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

Supporting Information

Hierarchy carbon nanotube forest supported metal phosphide electrode for the efficient overall water splitting

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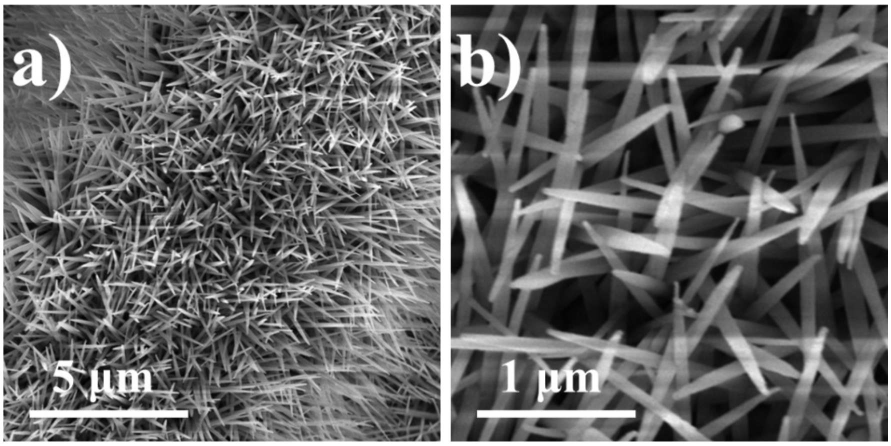

Fig. S1 a) low-magnification and b) high-magnification SEM images of NiCo-LDH/CP.

