Supplementary Information

Ordered porous Ni *in-situ* decorated by a thin-layer amorphous nickel-phosphorus via mild electrochemical-phosphorization for enhancing the hydrogen evolution performance

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1. Experimental section

Preparation of p-Ni and Ni-P/p-Ni: The porous Ni, named as p-Ni, was constructed by electrodepositing a porous Ni network on a clean Ni substrate (50.0 mm×10.0 mm×0.25 mm) using a facile hydrogen bubble dynamic template route. It was performed according to our previous method (RSC Adv., 2014, 4, 20521) in an electrolyte of 2.0 mol L^{-1} NH_4Cl and 0.1 mol L^{-1} $NiCl_2$ with a Ni foil as a counter electrode at a cathode current density of 2.0 A cm^{-2} for 100 s. Afterwards, the p-Ni acted as a working electrode in a three-electrode system and was electrochemical-phosphorization at -1.2 V versus Ag/AgCl for 2 h in an electrolyte containing NaH_2PO_2 to generate amorphous Ni-P on the surface of p-Ni.

Preparation of Ni_2P/p-Ni: The p-Ni and NaH_2PO_2 were placed in alumina boats and heated at 300 °C for 2 h in an Ar atmosphere to obtain traditional Ni_2P/p-Ni.

2. Characterizations and electrochemical measurements

The surface morphology and property of the catalysts were analyzed by X-ray diffraction (XRD-6000, Shimadzu), field-emission scanning electron microscopy (SEM, JSM-7800, Japan), and X-ray photoelectron spectroscopy (XPS, PE PHI-5400), respectively. Electrochemical measurements were conducted in a three-electrode system with an Electrochemical Workstation (Autolab electrochemical analyzer, PGSTAT302 N, Metrohm) and a CHI-660E electrochemical analyzer (CHI, Shanghai, China).

The electrode area of the working electrode is 1 cm^2. A graphite sheet in parallel orientation to the working electrode was used as the counter electrode and a mercuric oxide electrode (Hg/HgO) as the reference electrode. The catalytic performance of the prepared electrodes toward HER was systematically investigated in a 1.0 mol L^{-1} KOH electrolyte. All potentials mentioned in this work were converted to the values with reference to a reversible hydrogen electrode (RHE). Double layer capacitance of the electrodes was tested by cyclic voltammetry at scan rate from 5 to 100 mV s^{-1}. And the electrochemical active surface areas

(ECSAs) of the catalysts were determined by the equation: $ECSA=R_f \times S$, where S was 1 cm^2 and the R_f was determined by $Rf = C_{dl} / 60\ \mu F\ cm^{-2}$ based on the double-layer capacitance (C_{dl}) of a smooth oxide surface (60 $\mu F\ cm^{-2}$).

