

Supplementary Information

Tungsten-doped Ni-Co phosphides with catalytic multi-sites as efficient electrocatalyst for overall water splitting

Shan-Shan Lu ^a, Li-Ming Zhang ^a, Yi-Wen Dong ^{a,b}, Jia-Qi Zhang ^a, Xin-Tong Yan ^{a,b},

De-Fan Sun ^{a,b}, Xiao Shang ^{a,b}, Jing-Qi Chi ^a, Yong-Ming Chai ^a, Bin Dong ^{*a,b}

a State Key Laboratory of Heavy Oil Processing, Institute of New Energy, China University of Petroleum (East China), Qingdao 266580, PR China

b College of Science, China University of Petroleum (East China), Qingdao 266580, PR China

* Corresponding author. Email: dongbin@upc.edu.cn (B. Dong)

Tel: +86-532-86981156, Fax: +86-532-86981156

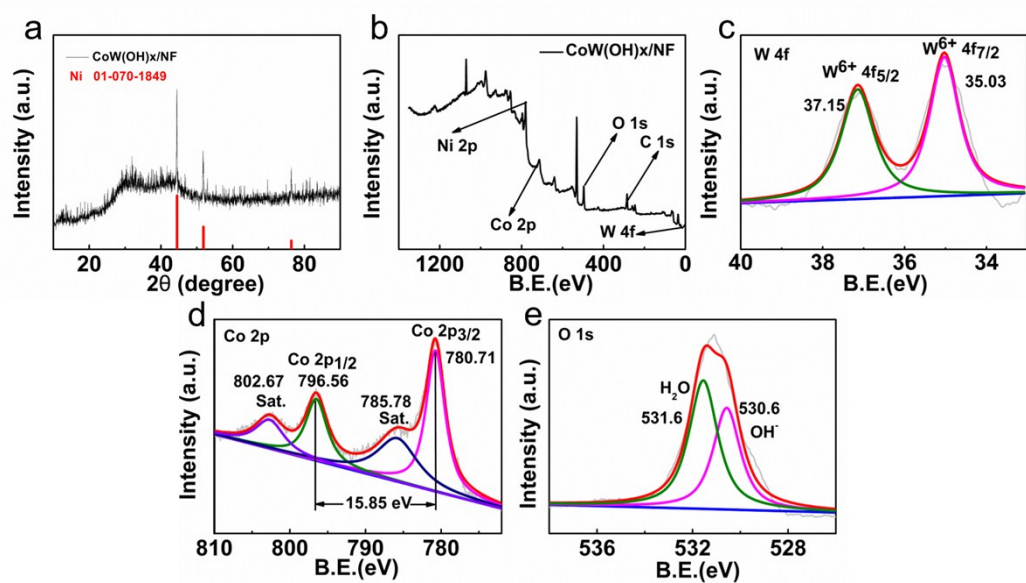


Fig. S1 (a) XRD pattern of $\text{CoW(OH)}_x/\text{NF}$, (b) Survey XPS spectrum and (c–e) high-resolution XPS scans of $\text{CoW(OH)}_x/\text{NF}$ in the (c) W 4f, (d) Co 2p, and (e) O 1s regions.

