Supporting Information

Interface Engineering of NiV-LDH@FeOOH Heterostructures as High-Performance Electrocatalysts for Oxygen Evolution Reaction in Alkaline Conditions

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1. Experimental Section

1.1Materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$), vanadium trichloride (VCl_3), urea ($CO(NH_2)_2$), sodium nitrate ($NaNO_3$), hexahydrate ferric chloride ($FeCl_3·6H_2O$), ruthenium dioxide (RuO_2), and Nafion (5 wt%) were purchased from Shinopharm Chemical Reagent Co., Ltd. Milli-Q ultrapure water was used for all experiments. Nickel foam (NF) were used as the substrate. All chemicals were used as received without further purification.

1.2. Synthesis of NiV-LDH/NF sample

The one-step hydrothermal method was employed to prepare the NiV-LDH/NF. In a typical synthesis process, a piece of Ni foam (1×4 cm^2) was treated in HCl solution (2.0 M) under the ultrasonication for 15 min to remove the surface oxide layer, followed by sonicating in ethanol and deionized water for 15 min, respectively. Then, 0.175 g $Ni(NO_3)_2·6H_2O$, 0.076 g VCl_3, and 0.24 g urea were dissolved in 30 mL deionized water and stirred for 30 min to form homogeneous solution. Afterwards, the precursor solution was transferred into a Teflon-lined stainless steel autoclave (50 mL). Subsequently, the as-cleaned Ni foam (1×4 cm^2) was submerged into the above solution. The autoclave was heated to 130 °C for 12 h in an electric oven. After cooling to room temperature, the as-prepared NiV-LDH/NF was washed with deionized water and ethanol for several times, and then dried in an oven at 60 °C, 12h.

1.3 Synthesis of NiV-LDH@FeOOH/NF sample

For preparing NiV-LDH@FeOOH/NF electrode, 2.547g $NaNO_3$ and 1.217g $FeCl_3·6H_2O$ was dissolved in 30 mL deionized water and kept at 100 °C for 8 min. Then, the as-prepared NiV-LDH/NF was immersed into the pre-heated solution within a certain amount of time. The as-prepared NiV-LDH@FeOOH/NF electrode was washed with ethanol for several times, and then further dried in an oven at 60 °C, 2h. The average mass loading of catalyst on Ni foam is about $3mg·cm^{-2}$.

1.4 Preparation of RuO_2 electrode on Ni foam

A total of 3 mg RuO_2 powder was dispersed in 200 μL deionized water, 200 μL of ethanol and 15 μL of 15wt% Nafion solution through ultrasound for 30 min to form a uniform suspension. Powder ink was loaded onto as-cleaned Ni foam ($1\times1cm^2$), followed with the dry in air at room temperature. The average mass loading of RuO_2 on Ni foam is about $3mg\cdot cm^{-2}$.

1.5 General characterizations

The morphology of as-prepared catalysts was characterized by field-emission scanning electron microscope (FESEM, JSM-7610F, 10 kV),_transmission electron microscope (TEM) (JSM-7610F, 10 kV). The surface characteristics of the samples were investigated using X-ray photoelectron spectroscopy (XPS) measurements (Kratos Axis Ultra DLD spectro meter.)

1.6 Electrochemical Test

All the electrochemical tests were proceeded in a standard three-electrode system by a CHI660E electrochemical station (CH Instruments, Inc., Shanghai) at room temperature. For detail, NiV-LDH/NF, NiV-LDH@FeOOH/NF and bare Ni foam were directly used as the working electrode, a graphite carbon rod was used as counter electrode and a mercury oxide electrode (Hg/HgO) was used as reference electrode. All electrochemical measurements were carried out in 1 M KOH solution. The measured potentials were transformed to reversible hydrogen electrode (RHE) according to the equation: $E_{RHE} = E_{Hg/HgO} + 0.059\times pH + 0.098$. The OER measurements were recorded by linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1}. All polarization curves were corrected by iR losses. The plots of electrochemical impedance spectroscopy (EIS) were measured with 5 mV amplitude in a frequency of 0.01 Hz ~ 100 kHz.

2. Supplementary Figures:

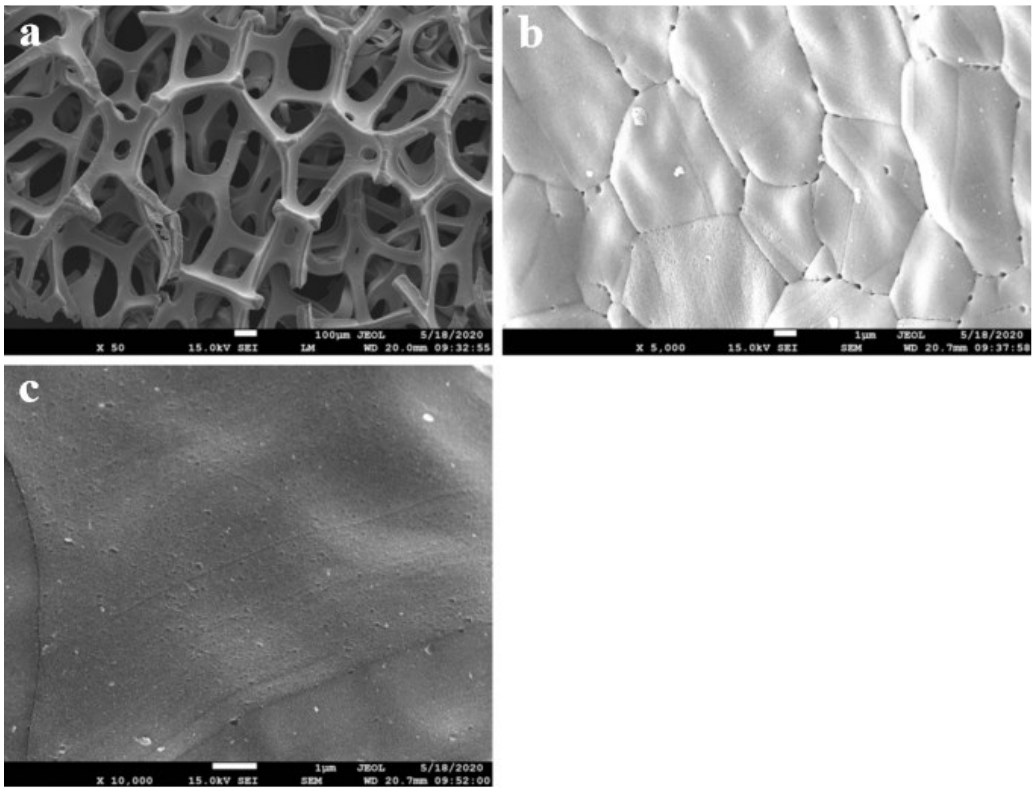

Figure S1. The SEM images of bare NF (a) with low-magnification (b, c) with high-magnification.

