

## Electronic Supplementary Information

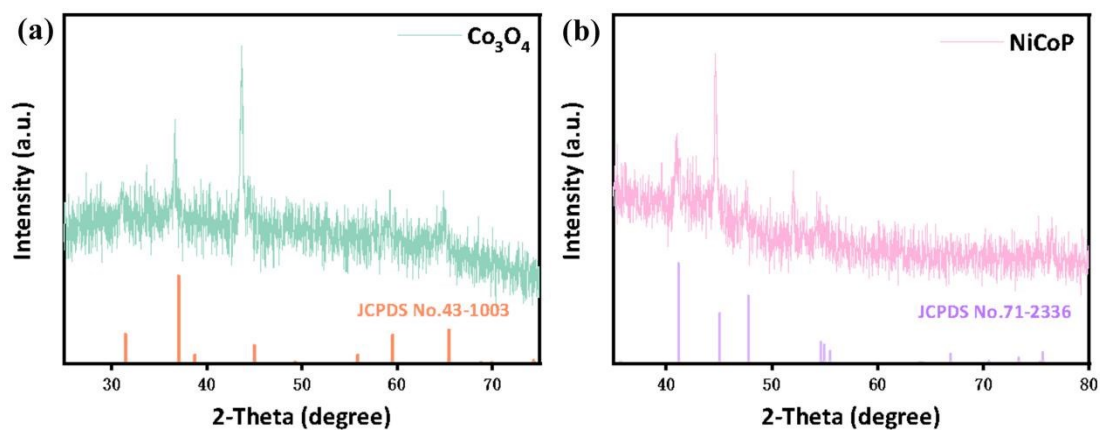


Fig. S1. XRD patterns of (a)  $\text{Co}_3\text{O}_4/\text{NF}$ ; (b)  $\text{NiCoP}/\text{NF}$ .