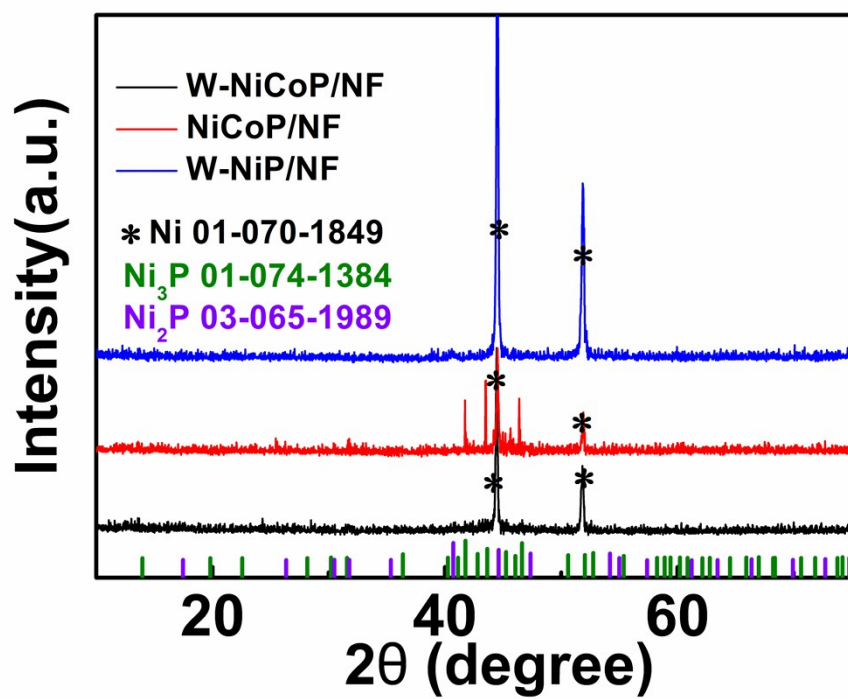


Fig. S2 XRD patterns of W-NiCoP/NF, NiCoP/NF, and W-NiP/NF after scratching off the samples from NF.

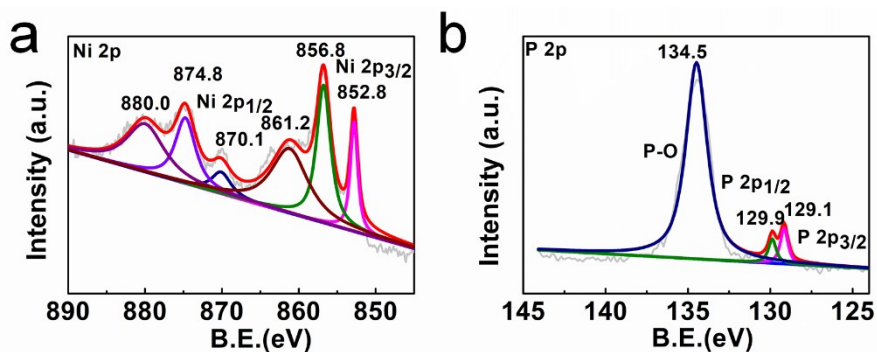


Fig. S3 XPS spectra of NiP/NF. (a) Ni 2p and (b) P 2p.

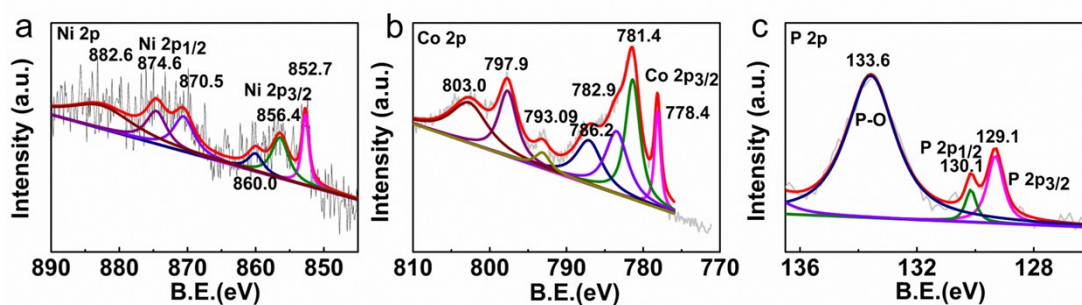


Fig. S4 XPS spectra of NiCoP/NF. (a) Ni 2p, (b) Co 2p, and (c) P 2p.

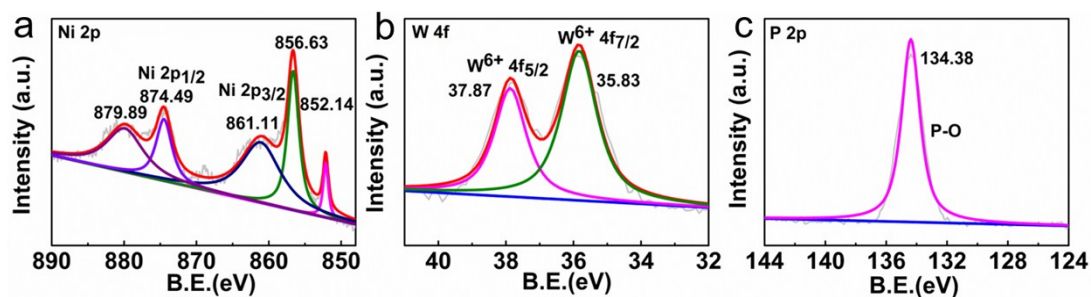


Fig. S5 XPS spectra of W-NiP/NF. (a) Ni 2p, (b) W 4f, and (c) P 2p.