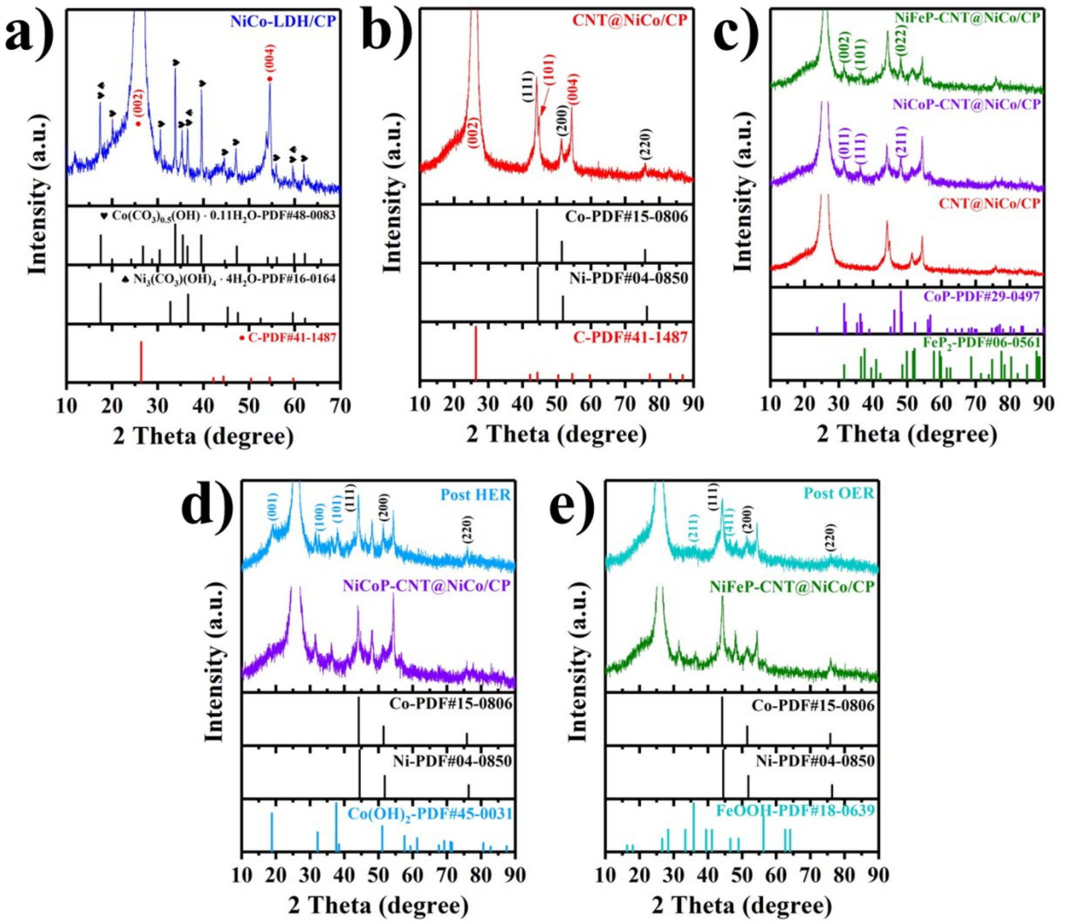

Fig. S2 XRD spectra of a) NiCo-LDH/CP, b) CNT@NiCo/CP, c) NiCoP-CNT@NiCo/CP and NiFeP-CNT@NiCo/CP, d) NiCoP-CNT@NiCo/CP and post-HER NiCoP-CNT@NiCo/CP, and e) NiFeP-CNT@NiCo/CP and post-OER NiFeP-CNT@NiCo/CP (three characteristic peaks of (111), (200) and (220) planes assigned to metallic cobalt and nickel still remain, meaning that the bulk of conductive NiCo nanowires were not changed in HER and OER operation).

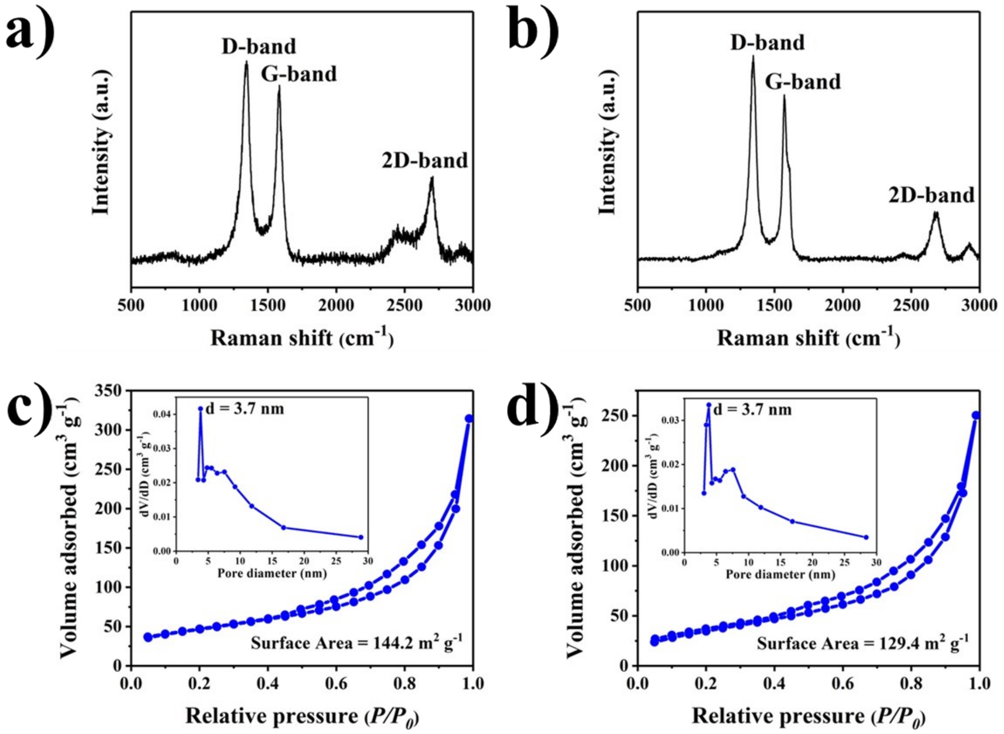

Fig. S3 Raman spectrum of a) NiCoP-CNT@NiCo/CP and b) NiFeP-CNT@NiCo/CP electrodes; N_2 adsorption-desorption isotherms and pore-size distribution curves of c) NiCoP-CNT@NiCo/CP and d) NiFeP-CNT@NiCo/CP.