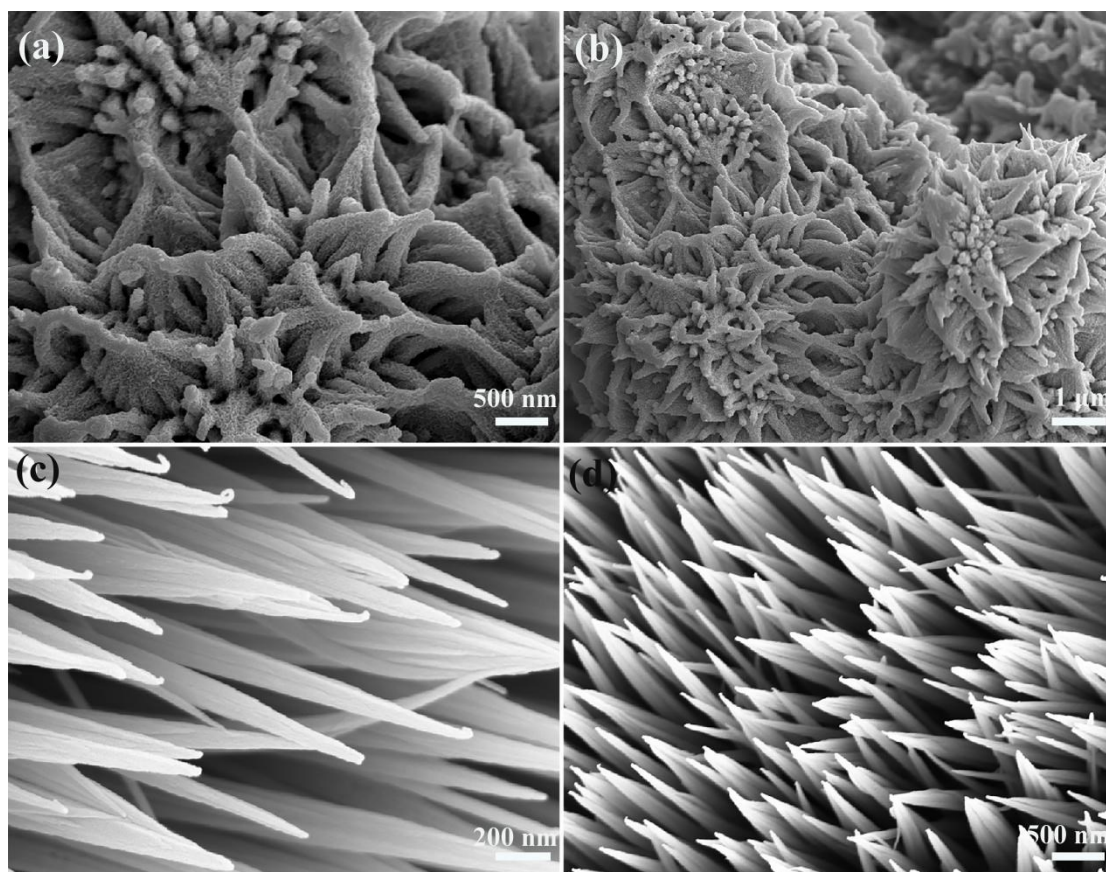
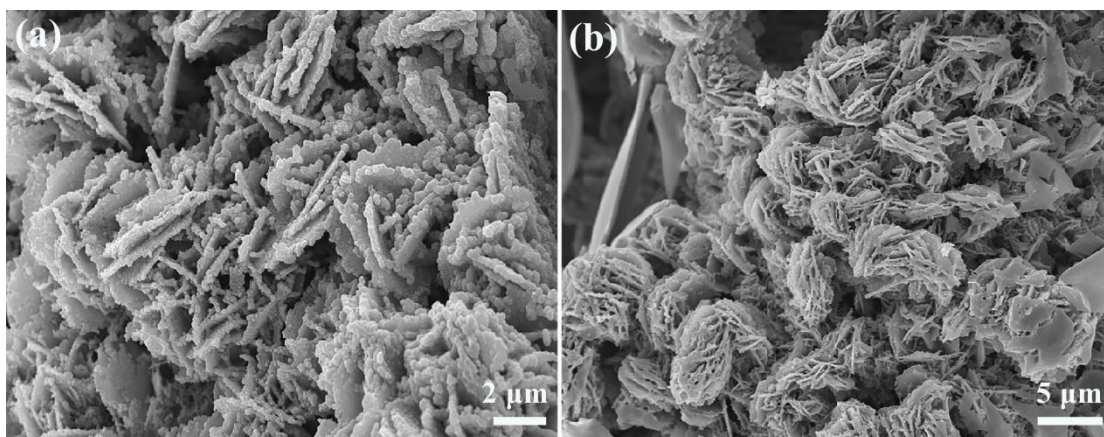
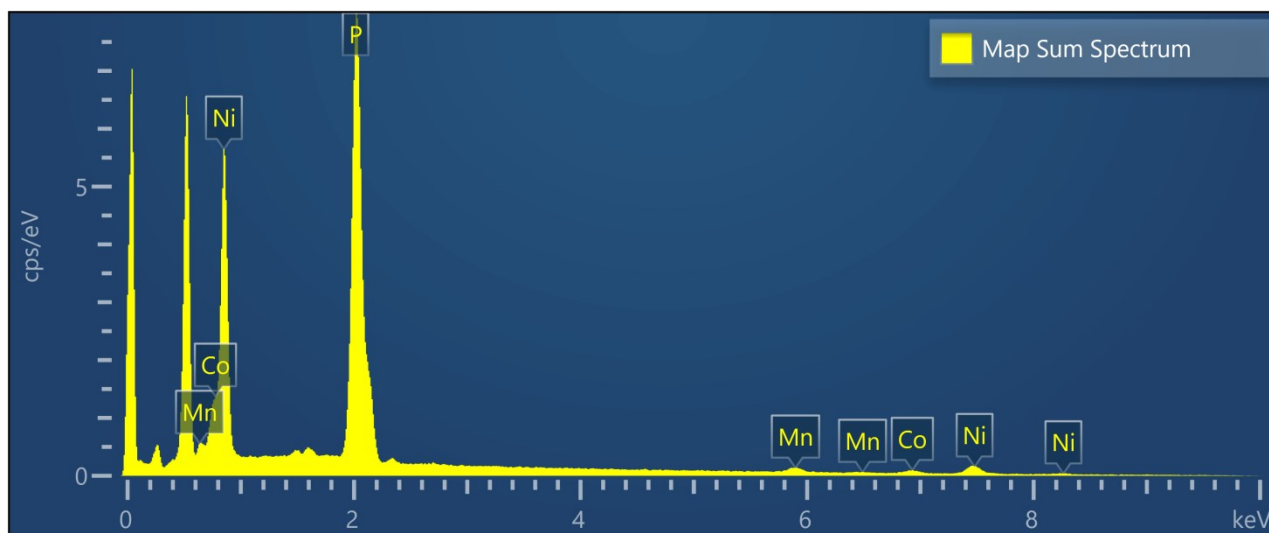


