitance of various electrocatalysts at non-faradaic overpotentials. By plotting the difference of current density (J) between the anodic and cathodic sweeps ($J_{anodic} - J_{cathodic}$) at 0.15 V vs. RHE against the scan rate, a linear trend was observed. The slope of the fitting line is equal to twice the geometric double layer capacitance (C_{dl}). Namely, $C_{dl} = (J_{anodic} - J_{cathodic})/2\nu$. All the potentials are referred to RHE, where $E_{RHE} = E_{SCE} + 0.241 \text{ V} + 0.0591 \times \text{pH}$. All voltages and potentials were corrected to eliminate electrolyte resistances unless noted.

1.4.3 Electrocatalytic overall water splitting testing.

Overall water splitting test was carried out with a two-electrode system, polarization curves were recorded with the scan rate of 5 mV s^{-1}, the stability is characterized by the chronoamperometry at 20 mA cm^{-2} current density for 50 h. And the EIS was carried out in the frequency range of 0.01 Hz to 100 KHz with an amplitude of 5 mV at the 1.6 V vs RHE (Tafel region).

2. Supplementary Figures

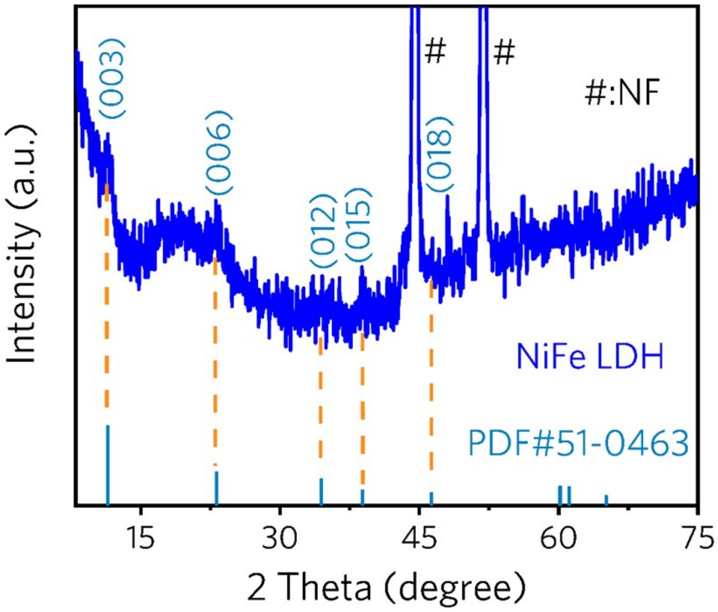

Figure S1. Enlarged XRD pattern of NiFe LDH. In the enlarged XRD pattern, the diffraction peaks of NiFe LDH are obvious at 11.5°, 23.2°, 34.5° and 39.0°.