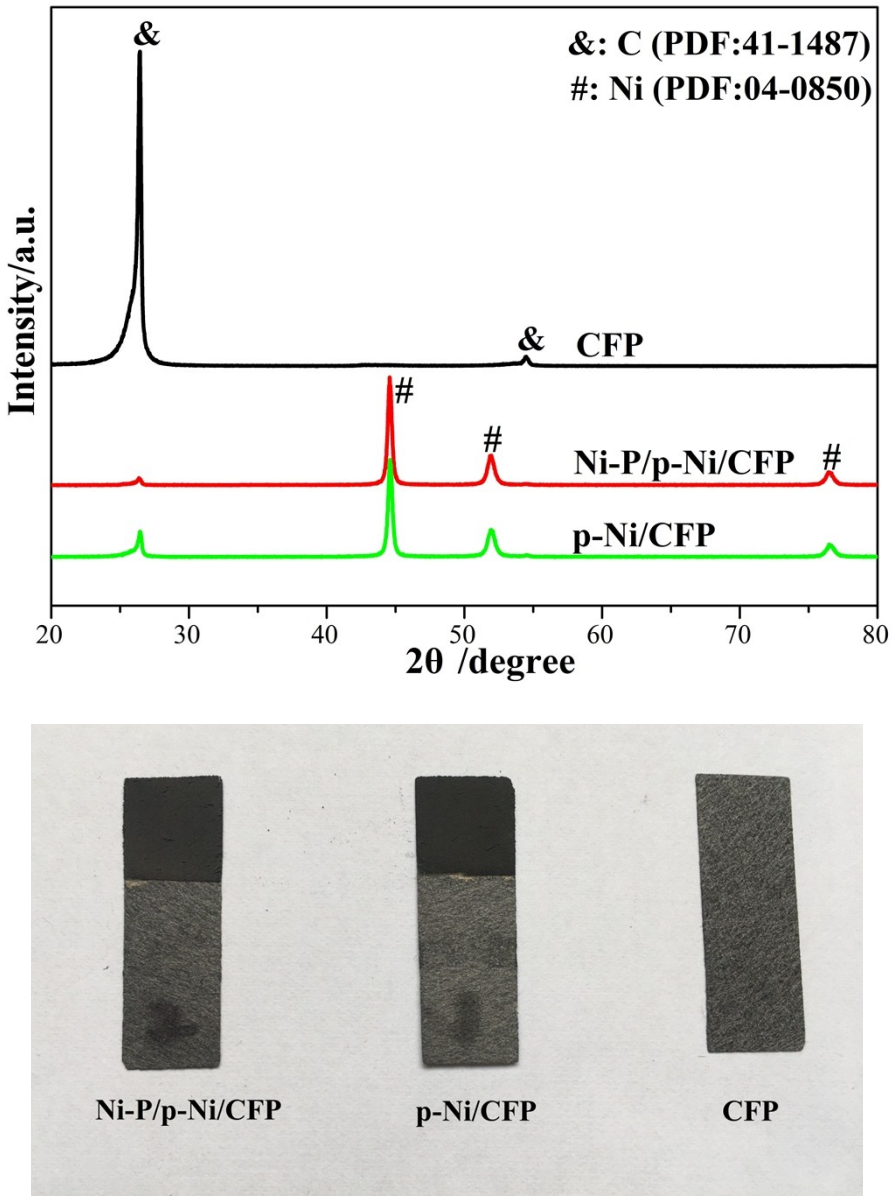

Fig. S1 XRD patterns and photograph of the CFP, p-Ni/CFP and Ni-P/p-Ni/CFP.

