Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Trace N introduction accelerates desorption of intermediates for HER and formation of MOOH species for OER on NiCoP to boost overall water splitting

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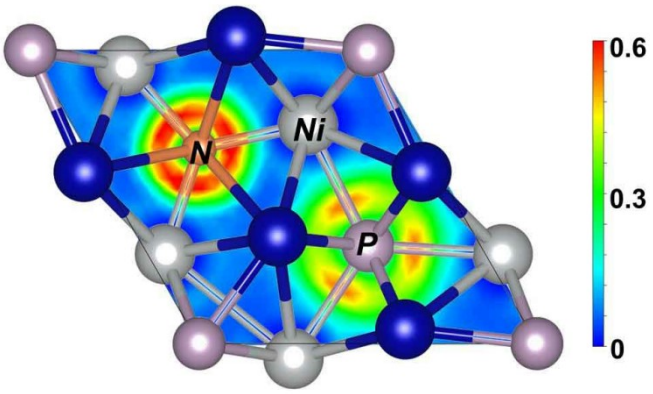


Fig. S1. 2D-ELF of N-NiCoP.

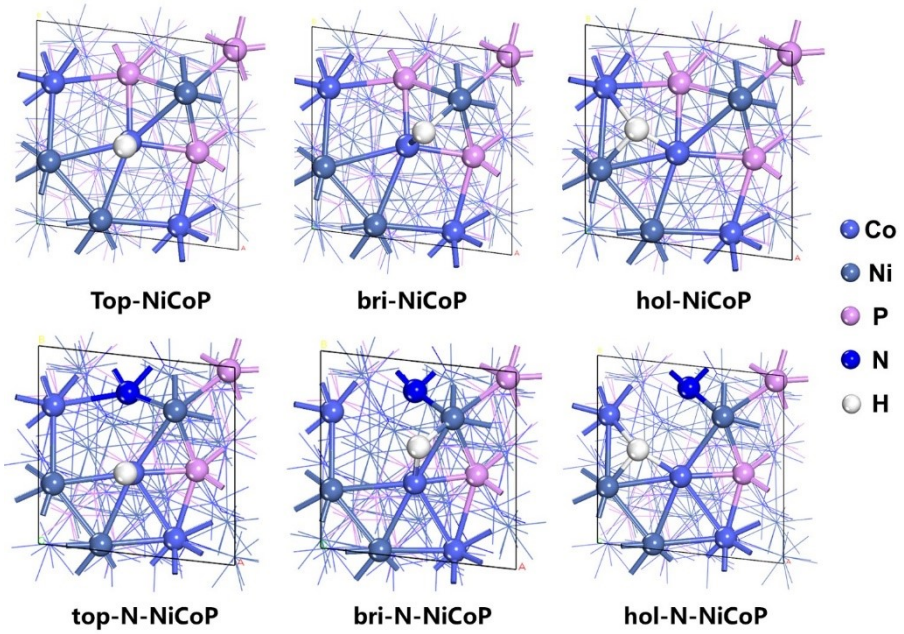


Fig. S2. The three positions (top, bridge, and hollow position) of the surface adsorption H models on NiCoP and N-NiCoP.

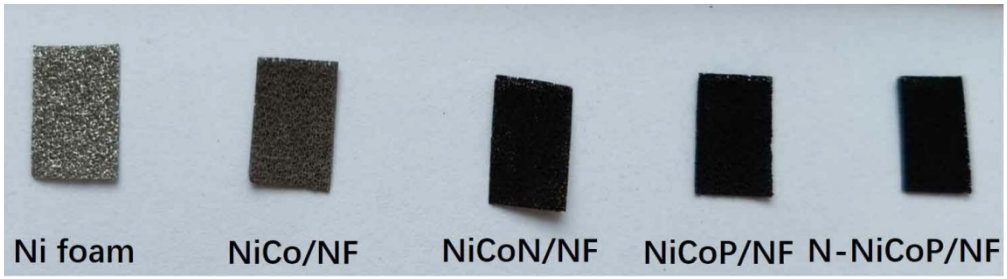


Fig. S3. Photo images of the different samples: bare clean Ni Foam, NiCo/NF, NiCoN/NF, NiCoP/NF and N-NiCoP/NF.

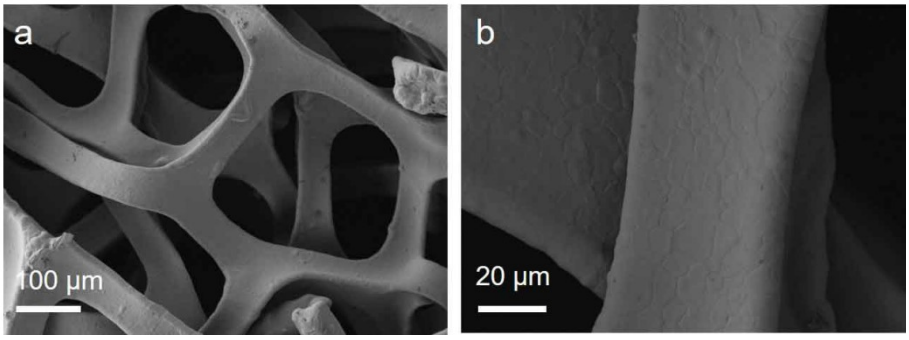


Fig. S4. SEM images of bare clean Ni Foam at different magnifications.

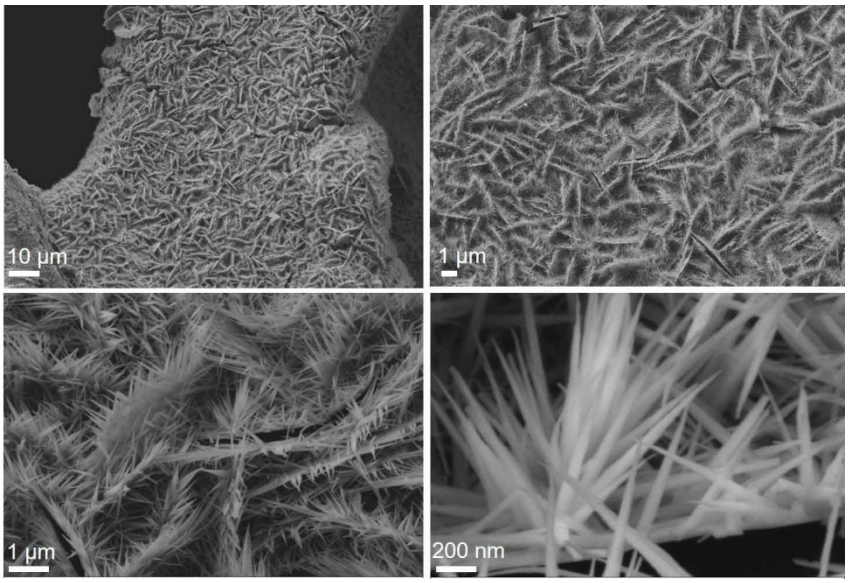


Fig. S5. SEM images of NiCo on Ni Foam at different magnifications.