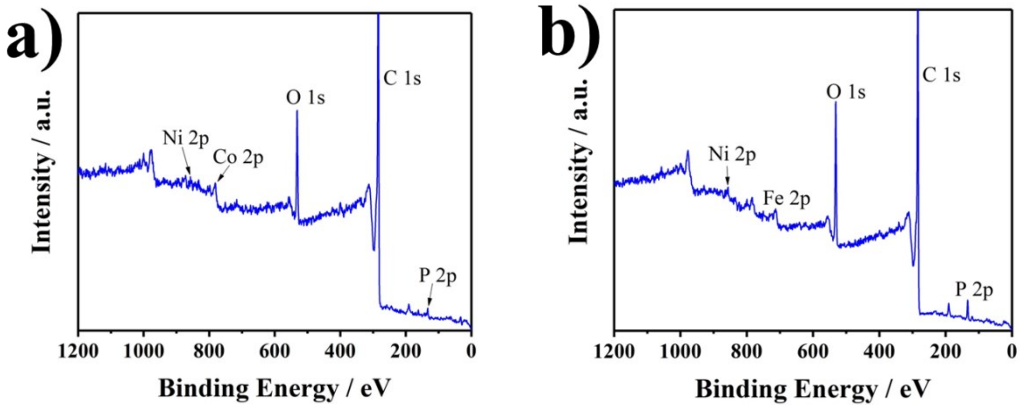

Fig. S4 XPS survey spectrum of a) NiCoP-CNT@NiCo/CP and b) NiFeP-CNT@NiCo/CP.

