Electronic Supplementary Information

Engineering Borate Modified NiFe Layer Double Hydroxides Nanoarrays as “Hydroxyl Ions Hungry” Electrocatalysts for Enhanced Oxygen Evolution

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Experimental methods

Materials:

Nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, Beijing Chemical Reagent Co., Ltd.), iron nitrate nonahydrate ($Fe(NO_3)_3·9H_2O$, Beijing Chemical Reagent Co., Ltd.), Cobaltous Nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, Beijing Chemical Reagent Co., Ltd.), Aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$, Beijing Chemical Reagent Co., Ltd.), ammonium fluoride (NH4F, Shanghai Macklin Biochemical Co.), urea (CH_4N_2O, Beijing Chemical Reagent Co., Ltd.), nitric acid (HNO_3, Beijing Chemical Reagent Co.,Ltd.), ethanol (C_2H_5OH, Beijing Chemical Reagent Co., Ltd.), potassium tetraborate tetrahydrate ($K_2B_4O_7·4H_2O$, Sigma-Aldrich Chemical Reagent Co., Ltd.) potassium hydroxide (KOH, Beijing Chemical Reagent Co.Ltd.), Nafion solution (Sigma-Aldrich Chemical Reagent Co. Ltd.), RuO_2 (Shanghai Macklin Biochemical Co. Ltd.). All the materials in this experiment were used directly without any purification.

Preparation of NiFe-LDHs /CP electrode:

The NiFe-LDHs/CP electrode was prepared *via* a facile hydrothermal method. 0.30 mmol $Ni(NO_3)_2·6H_2O$, 0.10 mmol $Fe(NO_3)_2·9H_2O$, 6 mmol NH_4F, 10 mmol urea and the carbon paper were dissolved into deionized water (80 mL) to ultrasonic treatment for 30 min. The carbon paper was pretreated in HNO_3 and then cleaned *via* sonication in deionized water and ethanol. Then, the mixture was transferred into a 100 ml Teflon-lined stainless steel autoclave to maintain at 120 ˚C for 12 h. After it was cooled to room temperature, the electrode was ultrasonicated with water and ethanol several times and then dried at 80 ˚C.

Preparation of BA-NiFe-LDHs /CP electrode:

The BA-NiFe-LDHs/CP electrode was prepared *via* second hydrothermal method procedure. The as-prepared NiFe-LDHs/CP was put into 80 mL saturated potassium tetraborate tetrahydrate solution and then transfered into 100 mL Teflon-lined stainless steel autoclave to maintain 12 h at 120 ˚C . After it was cooled to room temperature, the electrode was ultrasonicated with water and ethanol several times and then dried at 80 ˚C.

Preparation of CoFe-LDHs/CP, NiCo-LDHs/CP, NiAl-LDHs/CP and CoAl-LDHs/CP electrode: All these eletrodes were produced *via* a hydrothermal method, which was similar to the "Preparation of NiFe-LDHs /CP electrode"**.**

Preparation of BA-CoFe-LDHs/CP, BA-NiCo-LDHs/CP, BA-NiAl-LDHs/CP and BA-CoAl-LDHs/CP electrode:

All these eletrodes were produced *via* second hydrothermal method procedure, which was similar to the "Preparation of BA-NiFe-LDHs /CP electrode"**.**

Preparation of RuO_2 /CP electrode:

RuO_2 (5 mg) was dispersed in a 1 mL mixed solution (490 μL water, 15 μL 5 wt % Nafion solution, and 495 μL ethanol) and then followed by sonication to obtain catalyst ink. Put the catalyst ink on the surfaces of CP. Finally, the electrode was dried at 80 ˚C overnight.

Materials characterization:

X-Ray diffraction (XRD) was performed on a Phillips X'pert ProMPD diffractometer (CuKα, λ=1.54056 Å, the generator setting was 40 kV and 40 mA). Field emission scanning electronic microscope (FESEM) images were taken *via* a Hitachi scanning electron microscope with an acceleration voltage of 10 kV. High-resolution transmission electron microscopy (HRTEM) was measured by a FEI Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. The characteristic of the Fourier transform infrared spectroscopy (FT-IR) *via* n a Nicolet-380

FourierTransform infrared spectrometer. X-Ray photoelectron spectra (XPS) were conducted through ESCALAB 250Xi spectrometer (Thermo Fisher) with Al Kα radiation.

