Supplementary Information (SI) for Dalton Transactions.
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Supporting Information

Achieving advanced hydrogen evolution under large current density by amorphous/crystalline core/shell electrocatalyst of a-NiCoP/Co_2P

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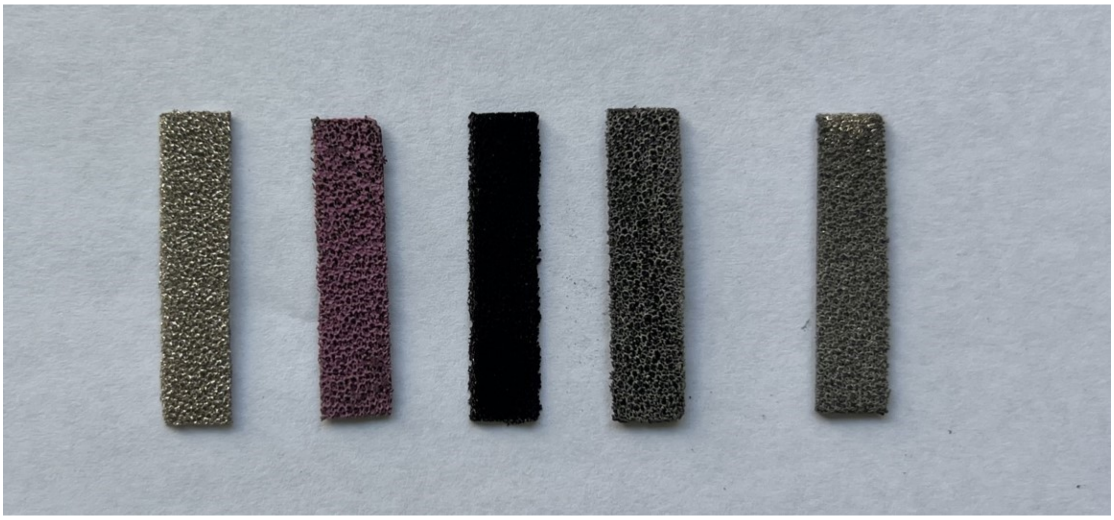

Figure S1. The optical pictures of Ni foam substrate, Co-CH@NF precuisor, Co_2P@NF, a-NiCoP/Co_2P@NF, and a-NiCoP@NF (from left to right).

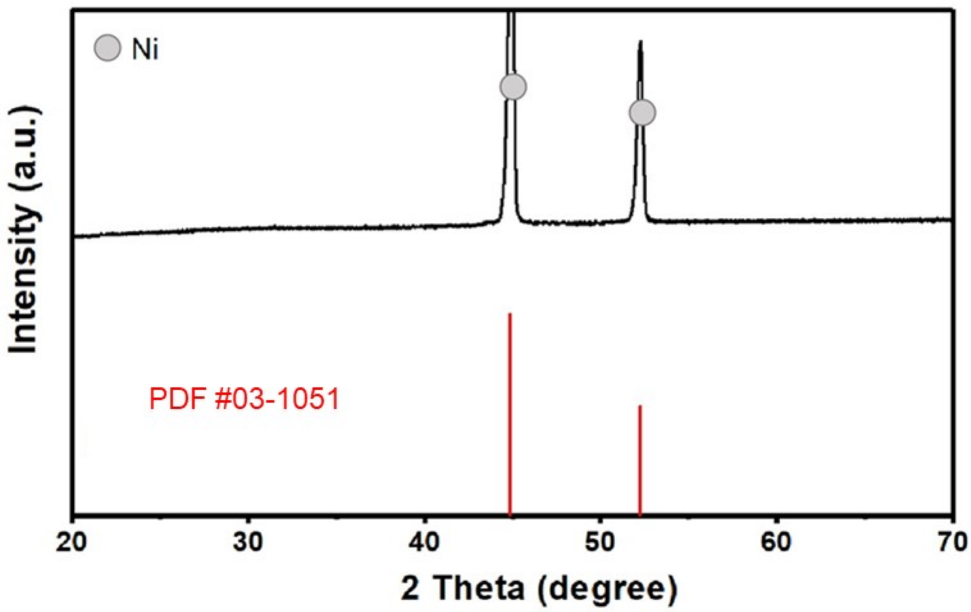

Figure S2. XRD pattern of Ni Foam substrate.

