

Supplementary materials

N/P-doped NiFeV oxide nanosheets with oxygen vacancy as Efficient Electrocatalysts for Oxygen Evolution Reactions

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Experimental section

Material preparation

Nickel nitrate hexahydrate (99 %), ferrous sulfate heptahydrate (99 %), urea (≥ 99 %), Ammonium fluoride (≥ 98 %), KOH (≥ 90 %), commercial IrO₂ (99 %) and Pt/C catalyst (20 wt%) were purchased from Shanghai Titan Technology Co., Ltd. Silver nitrate (≥ 99.8 %) was purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion solution (5 %) was purchased from Beijing Jingke Science Instrument Co., Ltd. Nick foam (thickness 1.7 mm) was purchased from Kunshan Longshengbao Electronic Materials Co., Ltd. All chemicals were used as received without further purification.

Synthesis of NiFeV-LDH/NF, NiFeVO /NF

Before used as based material, the NiO layer on the surface of NF need to be cleared. Thus, Ni foam (1.5 cm \times 3 cm) was soaked in HCl solution (3 M) for 15 min and washed with deionized water and absolute ethanol for three times. The 0.5 mmol of Fe(NO₃)₃·9H₂O, VCl₃ and 10 mmol of CO(NH₂)₂ were dissolved in the solvents of 36 mL of deionized water by stirring for 0.5 hours in a N₂ atmosphere. Afterward, the solution was transferred to a 50 mL Teflon-lined stainless steel autoclave for 3 hours with the cleaned Ni foam. Then, the autoclave was maintained at 120 °C for 8 h. After the reaction, the product covered on Ni foam was washed with deionized water and absolute ethanol for three times and air dried at 60 °C for 4 h to obtain NiFeV-LDH electrocatalyst.

As control samples, undoped NiFe LDH and undoped VOOH are also synthesized at the same conditions. For the synthesis of N/P-VO and N/P -Ni-Fe₂O₃, the feeding ratio of V: Fe is changed to 1:0, 0:1 and other parameters remain consistent.

For the synthesis of NiFeVO, the as-obtained NiFeV-LDH precursor was placed in the reaction chamber of a plasma-enhanced chemical vapor deposition (PECVD) system, and N₂/PH₃ plasma (N₂/PH₃: 20/50 sccm) treatment was performed at 100 W with a base pressure of 4 Pa. The N₂/PH₃ plasma process was maintained for 30 min.

Physicochemical characterization

X-ray diffraction (XRD) patterns were measured using a X'Pert PRO MPD diffractometer (Holland Panalytical) with Cu K α radiation. Raman spectroscopy with 532 nm excitation (Labram HR800 Evo) was adopted to confirm the structure and molecular structure. The sample morphology and composition were characterized by using a field-emission scanning electron microscope (FE-SEM, FEI, Quanta FEG 450) equipped with an energy dispersive X-ray spectrometer (EDS). Transmission electron microscopy (TEM) analysis was performed using a TECNAI F30 (FEI) microscope operated at 300 kV. For TEM observation, the catalyst nanosheets were dispersed in absolute ethanol by ultrasonic treatment for 30 min, and then dropped onto TEM grids. X-ray photoelectron spectroscopy (XPS) was performed by using ESCALAB250Xi (Thermo scientific) with a Mg K α X-ray source. All binding energies were calibrated via referencing to C 1s binding energy (284.6 eV).

Electrochemical measurements

The electrochemical measurements were conducted in a three-electrode cell with a Gamry interface 1010E GAMRY electrochemical workstation, using the prepared self-supporting catalysts as working electrode, a mercury oxide electrode (Hg/HgO) as reference electrode, Pt mesh as counter electrode for OER. The electrolyte is 1 M KOH solution. All the potentials were corrected with iR-compensation. Electrochemical impedance spectroscopy (EIS) was conducted from 100 kHz to 0.1 Hz.

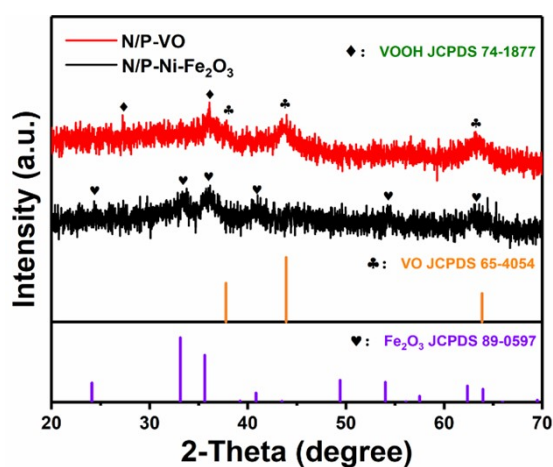


Fig. S1 XRD patterns of N/P-VO and N/P -Ni-Fe₂O₃.