Electrochemical measurements:

Electrochemical measurements were performed with a Zennium IM6 station electrochemical analyzer in a standard three-electrode system (a Pt wire as the counter electrode, Hg/HgO electrode as the reference electrode, and as-prepared working electrode as the working electrode). The OER performances were tested in 1.0 M KOH using the linear sweep voltammetry (LSV) curves with a scan rate of 5 mV s^{-1}. The potentials value was converted to the reversible hydrogen electrode (RHE) according to the following formula: $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.0591 * pH$ and the overpotentials (η) for OER is calculated according to the formula: $\eta = E_{RHE} - 1.23$ V. Electrochemical impedance spectroscopy (EIS) was measured with an AC voltage with 5 mV amplitude in the frequency range from 0.01 Hz to 100 kHz in a solution of 1.0 M KOH.

Computational Methods.

All the first-principles DFT calculations were performed using Vienna *ab initio* simulation package (VASP).[1] The exchange-correlation interactions were treated with the Pedrew-Burke-Ernzerhof (PBE) functional.[2] The interaction between the ionic cores and the valence electrons were described by the projector-augmented wave (PAW) approach.[3] The van der Waals interactions were considered using the Grimme's DFT-D3 method.[4] The structure optimization for atomic coordinates was performed with a 2 × 2 × 1 Monkhorst–Pack *k*-point mesh.[5] A plane-wave basis set with an energy cutoff of 400 eV was used with a 0.01 eV/Å convergence threshold on each atom for force.

All the adsorption models for BA-NiFe-LDHs and NiFe-LDHs were created and cut alone the (0 0 1) direction. To avoid the interaction between two neighboring images, the vacuum space along the *z* axis was set to be 15 Å.

The adsorption energies of OH groups on two substrates were defined as:

$$E_{ads} = E_{system} - E_{substrate} - E_{OH}$$

where E_{system} is the DFT calculated energy of the adsorption system, the $E_{substrate}$ is the energy of the substrate, and E_{OH} means the energy of OH.

Figures and Tables

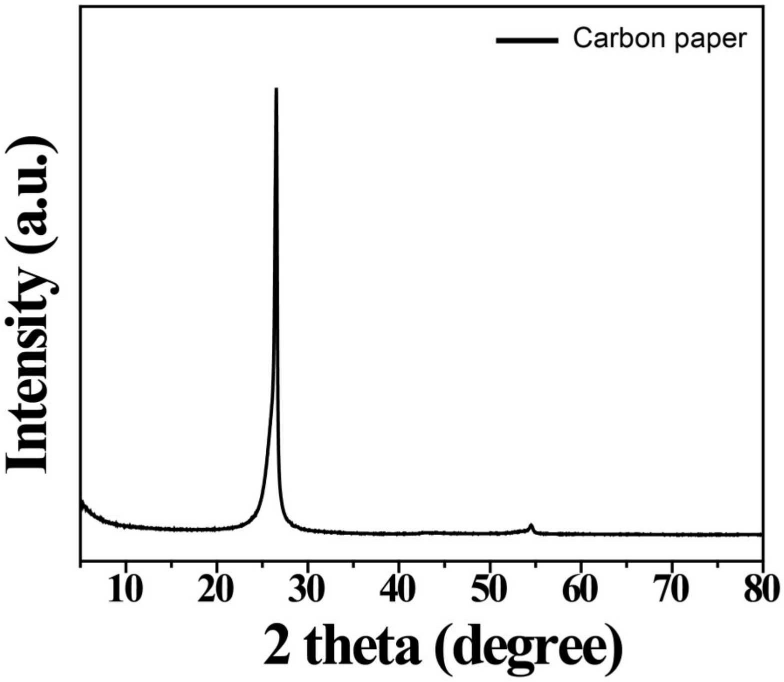

Figure S1 XRD patterns of carbon paper.