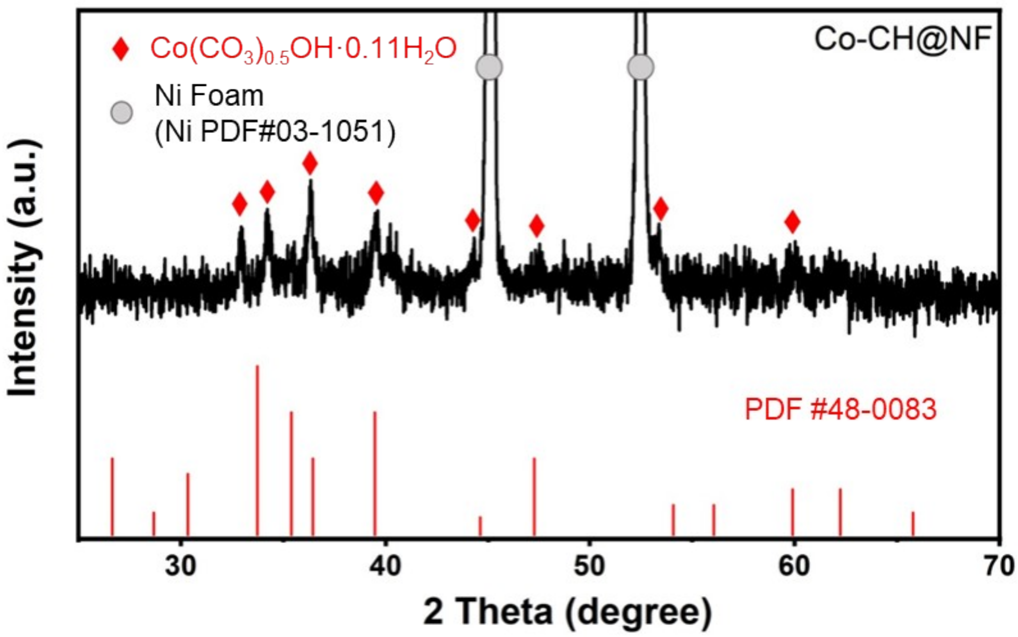

Figure S3. XRD pattern for Co-CH@NF precursor.

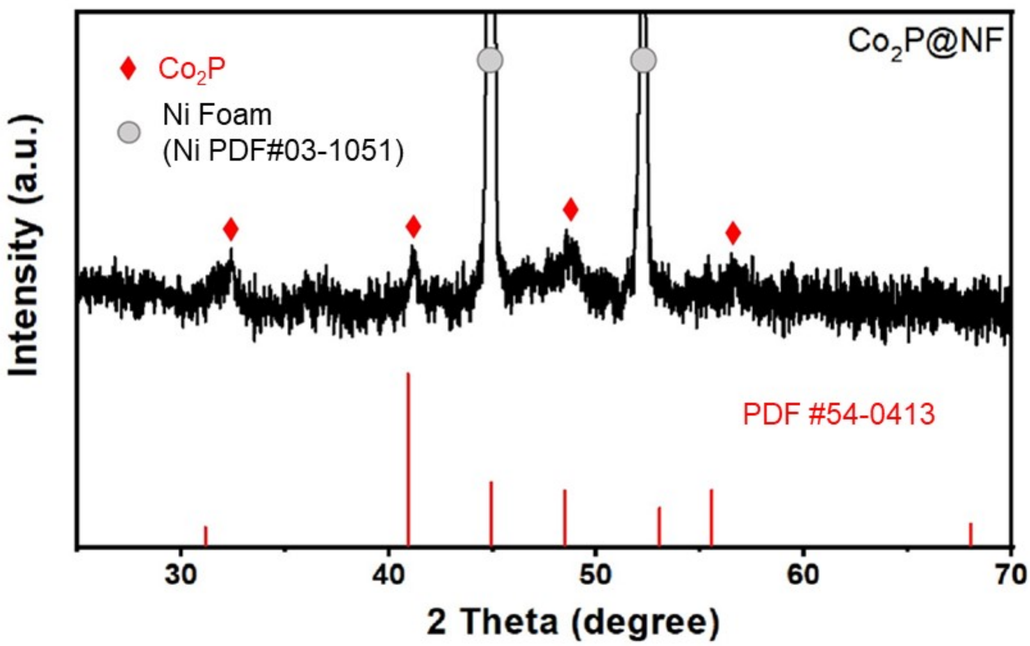

Figure S4. XRD pattern for Co_2P@NF.

