Supporting Information

High Wettable and Metallic NiFe-Phosphate/Phosphide Catalyst Synthesized by Plasma for High Efficient Oxygen Evolution Reaction

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Experimental details

Materials

All chemicals and solvents were used as received without further purification. The hydrochloric acid，acetone，ethanol were purchased from sigma. NiFe foams were purchased from Kunshan Tengerhui Electronic Technology Corporation.

Catalyst preparation

Synthesis of NiFePi: The NiFe foam was cleaned using diluted hydrochloric acid (HCl) for 15 min followed by sonication in acetone for 15 min and washing with ethanol and water, and then dried in the air before use. The NiFe foam was placed in the reaction chamber of a plasma-enhanced chemical vapor deposition (PECVD) system followed by PH_3, and a CO_2 plasma treatment was performed at 280°C for 20 min with a base pressure of 830 mTorr. The conditions for the plasma were as follows: $PH_3/CO_2/H_2$ (30:10:10 volumetric ratio), a flux of 50 sccm and a power of 150 W.

Synthesis of NiFeP: The NiFe foam was treated with a PH_3 plasma at 280°C for 20 min with a base pressure of 830 mTorr. The conditions for the plasma were as follows: PH_3/H_2 (40:10 volumetric ratio), a flux of 50 sccm and a power of 50 W.

Synthesis of NiFePi/P: The NiFe foam was managed by PH_3, H_2 and the CO_2 plasma treatment was performed at 280°C for 20 min with a base pressure of 830 mTorr and a power of 150 W, followed by treatment with the PH_3 and H_2 plasma for 20 min at that same pressure and a power of 50 W.

Catalyst characterization

Scanning electron microscopy (SEM) was used to characterize the top-down surface

morphology using a Hitachi SU8010 SEM in high vacuum mode. The cross-section energy dispersive spectroscopy (EDS) was performed using a JSM-7610F SEM. X-ray photoelectron spectroscopy (XPS) was performed using a PHI5000 VersaProbe spectrometer. The crystal structures of the samples were characterized using X-ray diffraction (XRD, Philips PANalytical X'Pert Pro) with a copper X-ray source.

Electrochemical measurements

Electrochemical characterization of catalyst is performed in a three-electrode configuration immersed in 1.0 M potassium hydroxide (KOH, pH=13.6). The potential of the working electrode is controlled with a Metrohm Autolab $_{B.V.}$ (PGSTAT 204). A Pt counter electrode, an Ag/AgCl reference electrode (saturated KCl and AgCl solution), and catalyst acting as the working electrode form the deployed three-electrode configuration. Linear sweep voltammetry (LSV) measurements with a scan rate of 1 mV s^{-1} are carried out to record the current density–potential (*J*–*E*) data of catalyst. To study the catalytic activity at the semiconductor/electrolyte interface of catalyst, potential EIS measurements were also performed from 10000 Hz to 0.1 Hz at 0.7 mV *vs*. RHE.

Electrochemical active surface area (ECSA) estimation

The active surface area of each catalyst was estimated from their electrochemical capacitance, which can be measured using a simple cyclic voltammetry method. We measured the currents in a narrow potential window with no faradic processes. Therefore, the currents should be primarily due to the charging of the double-layer, which is expected to be linearly proportional to the active surface area. By plotting the

capacitive currents (ΔJ, $J_{anodic} - J_{cathodic}$) as a function of the scan rate and linearly fitting the data, the double-layer capacitance (C_{DL}) can be estimated as half of the slope.