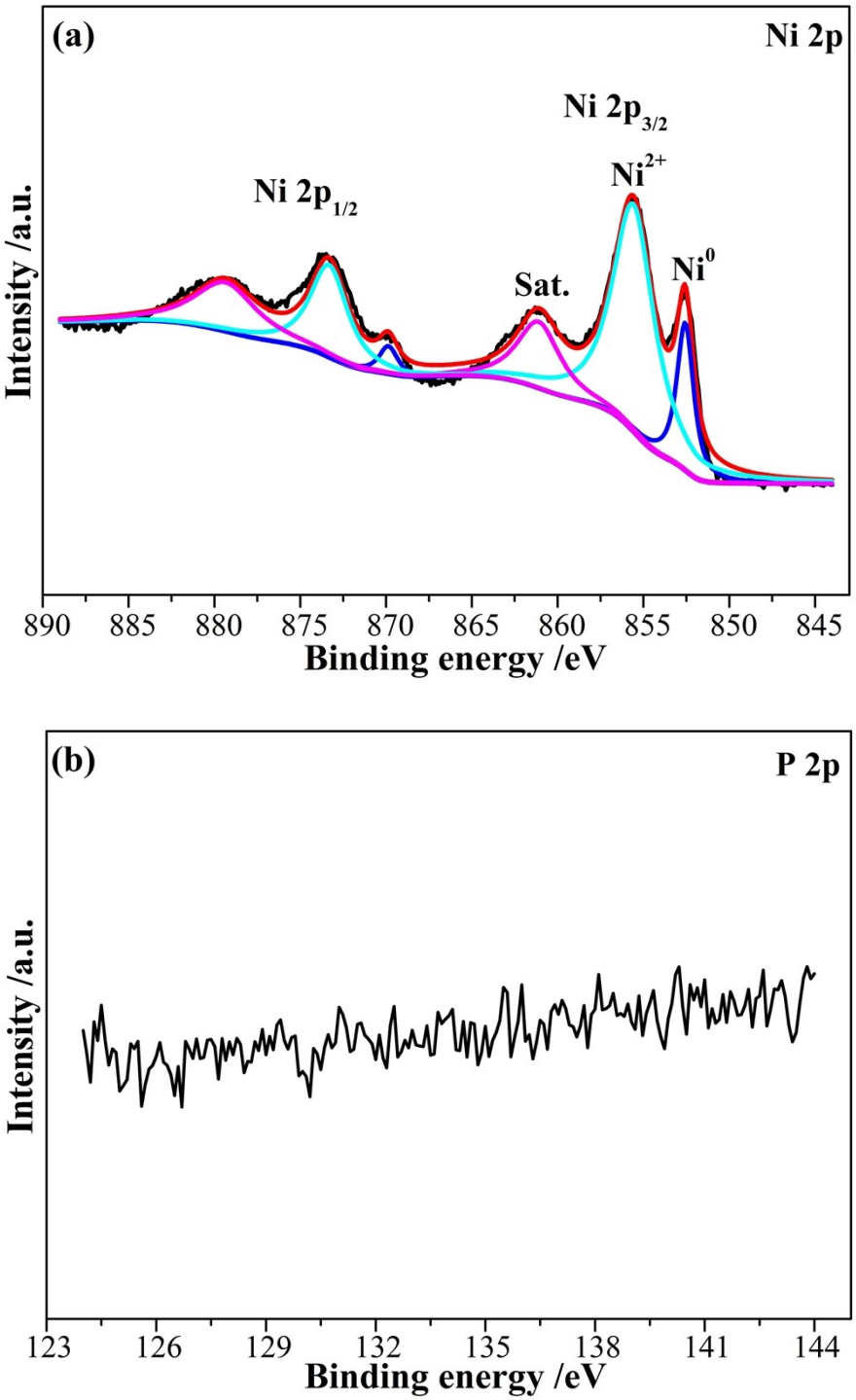

Fig. S2 High-resolution Ni 2p and P 2p XPS spectra of the p-Ni.