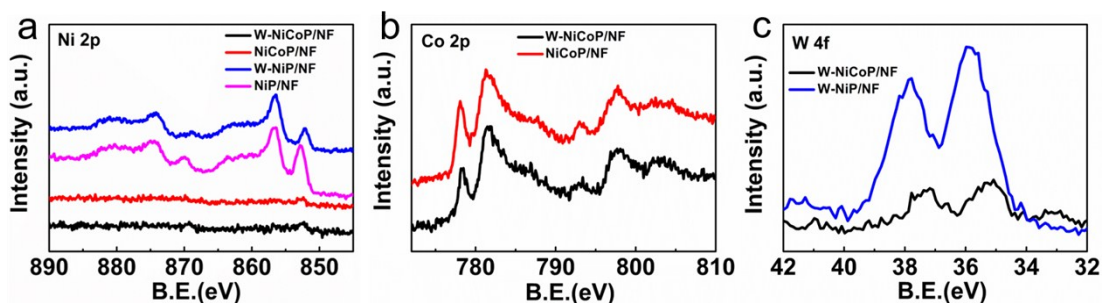


Fig. S6 (a) XPS spectra of W-NiCoP/NF, NiCoP/NF, W-NiP/NF, and NiP/NF in Ni 2p, (b) XPS spectra of W-NiCoP/NF and NiCoP/NF in Co 2p, (c) XPS spectra of W-NiCoP/NF and W-NiP/NF in W 4f.