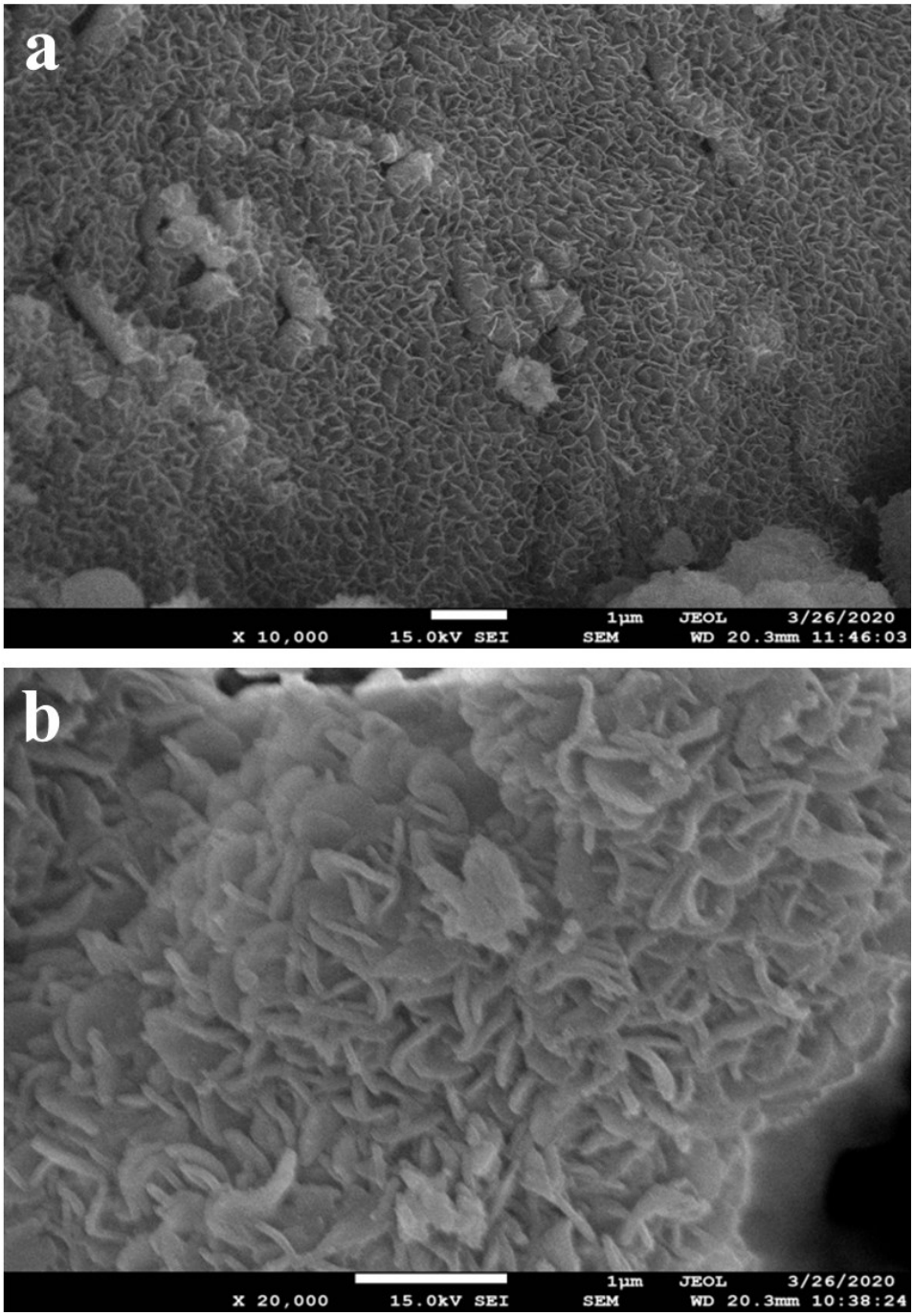

Figure S2. The SEM images of (a) NiV-LDH/NF and (b) NiV-LDH@FeOOH/NF electrodes.