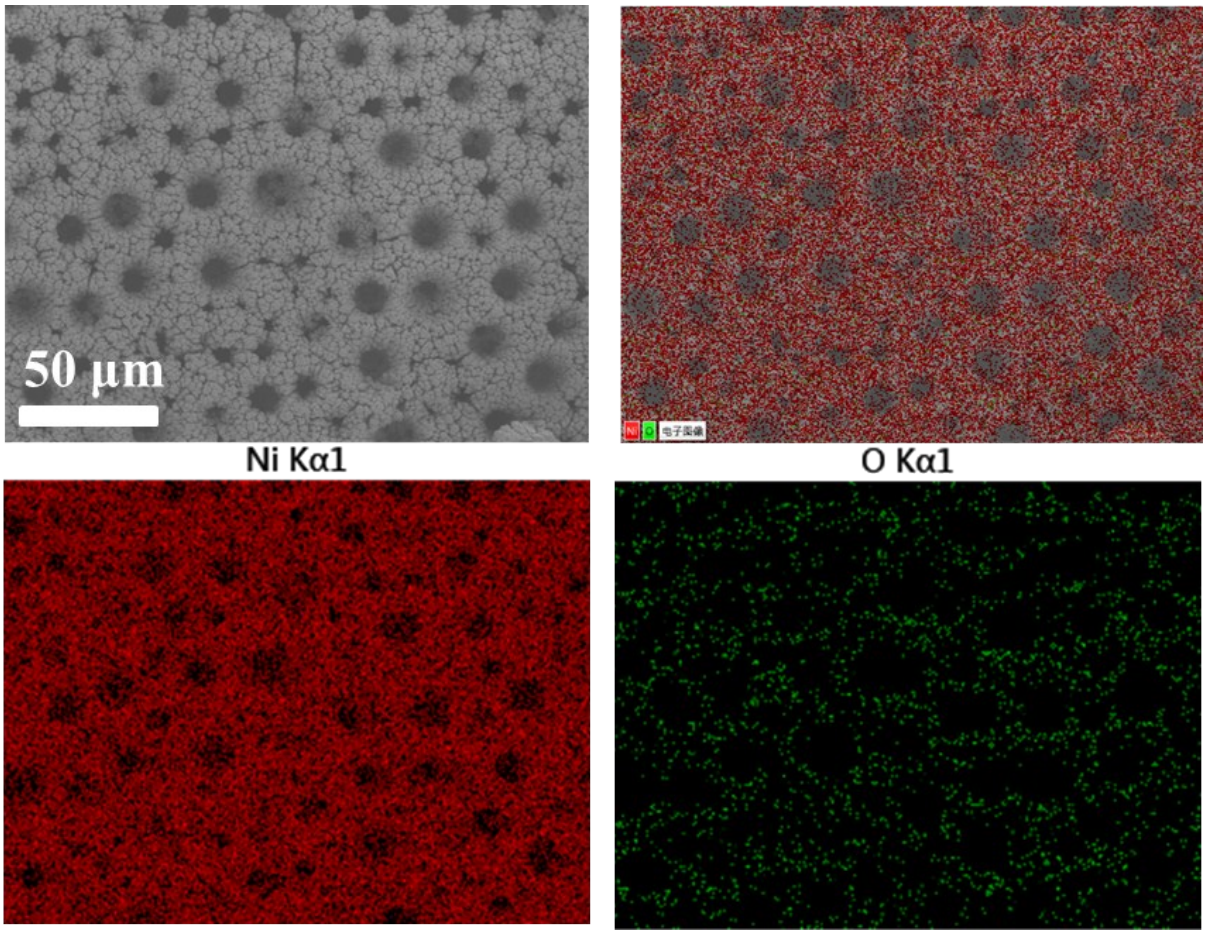

Fig. S3 SEM image and the corresponding elemental mapping images of Ni and O in the p-Ni.

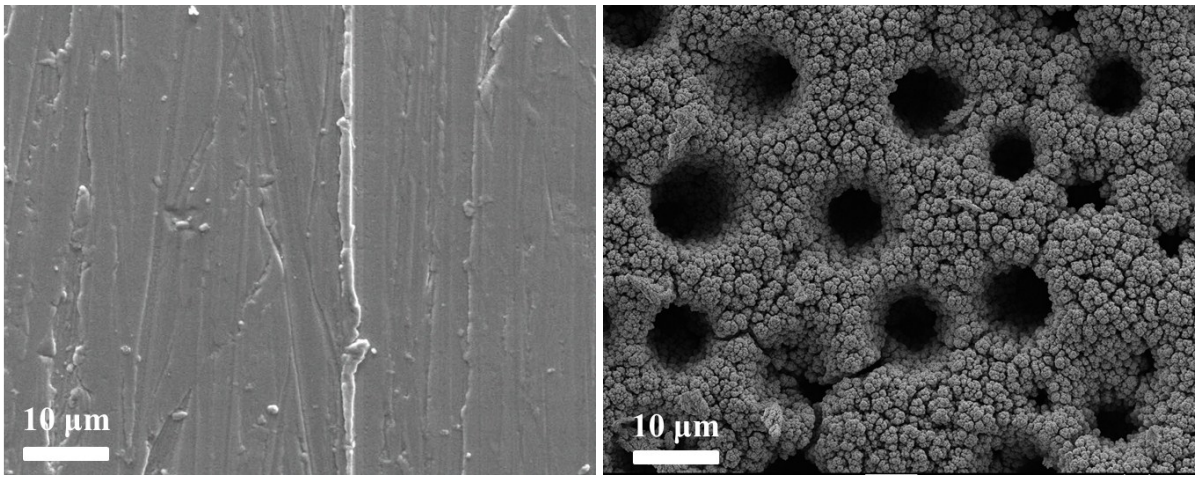

Fig. S4 SEM images of Ni substrate and the Ni_2P/p-Ni prepared by traditional solid-phosphorization process.

