Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Facile fabrication of 3D network composed of N-doped carbon-coated core-shell metal oxides/phosphides for highly efficient water splitting

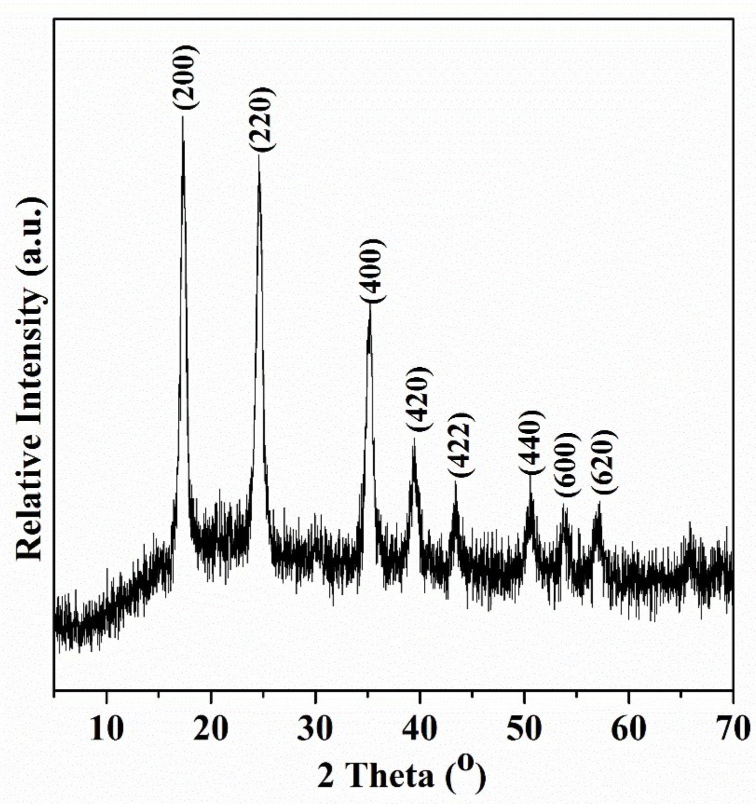

Fig. S1 The XRD pattern of NiFe-PBAs/PVP precursor