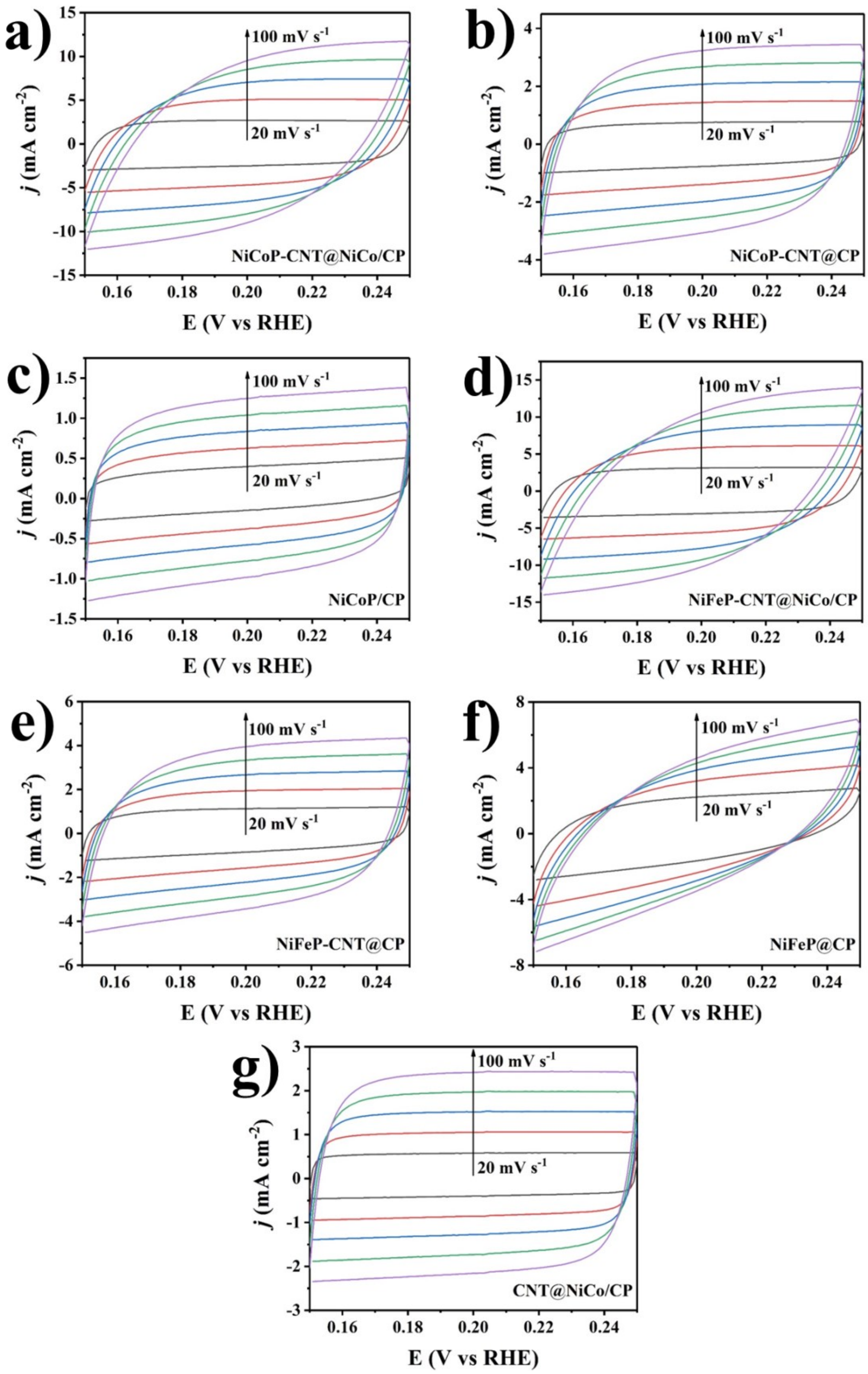

Fig. S5 CV curves of different catalysts in the non-Faradaic region (0.15-0.25 V vs RHE) obtained at different scanning rates.

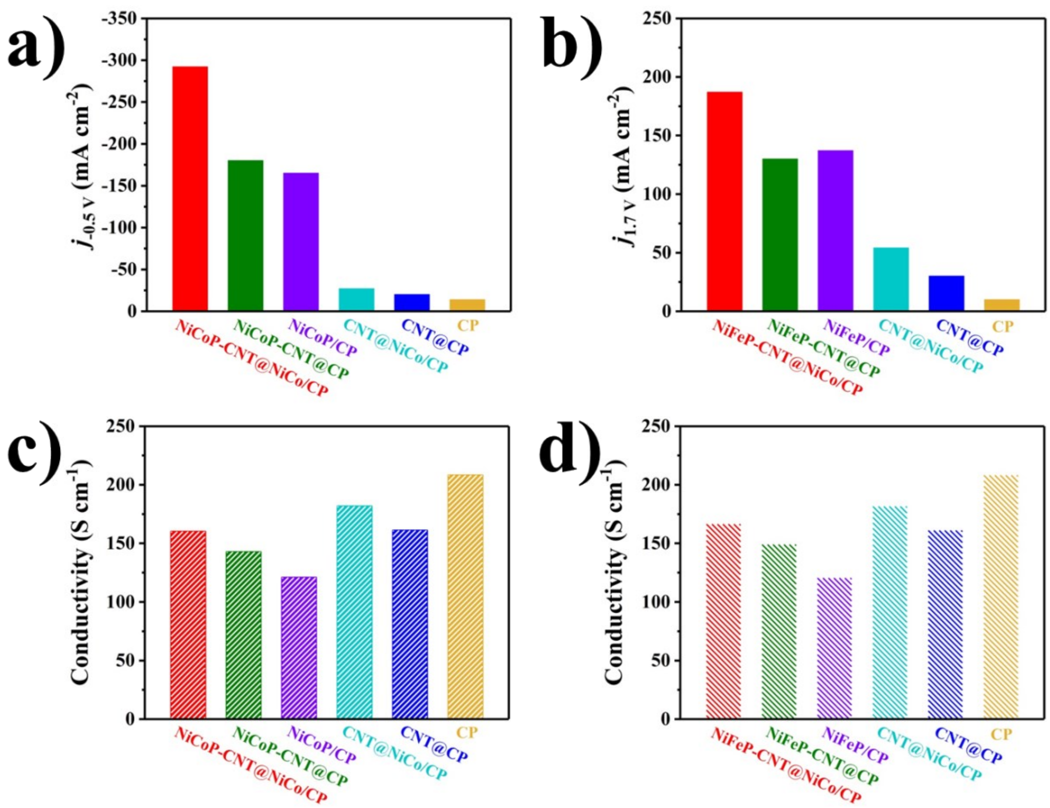

Fig. S6 Current density values based on the polarization curves a) for HER in Fig. 5c at the potential of -0.5 V and b) for OER in Fig. 6a at the potential of 1.7 V. Conductivity of different electrodes toward c) HER and d) OER.