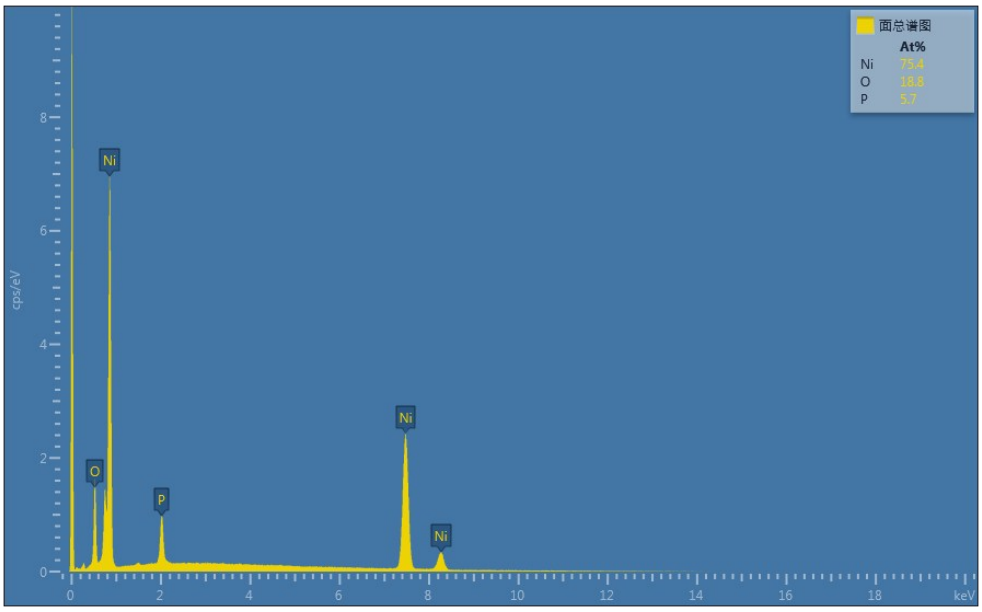

Fig. S5 EDX spectrum of the Ni-P/p-Ni

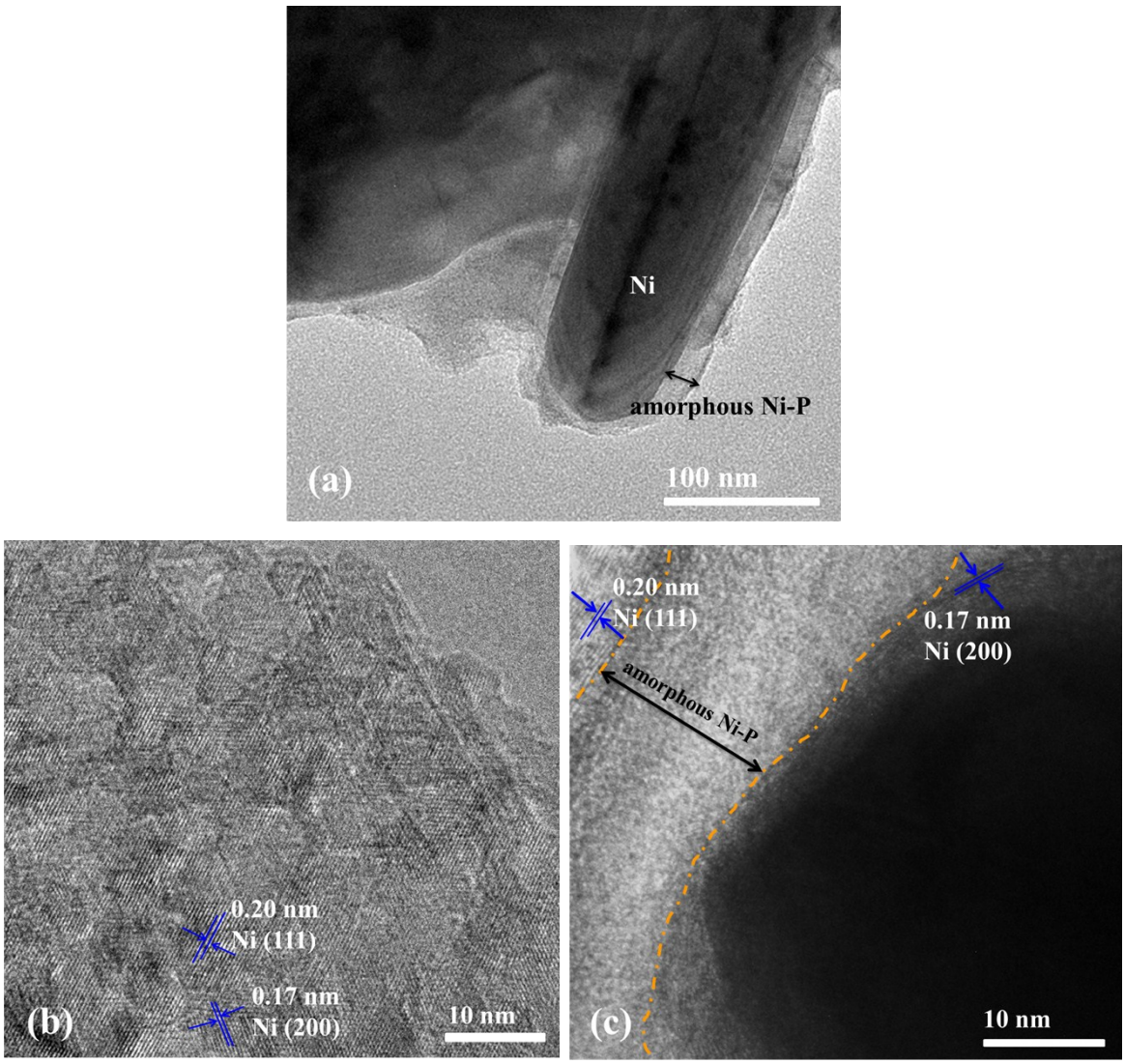

Fig. S6 (a) TEM and (b, c) HRTEM images of the the Ni-P/p-Ni.