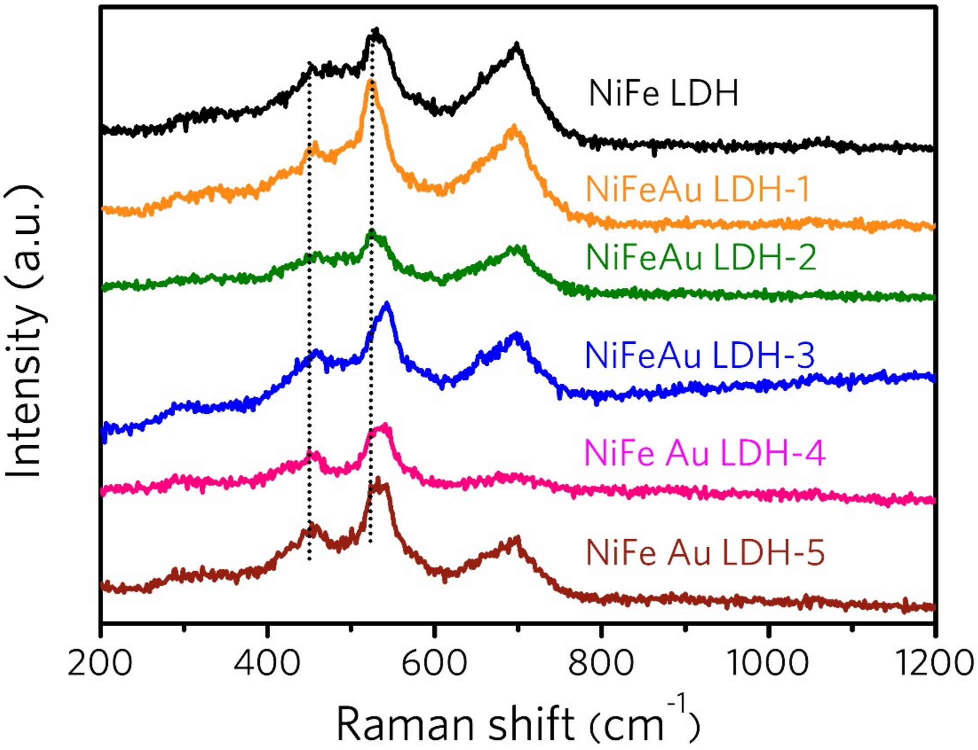

Figure S2. Raman spectra of catalysts. As shown in imagine, All samples (0.1 mL, 0.2 mL, 0.3 mL, 0.4 mL, 0.5 mL) have varying degrees of deviation for NiFe LDH at 526 cm^{-1}, which reveal the metal-oxygen of Fe^{3+}-O-Fe^{3+} was affected by the addition of Au.

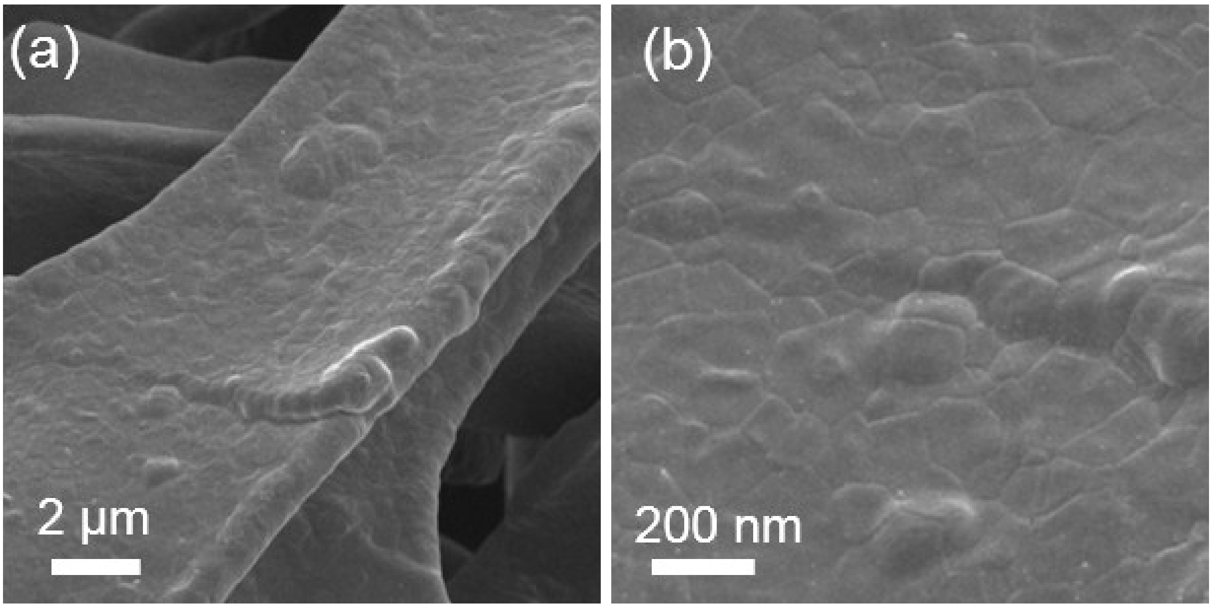

Figure S3. SEM image of Nickel foam (NF) cleaned by 3 M HCl, ethanol, and water sequentially.