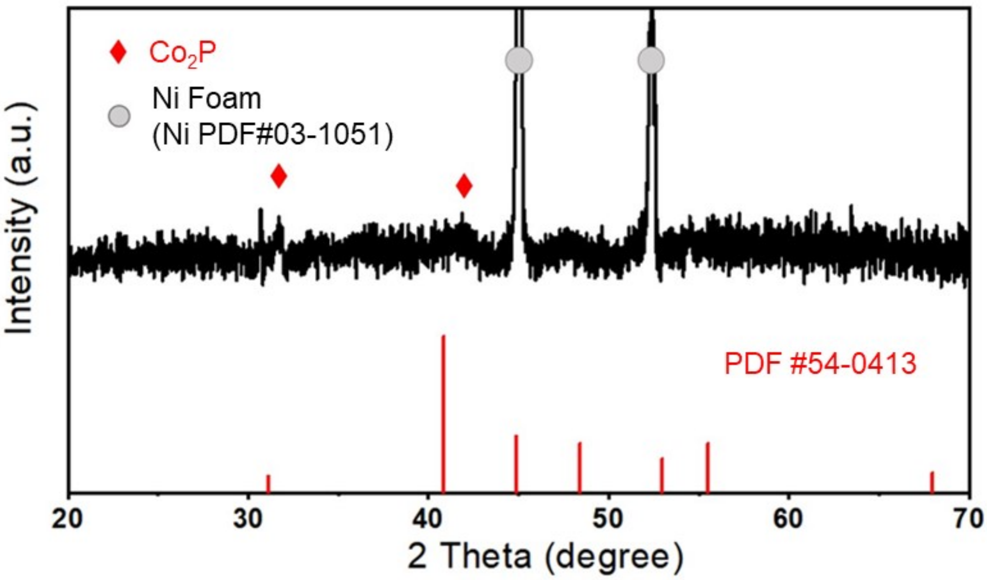

Figure S5. XRD pattern for a-NiCoP/Co_2P@NF.

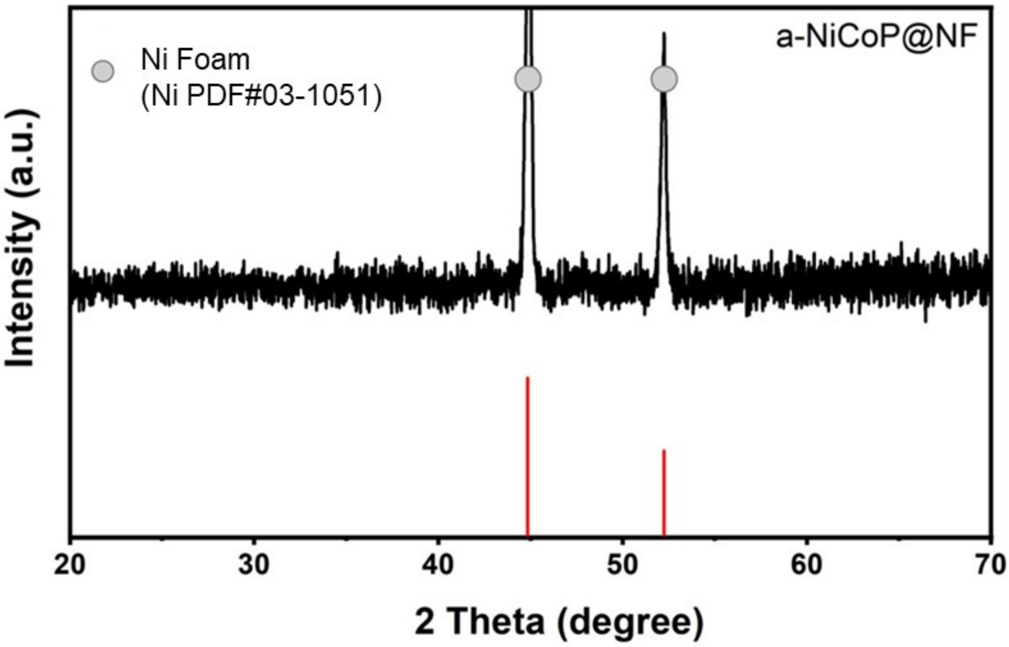

Figure S6. XRD pattern for a-NiCoP@NF.

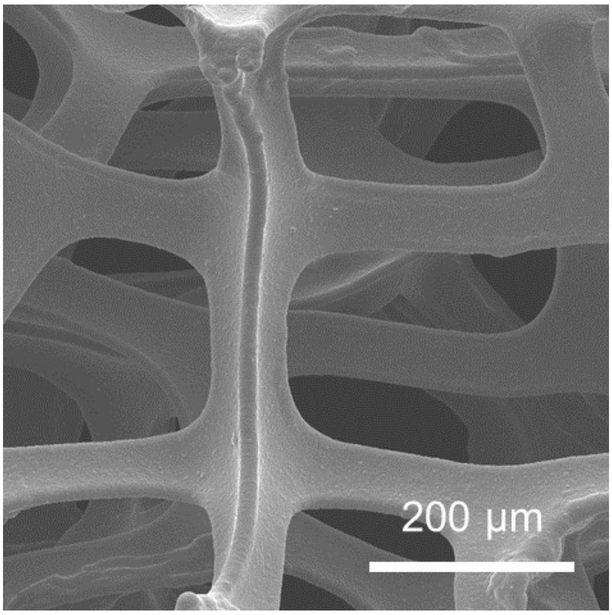

Figure S7. SEM image of Ni Foam substrate.