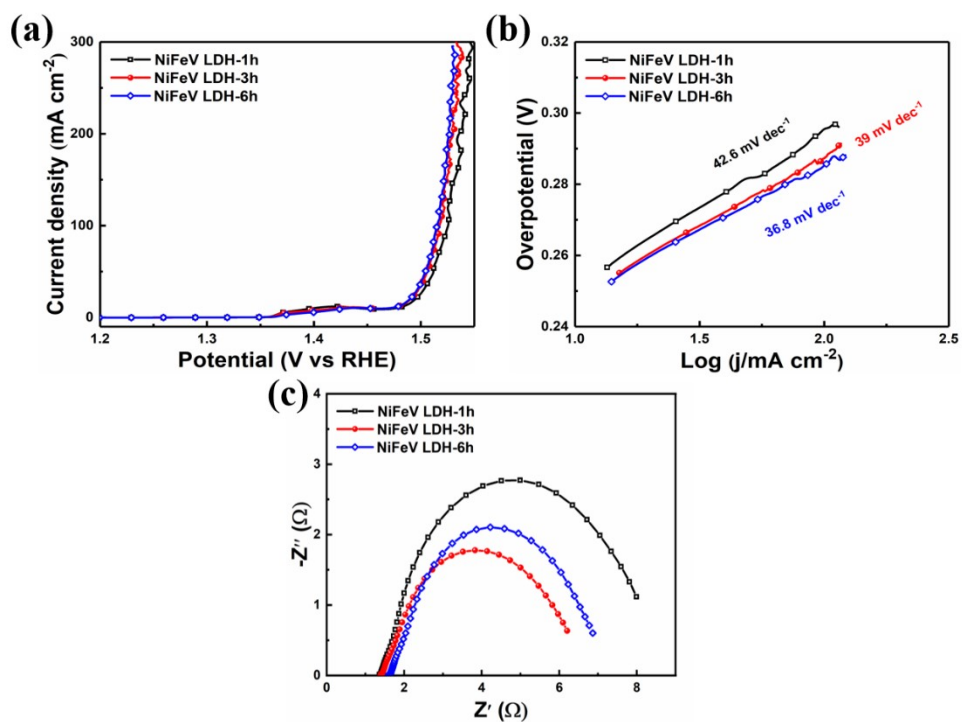


Fig. S2 OER electrocatalytic performance of the NiFeV LDH for hydrothermal reaction time. (a) LSV curve (with iR correction) at 2 mV s^{-1} , (b) Tafel plot, (c) Nyquist plot.