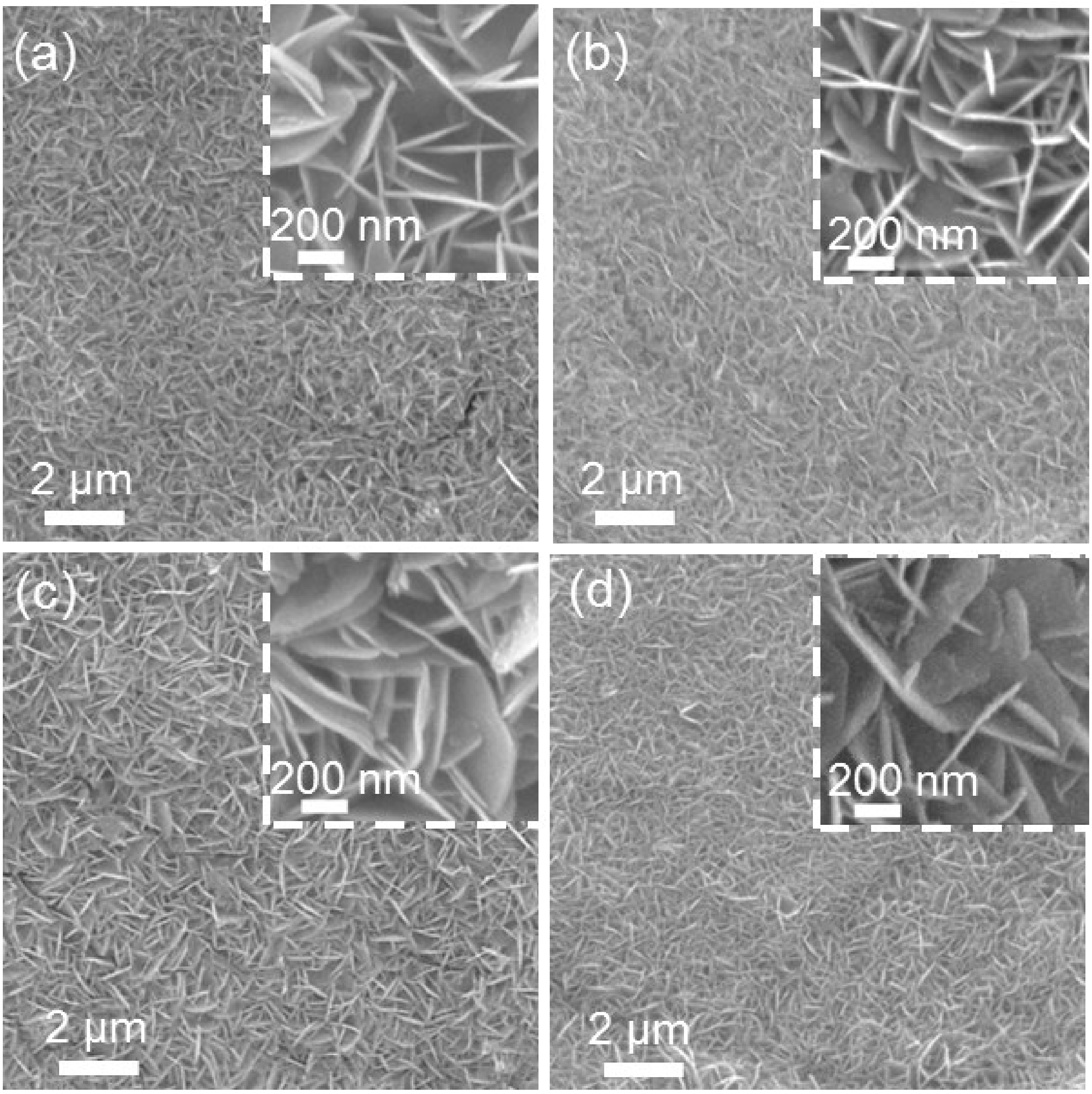

Figure S4. SEM images of the NiFeAu LDH prepared by adding different contenet $HAuCl_4$ (a) 0.1 mL (b) 0.2 mL (c) 0.4 mL (d) 0.5 mL, respectively.