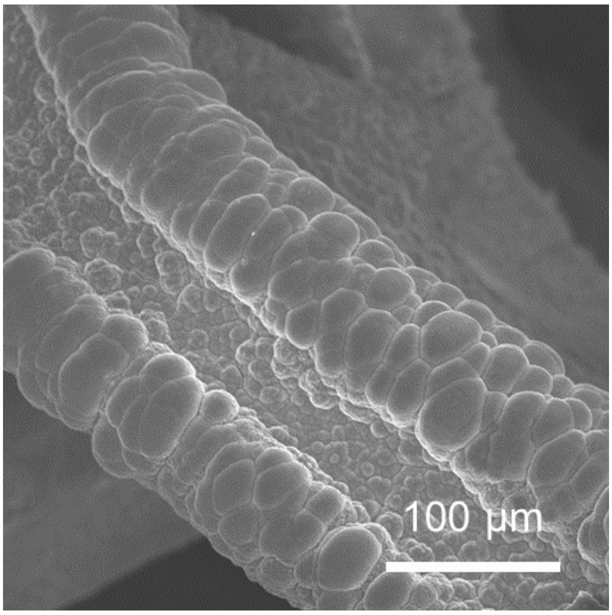

Figure S8. SEM image of a-NiCoP@NF.

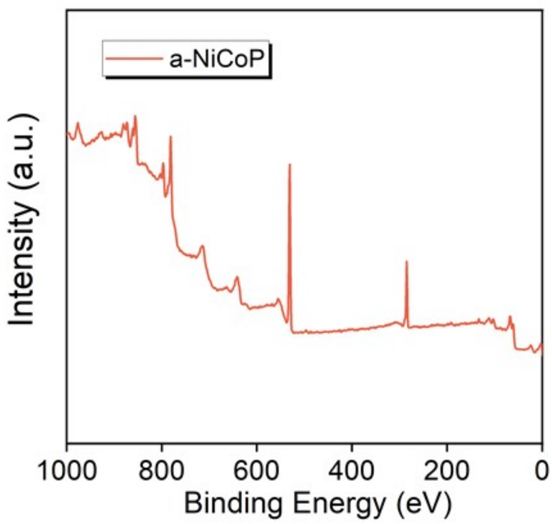

Figure S9. XPS survey of a-NiCoP@NF.

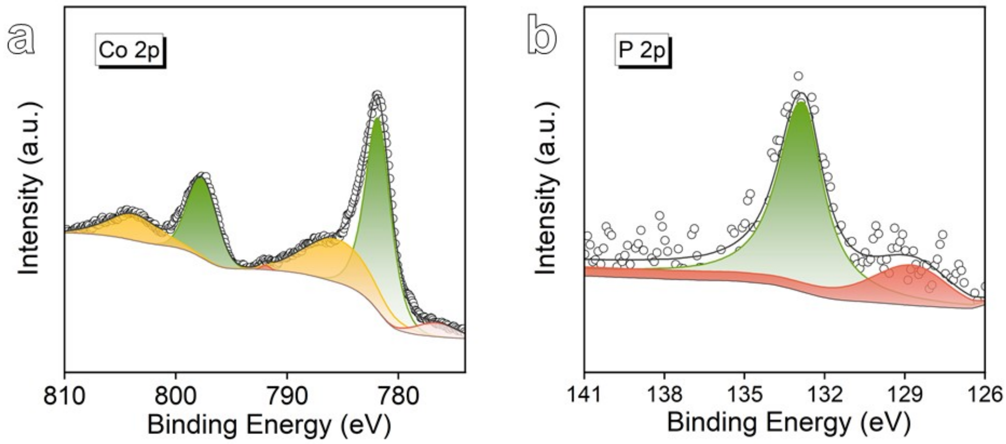

Figure S10. (a) Co 2p and (b) P 2p XPS spectra of a-NiCoP.

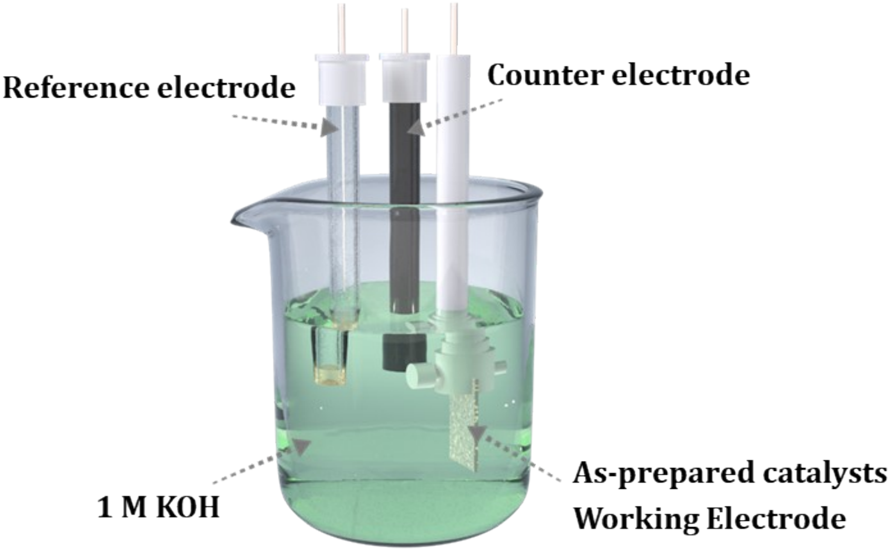

Figure S11. Schematic illustration of the three-electrode electrochemical testing system.