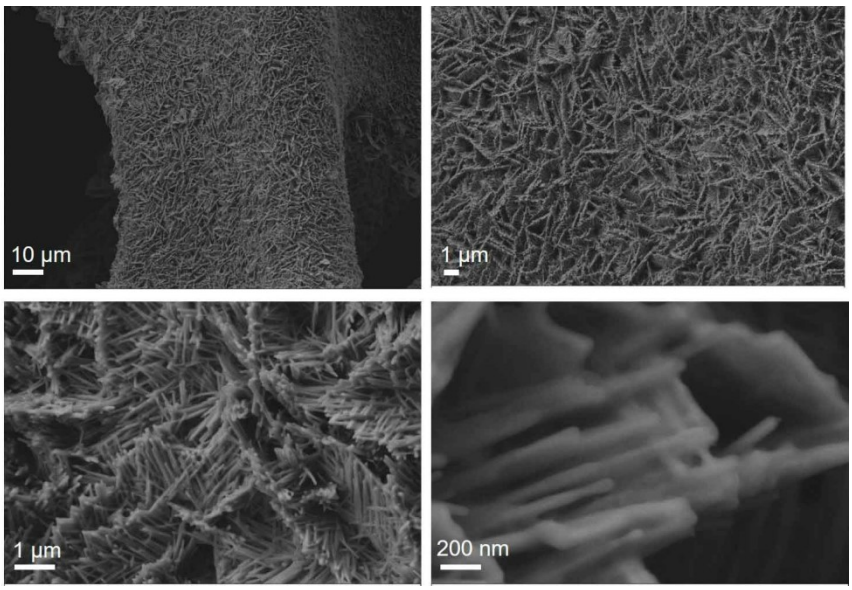


Fig. S6. SEM images of NiCoN on Ni Foam at different magnifications.

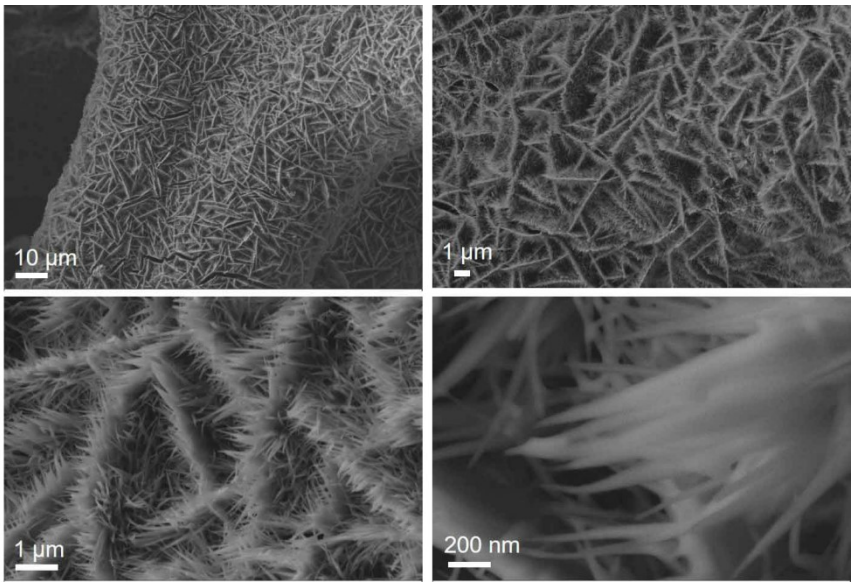


Fig. S7. SEM images of NiCoP on Ni Foam at different magnifications.

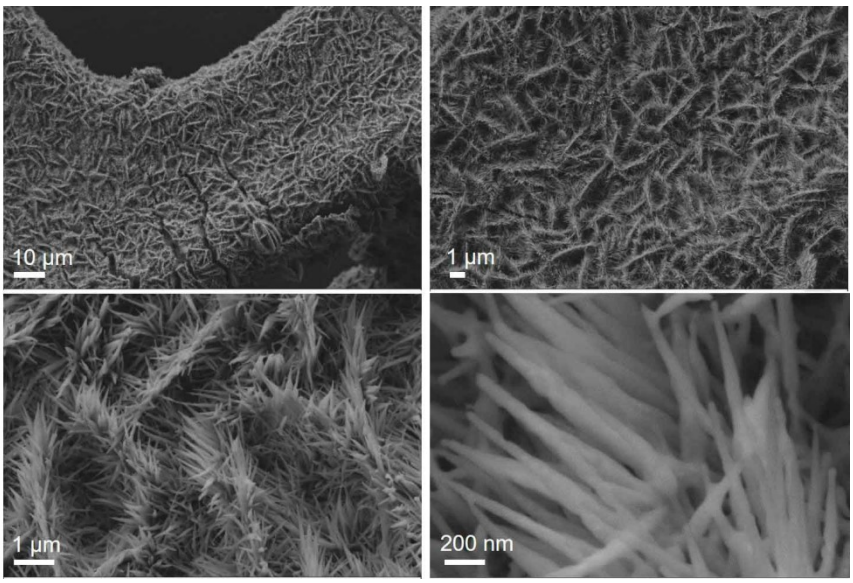


Fig. S8. SEM images of N-NiCoP on Ni Foam at different magnifications.