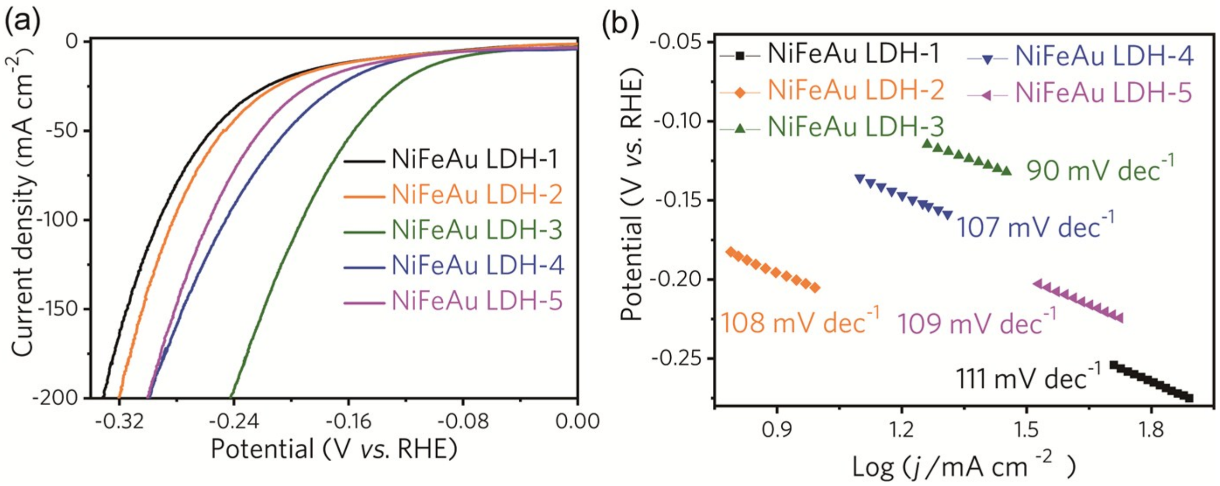

Figure S5. HER performance of NiFeAu LDH with different Au content (a) HER Polarization curves (b) Tafel slopes derived from polarization curves.

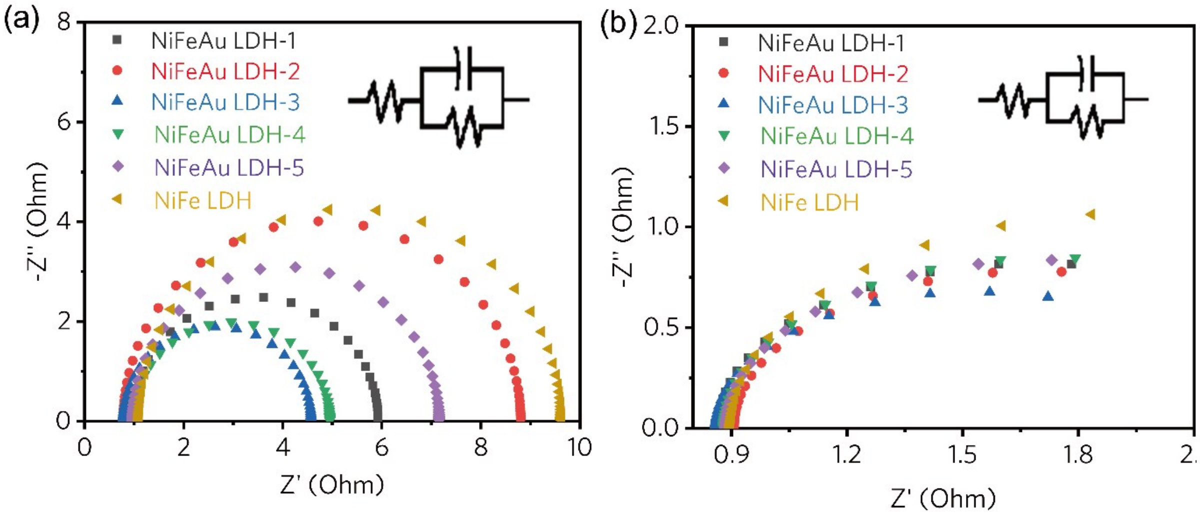

Figure S6. (a) EIS for the corresponding electrocatalysts at same potential (-0.18 V *vs*. RHE) for HER (b) EIS for the corresponding electrocatalysts at same potential (1.47 V *vs*. RHE) for OER

