Electronic Supplementary Information (ESI)

Hierarchical NiCoP nanocone arrays supported on Ni foam as an efficient and stable bifunctional electrocatalyst for overall water splitting

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Table S1

Methods of fabrication various nanoforms of phosphide or sulphide on conductive substrates.

Catalyst	Current collector	Catalyst morphology	Fabrication procedure	Ref.
CoP	CC	NWs	Step 1: Hydrothermally obtained Co(OH)F Step 2: Low-temperature phosphidation	S1
CoP	GCE	NCs ("urchin-like")	Step 1: Hydrothermally obtained $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ (at 120°C for 12 h) Step 2: Low-temperature phosphidation (at 120°C for 12 h)	S2
Co-P film	Cu foil	Films	Potentiodynamic electrodeposition	S3
Ni_5P_4	NF	TNS ("disklike")	Contact-conversion synthesis (nickel foil and red phosphorus for 1 h at 550°C under an inert atmosphere)	S4
Ni_5P_4-Ni_2P	NF	NS	Contact-conversion synthesis (nickel foil and red phosphorus heated to 400, 500, 600, or 800°C for 6 h in a flow of N2)	S5
Ni_8P_3	NF	NS	Contact-conversion synthesis (phosphorization at 250°C).	S6
Ni_9S_8	NF	NS	Contact-conversion synthesis (sulfurization at 250°C).	S6
$NiCo_2S_4$	NF	NWs	Step 1: Hydrothermally obtained Ni-Co-carbonates hydroxide NWs (at 120°C for 6 h) Step 2: Converted into $NiCo_2S_4$ NWs (precipitating process in a sodium sulfide environment at 160°C for 8 h)	S7
Ni_2P–CoP	CC	NWAs	Step 1: $Co(OH)_2$–$Ni(OH)_2$ electrodeposited Step 2: Converted into Ni_2P–CoP NS (phosphidation at 300°C for 1 h)	S8
NiCoP	Ti foil	NPs (nanospheres)	Synthesized using a reverse microemulsion method (tri-n-octylphosphine were used as phosphorus precursors)	S9
NiCoP	NF	NS	Step 1: Hydrothermally obtained NiCo precursor (at 100°C for 8 h) Step 2: Converted into NiCoP NS (phosphidation at 300°C for 2 h)	S10
NiCoP	NF	NWAs	Step 1: Hydrothermally obtained NiCo precursor NWAs (at 120 °C for 6 h). Step 2: Converted into NiCoP NWAs (phosphidation at 300°C for 3 h)	This work

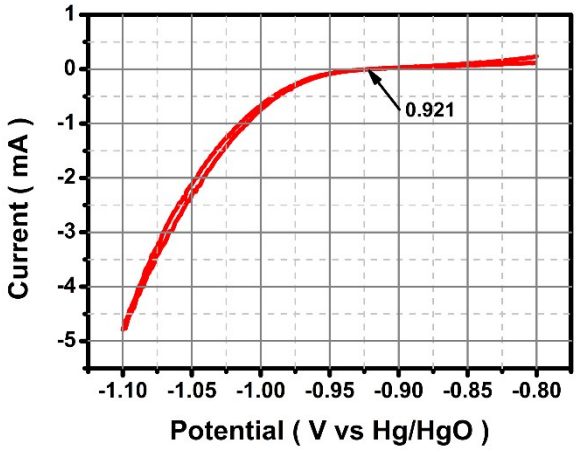

Fig S1. Cyclic voltammogram of calibration

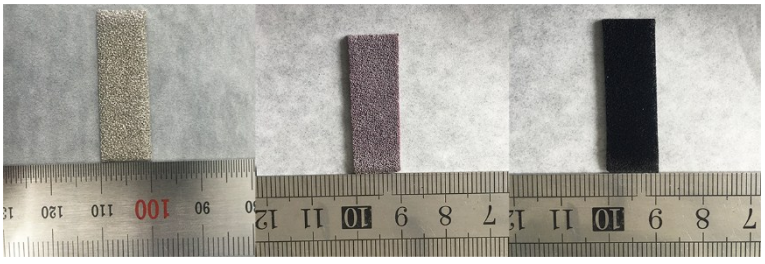

Fig S2. Optical photograph (from left to right) of Ni foam, NiCo-CH-NWAs/NF, NiCoP-NWAs/NF.