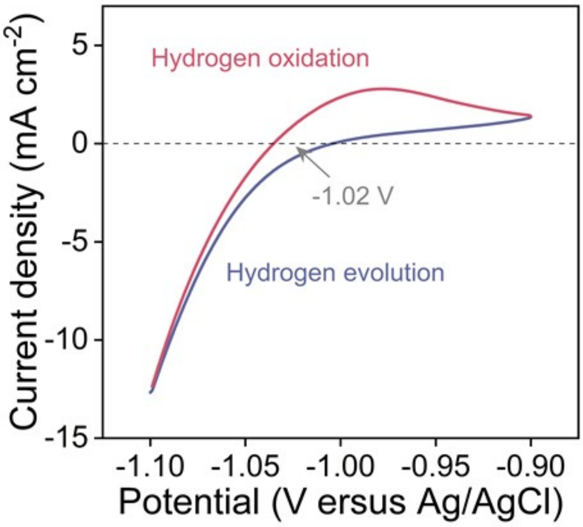

Figure S12. The reference electrode Ag/AgCl calibration in 1 M KOH.

Reference Electrode Calibration:

The correction was performed at three–electrode system with platinum sheets as counter electrode and working electrode under electrolyte hydrogen saturation. In 1 M KOH alkaline medium, corrected the Ag/AgCl reference electrode. The Cyclic Voltammetry (CV) cycles stable was operated at a scanning rate of 5 mV s^{-1}. Then, the average of the two potentials at which the current crossed zero in a single CV cycle were taken to be the thermodynamic potential for the hydrogen electrode reaction. Therefore, in 1 M KOH alkaline media, $E_{RHE}=E_{Ag/AgCl} + 1.02$ V.