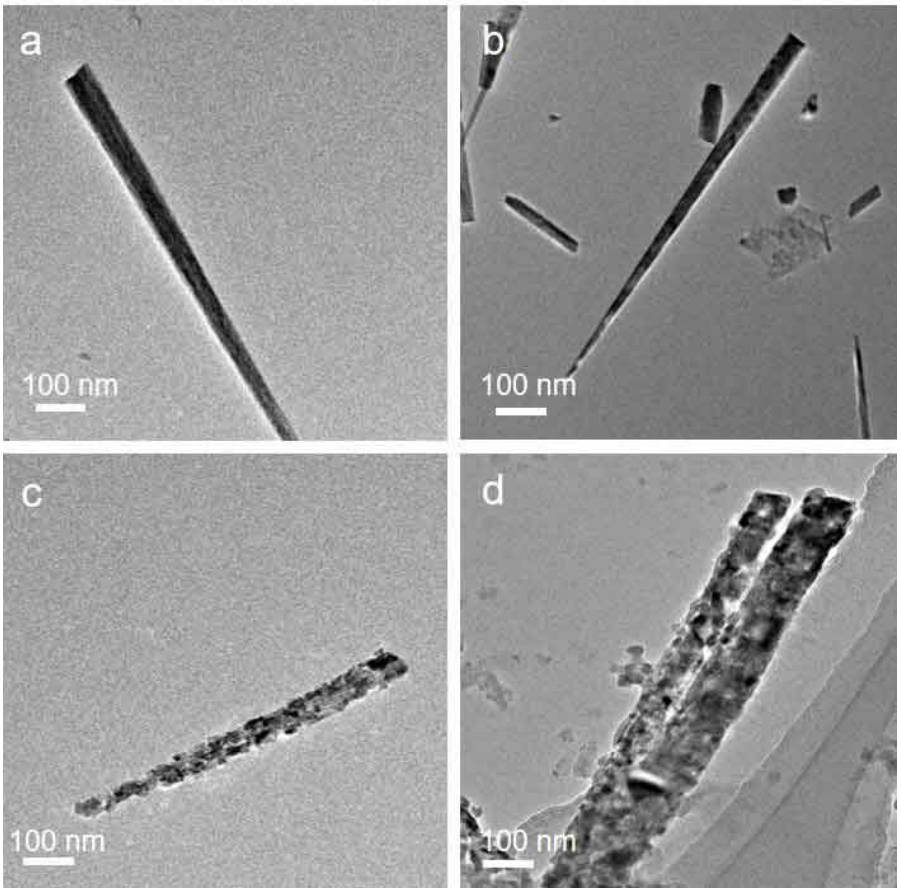


Fig. S9. TEM images of (a) NiCo, (b) NiCoP, (c) NiCoN and (d) N-NiCoP.

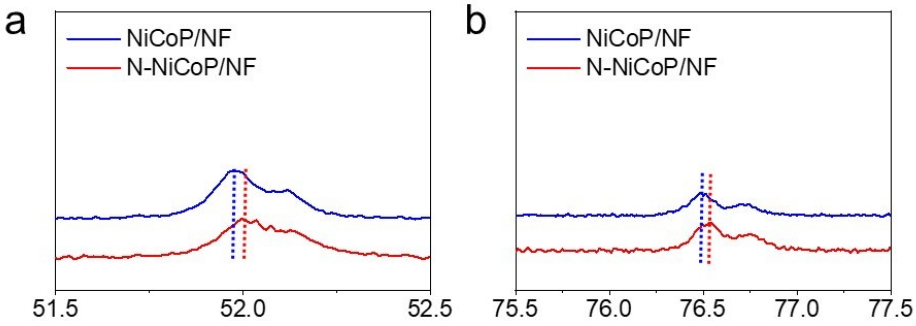
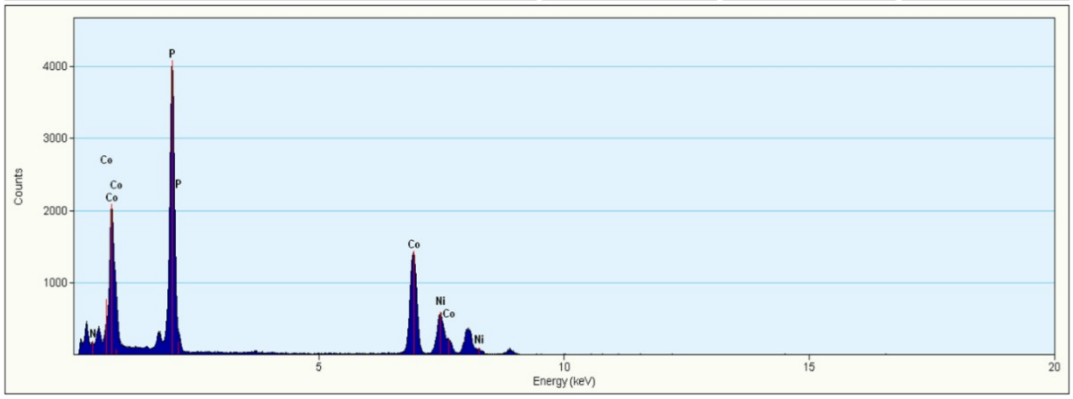


Fig. S10 Partial enlargement XRD patterns of NiCoP/NF and N-NiCoP/NF.



Element	Co	Ni	P	N	O
Atomic	19.04	17.30	35.98	2.91	24.77

Fig. S11. TEM-EDS spectrum of N-NiCoP.