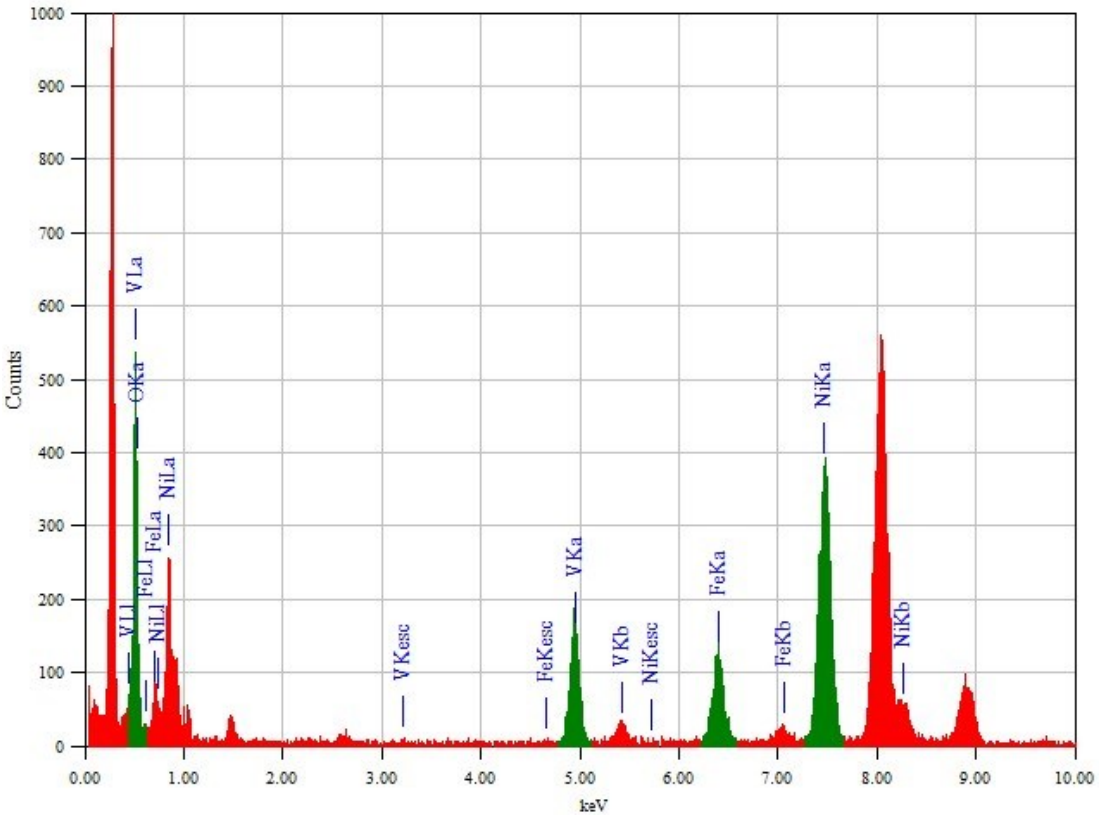

Figure S3. The EDS spectrum of NiV-LDH@FeOOH/NF electrode.

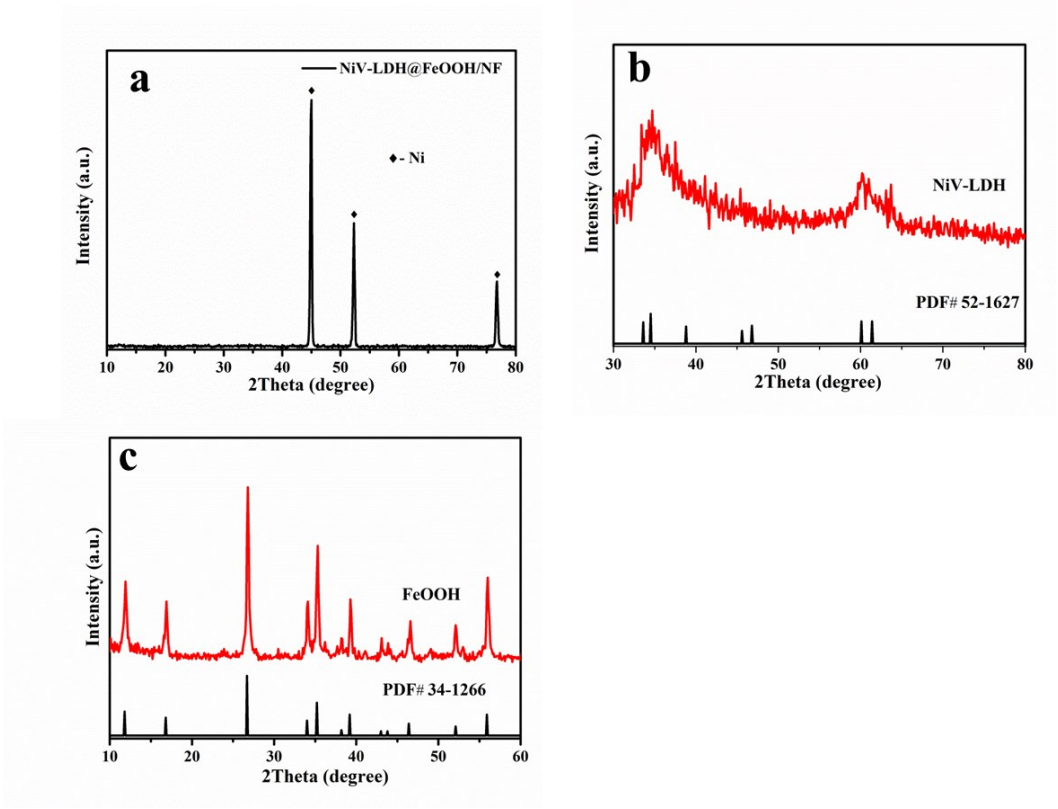

Figure S4. The XRD patterns of (a) NiV-LDH@FeOOH/NF hybrid electrode and NiV-LDH powder (b)and FeOOH powde (c).

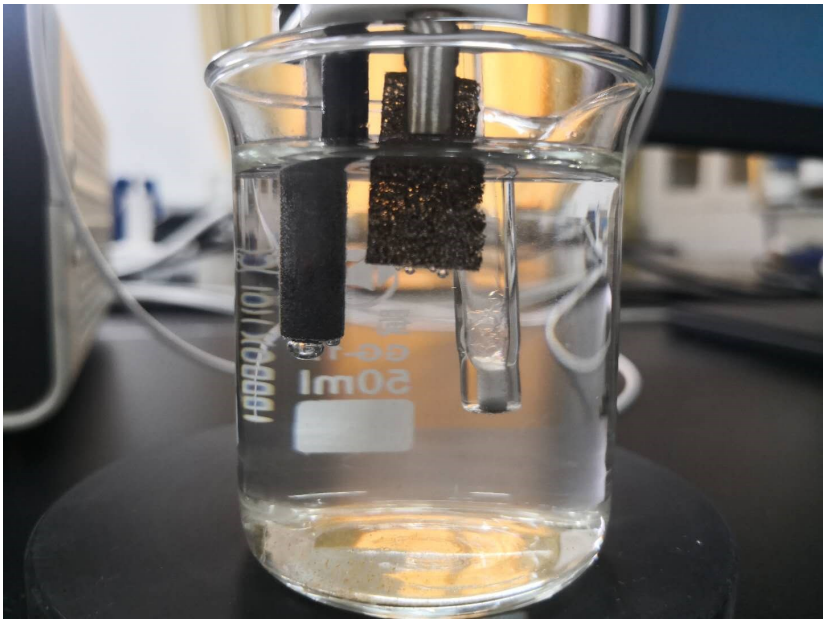

Figure S5. The photo of three electrode test system. NiV-LDH@FeOOH/NF was directly used as the working electrode, a graphite carbon rod was used as counter electrode and a mercury oxide electrode (Hg/HgO) was used as reference electrode.