Supplementary Figures

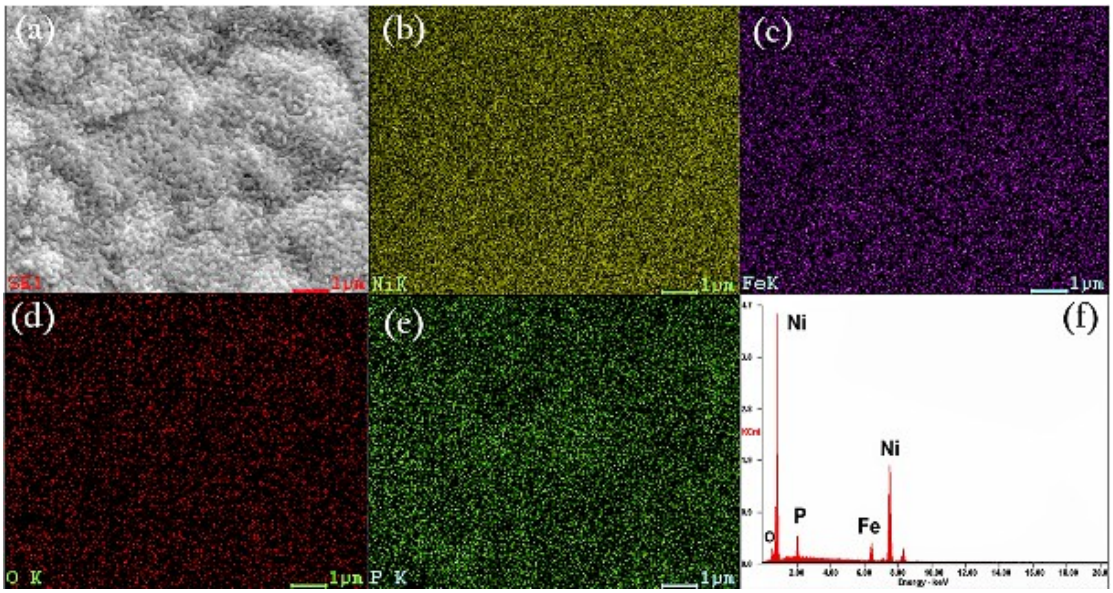

Fig S1. (a) The SEM images and elemental mapping images of (b) Ni, (c) Fe, (d) O, and (e) P. (f) EDS spectra of the NiFePi/P catalyst.

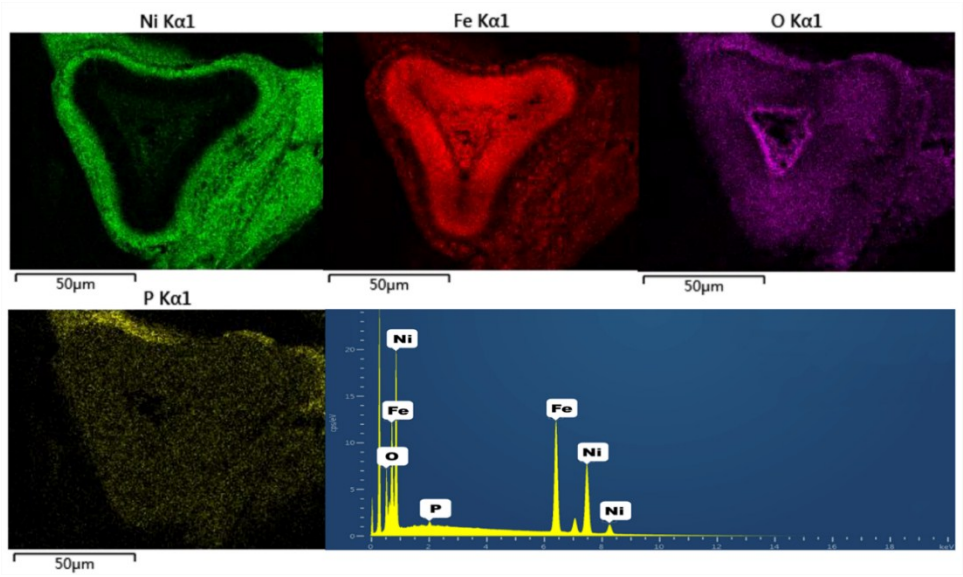

Fig S2. Cross-sectional EDS spectra of the NiFePi/P catalyst.