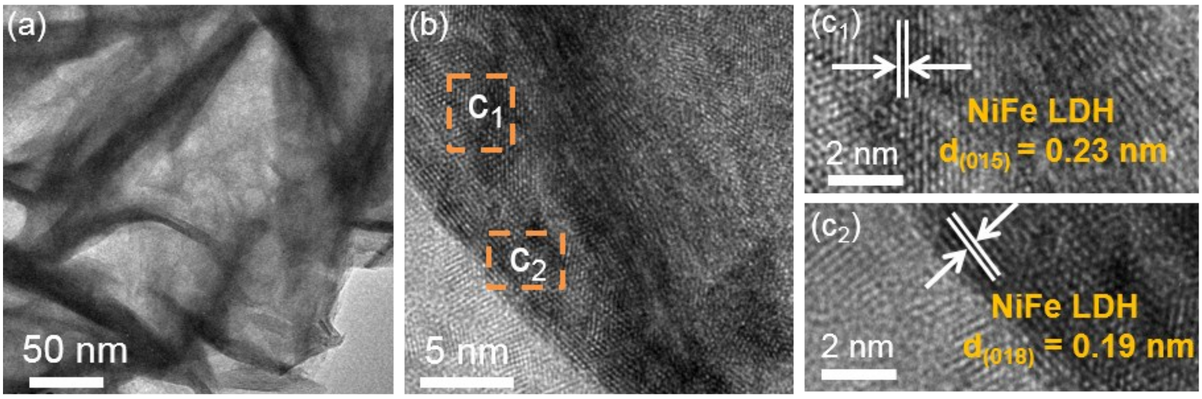

Figure S7. TEM image of NiFeAu LDH after HER: (a) the low-resolution, (b) the medium-resolution, (c) the high-resolution.

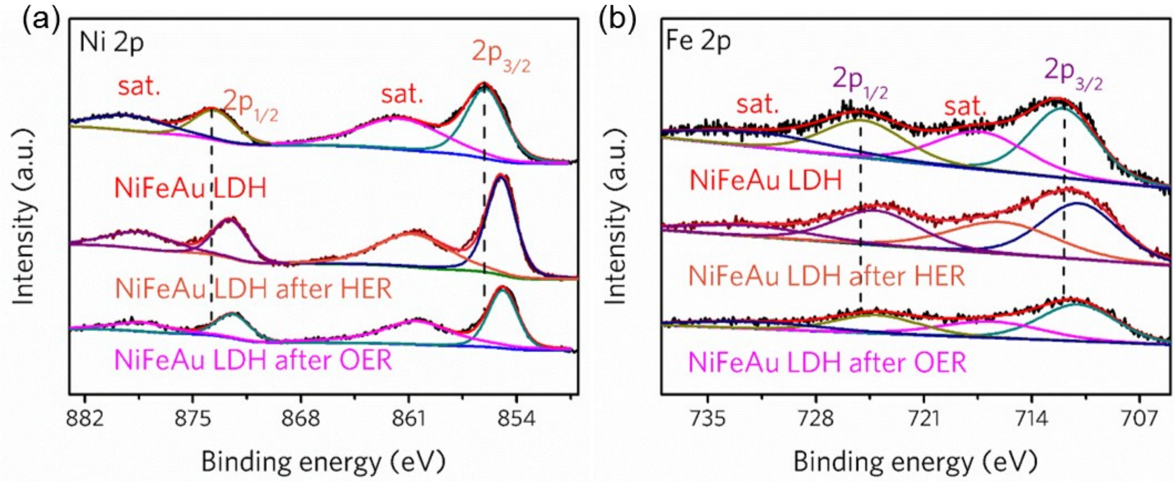

Figure S8. High-resolution XPS spectra of (a) Ni 2p, (b) Fe 2p in the NiFeAu LDH after HER and OER.