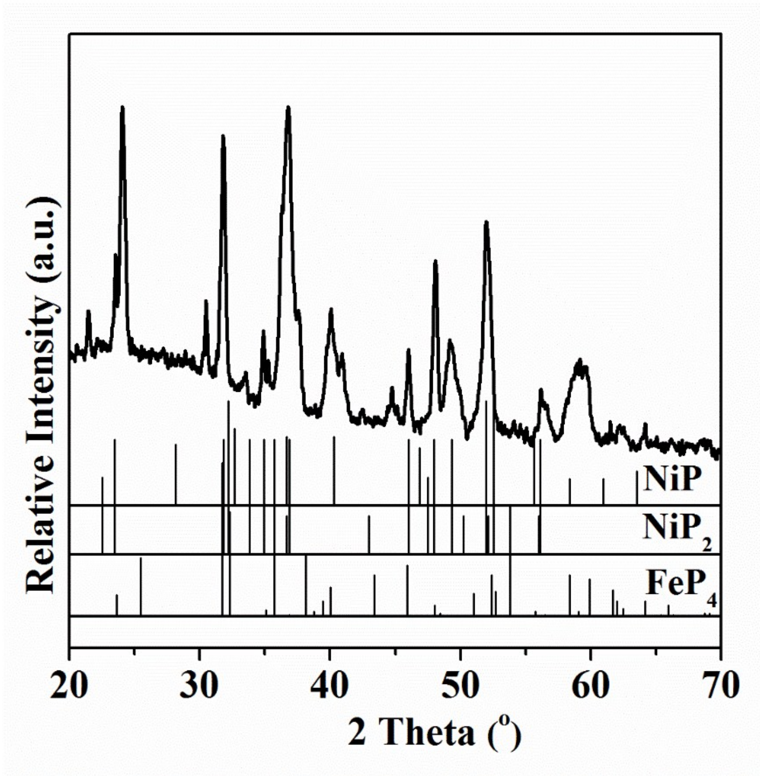

Fig. S2 The XRD pattern of NC-NiFeO$_x$@NiFe-P

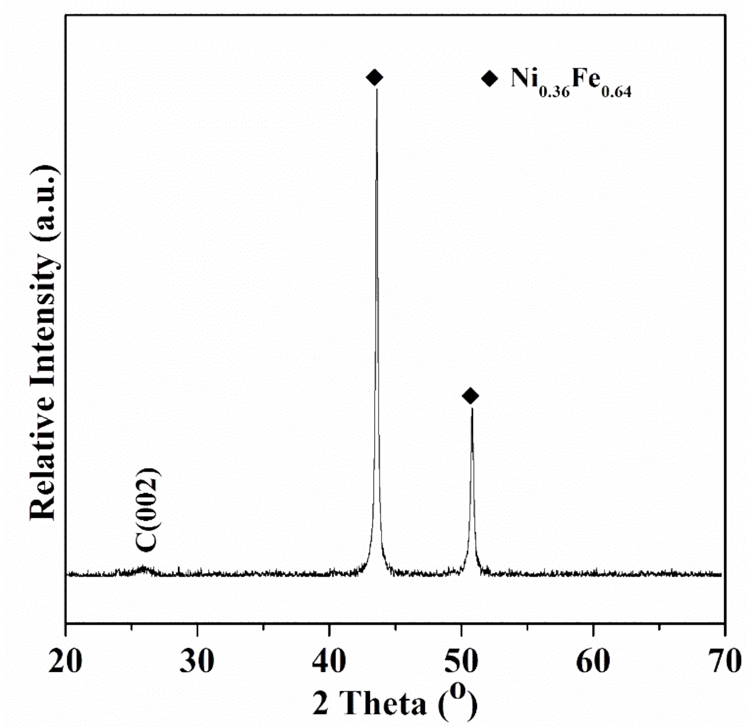

Fig. S3 The XRD pattern of NC-NiFe (served as control sample). The NC-NiFe was produced without phosphorization.