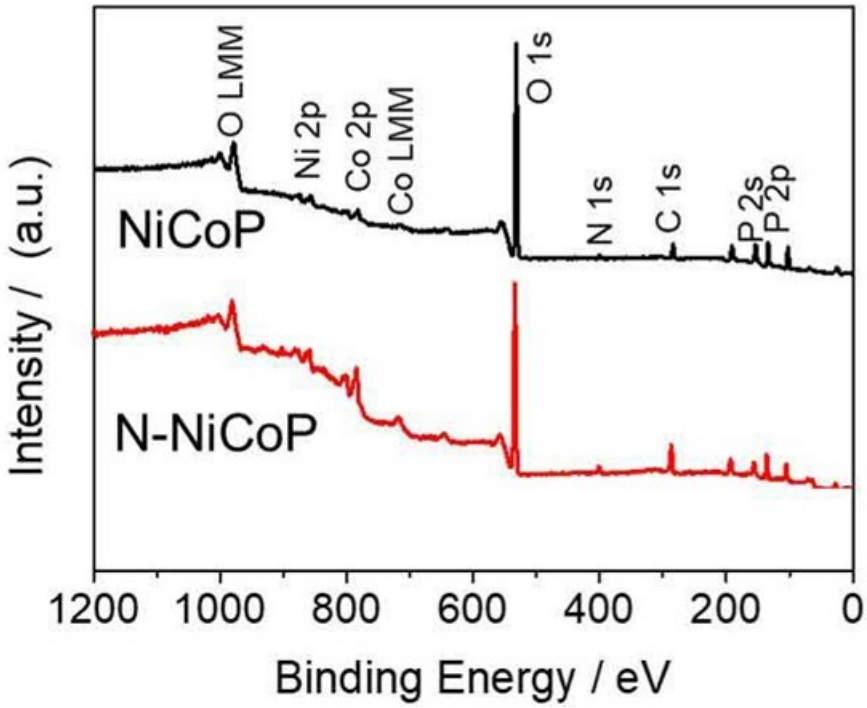


Fig. S12. High-resolution XPS spectrum of (a) full spectra in NiCoP and N-NiCoP samples

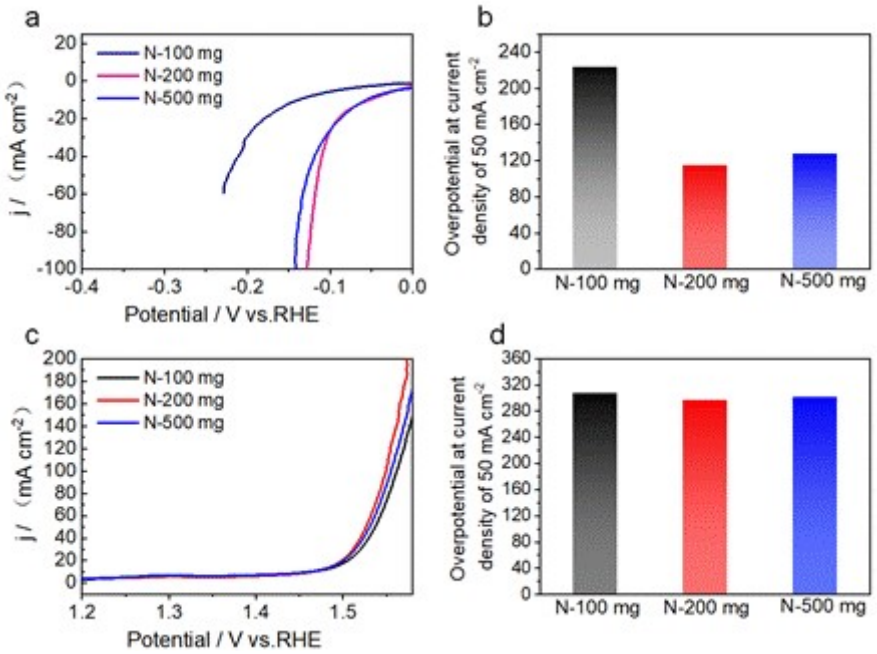


Fig. S13. Polarization curves of HER (a) and OER (b) in 1.0 M KOH with different contents of N samples, and Corresponding overpotential histogram in (c) and (d).

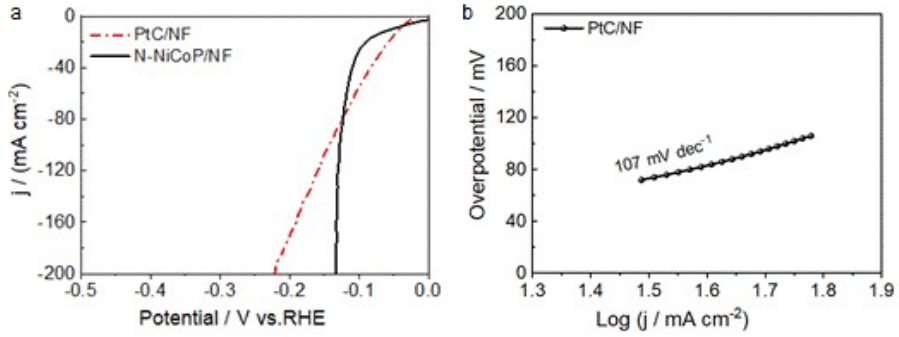


Fig. S14. (a) HER-LSV curves of PtC/NF and N-NiCoP/NF samples, (a) Tafel plot of PtC/NF.

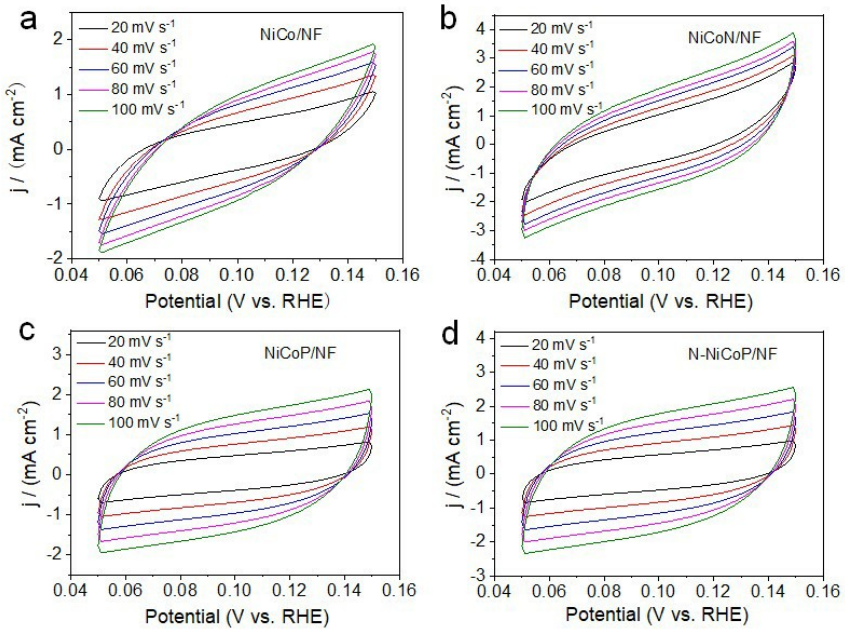


Fig. S15. (a) Cyclic voltammograms for (a) NiCo/NF, (b) NiCoN/NF, (c) NiCoP/NF and (d) N-NiCoP samples in the region of 0.05-0.15 V (vs RHE).