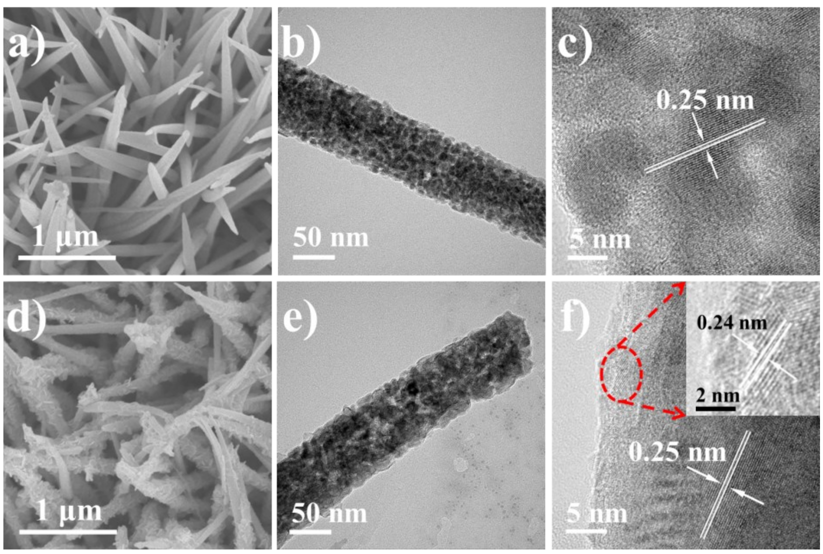

Fig. S7 Structural characterization of NiCoP/CP and post-HER NiCoP/CP. SEM images of a) NiCoP nanowire arrays and d) NiCoP nanowire arrays after 100 cycles; TEM images of b) NiCoP nanowire and e) post-HER NiCoP nanowire; HR-TEM images of c) NiCoP nanowire (It gave the spacing length of ~0.25 nm assigned to (111) plane of CoP in the original NiCoP); f) HR-TEM images of post-HER NiCoP nanowire (It gave the spacing length of ~0.24 nm indexed to (101) plane of $Co(OH)_2$ in the resultant material).