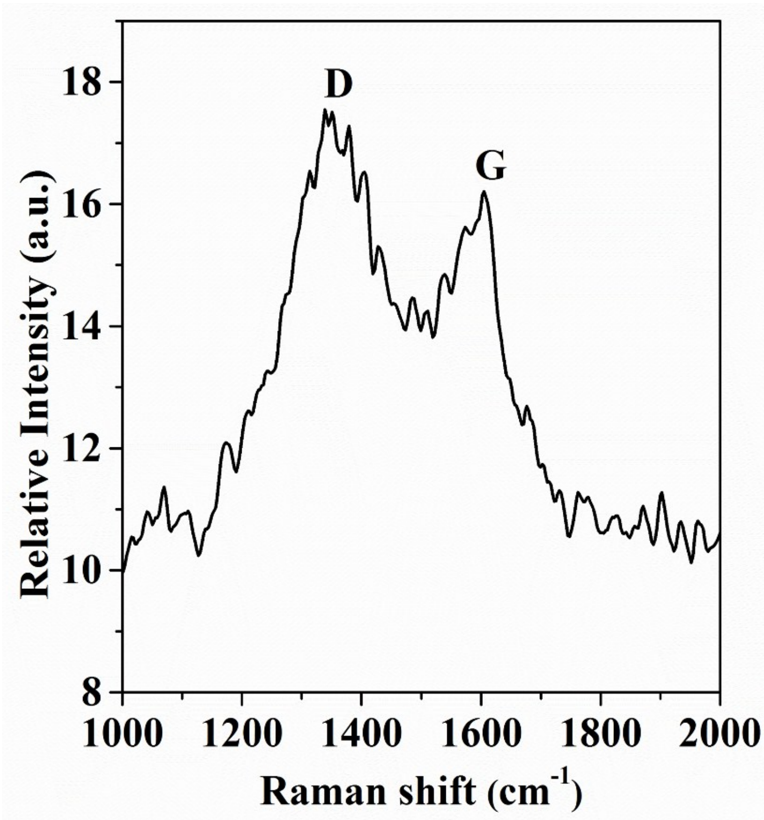

Fig. S4 The Raman spectrum of NC-NiFeO$_x$@NiFe-P

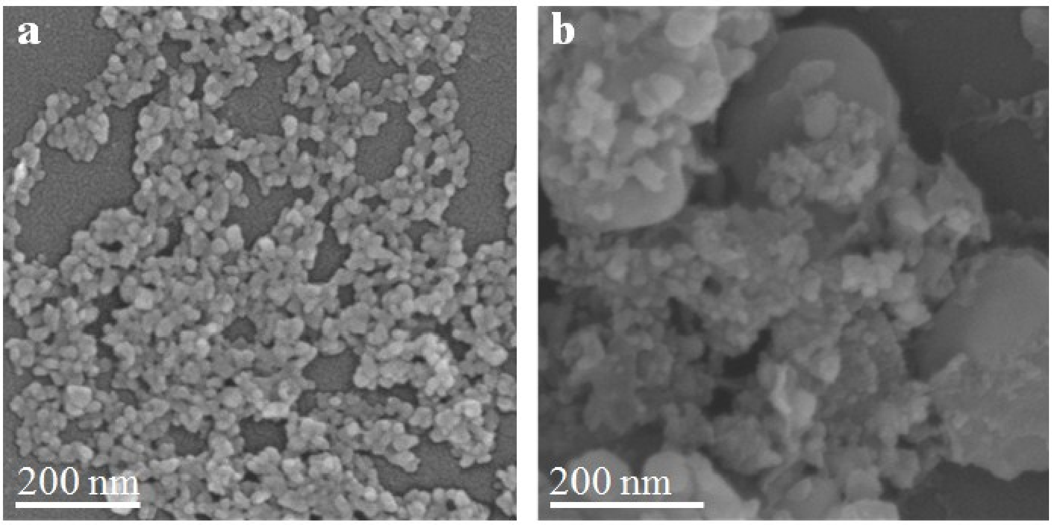

Fig. S5 The SEM images of (a) NiFe-PBAs and (b) NiFeO$_x$@NiFe-P. Both of NiFe-PBAs and NiFeO$_x$@NiFe-P were produced without addition of PVP.

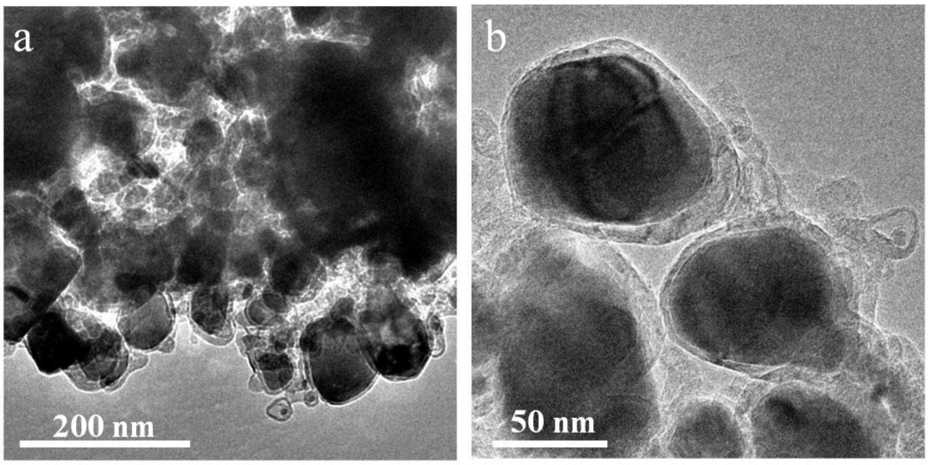

Fig. S6 The TEM images of $NiFeO_x$@NiFe-P.