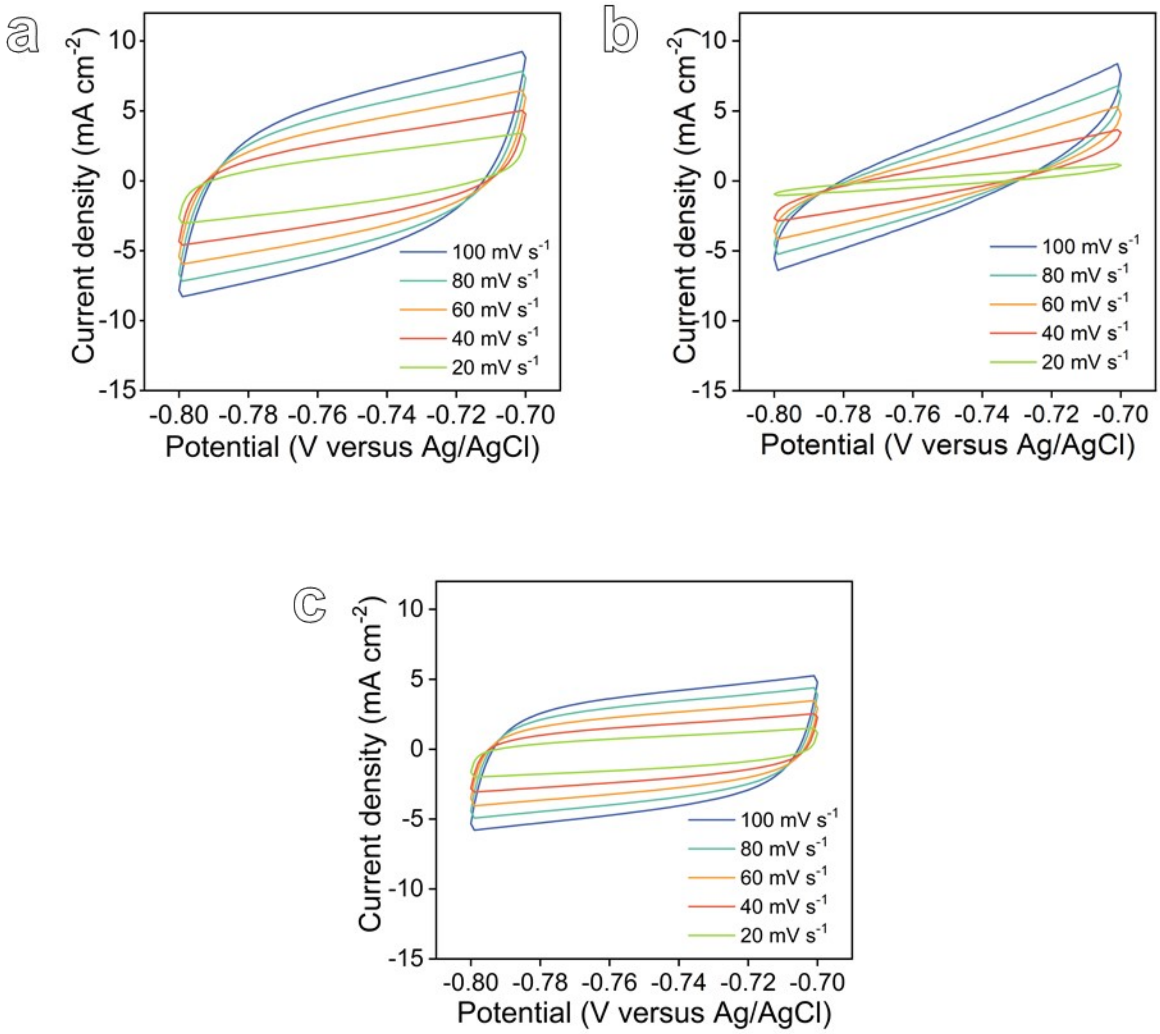

Figure S13. Cyclic voltammogram curves of (a) a-NiCoP/Co_2P@NF, (b) a-NiCoP@NF and (c) Co_2P@NF.

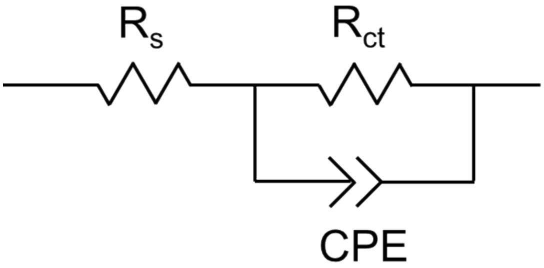

Figure S14. Schematic diagram of the electrode structure and the equivalent circuit mod.

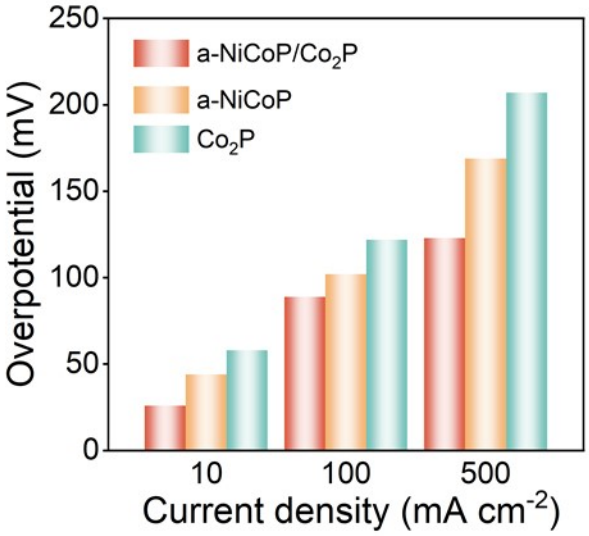

Figure S15. Comparison with η_{10}, η_{100}, η_{500} of a-NiCoP/Co_2P@NF, a-NiCoP@NF, Co_2P@NF measured in 1 M KOH.

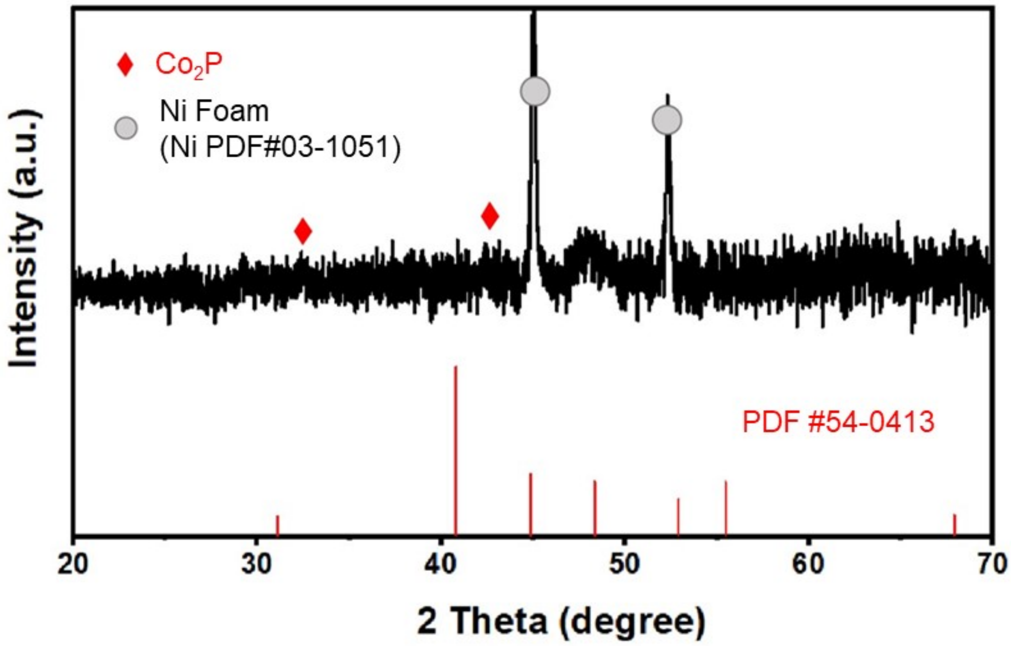

Figure S16. XRD pattern of a-NiCoP/Co_2P@NF after stability testing.