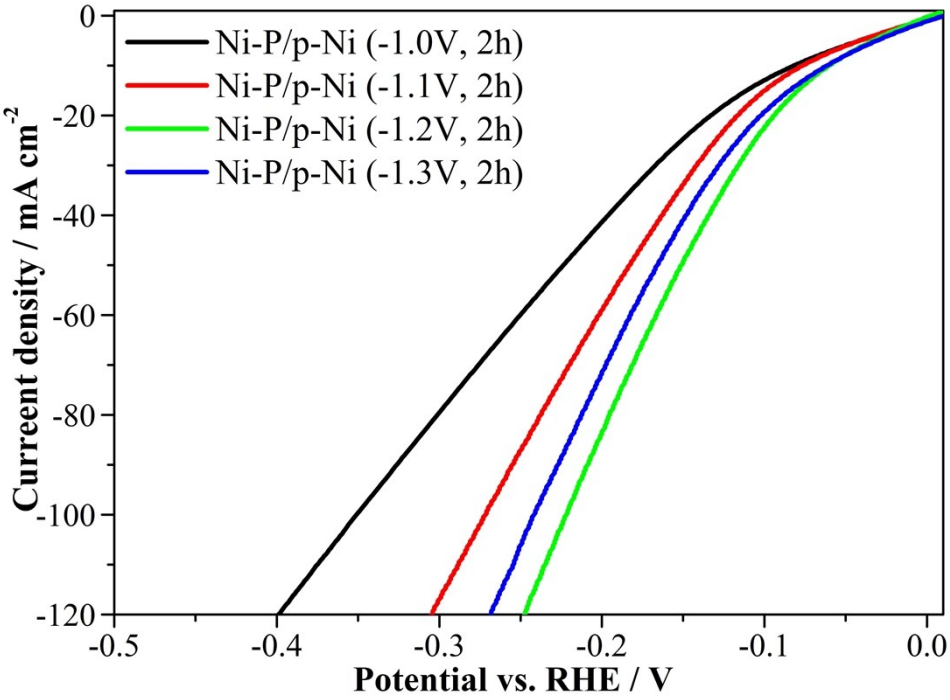

Fig. S7 Linear sweep voltammetry curves of the Ni-P/p-Ni synthesized at different potentials of electrochemical-phosphorization for 3 h.