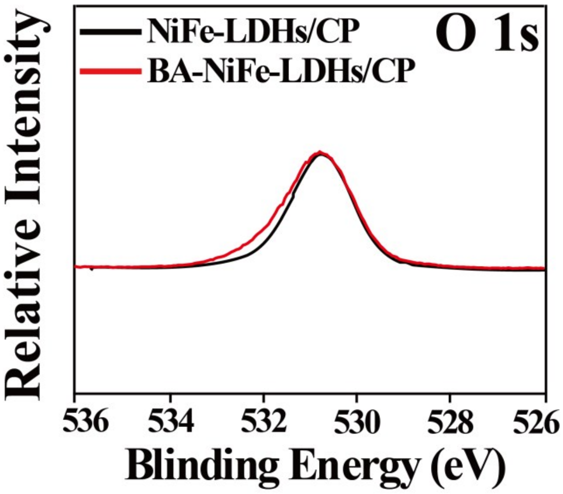

Figure S2 XPS images of O 1s region for NiFe-LDHs and BA-NiFe-LDHs respectively.

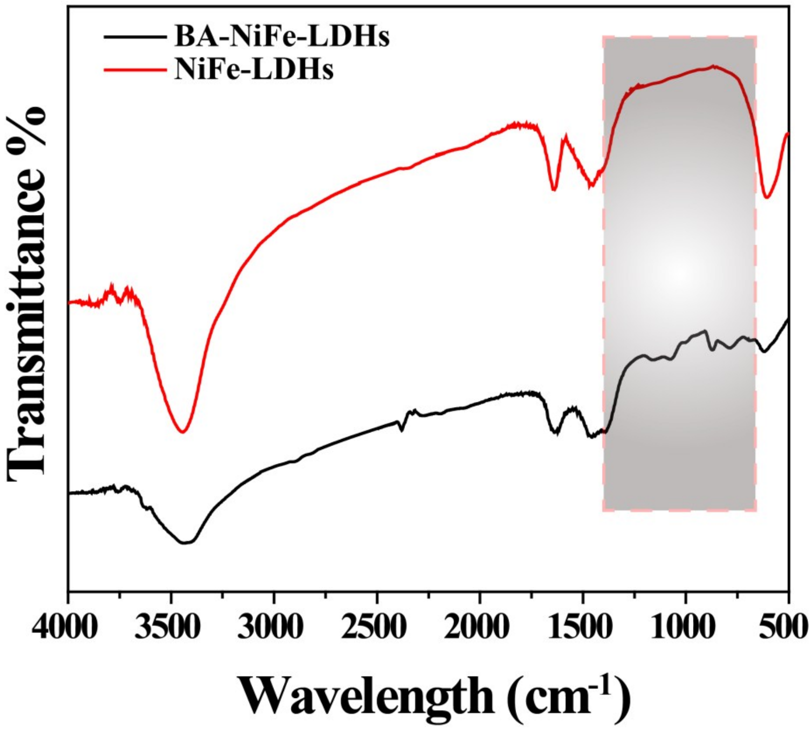

Figure S3 the FT-IR of BA-NiFe-LDHs and NiFe-LDHs.