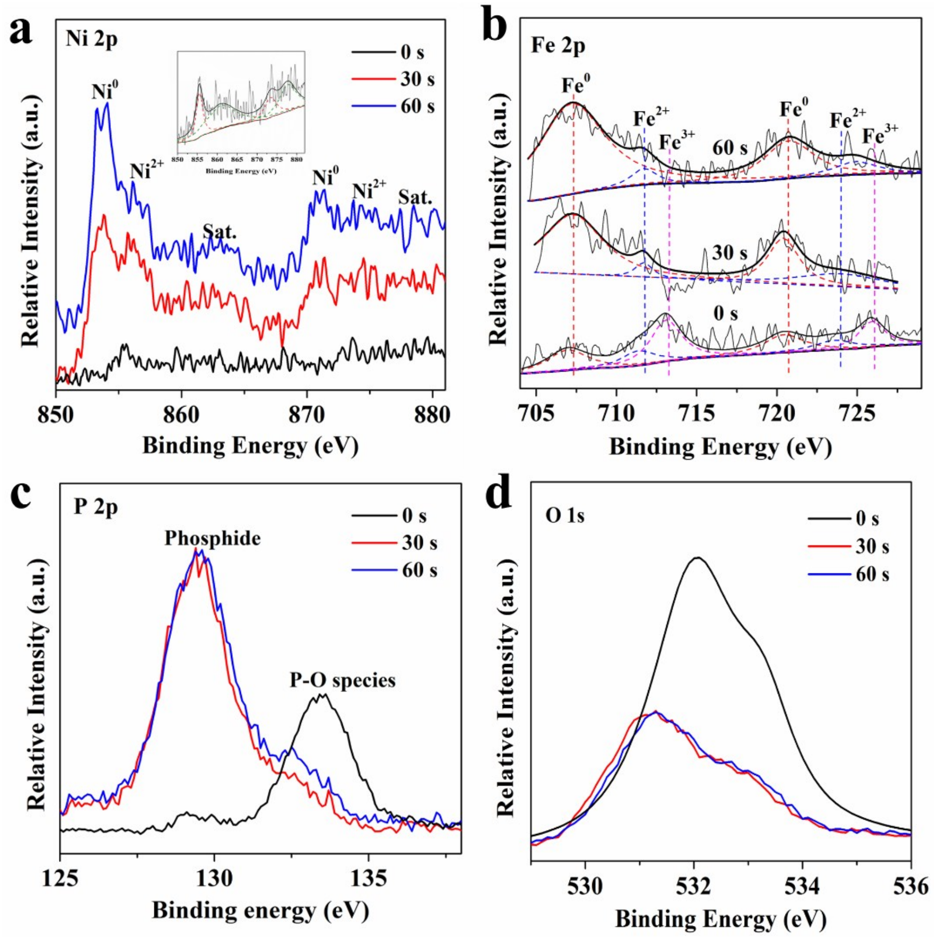

Fig. S7 XPS spectra of (a) Ni 2p, (b) Fe 2p, (c) P 2p, and (d) O 1s for NC-$NiFeO_x$@NiFe-P catalyst after Ar ions etching of different time (i.e. 0 s, 30 s, 60 s). The insert in (a) displayed the magnified spectrum of untreated NC-NiFeOx@NiFe-P sample