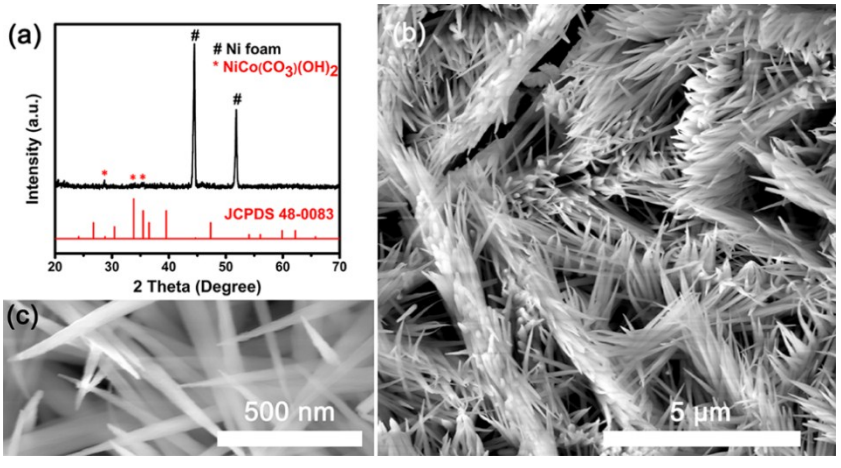

Fig S3. XRD and SEM images for NiCo-CH-NWAs/NF.

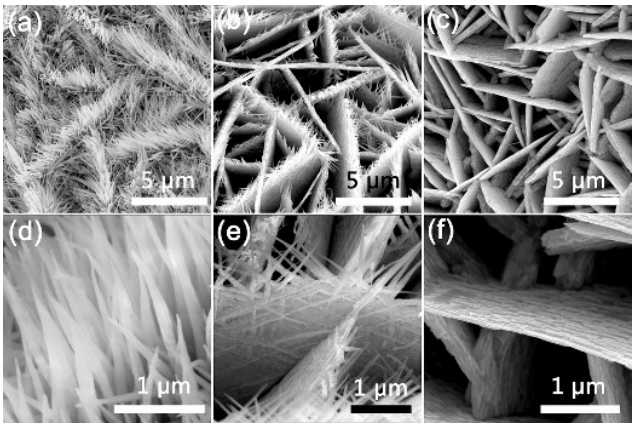

Fig.S4. SEM images of NiCoP nanostructures on foam which growing with different amounts of $CO(NH_2)_2$: (a, d) 25 mmol, (b, e) 15 mmol, (c, f) 10 mmol

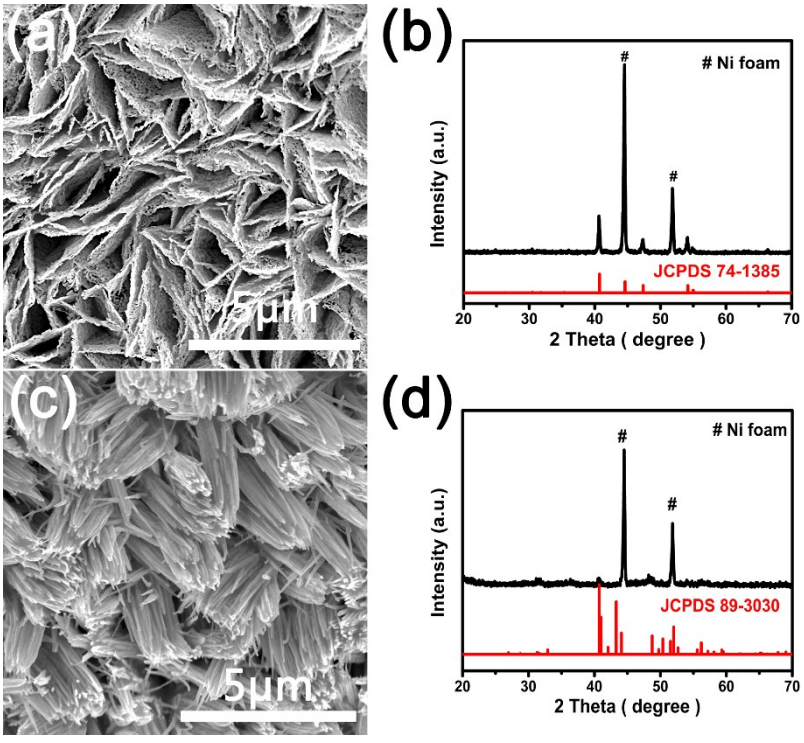

Fig S5. a) SEM image for Ni_2P-NSAs/NF; b) XRD patterns of Ni_2P-NSAs/NF; c) SEM image for

Co_2P-NWAs/NF; d) XRD patterns of Co_2P-NWAs/NF

Table S2
Comparison of HER activity of the NiCoP-NWAs/NF with that of some recently reported Co(or Ni)- phosphide- based catalysts tested in alkaline media.