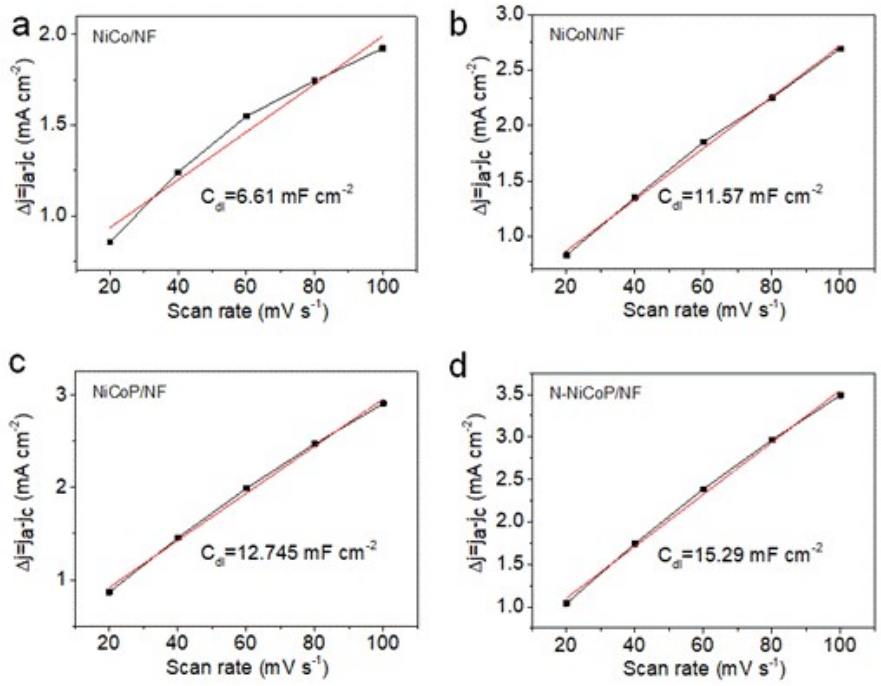


Fig. S16. Calculated C_{dl} for (a) NiCo/NF, (b) NiCoN/NF, (c) NiCoP/NF and (d) N-NiCoP samples.

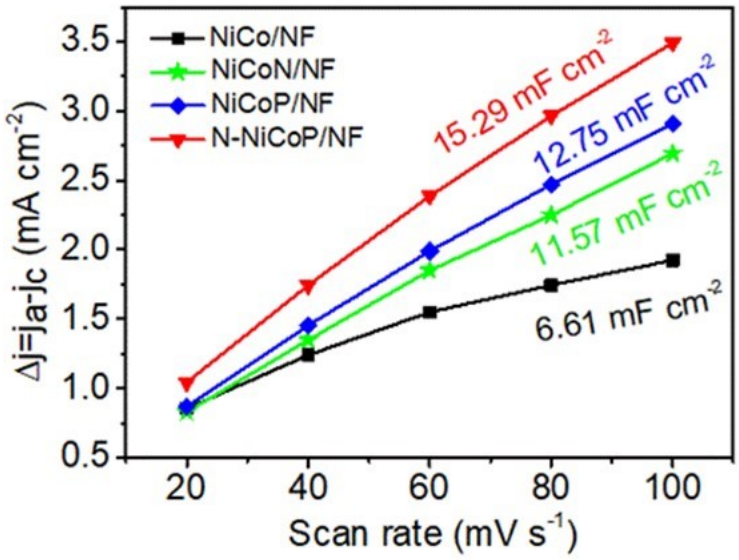


Fig. S17. The calculated C_{dl} of different samples.

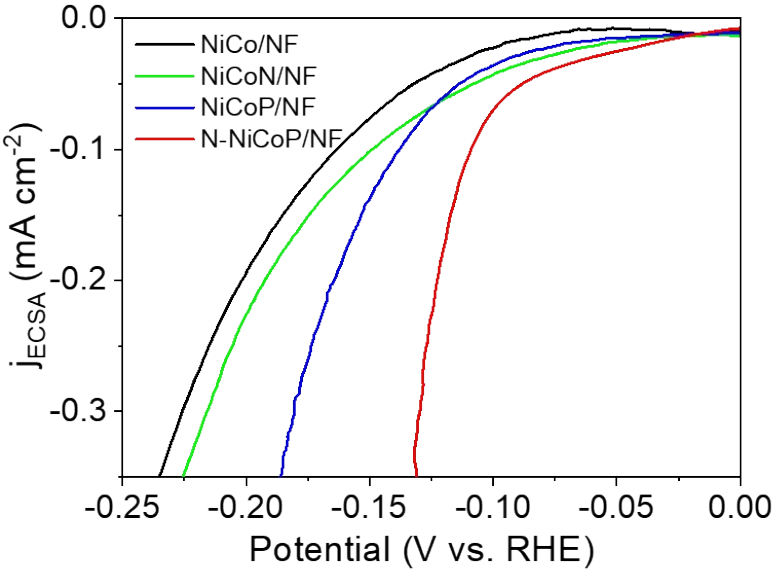


Fig. S18. The ECSA-normalized HER polarization curves.

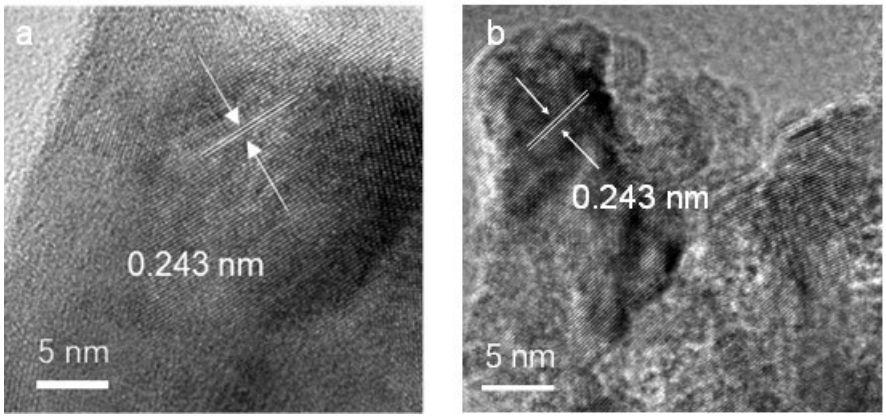


Fig. S19. HRTEM images of N-NiCoP/NF before and after 30 h HER process.