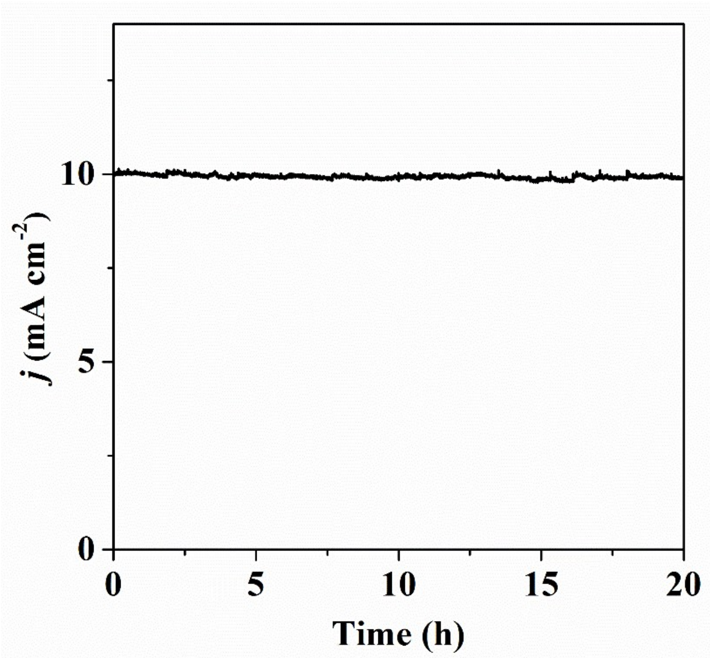

Fig. S8 Time-dependent current density curve for NC-NiFeO_x@NiFe-P catalyst at fixed potential of 1.53 V.

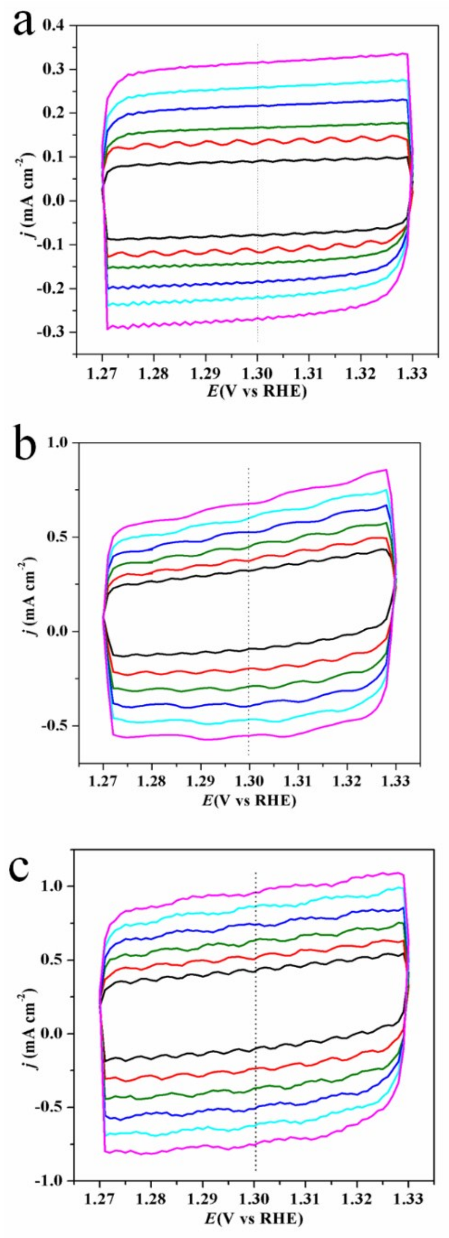

Fig. S9 CV curves for (a) $NiFeO_x$@NiFe-P, (b) NC-NiFe and (c) NC-$NiFeO_x$@NiFe-P at various scan rates