Catalyst	Current density (j)	Overpotential	Electrolyte	Reference
NiCoP-NWAs/NF	10 mA cm^{-2}	-104 mV	1.0 M KOH	This work
	100 mA cm^{-2}	-197 mV		
Co_2P-NWAs/NF	10 mA cm^{-2}	-131 mV	1.0 M KOH	This work
Ni_2P-NSAs/NF	10 mA cm^{-2}	-152 mV	1.0 M KOH	This work
Co-P film	10 mA cm^{-2}	-94 mV	1.0 M KOH	S3
CoP/CC	10 mA cm^{-2}	-209 mV	1.0 M KOH	S1
	20 mA cm^{-2}	-250 mV		
CoP-NR	10 mA cm^{-2}	-152 mV	1.0 M KOH	S11
	20 mA cm^{-2}	-171 mV		
Co phosphide/ phosphate	10 mA cm^{-2}	-380 mV	1.0 M KOH	S12
Ni-P/CP	10 mA cm^{-2}	-117 mV	1.0 M KOH	S13
	20 mA cm^{-2}	-150 mV		
	100 mA cm^{-2}	-250 mV		
Ni_2P/NF	10 mA cm^{-2}	-150 mV	1.0 M KOH	S14
Ni_2P/NF	20 mA cm^{-2}	-205 mV	1.0 M KOH	S15
NiP/Ni	10 mA cm^{-2}	-130 mV	1.0 M KOH	S6
Ni_2P	10 mA cm^{-2}	-110 mV	1.0 M KOH	S16
Ni_2P-NPs	20 mA cm^{-2}	-250 mV	1.0 M KOH	S17
Ni_2P/NF	10 mA cm^{-2}	-150 mV	1.0 M KOH	S18
	20 mA cm^{-2}	-190 mV		
Ni_5P_4/Ni foil	10 mA cm^{-2}	-150 mV	1.0 M KOH	S4