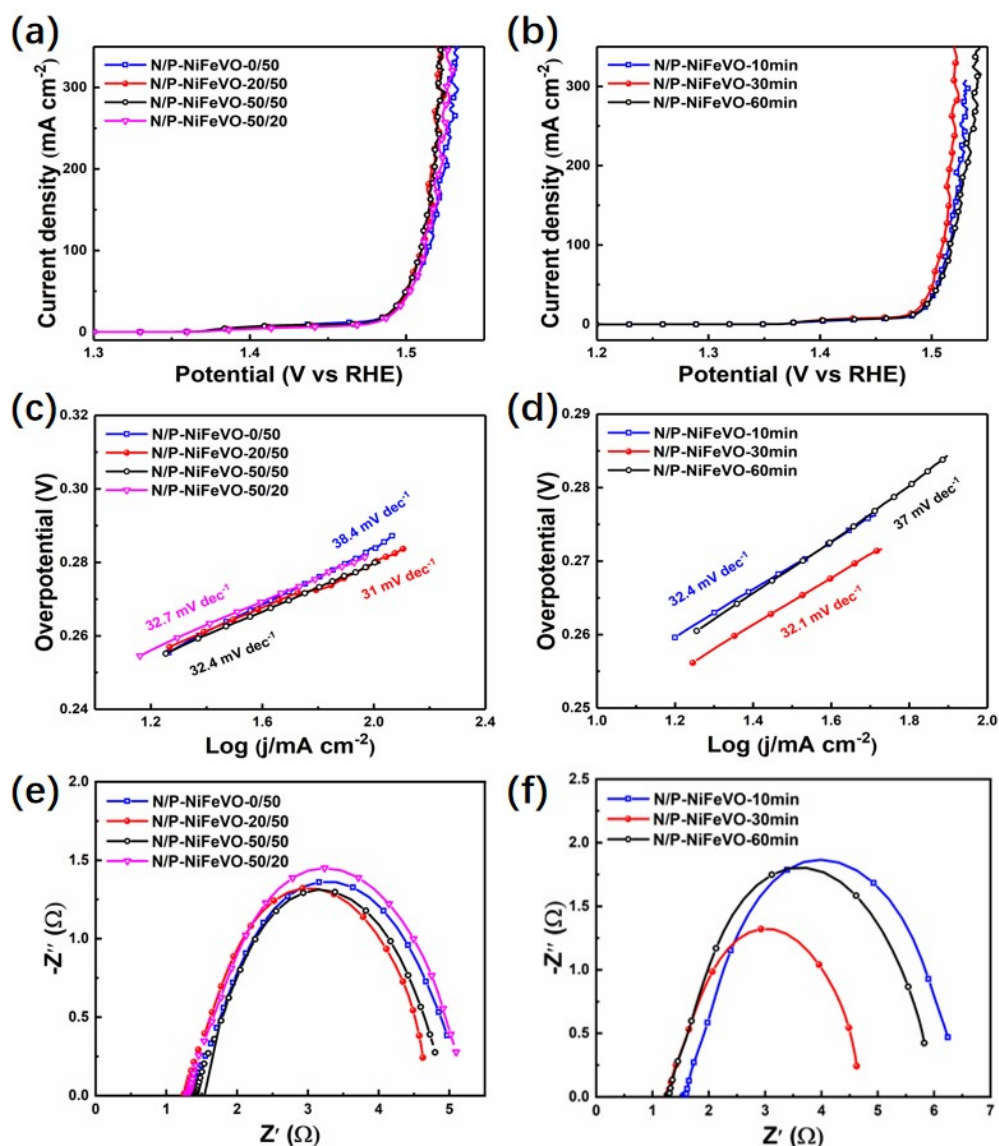


Fig. S3 OER electrocatalytic performance of the N/P-NiFeVO for plasma (N₂:PH₃ for 0:50, 20:50, 50:50, 50:20 sccm) treatment (a) LSV curve (with iR correction) at 2 mV s⁻¹, (b) Tafel plot, (c) Nyquist plot. OER electrocatalytic performance of the N/P-NiFeVO for plasma treatment for 10 min, 30 min and 60 min. (d) LSV curve (with iR correction) at 2 mV s⁻¹, (e) Tafel plot, (f) Nyquist plot.

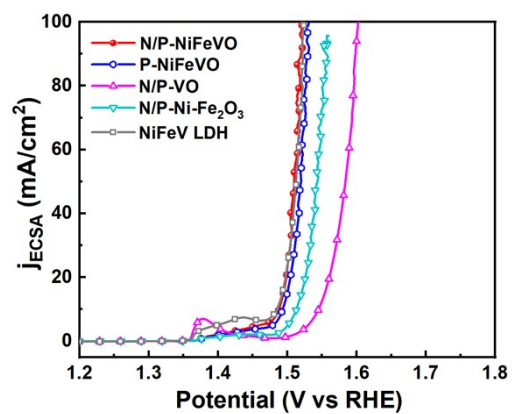


Fig. S4 C_{dl} -normalized polarization curves.

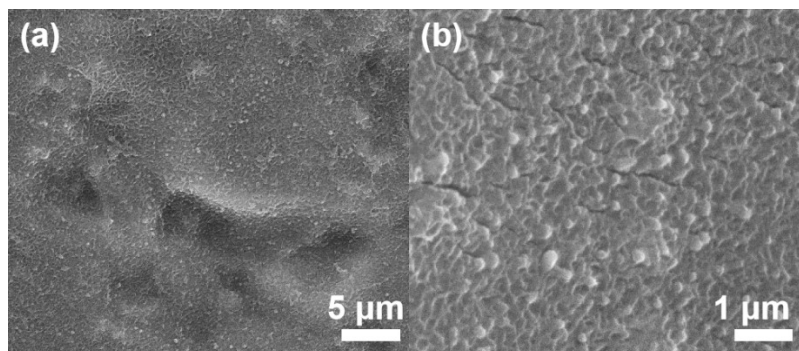


Fig. S5 The SEM images of post-OER catalyst.