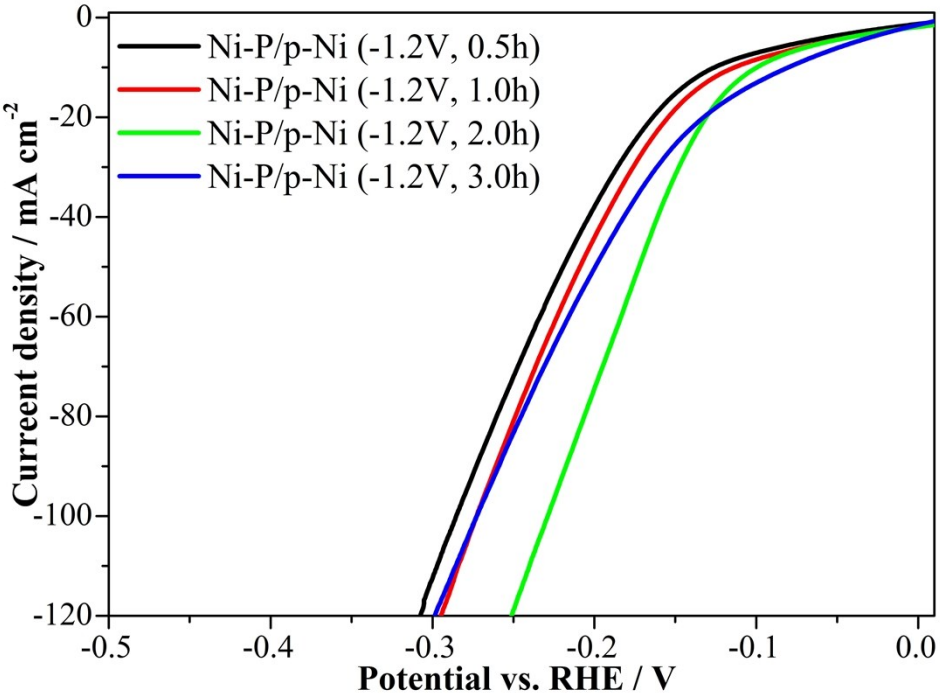

Fig. S8 (a) Linear sweep voltammetry curves of the Ni-P/p-Ni synthesized at different duration of electrochemical-phosphorization.