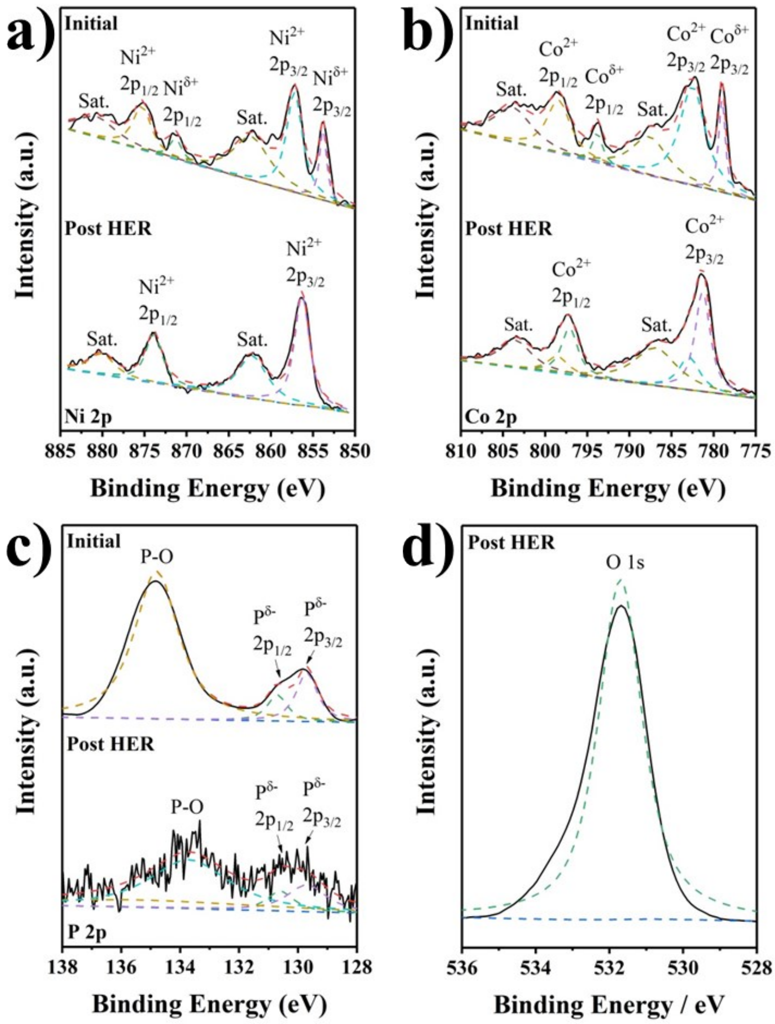

Fig. S8 XPS patterns of a) Ni 2p, b) Co 2p, c) P 2p and d) O 1s for NiCoP/CP and post-HER NiCoP/CP, respectively (The decline of P 2p peaks at the binding energies (129.8 and 130.5 eV) assigned to $P^{\delta-}$, as well as the disappearance of $Ni^{\delta+}$ 2p3/2 (853.7 eV) and $Co^{\delta+}$ 2p3/2 (778.9 eV) peaks evidenced that surface metal phosphides was transformed to metal hydroxide on NiCoP/CP surface after 100 cycles).

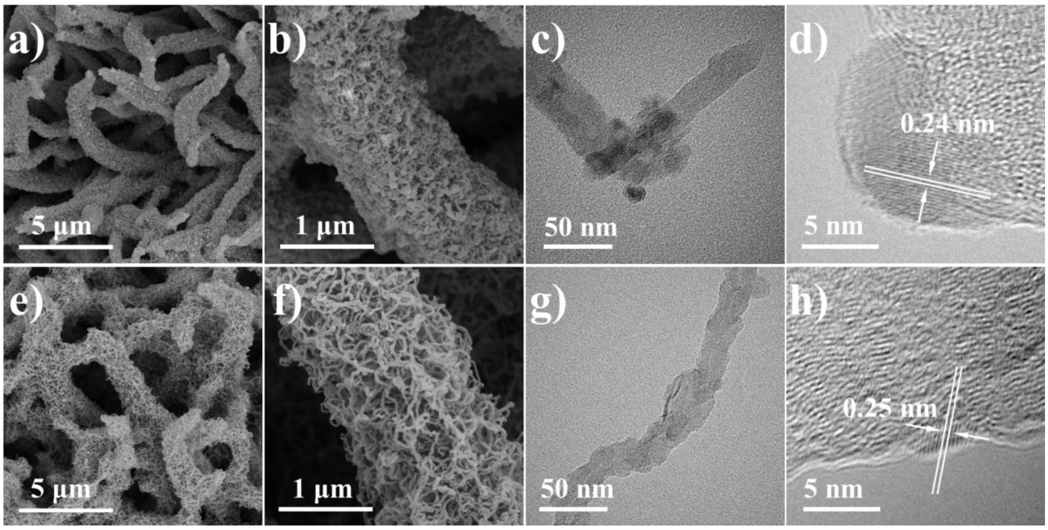

Fig. S9 Structural characterization of post-HER NiCoP-CNT@NiCo/CP and post-OER NiFeP-CNT@NiCo/CP. a) low-magnification, and b) high-magnification SEM image of post-HER NiCoP-CNT@NiCo/CP; c) TEM image of partial enlarged view CNTs in the post-HER NiCoP-CNT@NiCo/CP electrode; d) HR-TEM image of the NiCoP-derivative nanoparticles in the post-HER NiCoP-CNT@NiCo/CP electrode (The spacing length of ~0.24 nm can be assigned to (101) plane of $Co(OH)_2$ in the resultant material); e) low-magnification, and f) high-magnification SEM image of post-OER NiFeP-CNT@NiCo/CP; g) TEM image of partial enlarged view CNTs in the post-OER NiFeP-CNT@NiCo/CP electrode; h) HR-TEM image of the NiFeP-derivative nanoparticles in the post-OER NiFeP-CNT@NiCo/CP electrode (the spacing length of ~0.25 nm can be assigned to (211) plane of FeOOH in the resultant material).