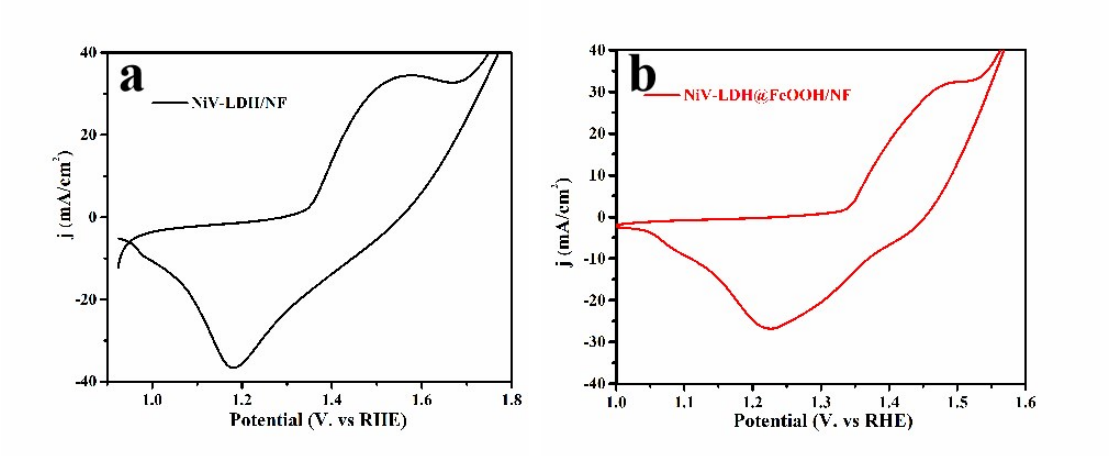

Figure S6. CV curve for NiV-LDH/NF (a) and NiV-LDH@FeOOH/NF (b) hybrid electrode.

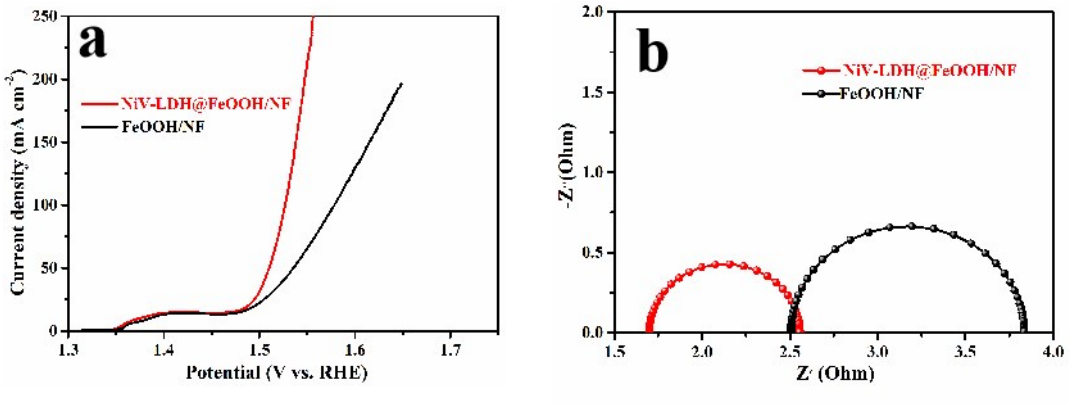

Figure S7. (a) The iR-corrected linear sweep voltammograms and (b) the EIS of the FeOOH/NF and NiV-LDH@FeOOH/NF hybrid electrode.