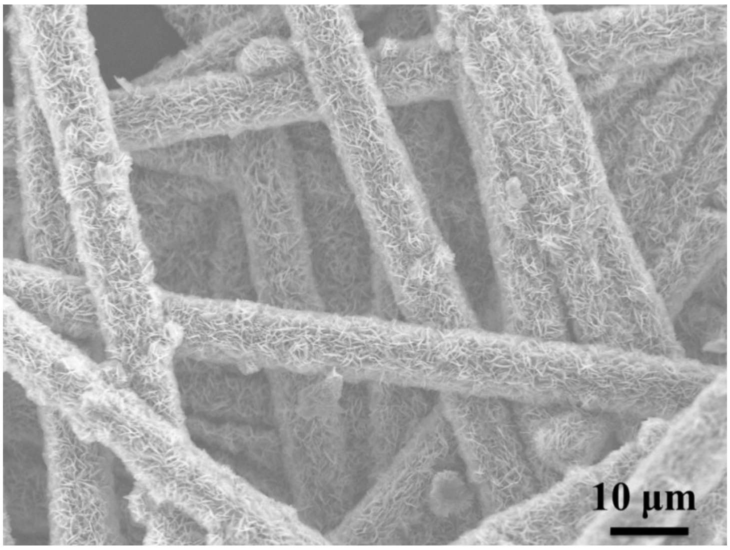

Figure S4 SEM of NiCo-LDHs /CP in low magnification

Figure S5 The digital image of electrolytic cell with electrode**.**

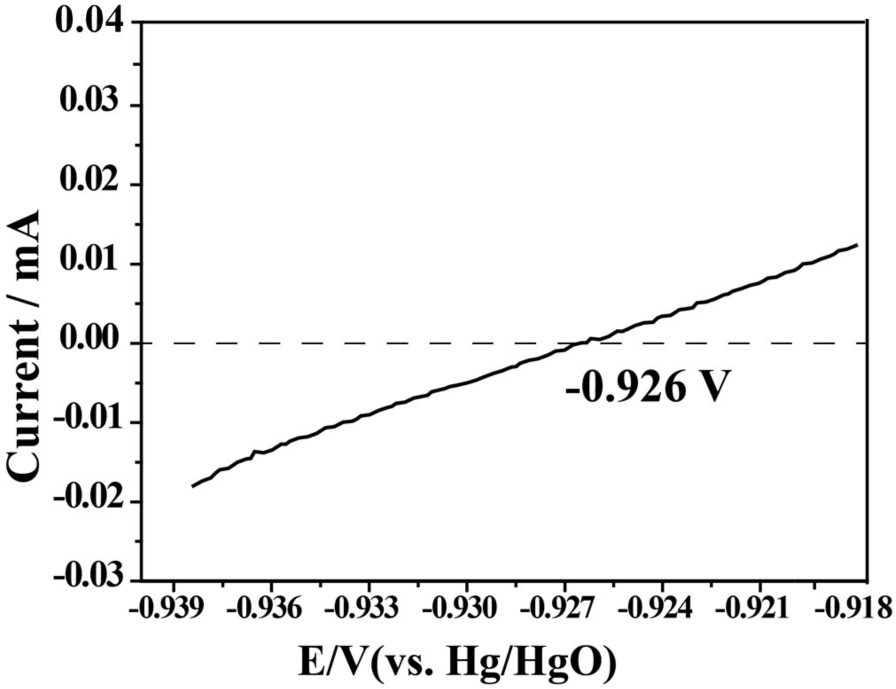

Figure S6 The LSV curves of hydrogen electrode reactions on Pt wire.

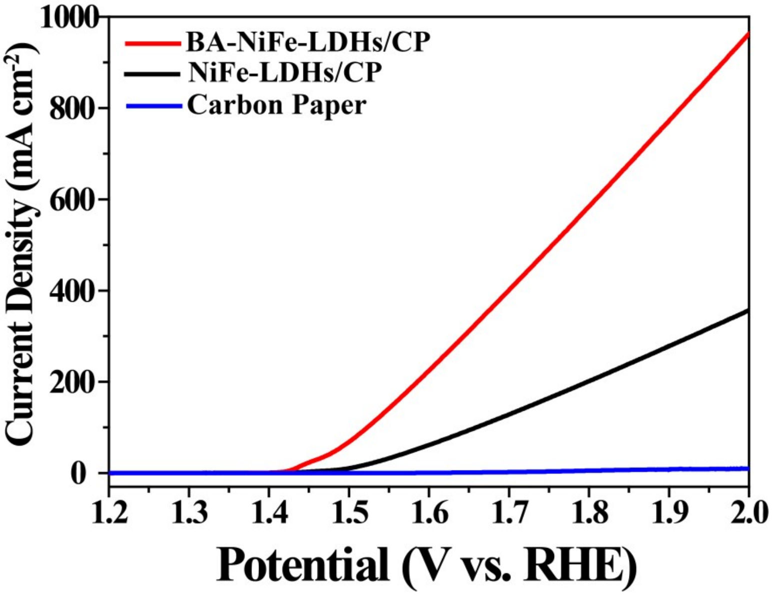

Figure S7 The polarization curves of CP, NiFe-LDHs/CP and BA-NiFe-LDHs/CP for the OER in 1.0 M KOH solution (scan rate 5 mV s^{-1})