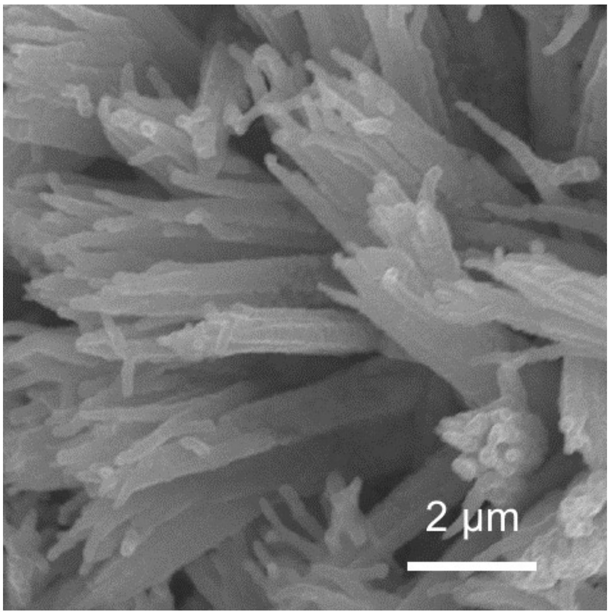

Figure S17. SEM image of a-NiCoP/Co_2P@NF after stability testing.

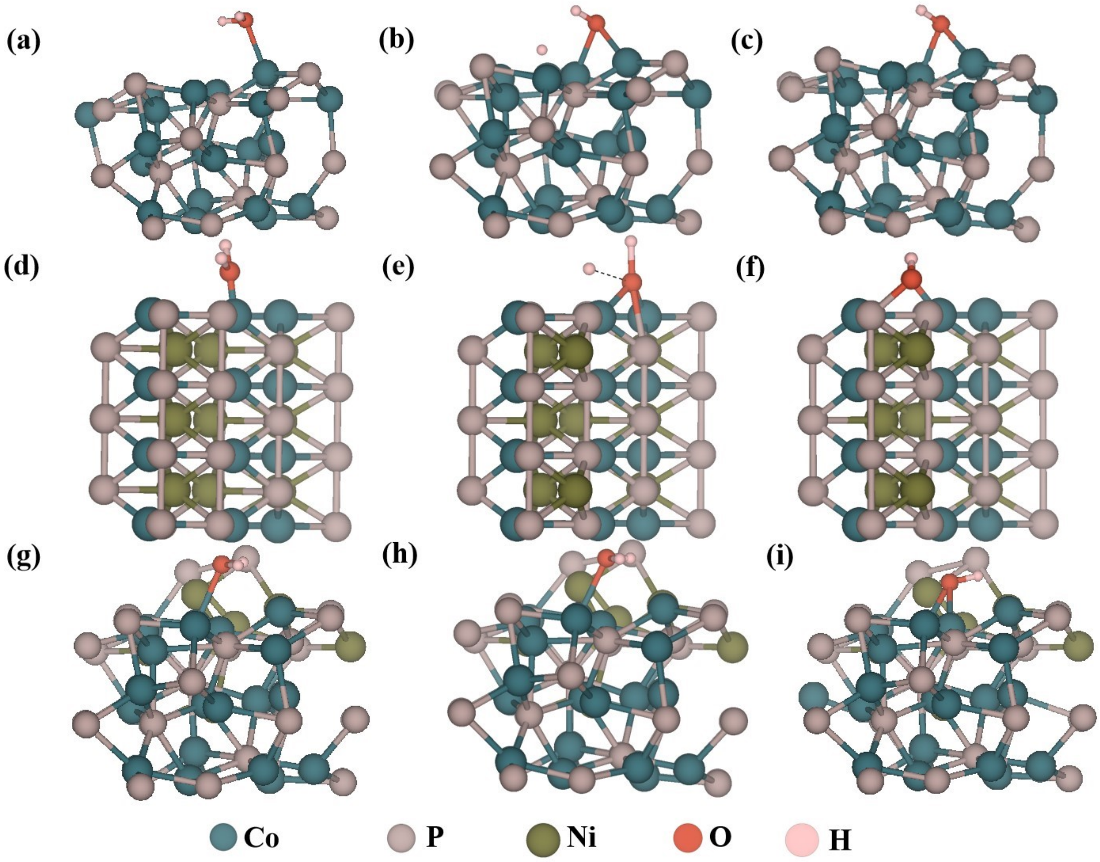

Figure S18. The optimized structure model and adsorption of different reaction intermediates: (a-c) Co_2P, (d-f) a-NiCoP, and (g-i) a-NiCoP/Co_2P.