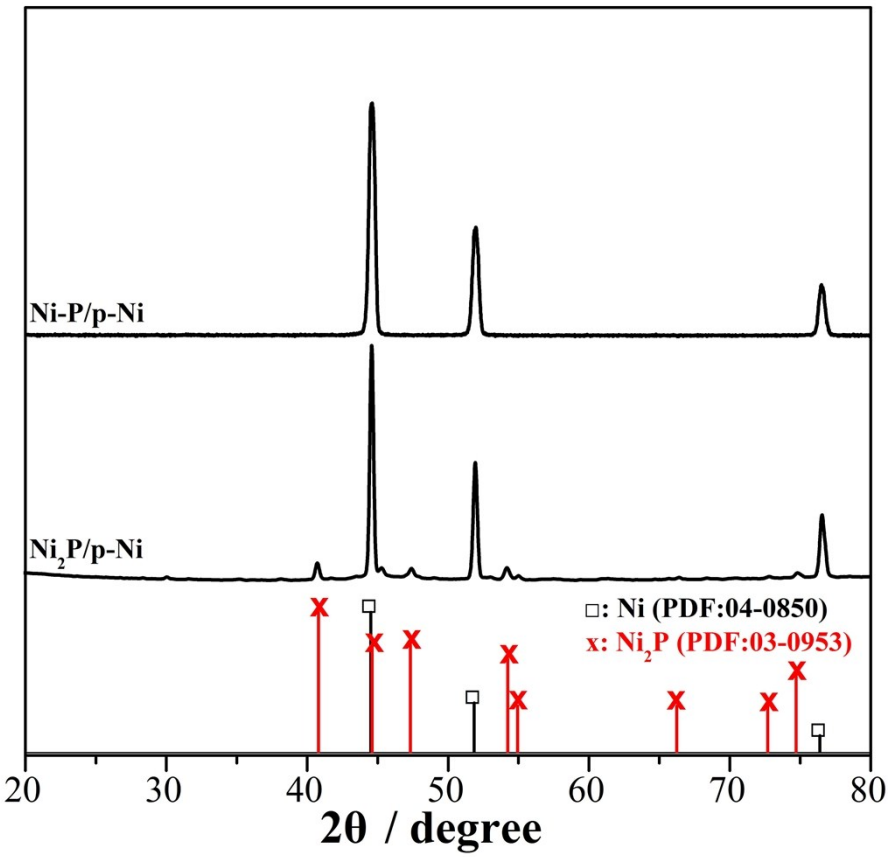

Fig. S9 XRD pattern of the Ni-P/p-Ni and Ni_2P/p-Ni.

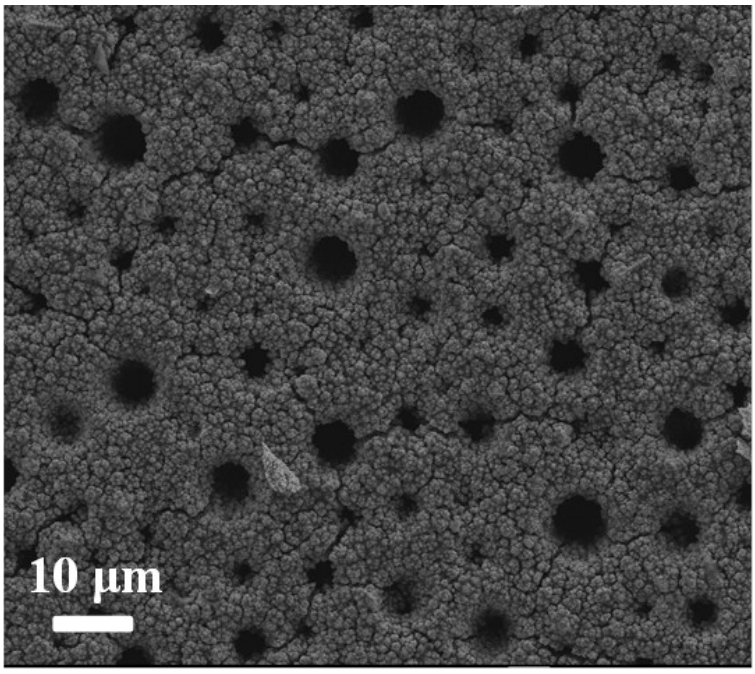

Fig. S10 SEM image of the Ni-P/p-Ni after HER stability test.

Table S1. HER performances of the Ni-P/p-Ni and other reported electrocatalysts in 1.0 M KOH. (j: current density; η: overpotential).

Catalysts	η_{10} (j=10 mA cm^{-2})	Tafel slope (mV dec^{-1})	References
Ni-P/p-Ni	69	76	This work
NiP_2/NiO nanorod	131	94	ACS Appl. Mater. Interfaces, 2018, 10, 17896
$Fe_{0.5}Co_{0.5}P$	143	94	ACS Catal., 2019, 9, 2956
Ni-Co-P/NF	156	108.4	J. Mater. Chem. A, 2018, 6, 12506
CoP/NPC/TF	80	50	Adv. Energy Mater., 2019, 9, 1803970
Co_2P/CoN-in-NCNTs	98	57	Adv. Funct. Mater., 2018, 28, 1805641
Co/CoP-5	193	73.8	Adv. Energy Mater. 2017, 7, 1602355
CoP-N/Co foam	60	50.9	J. Mater. Chem. A, 2019,7, 13242
CoNiP@NF	155	115	J. Mater. Chem. A, 2016, 4, 10195
CoMoP@C	133	92	Energy Environ. Sci., 2017, 10, 788
$Ni_{0.51}Co_{0.49}P$-NF	82	43	Adv. Funct. Mater., 2016, 26, 7644
$Ni_{1.5}Fe_{0.5}P$/CF	158	125	Nano Energy, 2017, 34, 472