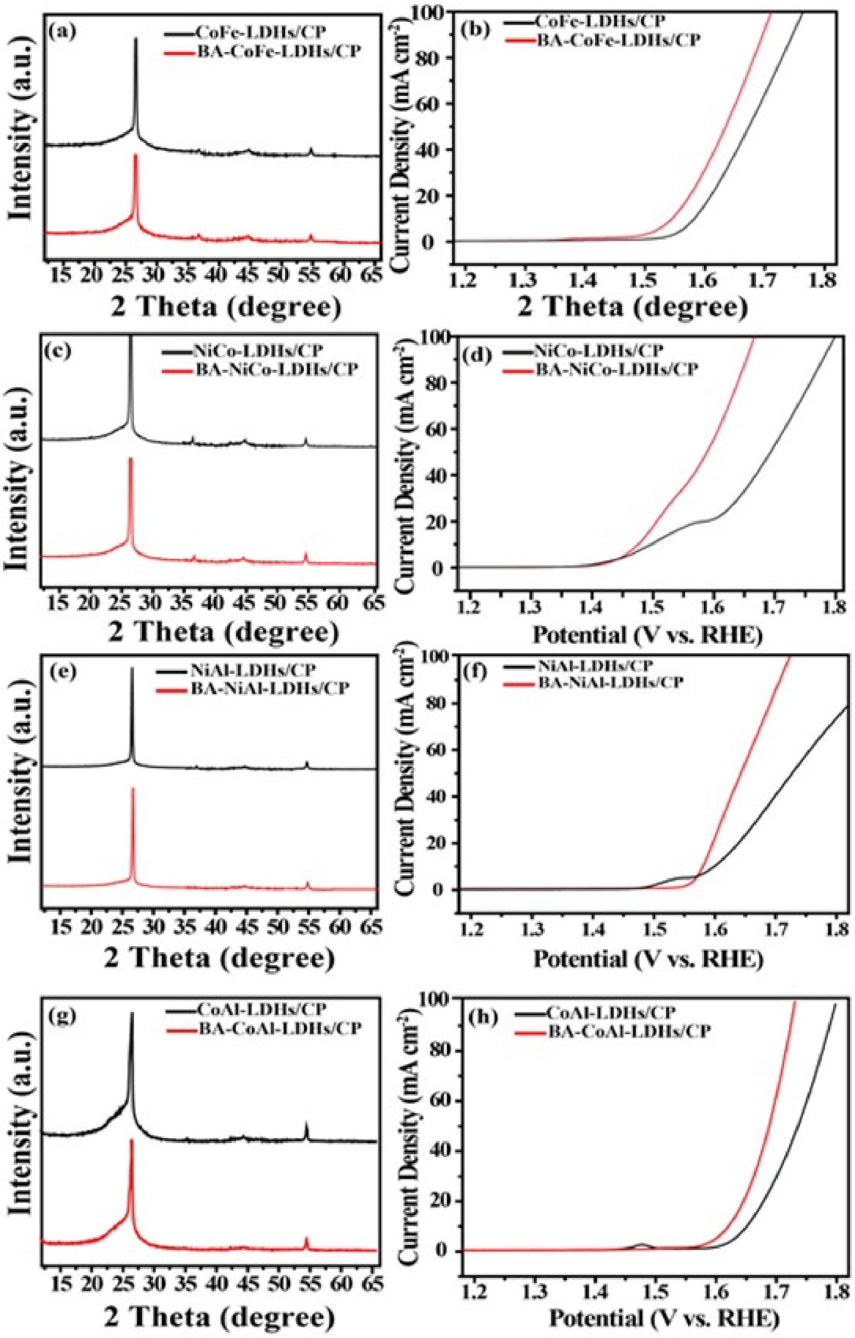

Figure S8 the XRD patterns and the polarization curves for the OER in 1.0 M KOH solution (scan rate 5 mV s^{-1}) of CoFe-LDHs/CP and BA-CoFe-LDHs/CP (a), (b); NiCo-LDHs/CP and BA-NiCo-LDHs/CP (c), (d); NiAl-LDHs/CP and BA-NiAl-LDHs/CP (e), (f) ; CoAl-LDHs/CP and BA-CoAl-LDHs/CP (g), (h) ;respectively.

