Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Inserting ultrafine NiO nanoparticles into amorphous NiP sheets by in-situ phase reconstruction for high-stability of the HER catalysts

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Physical characterizations

The X-ray diffraction (XRD) was done on Shimadzu XD-3A Instrument, which was fitted with filtered Cu-Kα radiation (λ = 0.15418 nm) and operated at 30 mA and 40 kV. The 2θ scan rate for XRD analysis was set at 5° min^{-1}. JEOL (JEM-2000 FX) microscope operated at 200 kV was used for transmission electron microscopy (TEM), high angle annular dark field scanning transmission electron microscopy (STEM) images and selected area electron diffraction (SAED) analysis. X-ray photoelectron spectra (XPS) were carried out on VG Escalab210 Spectrometer with Mg 300 W X-ray source.

Electrochemical measurements

A three-electrode electrochemical cell linked with a potentiostat/galvanostat (CHI 760, CH Instruments) was applied to evaluate the HER and electrocatalytic properties. In this three-electrode cell, Hg/HgO and graphite rod were used as reference electrode (RE) and counter electrode (CE) respectively. 1.0 M KOH aqueous solution was used as electrolyte for all electrocatalytic testing. Electrochemical impedance spectroscopy (EIS) spectra were measured at corresponding HER electrode potentials from 0.01 to 1,000,000 Hz with an amplitude of 5 mV. Linear sweep voltammetry (LSV) was done with a scan rate of 5 mV s^{-1}. All potentials stated in this work were normalized to the reversible hydrogen electrode (RHE). *iR* compensation was applied for all electrochemical experiments.

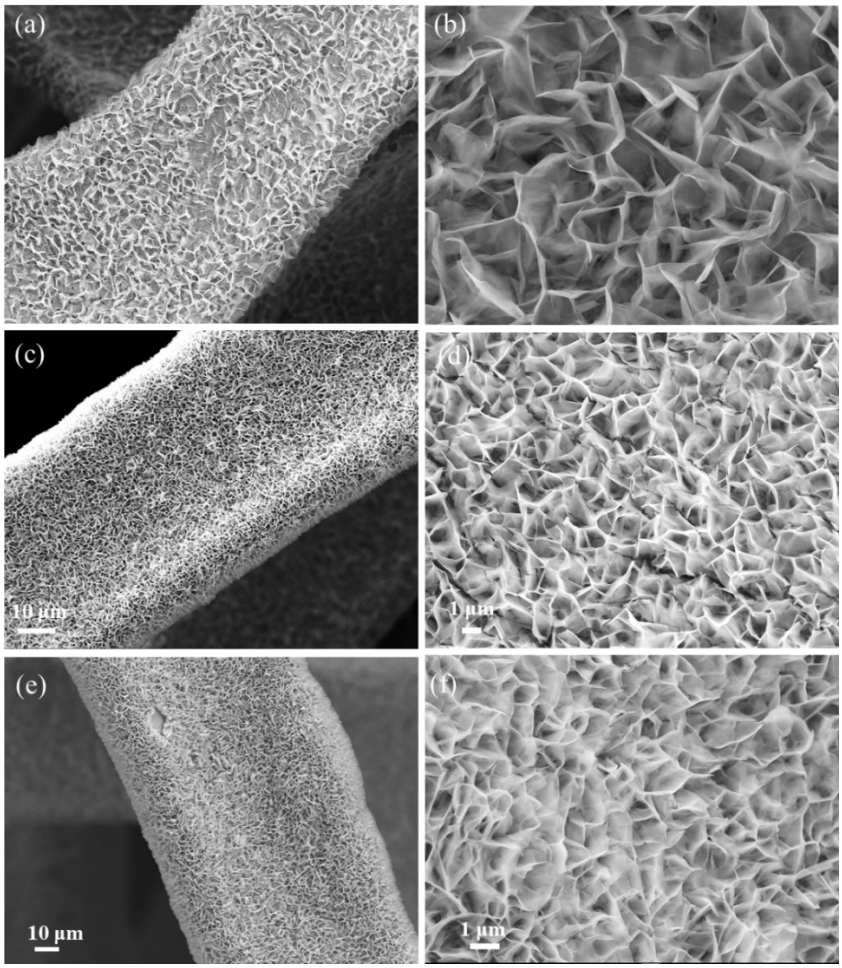

Figure S1. (a-b) SEM images of $Ni(OH)_2$/NF. (c-d) SEM images of Ni_2P/NF. (e-f) SEM images of NiO@NiP/NF.