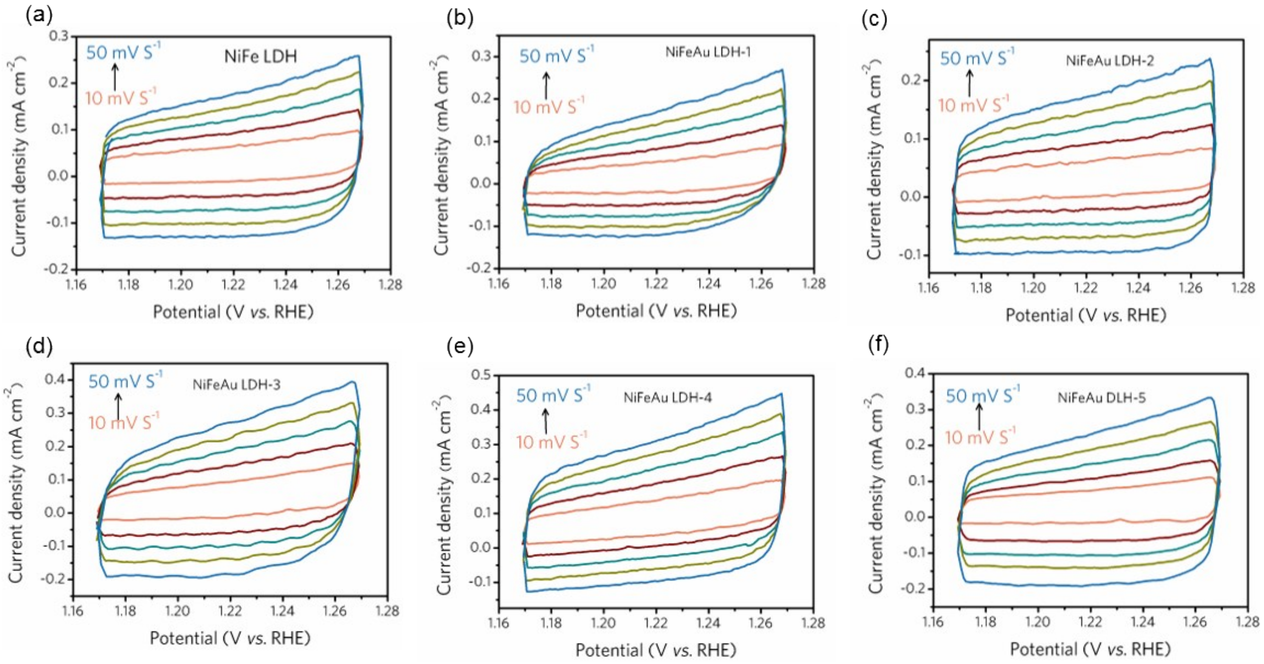

Figure S9. CV curves of different catalysts. (a) NiFe LDH, (b) adding $HAuO_4$ solution 0.1 mL NiFeAu LDH-1, (c) 0.2 mL $HAuO_4$ solution NiFeAu LDH-2, (d) 0.3 mL $HAuO_4$ solution NiFeAu LDH-3, (e) 0.4 mL $HAuO_4$ solution NiFeAu LDH-4, (f) 0.5 mL $HAuO_4$ solution NiFeAu LDH-5.

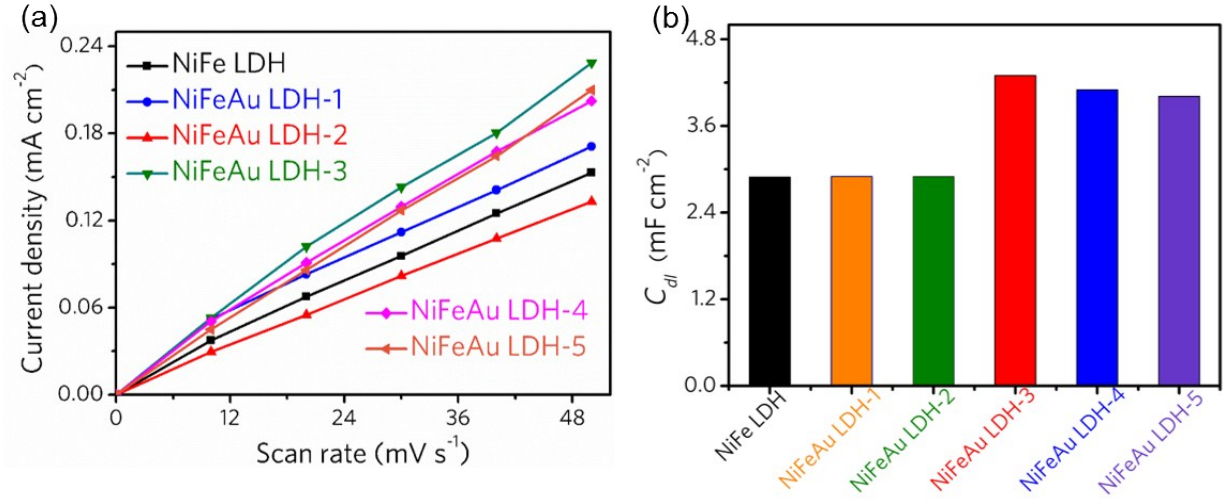

Figure S10. (a) charge current density differences of all catalysts (b) C_{dl} derived from ECSA of the catalysts. a~e corresponds to NiFeAu LDH with different content of $HAuCl_4$ (0.1 mL, 0.2 mL, 0.3 mL, 0.4 mL, 0.5 mL). The Cdl for NiFe LDH, NiFeAu LDH-1,NiFeAu LDH-2, NiFeAu LDH-4, and NiFeAu LDH-5 is 2.89, 2.9, 2.9, 4.1 and 4.0 mF cm^{-2}, the NiFeAu LDH presented largest C_{dl} value of 4.3 mF cm^{-2}, resulting in abundant exposed active sites for HER.