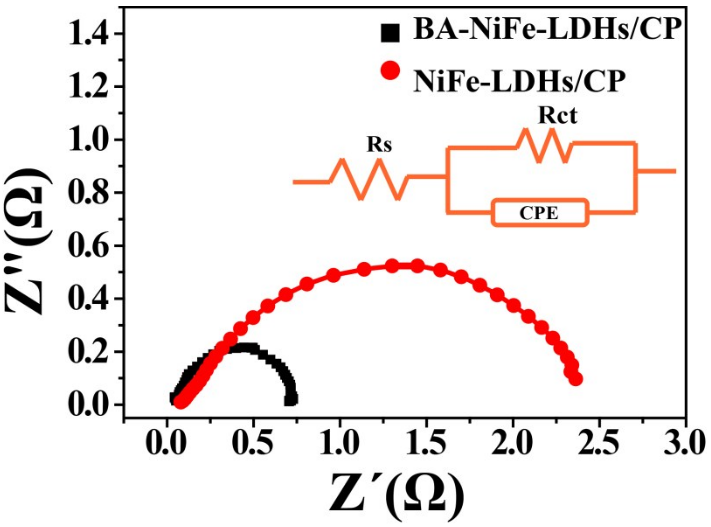

Figure S9 Nyquist plots of BA-NiFe-LDHs/CP and NiFe-LDHs/CP. Inset: an equivalent circuit used for fitting data.

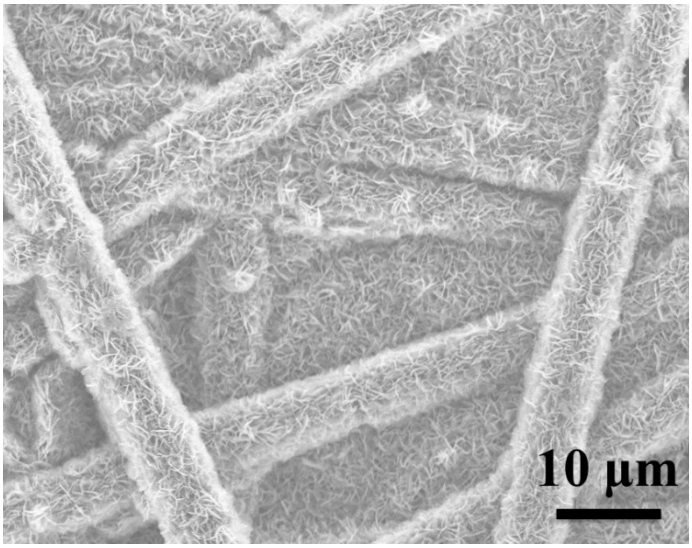

Figure S10 SEM of BA-NiFe-LDHs/CP after stability test in 1.0 M KOH.

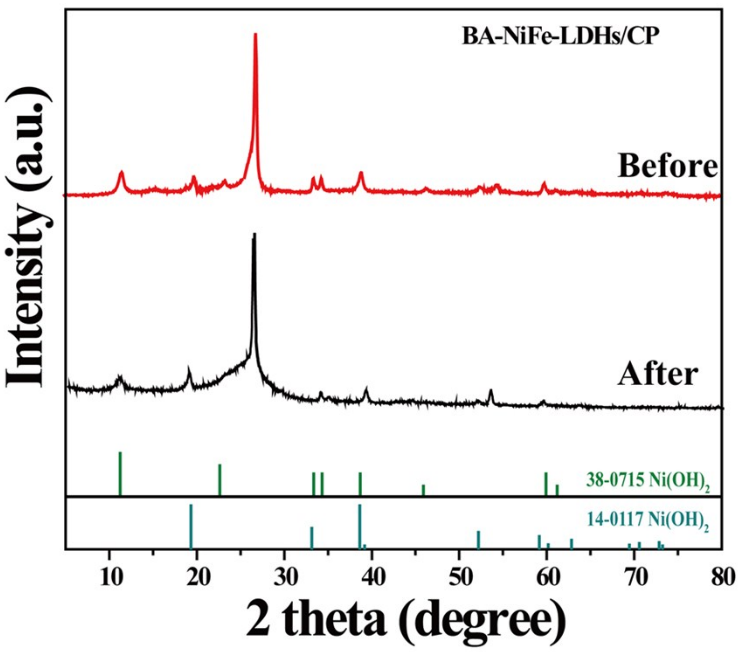

Figure S11 The XRD of the BA-NiFe-LDHs /CPbefore and after durability tests.