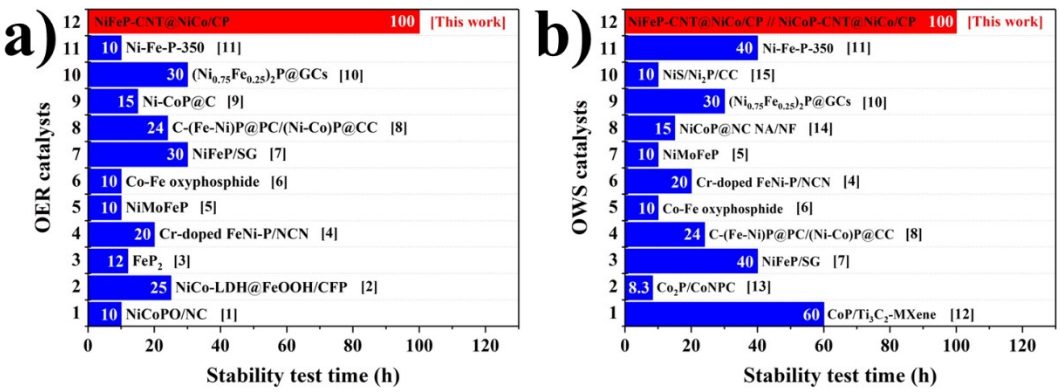

Fig. S10 Comparison of the stability test time at a current density of 10 mA cm^{-2} for a)

OER electrocatalysts and b) OWS electrocatalysts. (The list of references is as follows: [1] *Nano Energy*, 2020, **69**, 104453; [2] *Nano Energy*, 2020, **69**, 104367; [3] *Adv. Funct. Mater.*, 2020, **30**, 1907791; [4] *Adv. Mater.*, 2019, **31**, 1900178; [5] *Small*, 2019, **15**, 1905501; [6] *Adv. Sci.*, 2019, **6**, 1900576; [7] *Nano Energy*, 2019, **58**, 870-876; [8] *Nano Energy*, 2019, **65**, 103995; [9] *Nano Energy*, 2019, **62**, 136-143; [10] *J. Mater. Chem. A*, 2019, **7**, 20357-20368; [11] *ACS Appl. Mater. Interfaces*, 2017, **9**, 26134-26142; [12] *J. Mater. Chem. A*, 2020, **8**, 14234-14242; [13] *Adv. Mater.*, 2020, **32**, 2003649; [14] *Adv. Funct. Mater.*, 2019, **29**, 1906316; [15] *ACS Appl. Mater. Interfaces*, 2018, **10**, 4689-4696.)

Table S1. Comparison of the HER performance of NiCoP-CNT@NiCo/CP to other reported electrocatalysts in alkaline media.

Catalysts	electrolyte	$\eta_{10/HER}$ (mV)	Ref.
NiCoP-CNT@NiCo/CP	pH14 KOH	82	This work
CoP/Ti_3C_2-MXene	1M KOH	102	J. Mater. Chem. A, 2020, 8, 14234-14242
0.02Ni-MoP	1M KOH	162	Nano Energy, 2020, 70, 104445
Co_2P/CoNPC	1M KOH	130	Adv. Mater., 2020, 2003649
CoP@PNC-DoS	1M KOH	173	Energy Storage Materials, 2020, 28, 27-36
CoP-InNC@CNT	1M KOH	159	Adv. Sci., 2020, 1903195
NiCoFe-PS nanorod/NF	1M KOH	97.8	Small, 2019, 1905201
C-(Fe-Ni)P@PC/(Ni-Co)P@CC	1M KOH	142	Nano Energy, 2019, 65, 103995
CoP/Ni_2P	1M KOH	200	J. Mater. Chem. A, 2019, 7, 26177-26186
Co_4Ni_1P NTs	1M KOH	129	Adv. Funct. Mater., 2017, 1703455
Ni_2P/NiCoP@NCCs	1M KOH	116	J. Mater. Chem. A, 2017, 5, 16568-16572
Ce-doped CoP	1M KOH	92	Nano Energy, 2017, 38, 290-296
NiCoP/reduced graphene oxide	1M KOH	209	Adv. Funct. Mater., 2016, 26, 6785-6796

Table S2. Comparison of the OER performance of NiFeP-CNT@NiCo/CP to other reported electrocatalysts in alkaline media.