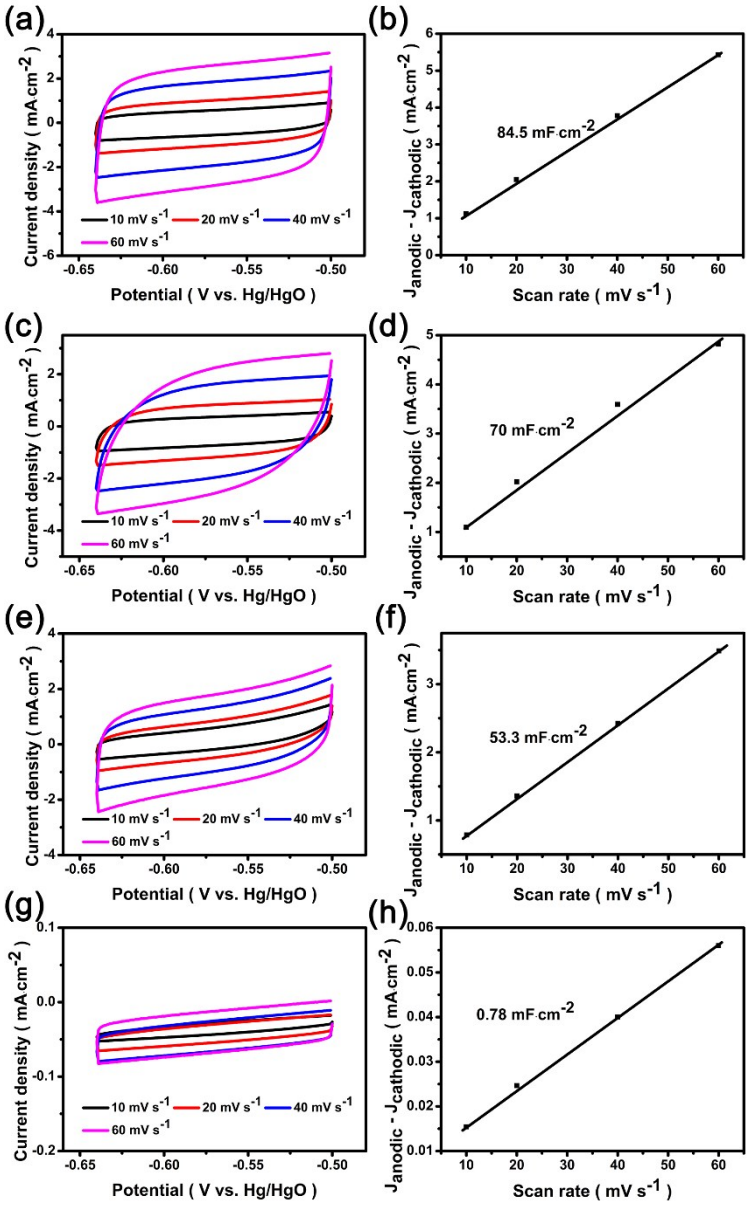

Fig S6. Cyclic voltammograms of NiCoP-NWAs/NF (a), Co_2P-NWAs/NF (c), Ni_2P-NSAs/NF (e) and Ni foam (g) at different scan rates in the region of -0.64 – -0.5 V. The current densities of NiCoP-NWAs/NF (b), Co_2P-NWAs/NF (d), Ni_2P-NSAs/NF (f) and Ni foam (h) at -0.57 V versus Hg/HgO with different scan rates.

The active surface area of catalysts can be evaluated by the electrochemical capacitances. The EDLC values of all catalysts can be calculated by the half of the slope of the capacitive current versus scan rate. The EDLC values can be converted into the ECSA using the specific capacitance value for a

standard with 1 cm2 of real surface area. The specific capacitance for a flat surface is about 0.02-0.06 mF cm^{-2}. The capacitance value of Ni foam is about 0.78 mF cm^{-2} larger than a flat surface. Therefore, the capacitance value of Ni foam is considered as the standard. The ECSA values of all electrodes can be calculated by the following formula:

$$A_{ECSA}=\frac{specific\ capacitance\ of\ catalysts}{specific\ capacitance\ of\ Ni\ foam\ per\ cm^2_{ECSA}}$$

The A_{ECSA} of NiCoP-NWAs/NF, Co_2P-NWAs/NF and Ni_2P-NSAs/NF are 54.2 cm^2, 44.9 cm^2 and 34.2 cm^2

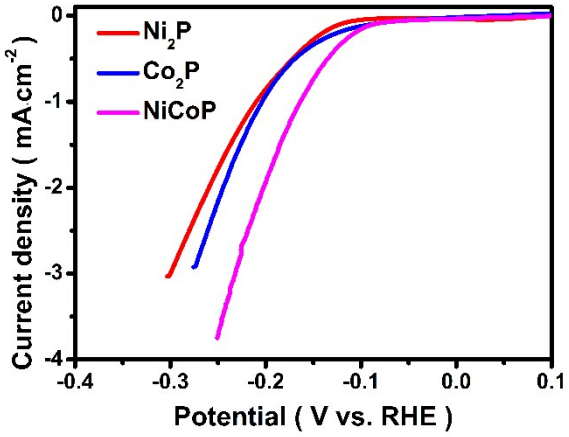

Fig S7. Polarization curves from normalized to the electrochemical active surface area (ECSA) for HER

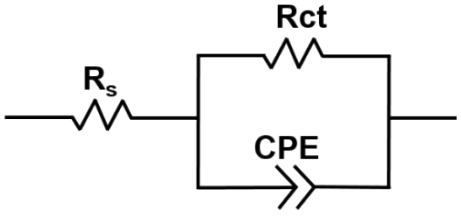

Fig S8. The equivalent circuit for fitting the EIS results.

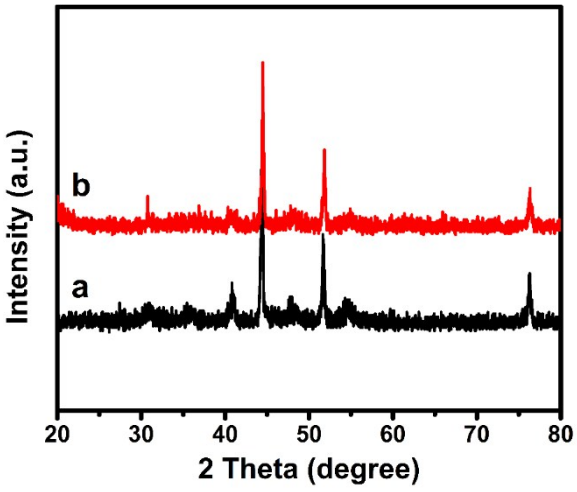

Fig S9. XRD patterns of NiCoP-NWAs/NF before (a) and after (b) 28h HER stability test in 1 M KOH.