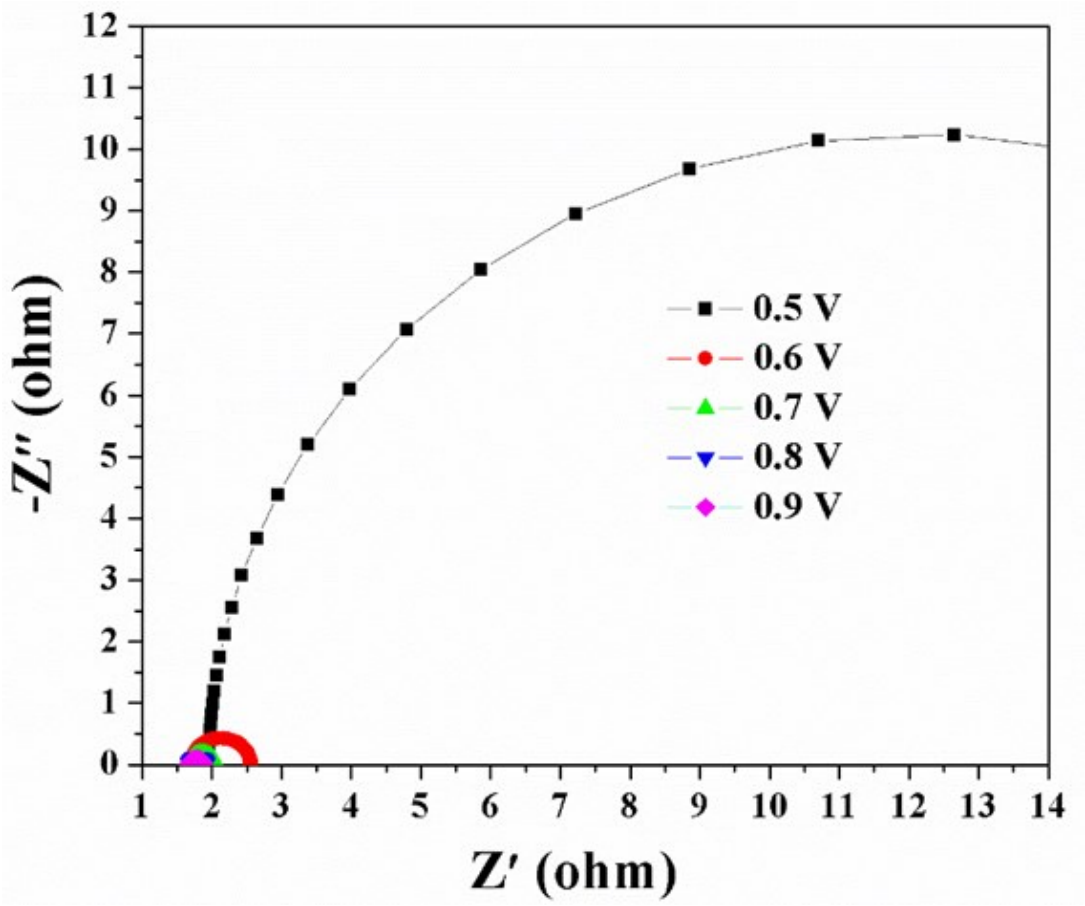

Figure S8. The EIS of NiV-LDH@FeOOH/NF electrode under different test conditions.

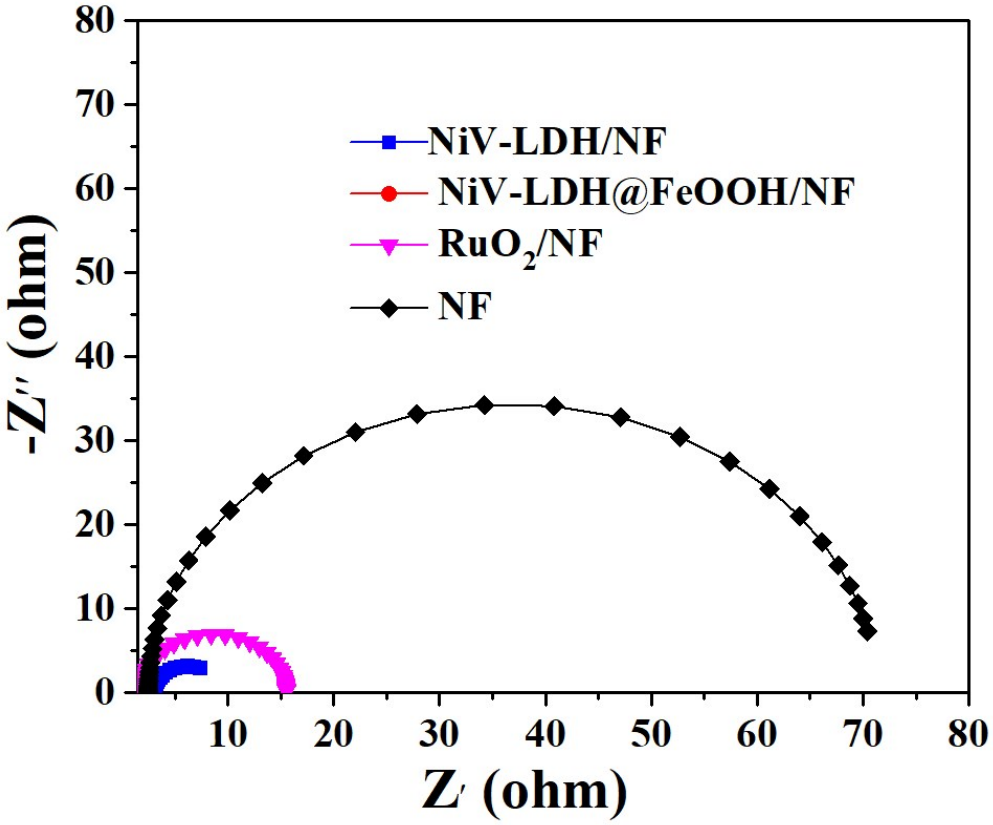

Figure S9. The EIS of the bare Ni foam, NiV-LDH/NF, NiV-LDH@FeOOH/NF and commercialized RuO_2 electrodes measured in O_2 saturated 1.0 M KOH solution (pH = 14).

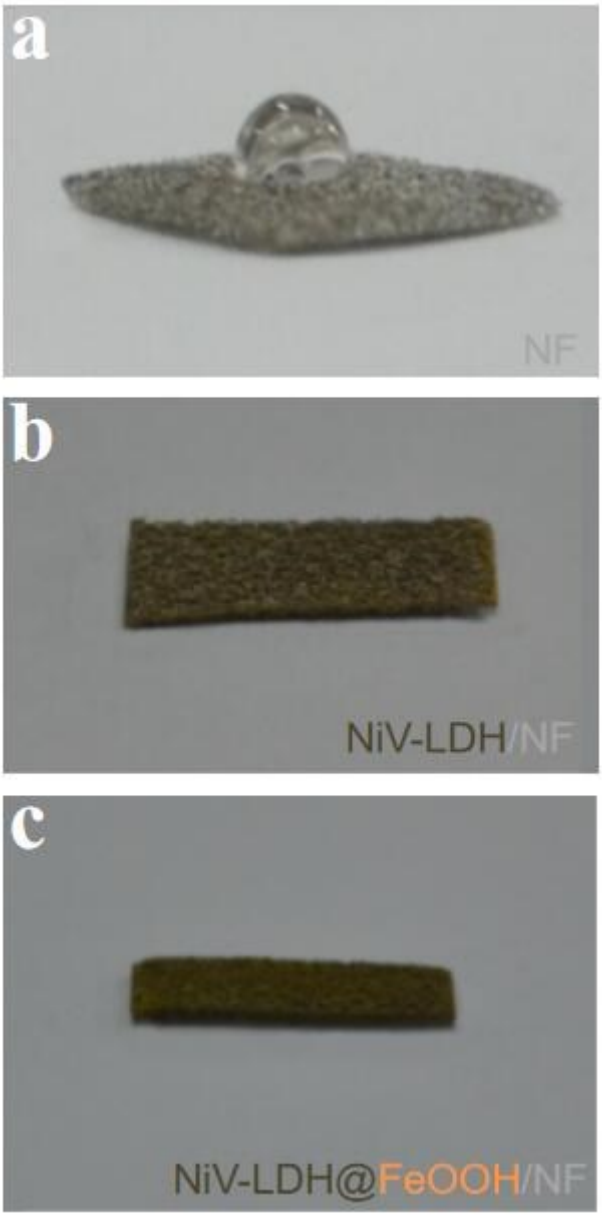

Figure S10. The direct hydrophilic and hydrophobic test.