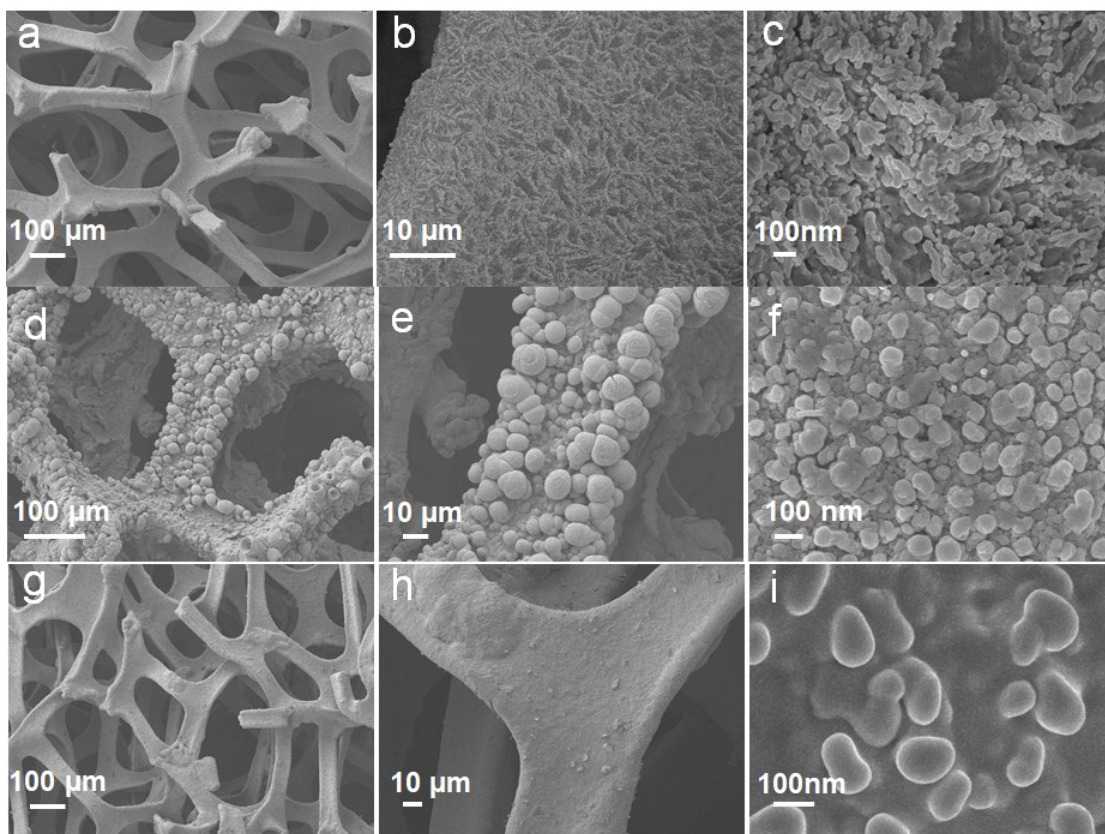


Fig. S7 SEM images of (a-c) NiP/NF, (d-f) NiCoP/NF, and (g-i) W-NiP/NF.

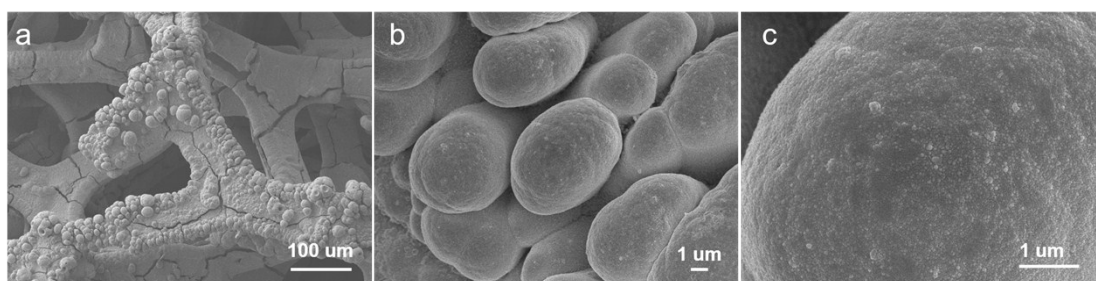


Fig. S8 (a, b, c) SEM images of CoW(OH)_x/NF.

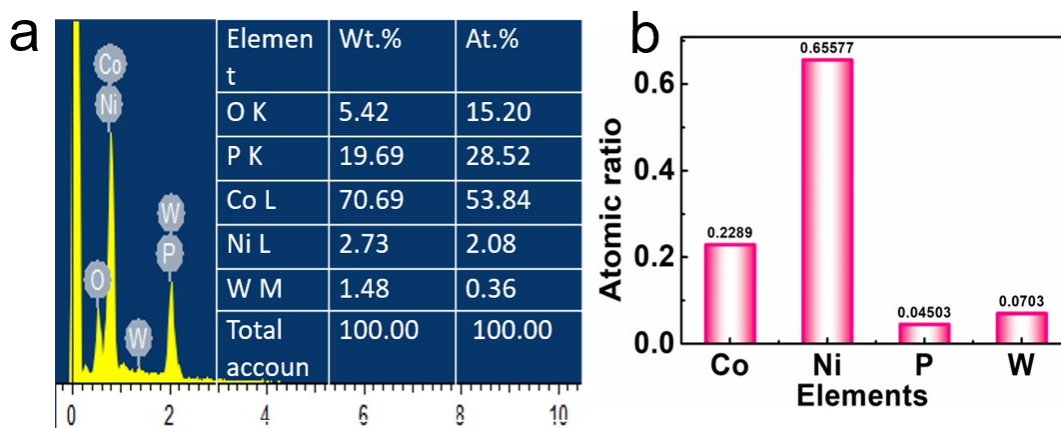


Fig. S9 (a) Elemental contents, (b) AES-ICP of W-NiCoP/NF.