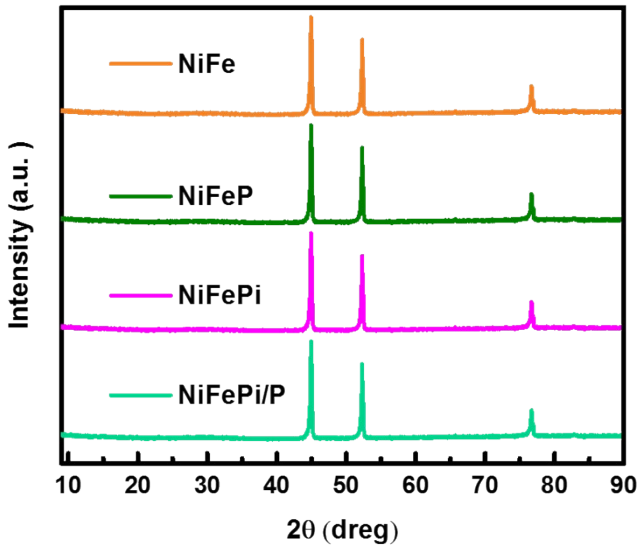

Fig S3. XRD patterns of the NiFePi/P, NiFePi, NiFeP and NiFe catalysts.

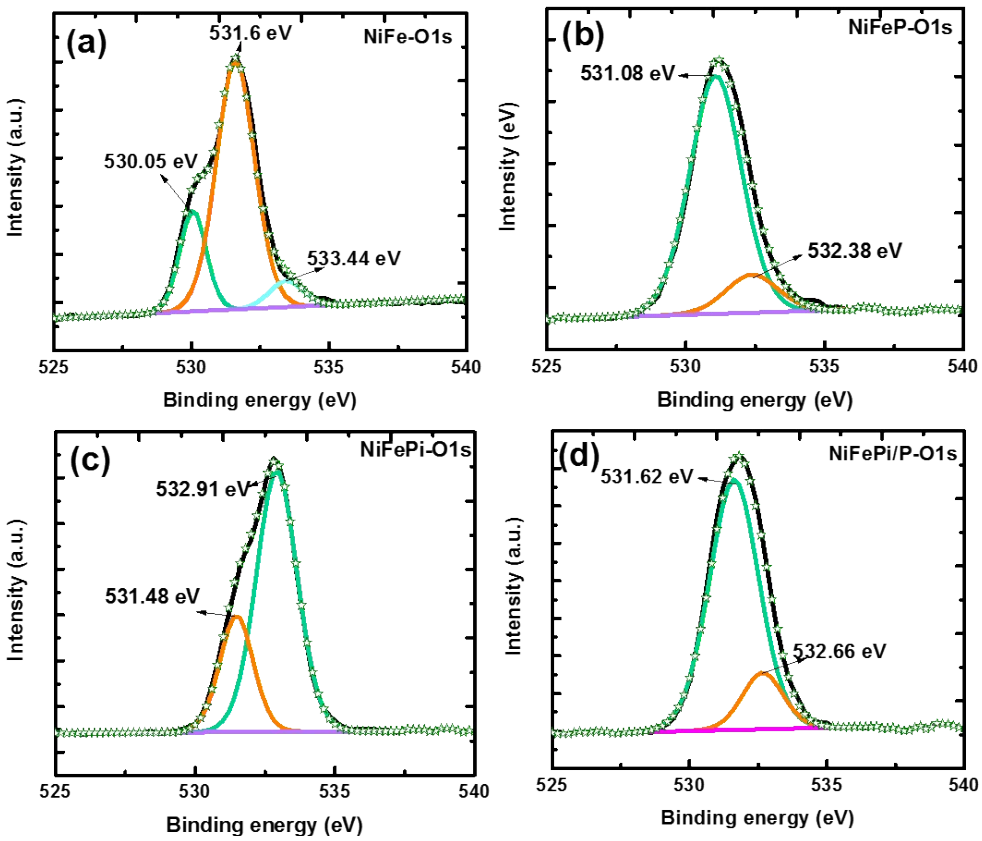

Fig S4. XPS spectra of O1s in (a)NiFe, (b)NiFeP, (c)NiFePi, and (d)NiFePi/P.