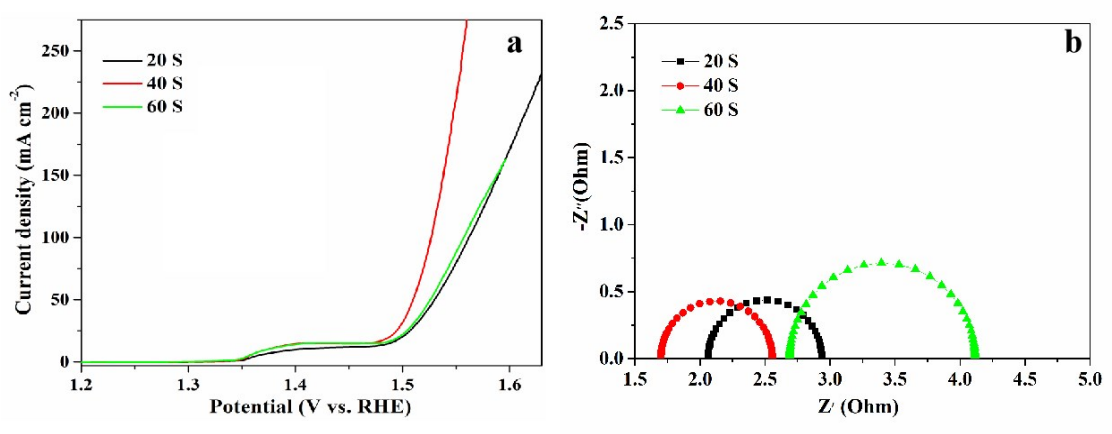

Figure S11. (a) The iR-corrected linear sweep voltammograms, (b) The EIS of the NiV-LDH@FeOOH/NF electrodes with different synthesis times measured in O_2 saturated 1.0 M KOH solution (pH = 14).

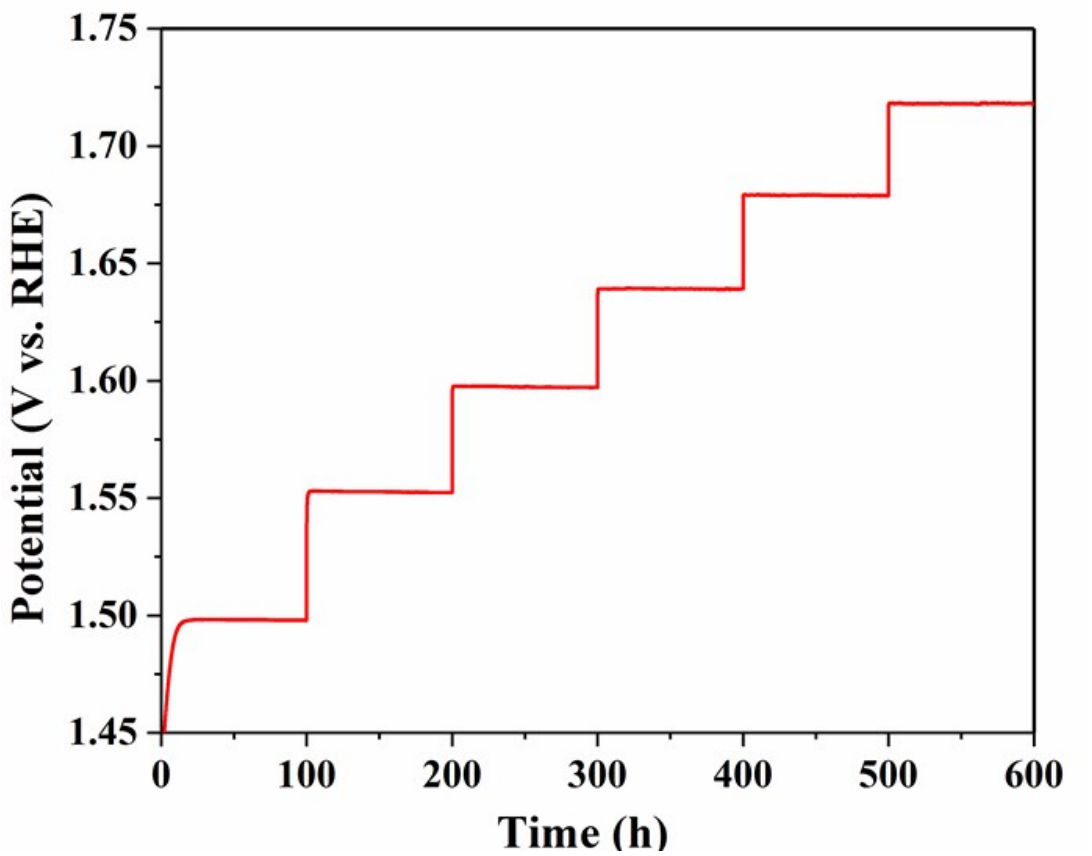

Figure S12. The multi-potential steps of NiV-LDH@FeOOH/NF electrodes.