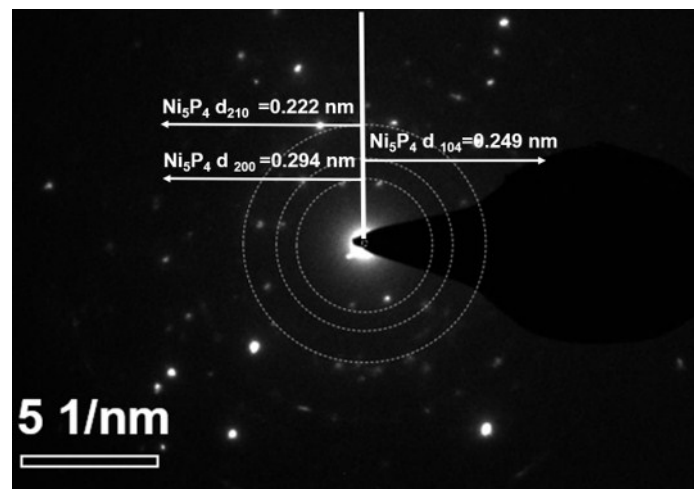


Fig. S10 SAED of W-NiCoP/NF.

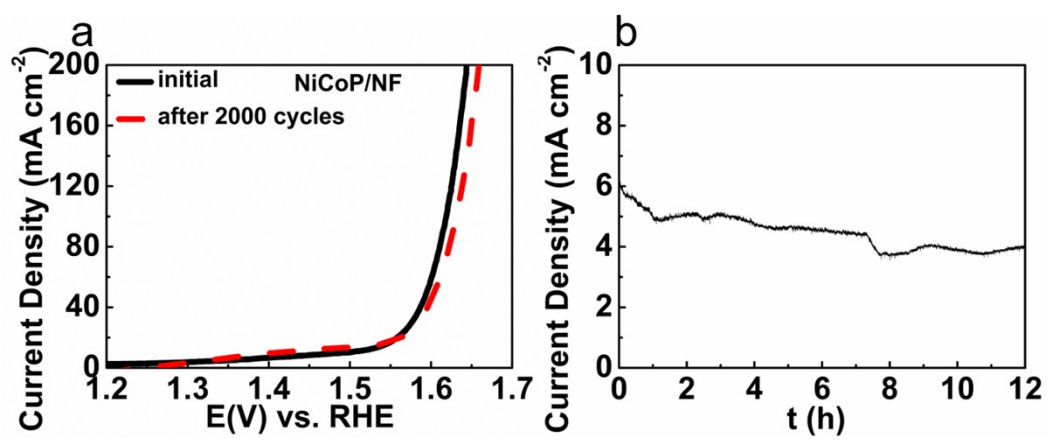


Fig. S11 (a) Stability tests for NiCoP/NF by 2000 cyclic voltammetry cycles in 1.0 M KOH, (b) Stability tests for NiCoP/NF through chronoamperometry for 12 h in 1.0 M.

KOH.