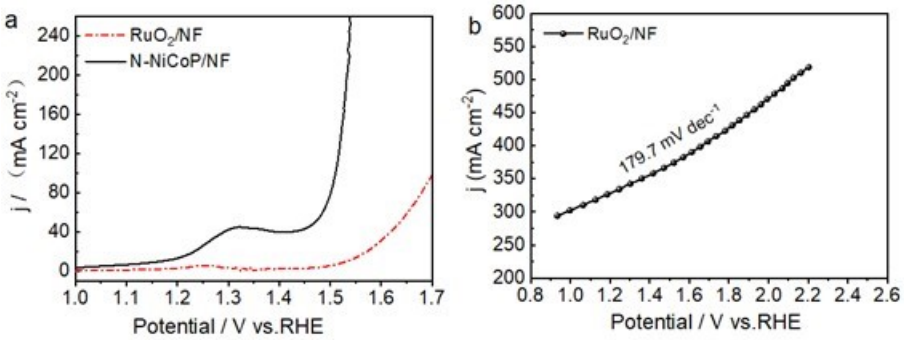


Fig. S20. (a) OER-LSV curves of RuO_2/NF and N-NiCoP samples, (b) Tafel slope of RuO_2/NF.

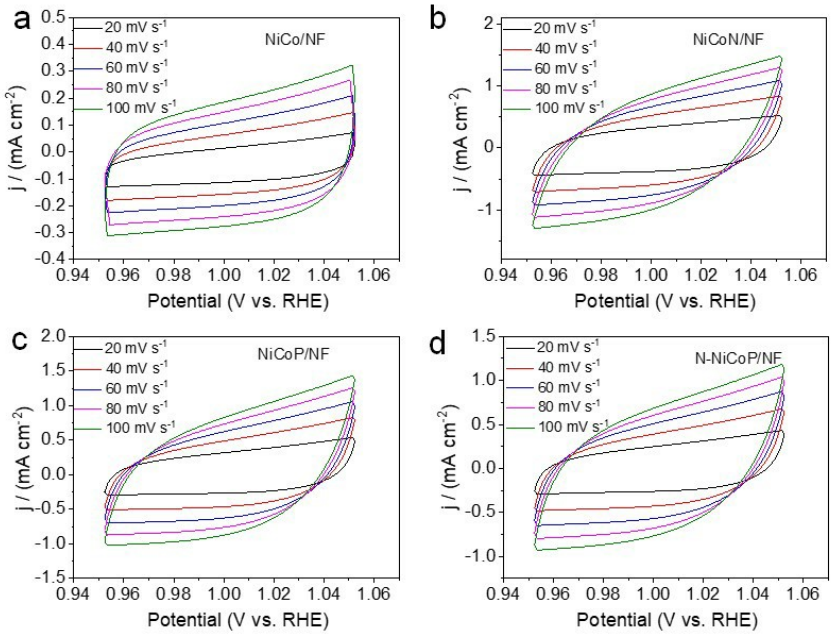


Fig. S21. (a) Cyclic voltammograms for (a) NiCo/NF, (b) NiCoN/NF, (c) NiCoP/NF and (d) N-NiCoP samples in the region of 0.05-0.15 V (vs RHE).

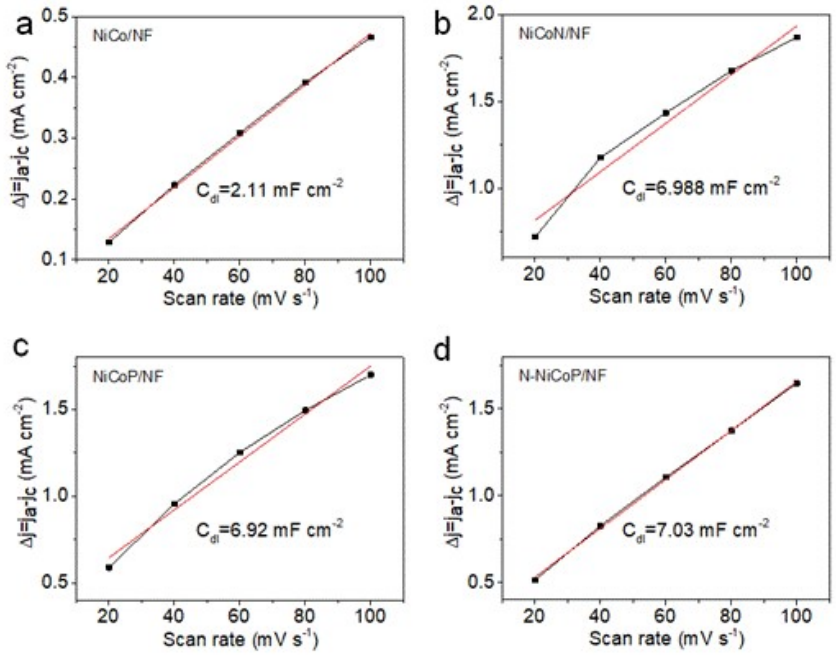


Fig. S22. Calculated C_{dl} for (a) NiCo/NF, (b) NiCoN/NF, (c) NiCoP/NF and (d) N-NiCoP samples.

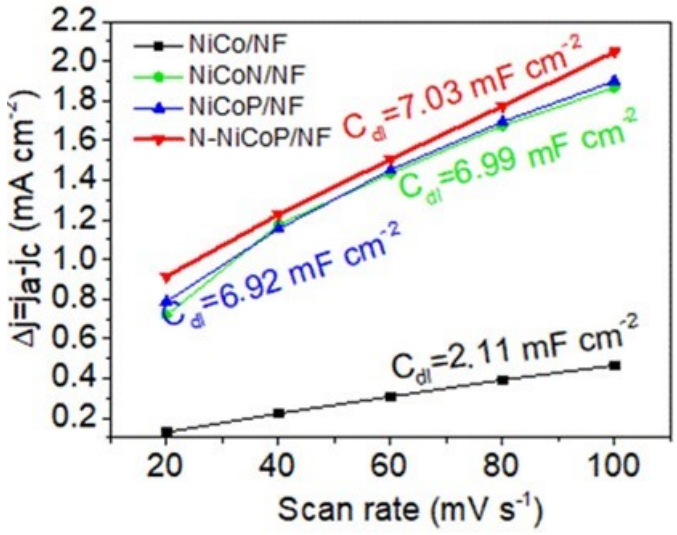


Fig. S23. The calculated C_{dl} of different samples.