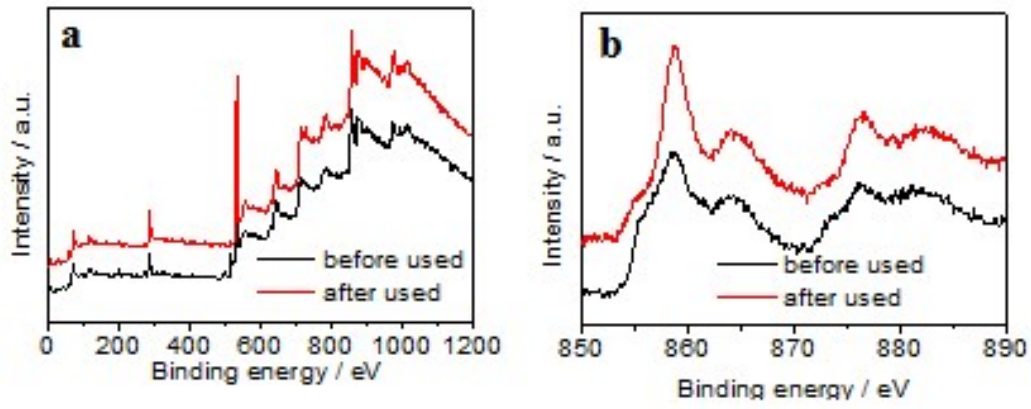

Figure S13. (a) XPS Spectrum and (b) high-resolution Ni 2p XPS spectrum of NiV-LDH@FeOOH/NF hybrid electrode before and after OER test.

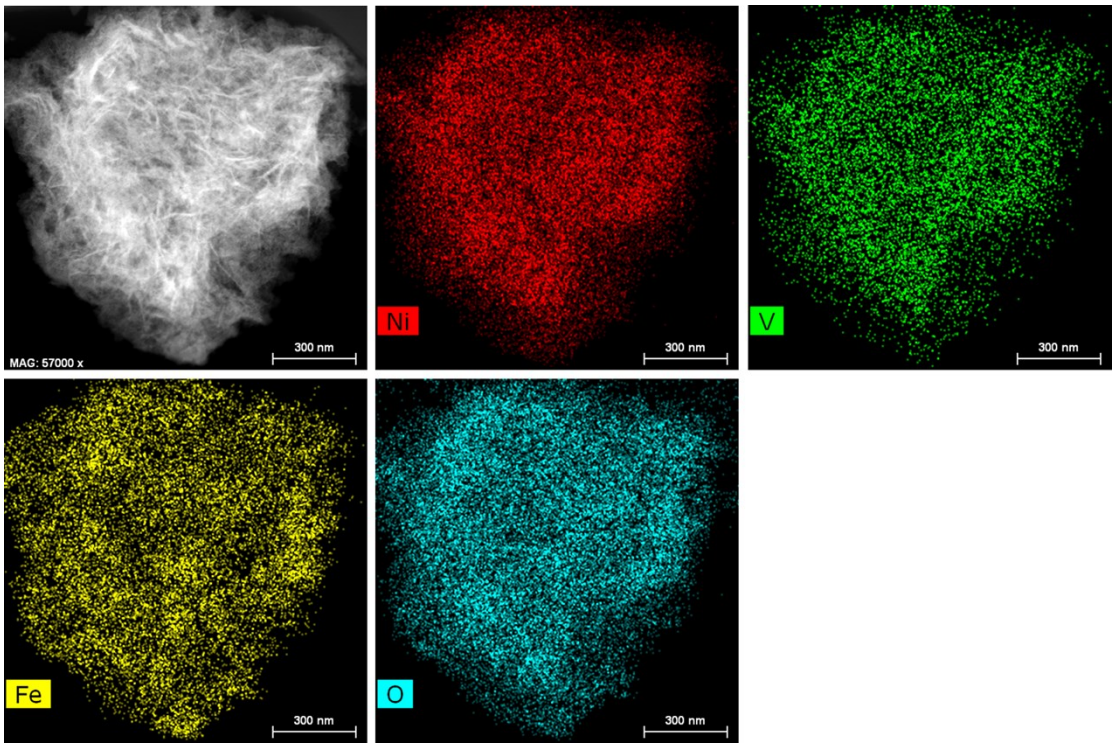

Figure S14. STEM image and corresponding EDX elemental mapping images for NiV-LDH@FeOOH/NF hybrid electrode after OER test.

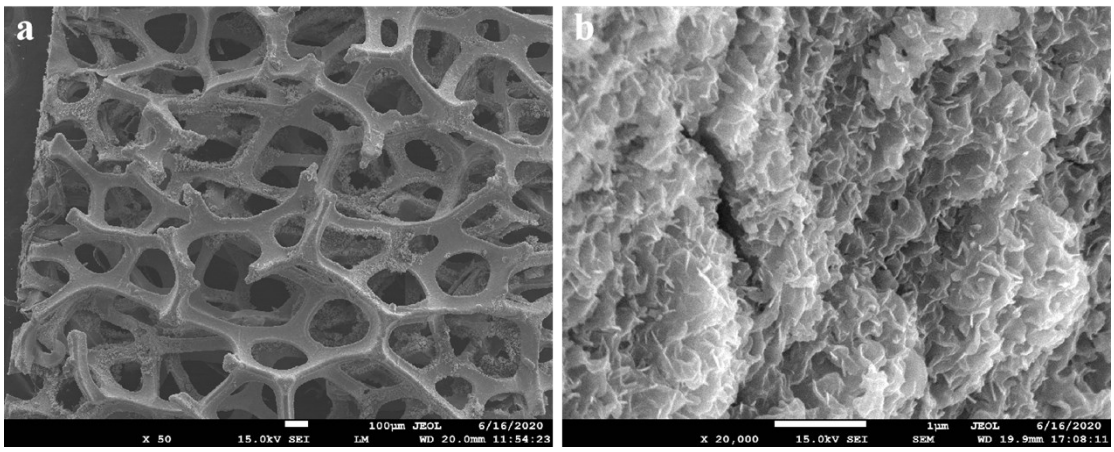

Figure S15. SEM image for NiV-LDH@FeOOH/NF hybrid electrode after OER test.