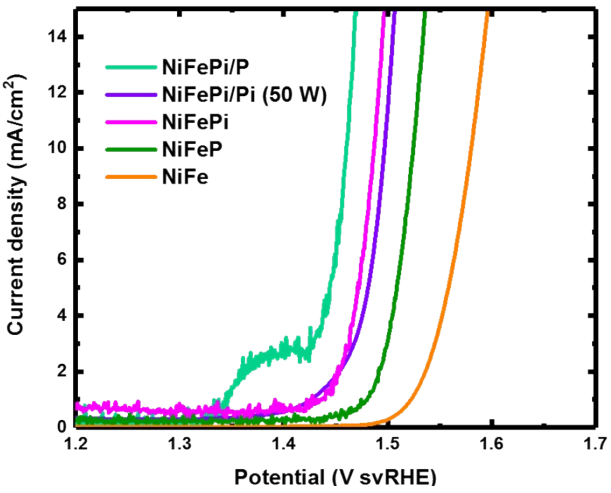

Fig S5. Comparing the LSV curves of NiFePi(prepared at 150 W)/P (prepared at 50 W), NiFePi (prepared at 150 W)/Pi (prepared at 50 W), NiFePi (prepared at 150 W), NiFeP (prepared at 50 W) and NiFe sample.

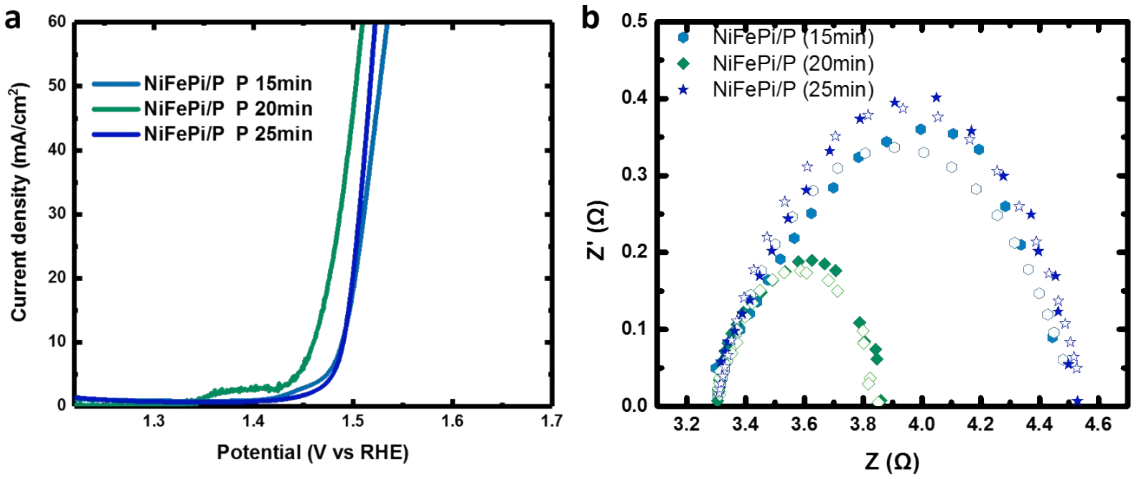

Fig S6. Comparing the (a) LSV curves and (b) EIS curves of NiFePi/P with different P contents: 15min, 20min and 25min by P treatment at a potential of 300 mV versus Ag/AgCl.