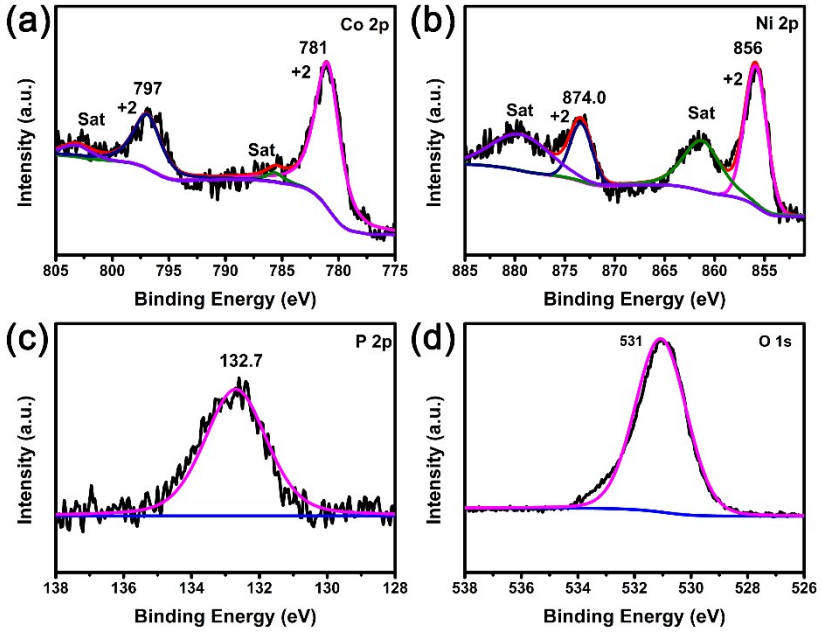

Fig S10. XPS spectra of (a) Co 2p, (b) Ni 2p, (c) P 2p and (d) O 2s for NiCoP-NWAs/NF after 28 h HER stability test.

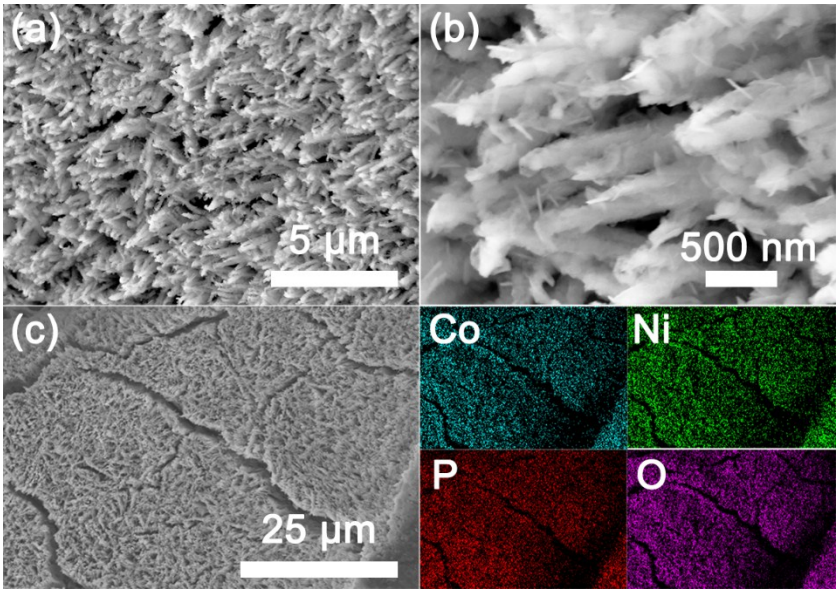

Fig S11. SEM images (a, b) and element mapping of NiCoP-NWAs/NF (c) after 28h HER stability test.

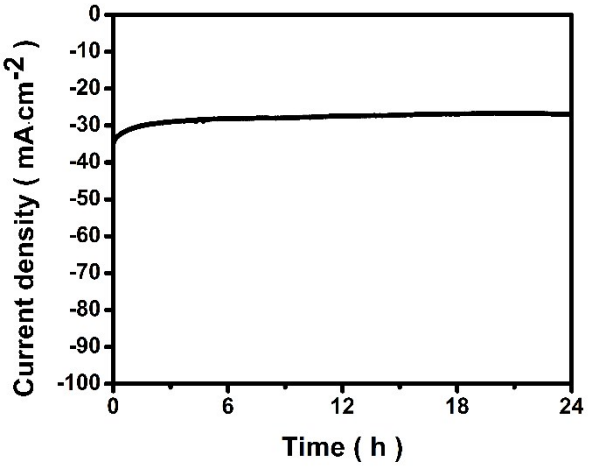

Fig S12. The time-dependent current density curve of NiCoP-NWAs/NF at -0.15 V vs. RHE.