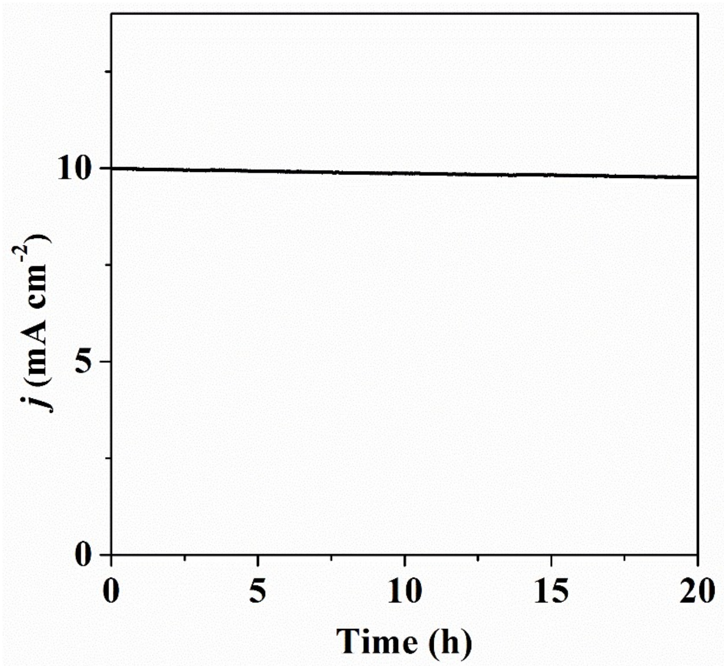

Fig. S10 Time-dependent current density curve for NC-NiFeO$_x$@NiFe-P catalyst at fixed potential of -0.23 V.

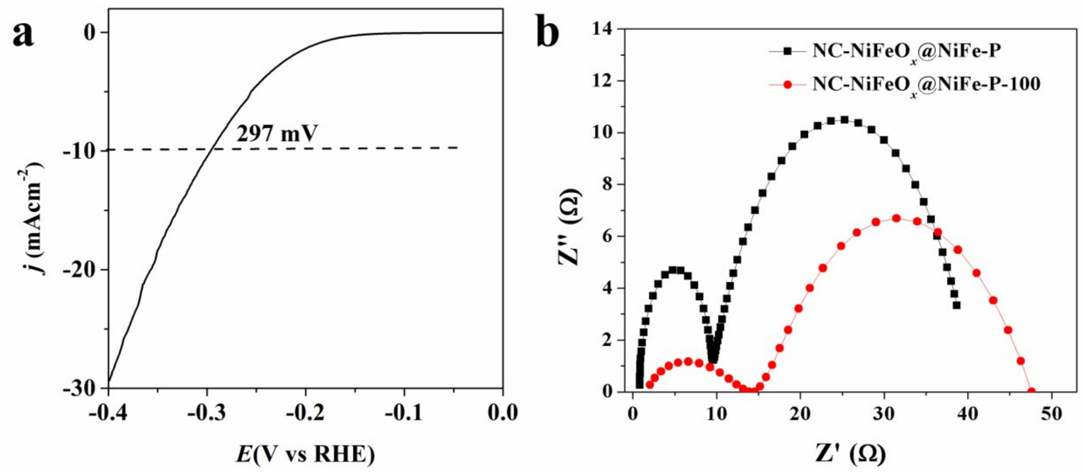

Fig. S11 (a) Steady-state HER polarization curves of NC-NiFeO$_x$@NiFe-P-100, (b) EIS of NC-NiFeO$_x$@NiFe-P and NC-NiFeO$_x$@NiFe-P-100

As shown in Fig. S11b, the Nyquist plots of all the two samples (i.e. NC-NiFeO$_x$@NiFe-P-100 and NC-NiFeO$_x$@NiFe-P) reveal two time-constants. As it well reported, the small constant at high frequency is belonged to series resistance, and the other big one at low frequency is related to the charge-transfer resistance (R_{ct}) during electrocatalytic processes. The charge-transfer resistance (R_{ct}) of NC-NiFeO$_x$@NiFe-P-100 (33.1 Ω) is found slightly larger than that of NC-NiFeO$_x$@NiFe-P (29.2 Ω) due to the presence of highly conductive N-doped carbon network. The result implies that the impaired electrocatalytic activity of NC-NiFeO$_x$@NiFe-P-100 could originate from the inefficiency of NiFeO$_x$ shell for the combination of active hydrogen atoms.