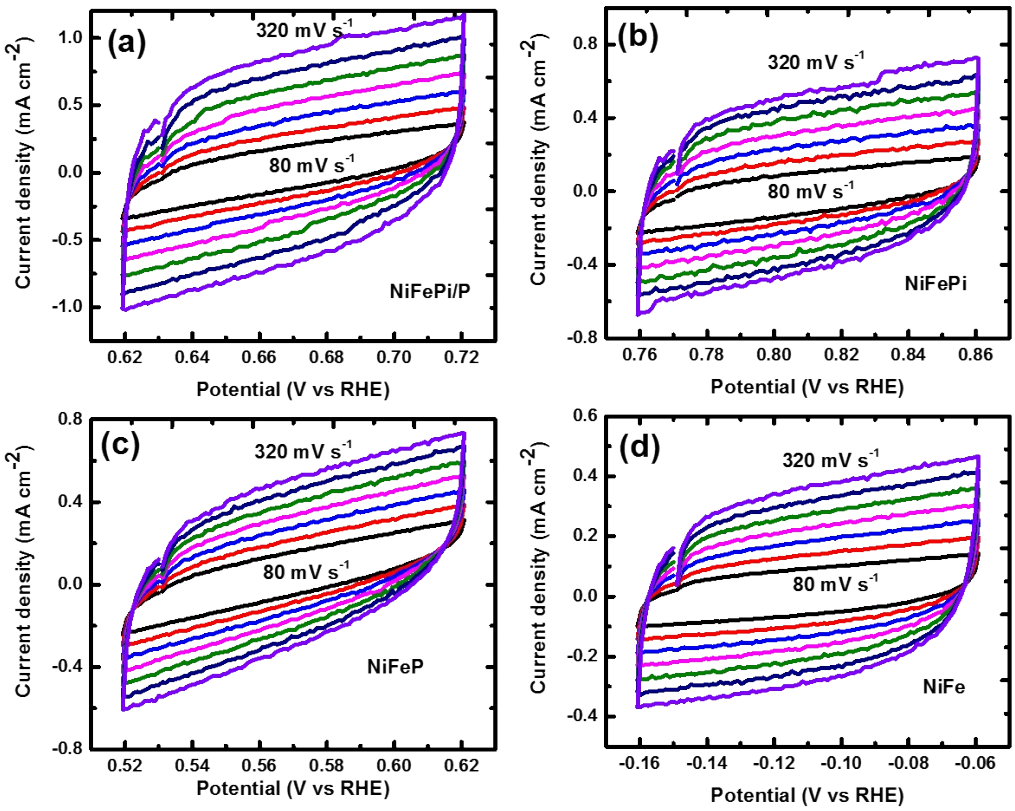

Fig S7. Cyclic voltammograms recorded at various scan rates for (a) NiFePi/P, (b) NiFePi, (c) NiFeP, and (d) NiFe.

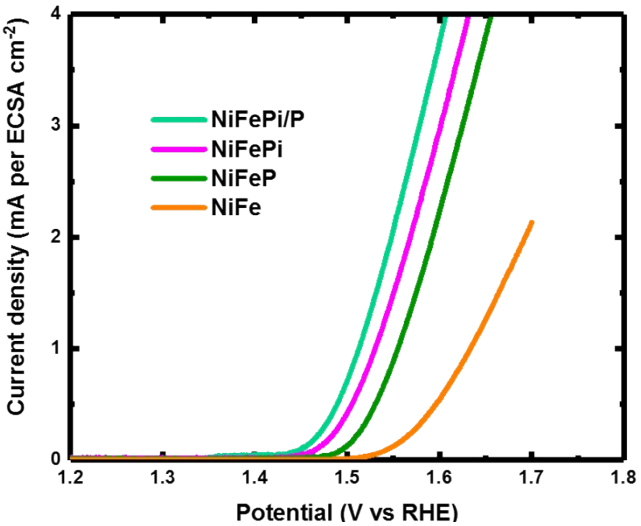

Fig S8. ECSA-normalized polarization curves for each of the four electrocatalysts.