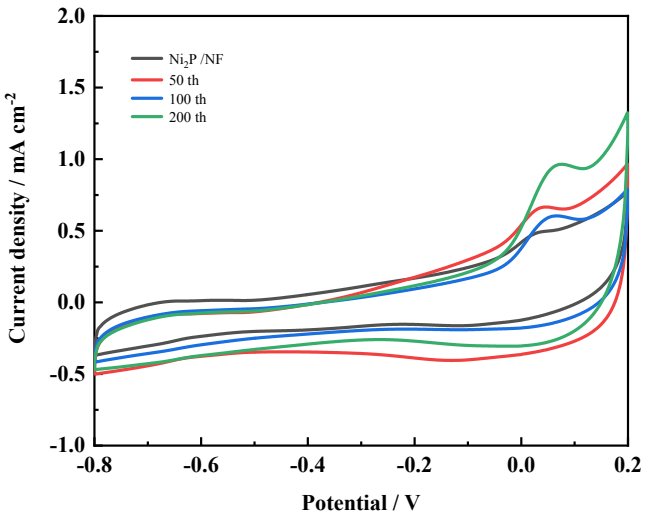

Figure S2. Cyclic voltammetry test of Ni_2P/NF,CV-50th, CV-100th, CV-200th.

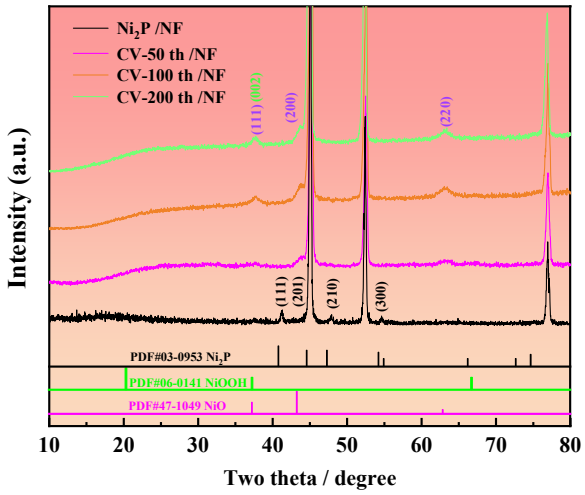

Figure S3. Comparison of XRD test of Ni_2P/NF after 50, 100, 200 CVs.

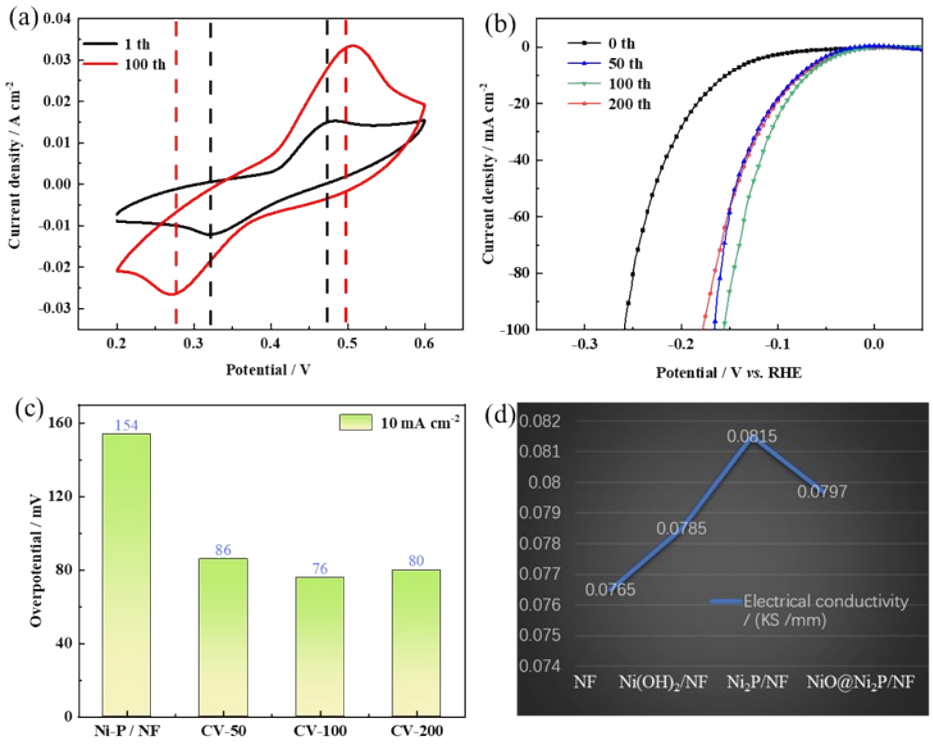

Figure S4. (a) Comparison of cyclic voltammetry curves before and after oxidation; (b) HER LSVs in 1.0 M KOH at a scan rate of 5 mV s^{-1} of different number of cycles; (c) corresponding overpotential at 10 mA cm^{-2} of different number of cycles; (d) Electrical conductivity of NF, $Ni(OH)_2$/NF, Ni_2P/NF, and NiO@NiP/NF.