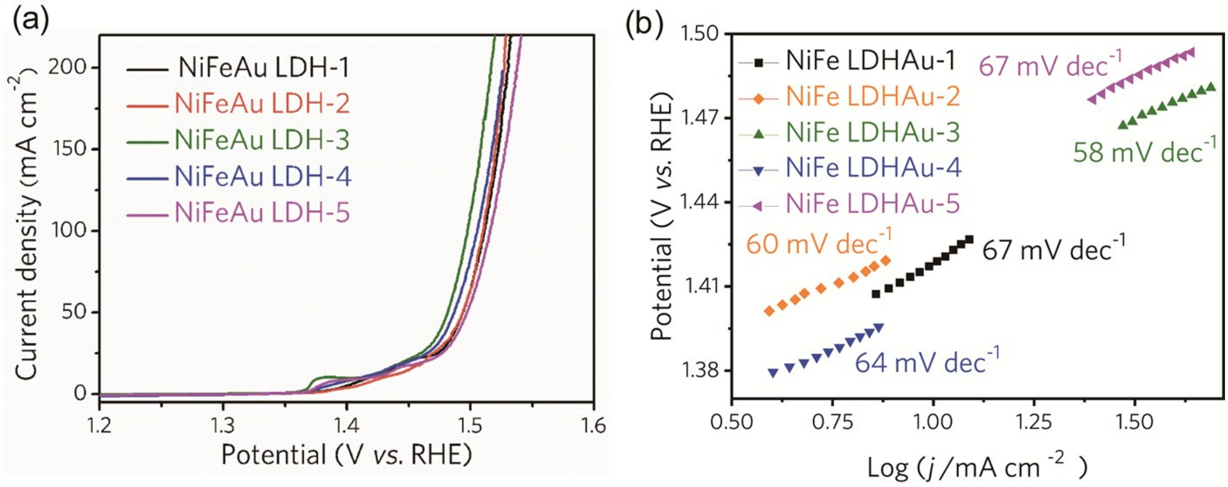

Figure S11. OER performance of NiFeAu LDH with different Au content (a) OER Polarization curves (b) Tafel slopes derived from polarization curves.

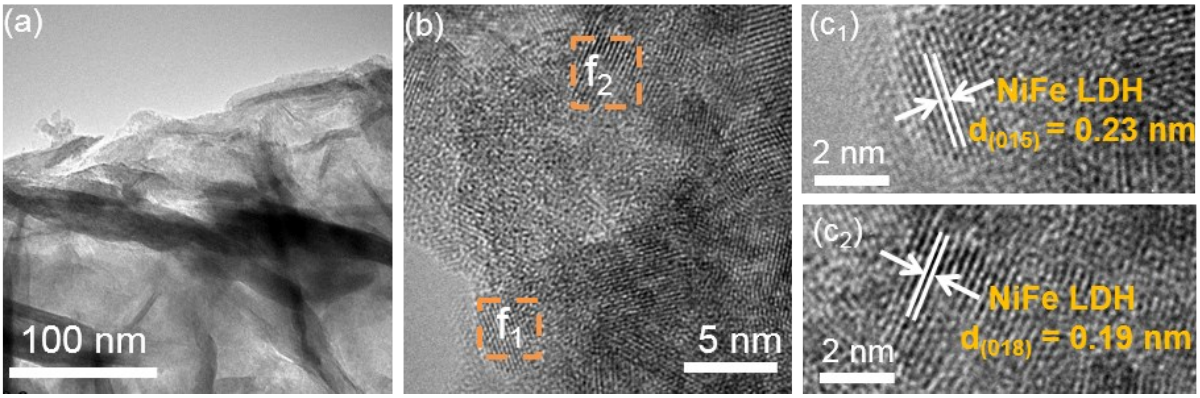

Figure S12. TEM image of NiFeAu LDH after OER: (a) the low- resolution, (b) the medium-resolution, (c) the high- resolution.

Table 1. Comparison HER performance of NiFeAu LDH with other electrocatalysts at 1M KOH solution.