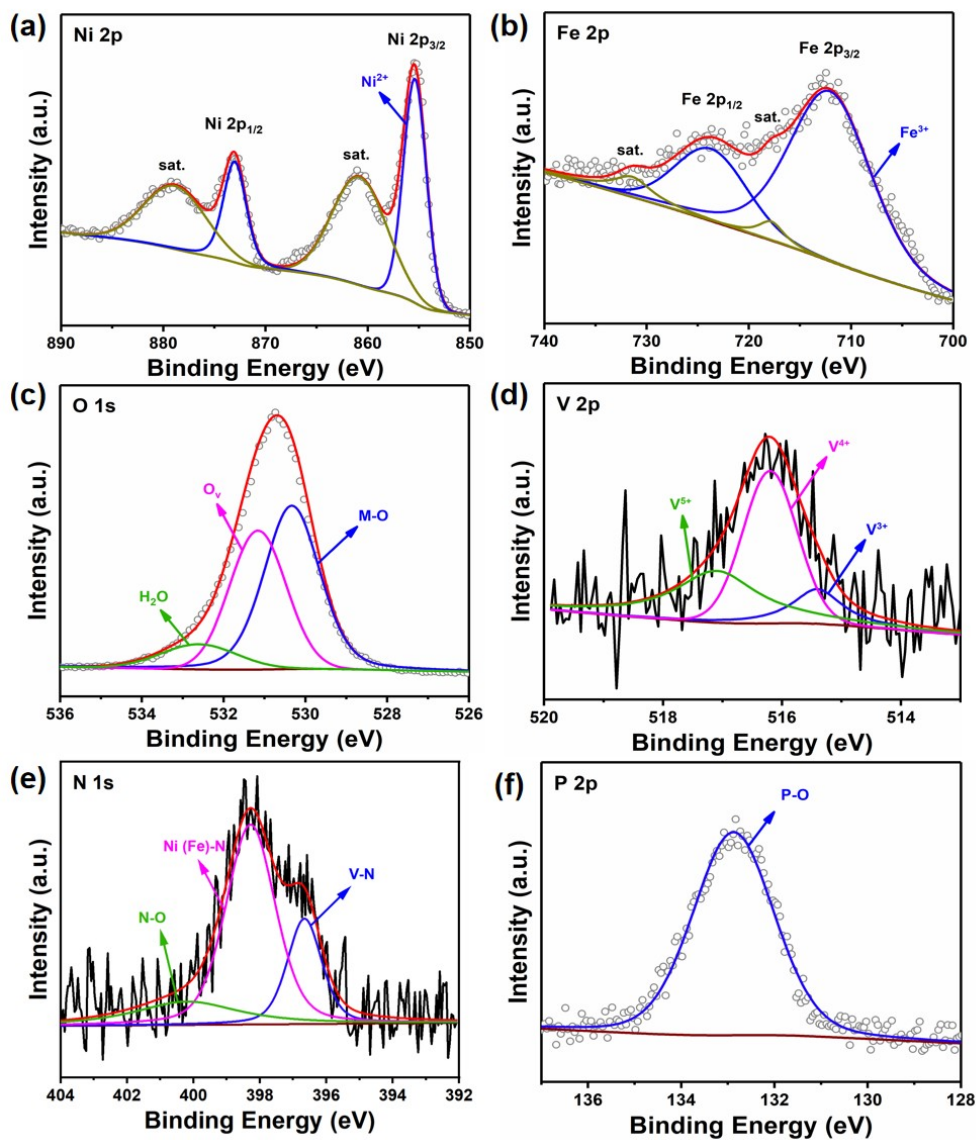


Fig. S6 XPS spectra of the N/P-NiFeVO catalyst after OER stability test: (a) Ni 2p, (b) Fe 2p, (c) O 1s, (d) V 2p, (e) N 1s and (f) P 2p.

Table S1 Comparison of OER performance of N/P-NiFeVO with other reported heterostructure electrocatalysts.

Catalyst	Electrolyte	η_{100} (mV)	Reference
Ag@Co(OH) _x	1 M KOH	440	[1]
Ni ₂ P-NiFe ₂ O ₄	1 M KOH	305	[2]
FeNiZn/FeNi ₃ @NiFe	1 M KOH	258	[3]
Ag@NiCo-LDH/NF	1 M KOH	324	[4]
NiFe ₂ O ₄ /NiFe LDH	1 M KOH	275	[5]
H-CoS _x @NiFe LDH/NF	1 M KOH	312	[6]
NiFe LDH/NiS	1 M KOH	277	[7]
Ag/NCMO/NF	1 M KOH	299	[8]
N-NiVFeP/NFF	1 M KOH	~320	[9]
N/P-NiFeVO	1 M KOH	273	This work

Table S2 Comparison of recent electrocatalysts for overall water splitting.

Catalyst	Electrolyte	Cell voltage	Reference
Ni ₂ P-Fe ₂ P/NF	1 M KOH	1.561 V @ 10 mA cm ⁻²	[10]
NiFe-LDH@NiCoP/NF	1 M KOH	1.57 V @ 10 mA cm ⁻²	[11]
NMS NFs	1 M KOH	1.6 V @ 10 mA cm ⁻²	[12]
δ -FeOOH NSs/NF	1 M KOH	1.62 V @ 10 mA cm ⁻²	[13]
Se-(NiCo)S/OH	1 M KOH	1.6 V @ 10 mA cm ⁻²	[14]
N/P-NiFeVO	1 M KOH	1.56 V @ 100 mA cm⁻²	This work

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