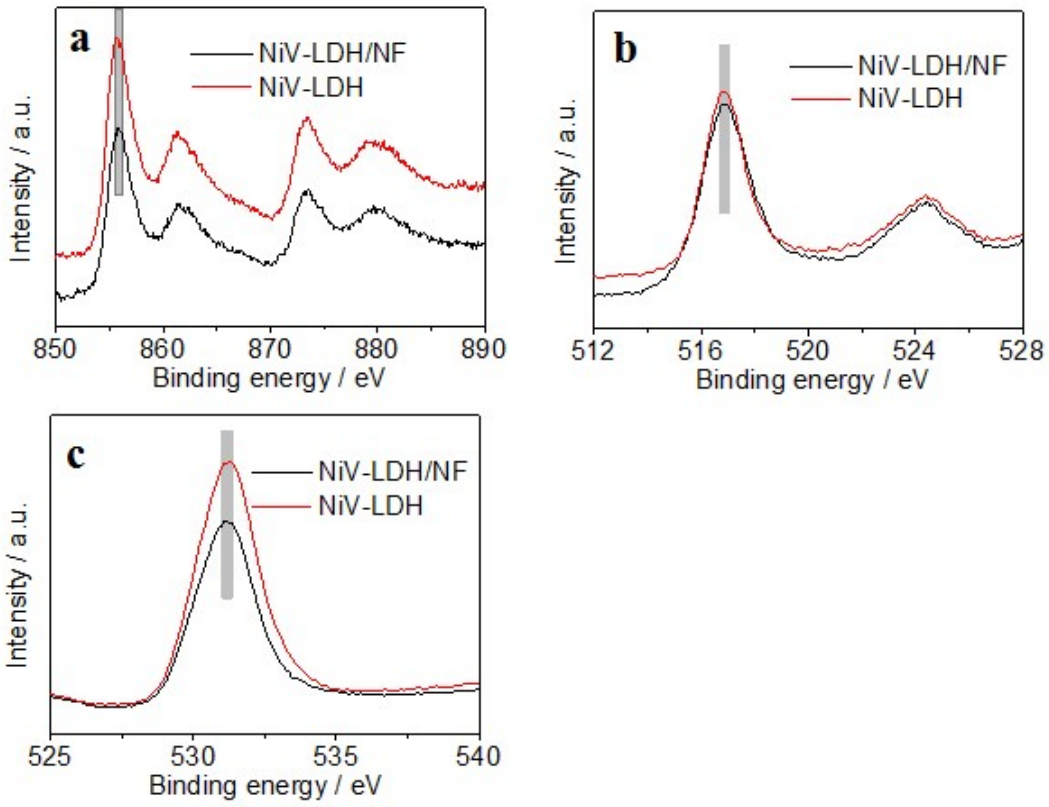

Figure S16. High-resolution (a) Ni 2p (b) V 2p and (c) O 1s XPS spectra of NiV-LDH/NF and NiV-LDH powder samples.

Supplementary Table S1 Comparison of the performance NiV-LDH@FeOOH/NF with other reference samples.

Samples	Onset potential / V vs. RHE	Over potential at j=100mA cm^{-2} (V vs. RHE)
NiV-LDH@FeOOH/NF	**1.49**	**297**
NiV-LDH/NF	**1.58**	**472**
RuO_2	**1.55**	**467**
Ni foam	**1.60**	**528**

Supplementary Table S2 Comparison of the OER activity of NiV-LDH@FeOOH/NF with other reported non-noble metal-based electrocatalysts in basic media (1 M KOH).

Catalysts	Loading/ mg cm^{-2}	Current density (mA/cm^2)	Overpotential (mV)	Reference
NiV-LDH@FeOOH/NF	3.0	100	297	**This work**
(Co-Pi)	0.285	100	420	1. Chem. Commun., 2020,56, 4575-4578
$NiCo_2O_4$	0.27	10	320	2. J. Mater. Chem. A, 2020,8, 8554-8565
NiCoP-rGO	0.15	10	270	3. Adv. Funct. Mater. 2016, 26, 6785-6796
NiFe LDH/graphene	2	100	325	4. Adv. Mater. 2017, 29, 1700017-1700024.
Ni-Fe-OH@Ni_3S_2/NF	22.2	100	300	5.Adv. Mater. 2017, 29, 1700404-17004010.
FeOOH/Co/FeOOH	0.5	100	308	6.Angew.Chem. Int. Ed. 2016, 55, 3694-3698.
$W_{0.5}Co_{0.4}Fe_{0.1}$/NF	-----	100	310	7.Angew. Chem. Int. Ed. 2017, 56, 4502-4506.
NiCo LDH/CFP	0.8	100	370	8.Carbon 2016, 110, 1-7.
NiFe LDH/NF	------	100	460	9.Science 2014, 345,1593-1596.
$Ni(OH)_2/Ni_3S_2$/NF	------	100	490	10.J. Mater. Chem. A. 2018, 6,6938-6946.
$NiCo_2S_4$ NW/NF	------	100	470	11.Adv. Funct. Mater. 2016, 26, 4661-4672.
Co_1Mn_1CH/NF	5.6	100	349	12.J. Am. Chem. Soc. 2017, 139, 8320-8328.
Hollow $NiCo_2O_4$	1	100	360	13.Angew. Chem. Int. Ed. 2016, 55, 6290-6294.
Ni_3S_2@NiV-LDH	0.71	100	320	14. Nanoscale, 2019,11, 8855-8863.
Co-CoO_x /CN	2.1	50	360	15. J. Am. Chem. Soc. 2015, 137, 2688-2694.
NiFe-LDH/$NiCo_2O_4$/NF	4.9	50	290	16.ACS Appl. Mater. Inter. 2017, 9, 1488-1495
Au-Ir	0.02	10	245	17.Nature Communications，2020，DOI:10.1038/s41467-020-15391-w
NiFeMn-LDH	0.102	10	310	18.Chem. Commun., 2016, 52, 908-911.
Ni_3FeAl_x–LDH/NF	0.5	20	304	19. Nano Energy 2017, 35, 350-357.
$Co_2Mo_3O_8$	0.14	10	241	20. Angew. Chem. Int. Ed. 2020, DOI: 10.1002/anie.202004533

Supplementary Table S3 Comparison of the EIS parameter of NiV-LDH@FeOOH/NF with other reference samples.

Samples	Rct/ ohm	RΩ/ ohm
NiV-LDH@FeOOH/NF	**0.85**	**1.699**
NiV-LDH/NF	**4.3**	**2.966**
RuO_2	**13.8**	**1.696**
Ni foam	**67.9**	**2.469**

4. Notes and references

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