Catalysts	electrolyte	$\eta_{10/OER}$ (mV)	Ref.
NiFeP-CNT@NiCo/CP	pH=14 KOH	230	This work
Cr-doped FeNi-P/NCN	1M KOH	240	Adv. Mater., 2019, 31, 1900178
FeP_2	1M KOH	240	Adv. Funct. Mater., 2020, 1907791
NiMoFeP	1M KOH	286	Small, 2019, 1905501
Fe-Co-P nanoboxes	1M KOH	269	Energy Environ. Sci., 2019, 12, 3348-3355
Co-Fe oxyphosphide	1M KOH	280	Adv. Sci., 2019, 1900576
CoFeP	1M KOH	233	ACS Energy Lett., 2019, 4, 2813-2820
C-(Fe-Ni)P@PC/(Ni-Co)P@CC	1M KOH	251	Nano Energy, 2019, 65, 103995
Ni-CoP@C	1M KOH	279	Nano Energy, 2019, 62, 136-143
Ni_3FeN/rGO	1M KOH	270	ACS Nano, 2018, 12, 245-253
NiS/Ni_2P/carbon cloth	1M KOH	265	ACS Appl. Mater. Interfaces, 2018, 10, 4689-4696
Ni-Fe-P-350	1M KOH	271	ACS Appl. Mater. Interfaces, 2017, 9, 26134-26142
$Ni_{0.9}Fe_{0.1}$/N-CNTs	1M KOH	270	ACS Catal., 2016, 6,

			580-588

Table S3. Comparison of the overall water splitting performance of NiCoP-CNT@NiCo/CP || NiFeP-CNT@NiCo/CP couple to other reported electrocatalysts in alkaline media.

Catalysts	**electrolyte**	**$V_{10/OWS}$ (V)**	**Ref.**
NiCoP-CNT@NiCo/CP‖ NiFeP-CNT@NiCo/CP	pH14 KOH	1.58	This work
Co_2P/CoNPC	1M KOH	1.64	Adv. Mater., 2020, 2003649
CoP@PNC-DoS	1M KOH	1.74	Energy Storage Materials, 2020, 28, 27-36
CoP/Ti_3C_2-MXene	1M KOH	1.58	J. Mater. Chem. A, 2020, 8, 14234-14242
CoP-InNC@CNT	1M KOH	1.58	Adv. Sci., 2020, 1903195
CoFeP	1M KOH	1.59	ACS Energy Lett., 2019, 4, 2813-2820
C-(Fe-Ni)P@PC/(Ni-Co)P@CC	1M KOH	1.63	Nano Energy, 2019, 65, 103995
Co-Fe oxyphosphide	1M KOH	1.69	Adv. Sci., 2019, 1900576
CoP/Ni_2P	1M KOH	1.60	J. Mater. Chem. A, 2019, 7, 26177-26186
NiS/Ni_2P/carbon cloth	1M KOH	1.67	ACS Appl. Mater. Interfaces, 2018, 10, 4689-4696
Ni-Fe-P-350	1M KOH	1.67	ACS Appl. Mater. Interfaces, 2017, 9, 26134-

			26142
Co_4Ni_1P NTs	1M KOH	1.59	Adv. Funct. Mater., 2017, 1703455

η_{10}/HER: the HER overpotentials at a current density of 10 mA cm^{-2}; $\eta_{10/OER:}$ the OER overpotentials at a current density of 10 mA cm^{-2}; $V_{10/OWS}$: the overall water splitting voltages at a current density of 10 mA cm^{-2}.