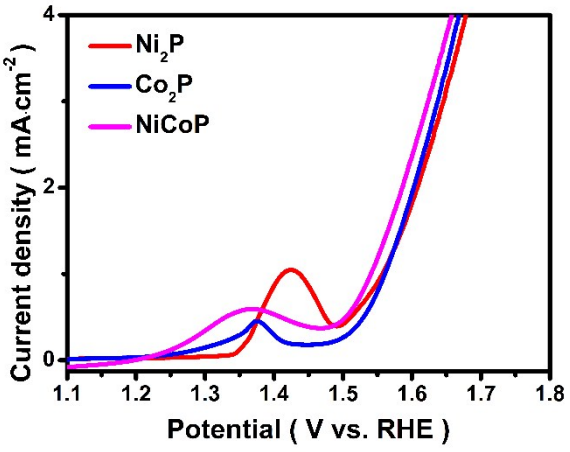

Fig S13. Polarization curves from normalized to the electrochemical active surface area (ECSA) for OER

Table S3
Comparison of OER activity of the NiCoP-CNWAs/NF with that of some recently reported Co(or Ni)- phosphide- based catalysts tested in alkaline media.

Catalyst	Current density (j)	Overpotential	Electrolyte	Reference
NiCoP-NWAs/NF	20 mA·cm^{-2}	270 mV	1.0 M KOH	This work
Co_2P-NWAs/NF	20 mA·cm^{-2}	306 mV	1.0 M KOH	This work
Ni_2P-NSAs/NF	20 mA·cm^{-2}	297 mV	1.0 M KOH	This work
Co-P film	10 mA·cm^{-2}	345 mV	1.0 M KOH	S3
CoP/GCE	10 mA·cm^{-2}	490 mV	1.0 M KOH	S19
CoP (hollow polyhedrons)	10 mA·cm^{-2}	400 mV	1.0 M KOH	S20
Co_2P-NSAs/NF	50 mA·cm^{-2}	330 mV	1.0 M KOH	S11
Co_xP-NP	10 mA·cm^{-2}	319 mV	1.0 M KOH	S21
Co phosphide/ phosphate	10 mA·cm^{-2}	300 mV	1.0 M KOH	S12
Ni_2P	10 mA·cm^{-2}	400 mV	1.0 M KOH	S16
Ni-P/CP	10 mA·cm^{-2} 20 mA·cm^{-2}	190 mV 230 mV	1.0 M KOH	S13
Ni_5P_4	10 mA·cm^{-2}	330 mV	1.0 M KOH	S4
Ni_2P-NSAs/NF	50 mA·cm^{-2}	376 mV	1.0 M KOH	S11
NiCoP-NSAs/NF	50 mA·cm^{-2}	308 mV	1.0 M KOH	S11

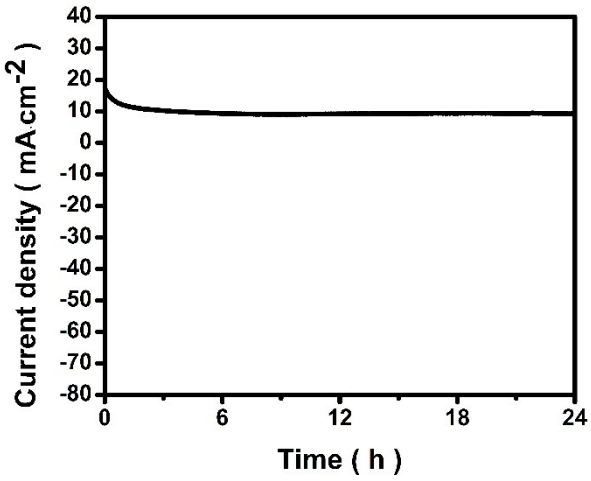

Fig S14. The time-dependent current density curve of NiCoP-NWAs/NF at 1.5V vs. RHE

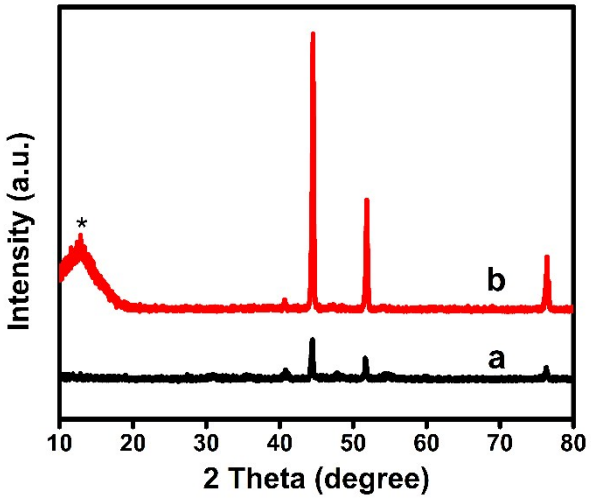

Fig S15. XRD patterns of NiCoP before (a) and after (b) 28h OER stability test in 1 M KOH.