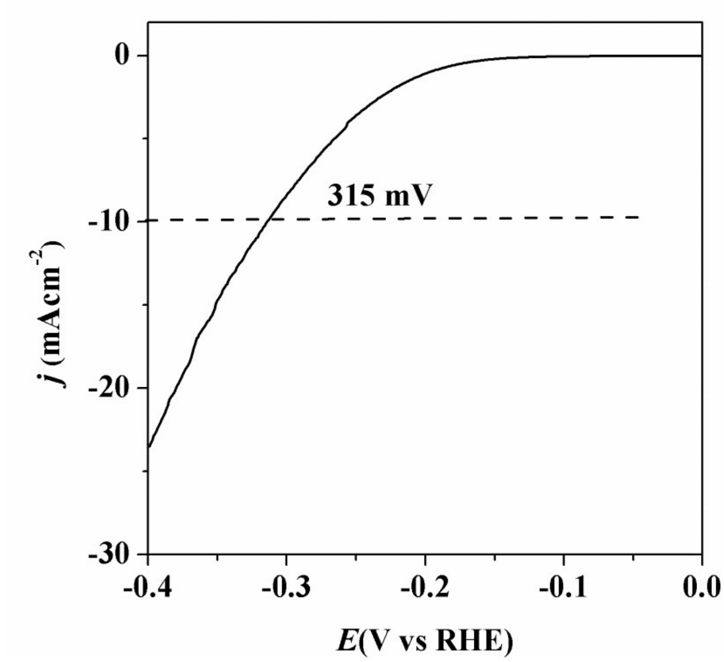

Fig. S12 Steady-state HER polarization curves of NC-NiFe-P

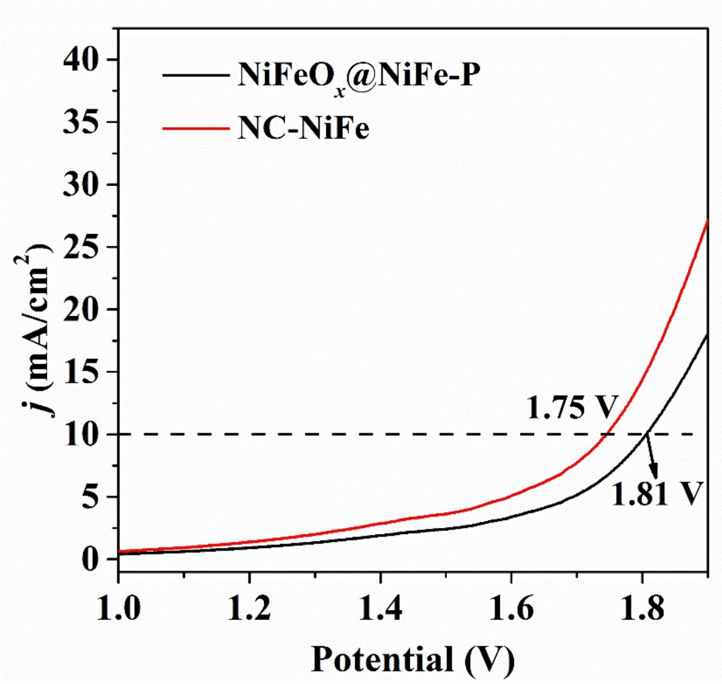

Fig. S13 LSV of water electrolysis based on the NiFeO$_x$@NiFe-P and NC-NiFe catalyst in 1 M KOH

Table S1 Element contents of NiFeO$_x$@NiFe-P and NC-NiFeO$_x$@NiFe-P determined by element analysis

Catalyst	C (wt%)	N (wt%)	H (wt%)
NiFeO$_x$@NiFe-P	12.23	0.76	0.69
NC-NiFeO$_x$@NiFe-P	28.62	2.23	0.82

Table S2 Comparison of the as-synthesized NC-NiFeO$_x$@NiFe-P catalyst with other recently reported catalysts for OER