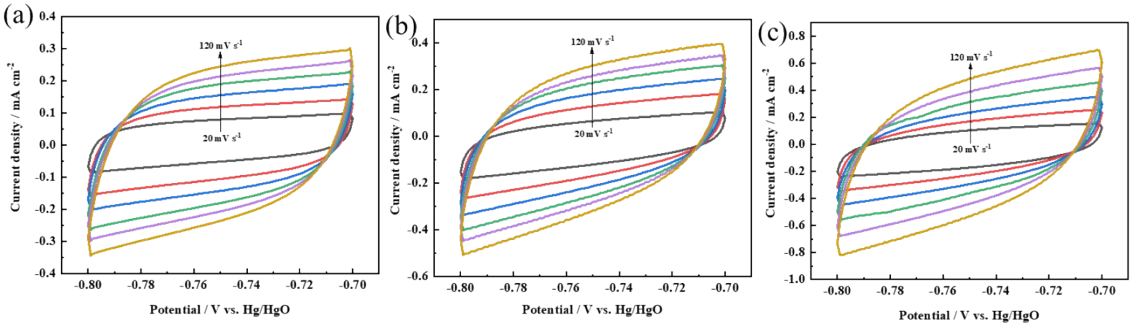

Figure S5. Cyclic voltammetry plots of (a) NF; (b) Ni_2P/NF; (c) NiO@NiP/NF for HER.

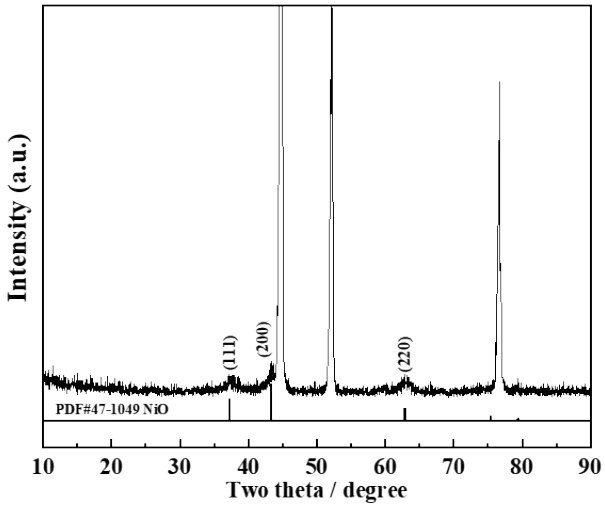

Figure S6. XRD pattern of NiO@NiP/NF after stability test.

Table S1. Element content of the samples based on XPS results.

Sample type	P element content(%)	Ni element content(%)
Ni_2P / NF	15.98	22.45
NiO@NiP/NF	0.9	21.52

Table S2. Comparison Table of Phosphide Sulfide Synthesized by Solid-gas Method.

Phases of nickel phosphide	Morphology	Overpotential (mV) 10 mA cm^{-2}	Stability (h)	Reference.
Ni_2P/Ni/NF	Porous Urchin-Like	98	20	[1]
$NiCo_2P_x$/CNTs	Nanosheets	47	48	[2]
$(Fe_{0.1}Ni_{0.9})_2P(O)$/NF	Nanosheets	87	40	[3]
Ni_5P_4	Disklike	140	24	[4]
CoS_x/Ni_3S_2@NF	Nanosheets	139	20	[5]
S-CoP@NF	Nanoparticles	109	20	[6]
Ni_3S_2/NF	Films	131	14	[7]
NiS/NF	Microsphere	158	20	[8]
NiO@NiP/NF	**Nanosheets**	**76**	**120**	**This work**

Table S3. Performance comparison table with the latest literature.

Phases of nickel phosphide	Morphology	Overpotential (mV) 10 mA cm^{-2}	Stability (h)	Reference
Fe-NiFe-LDH@NF	layered double	239	40	[9]
NiCo LDH@NiCoP/NF	Nanosheets	112	24	[10]
Ni@Ni-M@C	Nanosheets	123	25	[11]
Ni_3S_4/Ni/$Ni(OH)_2$	Irregular clump	54	15	[12]
FeNi–OH	Nanosheets	82	25	[13]
Ni-Cu-P@Ni-Cu	dendrite-like	70	10	[14]
NiCoP-WO_x	nanocoral reef	49	60	[15]
NiFe@Ni(Cu)/NF	3D hierarchical	36	20	[16]
NiO@NiP/NF	Nanosheets	76	120	This work

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