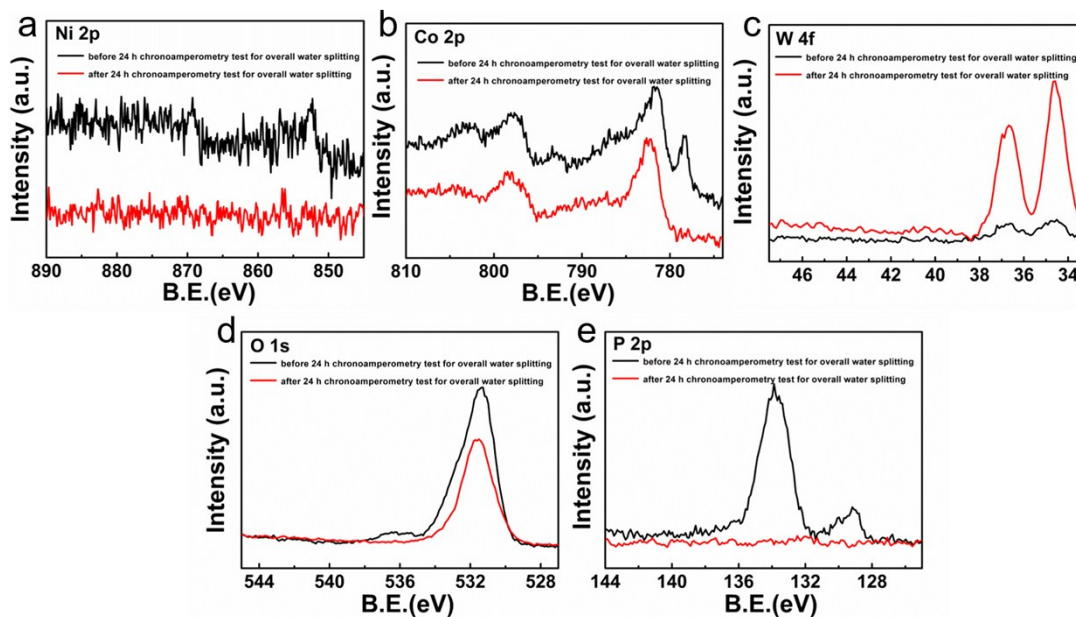


Fig. S12 High-resolution XPS scans of W-NiCoP/NF as counter electrode in the (a) Ni 2p, (b) Co 2p, (c) W 1f, (d) O 1s, and (e) P 2p regions before and after 24 h chronoamperometry test for overall water splitting in 1.0 M KOH.

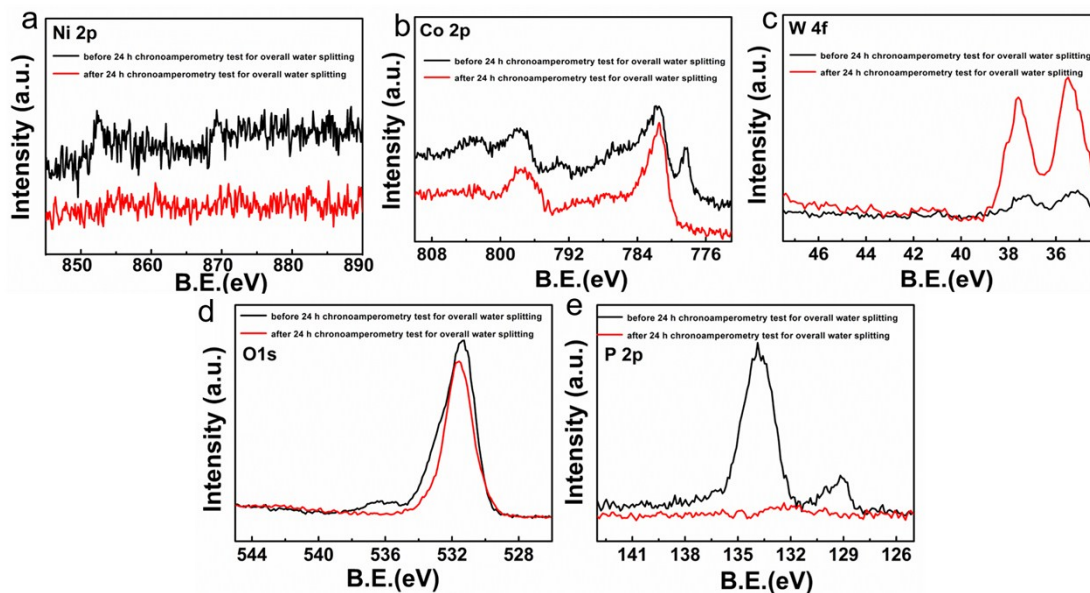


Fig. S13 High-resolution XPS scans of W-NiCoP/NF as working electrode in the (a) Ni 2p, (b) Co 2p, (c) W 1f, (d) O 1s, and (e) P 2p regions before and after 24 h chronoamperometry test for overall water splitting in 1.0 M KOH.

Table S1. Element contents (atom %) of the CoW(OH)_x/NF.

Element	Atom %
Ni	8.35
Co	15.42
W	2.69
O	73.55

Table S2. Comparison of the HER performance of W-NiCoP/NF with other recently reported HER electrocatalysts in alkaline media.