Fig. S2. (a-b) SEM images of  $\text{Co}(\text{OH})_2/\text{NF}$ ; (c-d) SEM images of  $\text{Co}_3\text{O}_4/\text{NF}$



**Fig. S3.** SEM images of Mn-NiCoP/NF after stability test.



**Fig. S4.** EDS spectrum of Mn-NiCoP/NF.

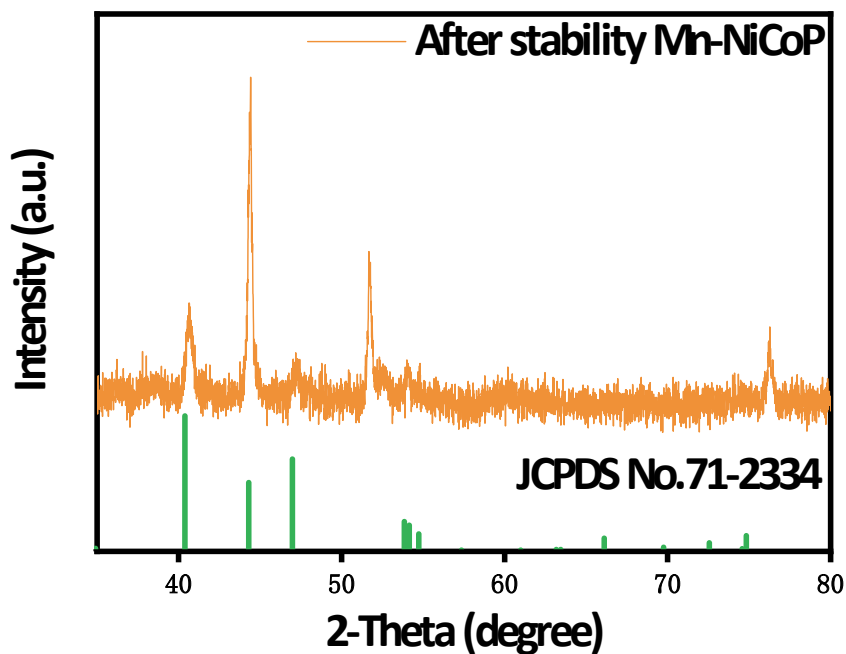


Fig. S5. XRD pattern of Mn-NiCoP/NF after 120h stability measure.