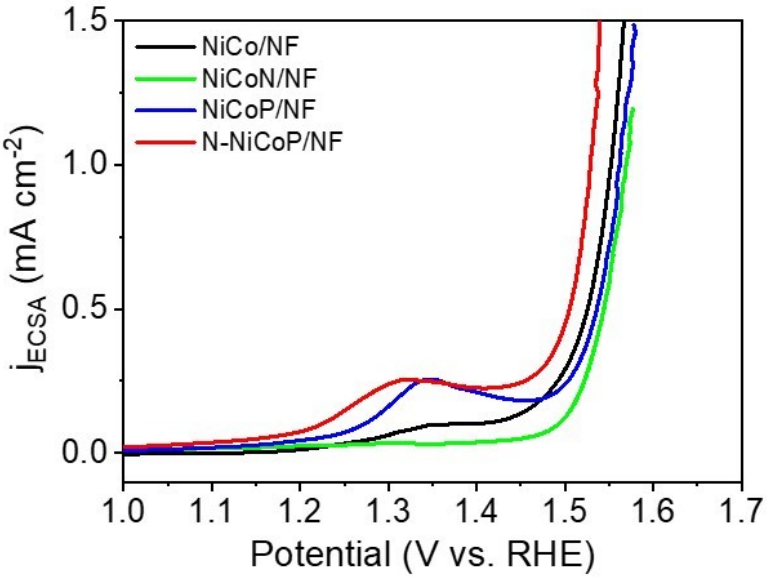


Fig. S24. The ECSA-normalized OER polarization curves.

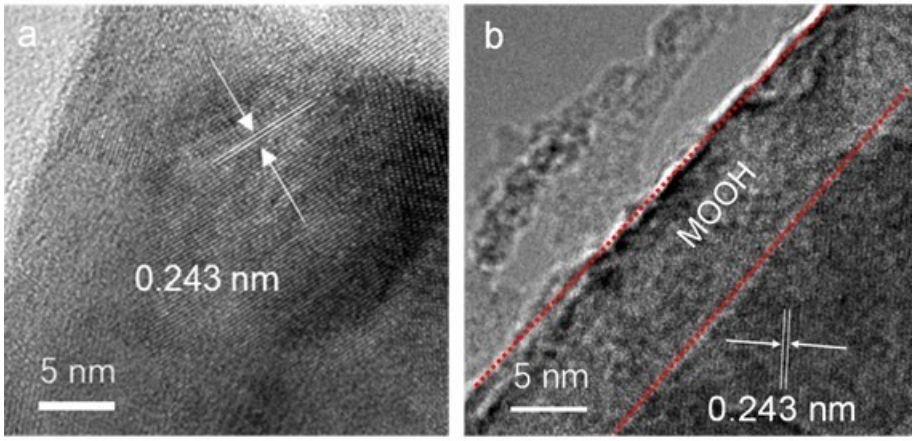


Fig. S25. HRTEM images of N-NiCoP/NF before and after 30 h OER process.

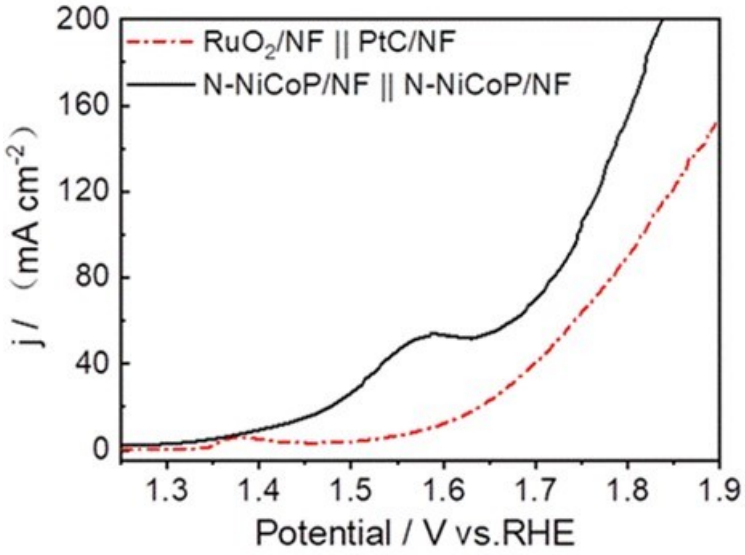


Fig. S26. Overall water splitting of LSV curves of RuO_2/NF||PtC/NF and N-NiCoP/NF|| N-NiCoP/NF samples

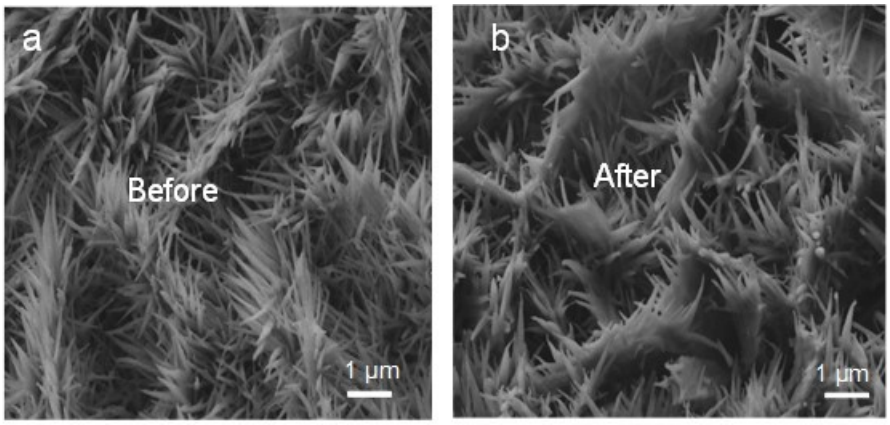


Fig. S27. SEM images of N-NiCoP on Ni Foam before and after 100 h overall water splitting in (a) and (b).