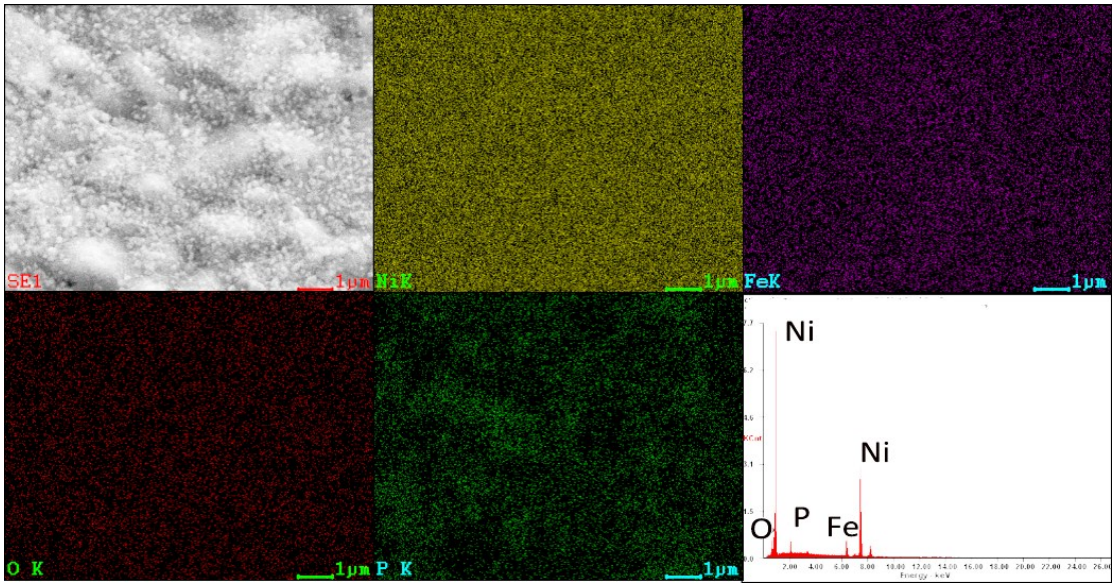

Fig S9. EDS spectra of NiFePi/P after catalysis for 24 hours in 1M KOH.

Supplementary Tables

Table S1. Comparison of the catalytic OER performance of the catalysts developed in this study and other OER catalysts in 1 M KOH.

Catalyst	η at 10mA cm^{-2} (mV)	Substrate	Electrolyte	Reference
NiFePi/P	230	NiFe foam	1 M KOH	This work
NiFe-LDH/CNT	247	Carbon fiber paper	1 M KOH	J. Am. Chem. Soc. 2013, 135, 8452−8455
Ni–Fe/3D-ErGO	259	Au	1M KOH	J. Mater. Chem. A. 2015, 3, 6921.
NiFeP	270	Ni foam	1 M KOH	ACS Energy Lett. 2017, 2, 1035−1042
NiFe-LDH NP	270	Carbon fiber paper	1 M KOH	J. Am. Chem. Soc. 2013, 135, 8452−8455
Fe:$Ni(OH)_2$ film	280	Au	1M KOH	J. Phys. Chem. C 2015, 119, 7243.
$NiFeO_x$	280	Carbon black	1 M KOH	Langmuir. 2014, 30, 7893−7901
NiFe/NiFePi	290	Carbon fiber paper	1 M KOH	ACS Catal. 2017, 7, 2535−2541

NiFe-DH	323	Ni foam	1 M KOH	ACS Energy Lett. 2017, 2, 1035−1042
$NiFeO_x$	350	FTO	1 M KOH	Nano Research 2015, 8, 23–39

LDH represent layered double hydroxide, CNT is carbon nanotubes，NiFe-DH represent NiFe-OH, 3D-ErGO is three-dimensional electrochemically reduced graphene oxide graphene oxide.

Table S2 The ratio of P-O and P-O-P with NiFeP, NiFePi and NiFePi/P samples.

Samples	P-O (%)	P-O-P (%)
NiFeP	86.2	13.8
NiFePi	26.8	73.2
NiFePi/P	83.3	15.7

Table S3. The R_s and R_{ct} of EIS parameters for different P contents in NiFePi/P.

Samples	R_s (Ω)	R_{ct} (Ω)
NiFePi/P (15 min)	3.296	1.23
NiFePi/P (20 min)	3.290	0.57
NiFePi/P (25 min)	3.301	1.25