Catalysts	Electrolyte	Loading (mg cm^{-2})	η (mV) at 10 mA/cm^2	Reference
NC-NiFeO$_x$@NiFe-P	1 M KOH	0.2	285	This work
Ni_2P	1 M KOH	0.14	290	Energy Environ. Sci., 2015, **8**, 2347
Co_2P	1 M KOH	0.2	310	ACS Energy Lett., 2016, **1**, 169
CoMnP	1 M KOH	0.284	330	J. Am. Chem. Soc., 2016, **138**, 4006.
Co@Co_3O_4/NC	0.1 M KOH	0.21	410	Angew. Chem. Int. Ed., 2016, **55**, 4087
$Ni_xCo_{3-x}O_4$	1 M NaOH	3	370	Adv. Mater., 2010, **22**, 1926
PNG-$NiCo_2O_4$	0.1 M KOH	N/A	310	ACS Nano 2013, **7**, 10190
CoCo LDH	1 M KOH	0.07	393	Nat. Commun., 2014, **5**, 4477
NiCo LDH	NiCo LDH	N/A	367	Nano Lett., 2015, **15**, 1421

NC: N-doped carbon nanotube, PNG: porous N-doped graphene, LDH: layered double hydroxides

Table S3 Comparison of the as-synthesized NC-NiFeO$_x$@NiFe-P catalyst with other recently reported catalysts for HER

Catalysts	Electrolyte	Loading (mg cm^{-2})	η (mV) at 10 mA/cm^2	Reference
NC-$NiFeO_x$@NiFe-P	1 M KOH	0.2	237	This work
Co-NRCNTs	1 M KOH	0.28	370	Angew. Chem., Int. Ed.,2014, **53**, 4372
MnNi	0.1 M KOH	0.28	360	Adv. Funct. Mater., 2015, **25**, 393
Co@Co-N-C	0.1M KOH	0.6	314	Chem. Commun., 2015, **51**, 8942
Co_3O_4 NCs	1 M KOH	0.35	380	Chem. Commun. 2015, **51**, 8066
MoB	1 M KOH	2.3	~210	Angew. Chem., Int. Ed., 2012, **51**, 12703
NiO/Ni-CNT	1 M KOH	0.28	~100	Nat. Commun., 2014, **5**,4695
Co_x@CN	1 M KOH	0.12	232	J. Am. Chem. Soc., 2015, **137**, 2688
FeCo@CN	1 M KOH	0.32	211	ACS Catal., 2017, **7**, 469
NRCNTs: N-rich carbon nanotubes, NCs: nanocrystals, CNT: carbon nanotube, CN: N-doped carbon				

Table S4 Comparison of the as-synthesized NC-$NiFeO_x$@NiFe-P catalyst with other recently reported bifunctional catalysts for overall splitting of water

Catalysts	Substrate	Loading (mg/cm^2)	Voltage (V) at 10 mA/cm^2	Reference
NC-$NiFeO_x$@NiFe-P	Ni foam	1	1.59	This work
CoO_x@CN	Ni foam	2	1.55	J. Am. Chem. Soc., 2015, **137**, 2688.
Ni_2P/NiO_x	Ni foam	5	1.63	Energy Environ., Sci. 2015, **8**, 2347.
Co-P	Cu foil	2.6	1.65	Angew. Chem. Int. Ed., 2015, **54**, 6251.
Ni/NiP	Ni foam	N/A	1.61	Adv. Funct. Mater., 2016, **26**, 3314.
Ni_2P	FTO	1	1.58	ACS Catal., 2017, **7**, 103
Co-Fe-P-1.7	Ni foam	1	1.60	ACS Appl. Mater. Interfaces 2017, **9**, 362
Ni-B	Ni foam	12.3	1.68	Nanotechnology., 2016, 27,
NiSe NWs	Ni foam	2.8	1.63	Angew. Chem. Int. Ed., 2015, **54**, 9351
Fe-Co	CFP	1.2 or 2	1.68	Nano Energy, 2017, **38**, 576
CN: N-doped carbon, NWs: nanowires				