Electrocatalyst	j (mA cm ⁻²)	η (mV)	Ref.
W-NiCoP/NF	10	29.6	This work
Ni-Co-P HNBS	10	107	Energy Environ. Sci., 2018, 11, 87
CoNiP@NF	10	155	J. Mater. Chem. A, 2016, 4, 10195
CoO _x @CN	10	232	<i>J. Am. Chem. Soc.</i> 2015 , 137, 2688
Ni/Ni ₃ N foam	10	~399	J. Mater. Chem. A, 2015, 3, 8171
CoP/rGO-T	10	150	Chem. Sci., 2016, 7, 1690
CoP NA/Ti	10	90	Chem. Mater., 2014, 26, 4326
CoP ₂ /RGO	10	88	J. Mater. Chem. A, 2016, 4, 4686
Mn-Co-P/Ti	10	76	ACS Catal., 2016, 7, 98
Ni ₃ FeN-NPs	10	158	Adv. Energy Mater., 2016, 6, 1502585.
Co ₉ S ₈ /CC	–	175	J. Mater. Chem. A, 2016, 4, 6860

Table S3. Elemental values of simulated equivalent circuit for NiP/NF, W-NiP/NF, NiCoP/NF, and W-NiCoP/NF in alkaline solution.

Samples	R_s/Ω	R_{ct}/Ω
W-NiCoP/NF	1.053	2.216
NiCoP/NF	1.969	90.1
W-NiP/NF	1.198	9.166
NiP/NF	1.869	70.35

Table S4. Comparison of the OER performance of W-NiCoP/NF with other recently reported electrocatalysts in alkaline media.

Electrocatalyst	j (mA cm ⁻²)	η (mV)	Ref.
W-NiCoP/NF	20	200	This work
Ni-Co-P HNBS	10	270	<i>Energy Environ.Sci.</i> , 2018, 11, 872
NiCoP nanoparticle	10	310	<i>Adv. Mater. Interfaces</i> 2016, 3,1500454
FeP	10	288	<i>Chem. Eur. J.</i> 2015, 21, 18062
Co4N/CC	10	257	<i>Angew. Chem. Int. Ed.</i> 2015, 54, 14710
np-(Co _{0.52} Fe _{0.48}) ₂ P	10	270	<i>Energy Environ. Sci.</i> 2016, 9, 2257
Cu _{0.3} Co _{2.7} P/NC	10	190	<i>Adv. Energy. Mater.</i> 2017, 7, 1601555
W _{0.5} Co _{0.4} Fe _{0.1} /NF	10	310	<i>Angew. Chem. Int. Ed.</i> 2017, 56, 4502-4506
N-doped carbon	10	158	<i>Nat. Commun.</i> 2017, 8, 13592
NiFe-NS	10	302	<i>Nat. Commun.</i> 2014, 5, 4477
Ni _{0.9} Fe _{0.1} /NC	10	330	<i>ACS Catal.</i> 2016, 6, 580-588

Table S5. Comparison of the overall water splitting performance of W-NiCoP/NF with other recently reported electrocatalysts in alkaline media.

Electrocatalyst	j (mA cm ⁻²)	η (mV)	Ref.
W-NiCoP/NF	20	1.54	This work
Ni5P4/ Ni5P4	10	1.7	<i>Angew.Chem.Int.Ed.</i> 2015,54,12361
CP@Ni-P/CP@Ni-P	10	1.63	<i>Adv.Funct.Mater.</i> 2016,26,4067
CoP-Cu/CoP-Cu	10	1.645	<i>Angew.Chem. .Int.Ed.</i> 2015,127,6349.
Ni2P-NF/Ni2P-NF	10	1.63	<i>Energy Environ. Sci.</i> 2015,8,1027.
Ni12P5-NF/ Ni12P5-NF	10	1.64	<i>ACS Catal.</i> 2015,7.103
CoSe2-CC/CoSe2-CC	10	1.63	<i>Adv. Mater.</i> 2016,28,7527.
NiCo2O4	10	1.65	<i>Angew. Chem. Int. Ed.</i> 2016, 55, 6290
Ni2P	10	1.63	<i>Energy Environ. Sci.</i> 2015, 8, 2347
CoSe film	10	1.65	<i>Chem. Commun.</i> 2015, 51, 16683
NiFeOx	10	1.51	<i>Nat. Commun.</i> 2015, 6, 7261

Table S6 Element contents (atom %) of the W-NiCoP/NF before and after overall water splitting

Samples	Ni	Co	W	P	O
W-NiCoP/NF	2.68	8.23	0.28	21.96	66.84
W-NiCoP/NF-HER	3.31	11.68	3.55	6.47	74.99
W-NiCoP/NF-OER	3.01	11.26	2.84	5.13	77.75