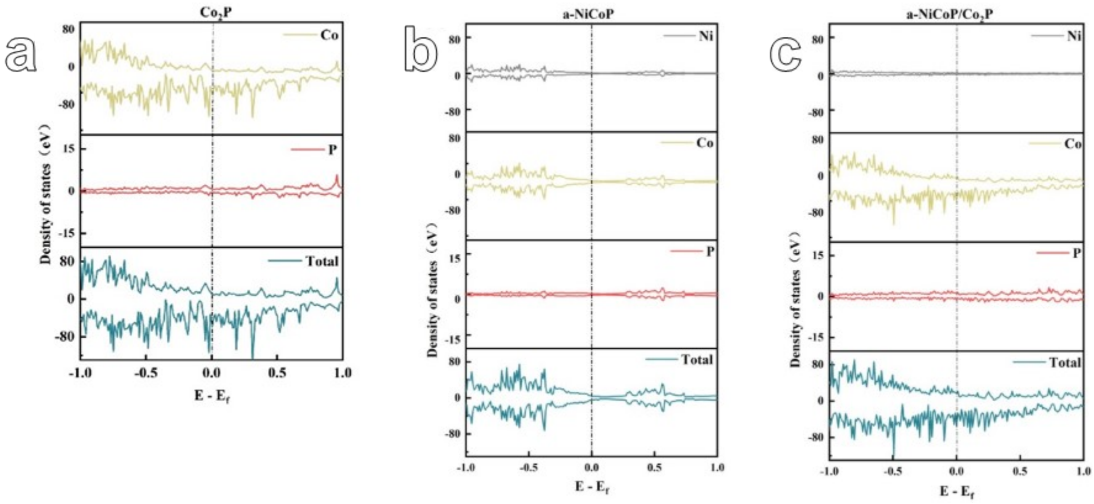

Figure S19. Density of states of (a) Co_2P, (b) a-NiCoP, and (c) a-NiCoP/Co_2P, respectively.

Table S1. Comparison with the recently reported performance of some non-precious metal HER electrocatalysts measured in 1 M KOH.

Electrocatalysts	Electrode	η_{10} (mV)	η_{100} (mV)	η_{500} (mV)	Reference
a-NiCoP/Co_2P	Ni Foam	26	89	123	this work
CoP/$Ni(OH)_2$	Cu Foam	48	108	175	[1]
A-NiCo LDH/NF	Ni Foam	36	151	286	[2]
Cr-CoP-NR/CC	Carbon cloth	38	101	209	[3]
MoC-Mo_2C-790	Mo Sheet	98.2	NA	292	[4]
NiFeMo IOS	Ni Foam	33	NA	249	[5]
CoP/Ni_2P	Ni Foam	16	85	209	[6]
$(Ni_xFe_yCo_{6-x-y})Mo_6C$	Ni Foam	20	NA	194	[7]
OH-Ni/Ni_3C	Glassy Carbon	72	NA	276	[8]
NiFe-LDH/MXene/NF	Ni Foam	132	NA	205	[9]
$CoMoS_x$/NF	Ni Foam	89	NA	269	[10]
NiCo/NiCo−OH	Ni Foam	19	104	184	[11]
SANi-I	Ni Foam	NA	60	160	[12]
A-CFC	Carbon Fiber Cloth	78	160	260	[13]
Ni/$NiFeMoO_x$/NF	Ni Foam	22	117	NA	[14]
MFN-MOFs/NF	Ni Foam	79	NA	234	[15]

NiMnOP/NF	Ni Foam	91	NA	195	[16]
2H-MoS_2	Carbon Cloth	115	231	332	[17]
CoOx–CoSe	Ni Foam	90	300	380	[18]
Cu-FeOOH/Fe_3O_4	Iron foam	NA	129	285	[19]
NiCoSx@CoCH NAs/NF	Ni Foam	55	199	338	[20]

Table S2. ECSA of a-NiCoP/CoP@NF、a-NiCoP/CoP@NF、CoP@NF.

Sample	C_{dl} (mF)	C_s (mF cm^{-2})	ECSA (cm^{-2})
a-NiCoP@NF	4	0.04	100
Co_2P@NF	38	0.04	950
a-NiCoP/Co_2P@NF	50	0.04	1250

Table S3. The adsorption energy of different positions in a-NiCoP/CoP.

Site	Adsorption Energy
I	E_{ads} = -0.10 eV
II	E_{ads} = -0.39 eV
III	E_{ads} = 0.02 eV

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