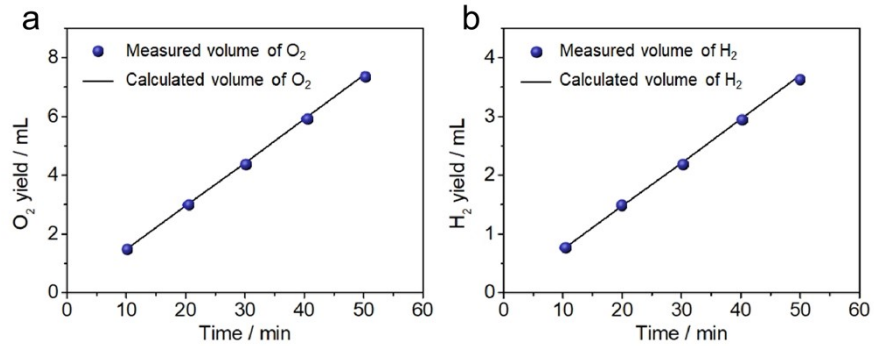


Fig. S28. (a) The volume of oxygen was theoretically calculated and actually measured for N-NiCoP/NF sample in 1.0 M KOH, (b) the Volume of hydrogen was theoretically calculated and measured simultaneously.

Table S1. Comparison of N-NiCoP HER performance with that of recently reported electrocatalysts.

Catalyst	η_{10} /mV	η_{50} /mV	Electrolyte	References
N-NiCoP/NF	53	138	1.0 M KOH	This work
O-NiCoP/Ni_2P	58	119	1.0 M KOH	1
O-NiCoP	44	/	1.0 M KOH	2
S-Ni_5P_4	56	104	0.5 M H_2SO_4	3
CoP/NiCoP/NC	75	/	1.0 M KOH	4
NiCo foam	86	135	1.0 M KOH	5
Ni_3S_2/Cu–NiCo/NF	156	274	1.0 M KOH	6
Se-(NiCo)S_x/$(OH)_x$	103	175	1.0 M KOH	7
CoNi-inf	72	150	1.0 M KOH	8
MoS_2/(CoNi@G)	150	207	0.5 M H_2SO_4	9

Table S2. Fitted values of equivalent circuit, R_s and R_{ct} in 1.0 M KOH for HER

	NiCo/NF	NiCoN/NF	NiCoP/NF	N-NiCoP/NF
R_s/ Ω	1.44	1.25	1.02	0.89
R_{ct} / Ω	63.1	8.5	4.6	2.5

Table S3 Comparison of N-NiCoP OER performance with that of recently reported electrocatalysts.

Catalyst	η_{10} /mV	η_{50} /mV	Electrolyte	References

N-NiCoP/NF	/	250	1.0 M KOH	This work
NiFe foam	206	242	1.0 M KOH	5
SO_4^{2-} modified NiFe (oxy)hydroxide	/	234	1.0 M KOH	10
$NiCo(OH)_2/NiS_2$ CHCs	258	/	1.0 M KOH	11
NiCo@CuO	262	/	1.0 M KOH	12
$NiFe\text{-}OOH_{OV}$	/	330	1.0 M KOH	13
$NiCoFeO_x$	201	/	1.0 M KOH	14
$NiCo/Fe_3O_4$/MOF-74	238	261	1.0 M KOH	15
$NiCoSe_2$@NiO@$CoNi_2S_4$@CoS_2/NF	/	350	1.0 M KOH	16
$NiMoO_4$(Vo)	/	220	1.0 M KOH	17

Table S4. Fitted values of equivalent circuit, R_s and R_{ct} in 1.0 M KOH for OER

	NiCo/NF	**NiCoN/NF**	**NiCoP/NF**	**N-NiCoP/NF**
R_s/ Ω	1.01	0.95	0.79	0.69
R_{ct} / Ω	4.3	3.71	1.96	1.85

Table S5. Comparison of N-NiCoP OWS performance in 1.0 M KOH electrolyte with recently reported electrocatalysts.

Catalyst	**E/mV**	**Stability/h**	**References**
N-NiCoP/NF||N-NiCoP/NF	J_{52}=1.62 J_{100}=1.74	100	This work
CVN/CC||CVN/CC	J_{10}=1.64 J_{50}=1.88 J_{100}=2.12	100	18

NiCoP||NiCoP	J_{10}=1.53 J_{50}=1.75 J_{100}=1.86	20	19
NiCo foam(-)||NiFe foam(+)	J_{50}=1.59 J_{100}=1.64	50	5
Ni_3S_2/Cu–NiCo/NF||Ni_3S_2/Cu–NiCo/NF	J_{50}=1.70 J_{100}=1.75	12	6
Co-Ni_xP_y@Co_3O_4/NF||Co-Ni_xP_y@Co_3O_4/NF	J_{50}=1.62	36	20
NiCoP||NiCoP	J_{50}=1.72 J_{100}=1.80	24	21
Mo–NiCoP||Mo–NiCoP	J_{10}=1.61 J_{50}=1.7	48	22
$NiCoSe_2$@NiO@$CoNi_2S_4$@CoS_2/NF||$NiCoSe_2$@NiO@$CoNi_2S_4$@CoS_2/NF	J_{10}=1.583 J_{50}=1.952	24	16
Se-(NiCo)S_x/$(OH)_x$||Se-(NiCo)S_x/$(OH)_x$	J_{10}=1.6 J_{50}=1.84 J_{100}=2.05	66	7
$CoNiMoO_4$/CuOx/CF||CoNiMoO_4/CuOx/CF	J_{50}=1.532	20	23
Al, Fe-CoP/RGO||Al, Fe-CoP/RGO	J_{10}=1.66 J_{50}=1.78	15	24
O-CoP||O-CoP	J_{10}=1.6 J_{50}=1.74	18	25
NF/NiCoMoO-H_2||NF/NiCoMoO-H_2	J_{50}=1.6 J_{100}=1.73	60	26
Co-Mo-P/CoNWS/NF||Co-Mo-P/CoNWS/NF	J_{50}=1.71 J_{100}=1.78	35	27
NiFeOH/CoS_x/NF||NiFeOH/CoS_x/NF	J_{50}=1.71 J_{100}=1.75	24	28
Ni_3S_2/VG@NiCo||Ni_3S_2/VG@NiCo	J_{50}=1.85 J_{100}=1.95	24	29

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