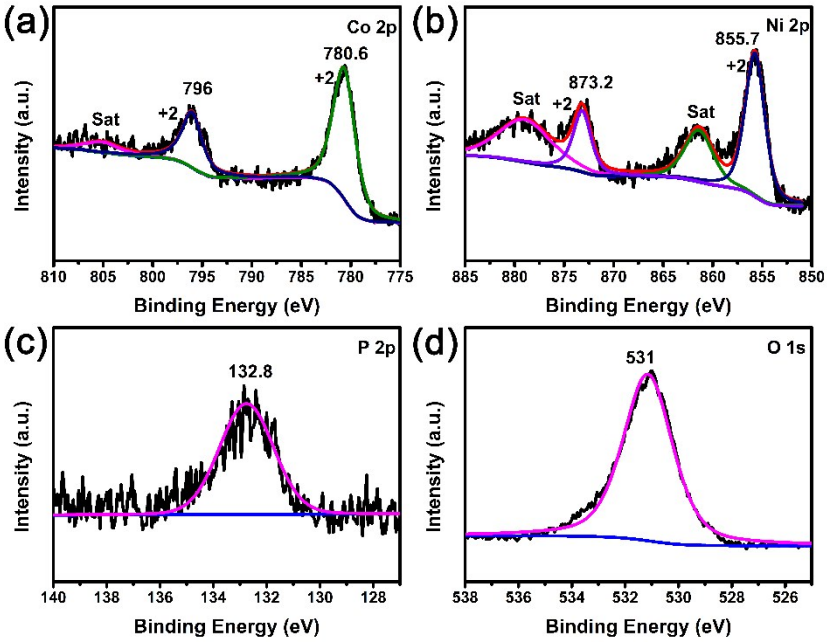

Fig S16. XPS spectra of (a) Co 2p, (b) Ni 2p, (c) P 2p and (d) O 2s for NiCoP-NWAs/NF after 28 h OER stability test.

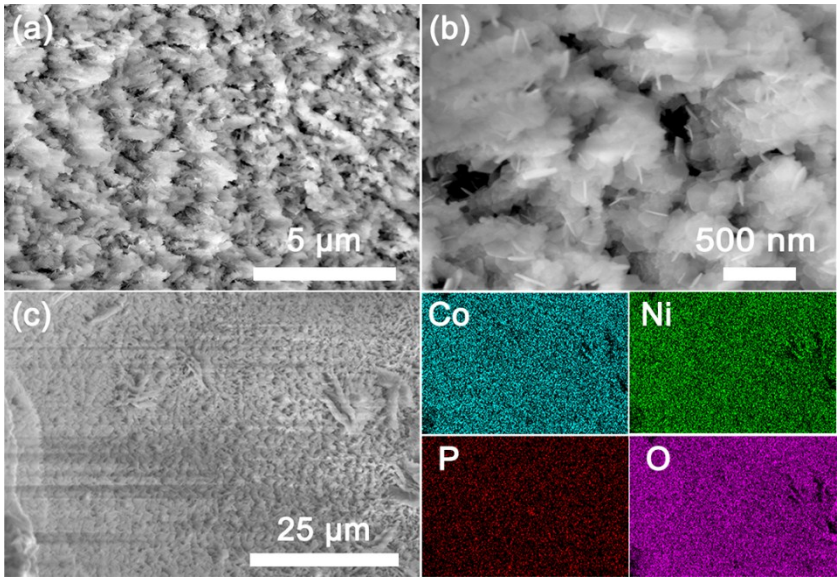

Fig S17. (a)-(b) SEM images and (c) element mapping of NiCoP-NWAs/NF after 28h OER stability test.