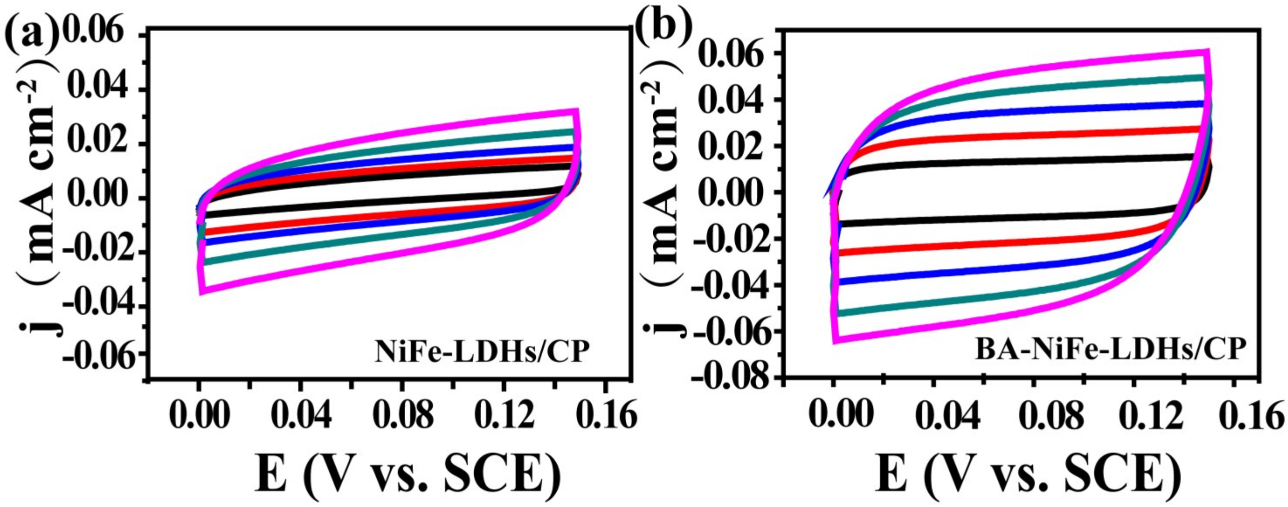

Figure S12 CVs of (a) NiFe-LDHs/CP and (b) BA-NiFe-LDHs/CP in the non-faradaic capacitance current range at scan rates of 20, 40, 60, 80, and 100 mV s^{-1}

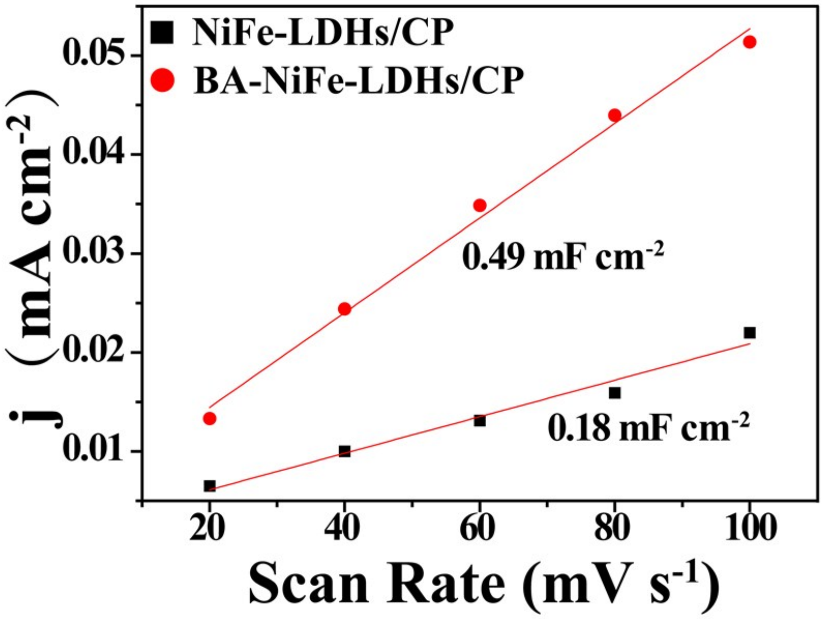

Figure S13 The capacitive currents at 0.075 V vs. SCE as a function of scan rate for electrodes. The determined double-layer capacitance of the system is taken as the average of the absolute value of the slope for the linear fits to the data.