Catalyst	Support	η_{mV} @ j mA cm^{-2}	Tafel slope mV dec^{-1})	Ref.
NiFeAu LDH	Ni Foam	89@10	90	This work
CoFe@ NiFe LDH	Ni Foam	240@10	84	*Appl. Catal. B-Enviro.***2019**,*253*,131.
$NiCo_2S_4$@NiFe LDH	Ni Foam	200@10	101	*ACS Appl. Mater. Interfaces* **2017**, *9*, 15364.
NiFe LDH@ NiCoP	Ni Foam	120@10	88	*Adv. Funct. Mater.* **2018**, *28*, 1706847.
Ni_5P_4/NiP_2/NiFe LDH	Ni Foam	124@10	/	*J. Mater. Chem. A,* **2018**, *6*,13619.
Cu@ NiFe LDH	Cu foam	116@10	59	*Energy Environ. Sci.*, **2017**, *10*,1820.
NiFe LDH NS@DG10	Glassy carbon	300@10	110	*Adv. Mater.*, **2017**, *29*, 1700017.
NiFeOx/CFP	CFP	88@10	118	*Nat. Commun.* **2015**, *6*, 7261.
NiCoFe/CFP	CFP	200@10	70	*ACS Energy Lett.* **2016**, *1*, 445.
NiFeV LDH	Ni Foam	125@10	62	*Small* **2018**, *14*, 1703257-1703266.
$Co_{0.85}Se$/NiFe-LDH	Graphite foil	260@10	160	*Energy Environ. Sci.* **2016**, *9*, 478.

Table 2. Comparison OER performance of NiFeAu LDH with other electrocatalysts at 1M KOH solution.

Catalyst	Support	η_{mV}@ jmA cm^{-2}	Tafel slope (mV dec^{-1})	Ref.
NiFeAu LDH	Ni Foam	181@10	58	This work
CoFe@ NiFe LDH	Ni Foam	190@10	45	*Appl. Catal. B-Enviro*.**2019**,*253*,131.
$NiCo_2S_4$@NiFe LDH	Ni Foam	201@60	46	*ACS Appl. Mater. Interfaces* **2017**, *9*, 15364.
Ultrathin NiFe LDH	Ni Foam	210@10	31	*ACS Catal.* **2019**, *9*, 6027.
NiFe LDH@ NiCoP	Ni Foam	220@10	48	*Adv. Funct. Mater.* **2018**, *28*, 1706847.
Ni_5P_4/NiP_2 /NiFe LDH	Ni Foam	197@10	47	*J. Mater. Chem. A,* **2018**, *6*, 13619.
NiFe LDH HMS	Glassy carbon	239@10	53	*ACS Appl. Mater. Interfaces,* **2016**, *8*, 33697.
Cu@ NiFe LDH	Cu foam	240@10	44	*Energy Environ. Sci.*, **2017**, *10*, 1820.
NiFe LDH NS@DG10	Glassy carbon	210 @10	52	*Adv. Mater.*, **2017**, *29*, 1700017.
NiFe LDH@ Au	Ni foam	235@100	48	*ACS Appl. Mater. Interfaces,* **2017**, *9*,19807.
NiFeRu-LDH	Ni foam	225@10	32	*Adv. Mater*. **2018**, 1706279.
NiFeV LDH	Ni Foam	231@10	34	*Small*. **2018**, *14*, 1703257.
$Co_{0.85}Se$/NiFe-LDH/GF	Graphite foil	260@100	57	*Energy Environ. Sci*. **2016**, *9*, 478

Table 3. Comparison of two electrode water splitting voltage of NiFeAu LDH electrocatalyst with other bifunctional electrocatalyst at 1 M KOH solution.

Catalyst	Support	voltage V @ *j* mA cm^{-2}	Ref.
NiFeAu LDH	Ni Foam	1.57@10	This work
CoFe@NiFe/NF	Ni Foam	1.59@10	*Appl. Catal. B-Enviro.***2019**,*253*:131-139.
NiCoP	Ni Foam	1.58@10	*Nano Lett.* **2016**, *16*, 7718
NiFe LDH @NiCoP/NF	Ni Foam	1.57@10	*Adv. Funct. Mater.* **2018**, *28*, 1706847.
NiFeRu-LDH	Ni foam	1.52@10	*Adv. Mater.* **2018**, 1706279.
NiFeV LDH	Ni Foam	1.59@10	*Small*. **2018**, *14*, 1703257.
Ni_3Se_4@NiFe LDH/CFC	CFP	1.54@10	*Nanoscale Horiz.*, **2019**,*4*, 1132
NiFe LDH@$NiCo_2S_4$	Ni foam	1.6@10	*ACS Appl. Mater. Interfaces,* **2017**, *9*, 15364.
EG/$Co_{0.85}$Se/NiFe-LDH	Graphite foil	1.67@10	*Energy Environ. Sci.* **2016**, *9*, 478.