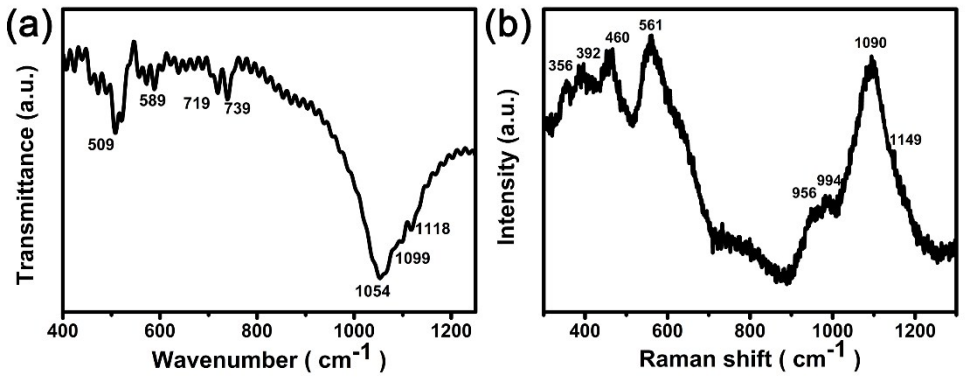

Fig S18. (a) FTIR spectra of NiCoP-NWAs/NF and (b) Raman spectra of NiCoP-NWAs/NF after 28h OER stability test.

References

[S1] J. Q. Tian, Q. Liu, A. M. Asiri and X. P. Sun, *J. Am. Chem. Soc.*, 2014, **136**, 7587.

[S2] H. C. Yang, Y. J. Zhang, F. Hu and Q. B. Wang, *Nano Lett.*, 2015, **15**, 7616.

[S3] N. Jiang, B. You, M. Sheng and Y. Sun, *Angew. Chem. Int. Ed.*, 2015, **54**, 6251.

[S4] M. Ledendecker, S. K. Calderýn, C. Papp, H. P. Steinrîck, M. Antonietti, and M. Shalom, *Angew.Chem.* 2015, **127**,12538.

[S5] X. G. Wang, Y. V. Kolen'ko, X. Q. Bao, K. Kovnir and L. F. Liu, *Angew. Chem. Int. Ed.*, 2015, **54**, 8188.

[S6] G. F. Chen, T. Y. Ma, Z. Q. Liu, N. Li, Y. Z. Su and K. Davey, S. Z. Qiao, *Adv. Funct. Mater.*, 2016, **26**, 3314.

[S7] A. Sivanantham, P. Ganesan and S. Shanmugam, *Adv. Funct. Mater.*, 2016, **26**, 4661.

[S8] A. L. Wang, J. Lin, H. Xu, Y. X. Tong and G. R. Li, *J. Mater. Chem. A*, 2016, **4**, 16992.

[S9] C. D. Wang, J. Jiang, T. Ding, G. H. Chen, W. J. Xu and, Q. Yang, *Adv. Mater. Interfaces*, 2016, **3**, 1500454.

[S10] Y. J. Li, H. C. Zhang, M. Jiang, Y. Kuang, X. M. Sun and X. Duan, *Nano Res.*, 2016, **9**, 2251.

[S11] Z. P. Huang, Z. Z. Chen, Z. B. Chen, C. C. Lv, M. G. Humphrey and C. Zhang, *Nano Energy*, 2014, **9**, 373.

[S12] Y. Yang, H. L. Fei, G. D. Ruan and J. M. Tour, *Adv. Mater*, 2015, **27**, 3175.

[S13] X. G. Wang, W. Li, D. H. Xiong, D. Y. Petrovykh and L. F. Liu, *Adv. Funct. Mater.*, 2016, **26**, 4067.

[S14] B. You, N. Jiang, M. L. Sheng, M. W. Bushan and Y. J. Sun, *ACS Catal*., 2016, **6**, 714.

[S15] E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, *J. Am. Chem. Soc*., 2013, **135***,* 9267.

[S16] L. A. Stern, L. G. Feng, F. Song and X. L Hu *Energy Environ. Sci.*, 2015, **8**, 2347.

[S17] L. G. Feng, H. Vrubel, M. Bensimon and X. L. Hu *Phys. Chem. Chem. Phys.*, 2014, **16**, 5917.

[S18] A. L. Han, S. Jin, H. L. Chen, H. X. Ji, Z. J. Sun and P. W. Du *J. Mater. Chem. A*, 2015, **3**, 1941.

[S19] J. F. Chang, Y. Xiao, M. L. Xiao, J. J. Ge, C. P. Liu and W. Xing, *ACS Catal.*, 2015, **5**, 6874.

[S20] M. J. Liu and J. H. Li, *ACS Appl. Mater. Interfaces*, 2016, **8**, 2158.

[S21] B. You, N. Jiang, M. L. Sheng, S. Gul, J. Yano and Y. J. Sun *Chem. Mater.*, 2015, **27**, 7636.