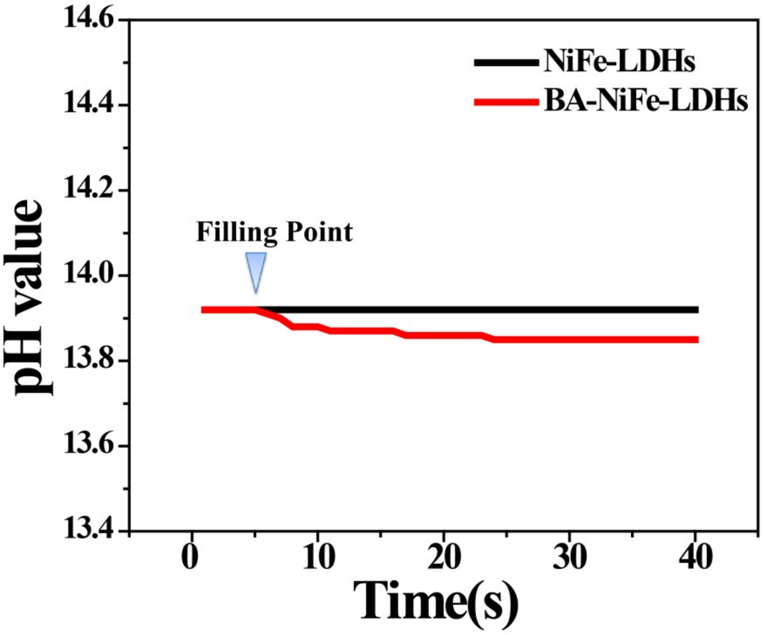

Figure S14 the pH value-time curve with NiFe-LDHs and BA-NiFe-LDHs added in the fifth min (the same weight NiFe-LDHs and BA-NiFe-LDHs powder in the same volume of solution (0.1 mg/ml)) .

Table S1 Comparison of OER performance in alkaline for NiFe-LDHs@B_2O_3/CP with other Ni-based and Co-based OER electrocatalysts

Catalyst	j(mAcm^{-2})	Mass loading (mg/cm^{-2})	η (mV)	Electrolyte	Ref.
BA-NiFe-LDHs /CP	**10**	**0.21**	**203**	**1M KOH**	**This work**
	50	**0.21**	**255**	**1M KOH**	**This work**
	100	**0.21**	**293**	**1M KOH**	**This work**
NiFe-LDHs/Ni Foam	50	-	336	1M KOH	Science, 2014, 345, 1593–1596
NiFeCr LDHs/GC	10	0.20	280	1M KOH	Adv. Energy Mater. 2018, 8, 1703189
CoFe2O4/PANIMWCNTs	10	0.28	314	1M KOH	J. Mater. Chem. A, 2016, 4, 4472-4478.
CoFeMo (oxy)hydroxides/GC	10	0.20	277	1M KOH	Chem. Sci. 2017, 8, 3484
FeOOH/NiFe LDHs@CCH NAs-NF	10	-	220	1M KOH	J. Mater. Chem. A, 2018, 6, 3397
NiFe LDH@CNT/CP	10	0.25	247	1M KOH	J. Am. Chem. Soc. 2013, 135, 8452
$Ni_{0.08}FeAl_{0.91}$-LDHs/NF	20	-	304	1M KOH	Nano Energy 2017, 35, 350.
NiFeMn LDH/CP	20	~0.20	289	1M KOH	Chem. Commun. 2016, 52, 908
Fe-Ni_3S_2/FeNi foil	10	-	282	1M KOH	Small, 2017, 13, 1604161.

(array)					
Fe-CoP/Ti foil (array)	100	1.03	310	1M KOH	Adv. Mater., 2017, 29, 1602441
α-$Co_4Fe(OH)_x$	10	0.28	295	1M KOH	J. Mater. Chem. A, 2017, 5, 1078–84
FexN/graphene/Ni foam	10	4 .0	238	1M KOH	ACS Catal., 2017, 7, 2052-2057.
$NiCo_2S_4$/Ni foam (array)	10	-	260	1M KOH	Adv. Funct. Mater., 2016, 26, 4661- 4672.
H_2O-Plasma-Exfoliated NiFe-LDHs	10	0.41	278	1M KOH	Adv. Mater. 2017, 29, 1701546

Table S2 Geometric values of the electronic elements estimated from electrical Equivalent

Sample	Rs	Rct	CPE
NiFe-LDHs/CP	0.05	0.67	0.04
BA-NiFe-LDHs/CP	0.16	2.11	0.12

Reference

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2. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-3868.
3. P. E. Blochl, Phys. Rev. B, 1994, 50, 17953-17979.
4. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132.
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