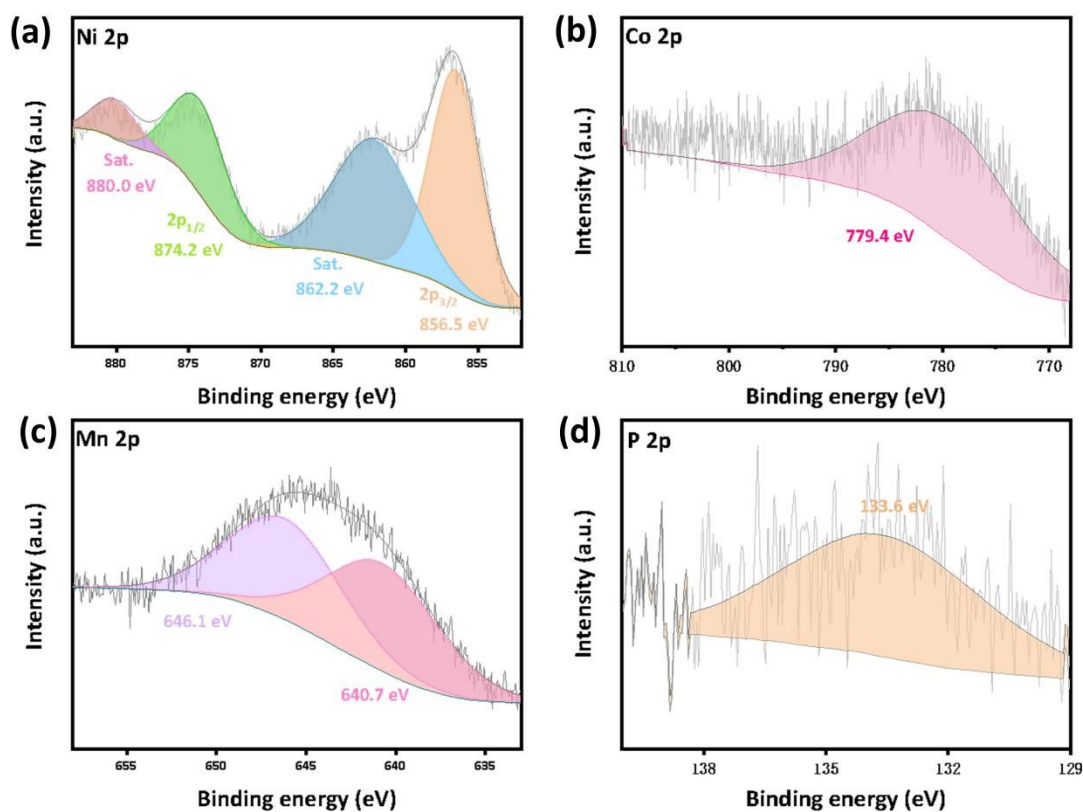
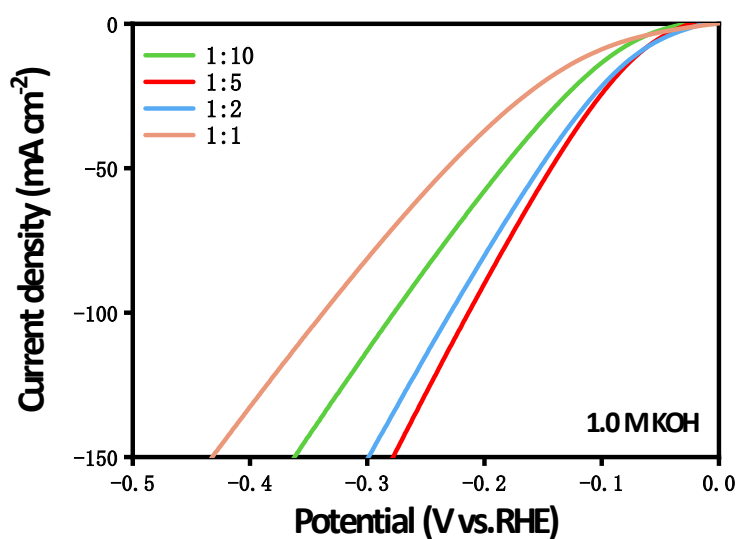
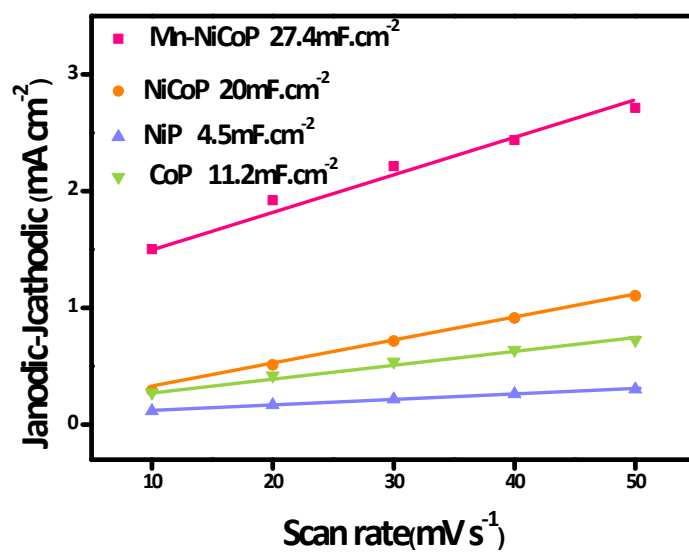


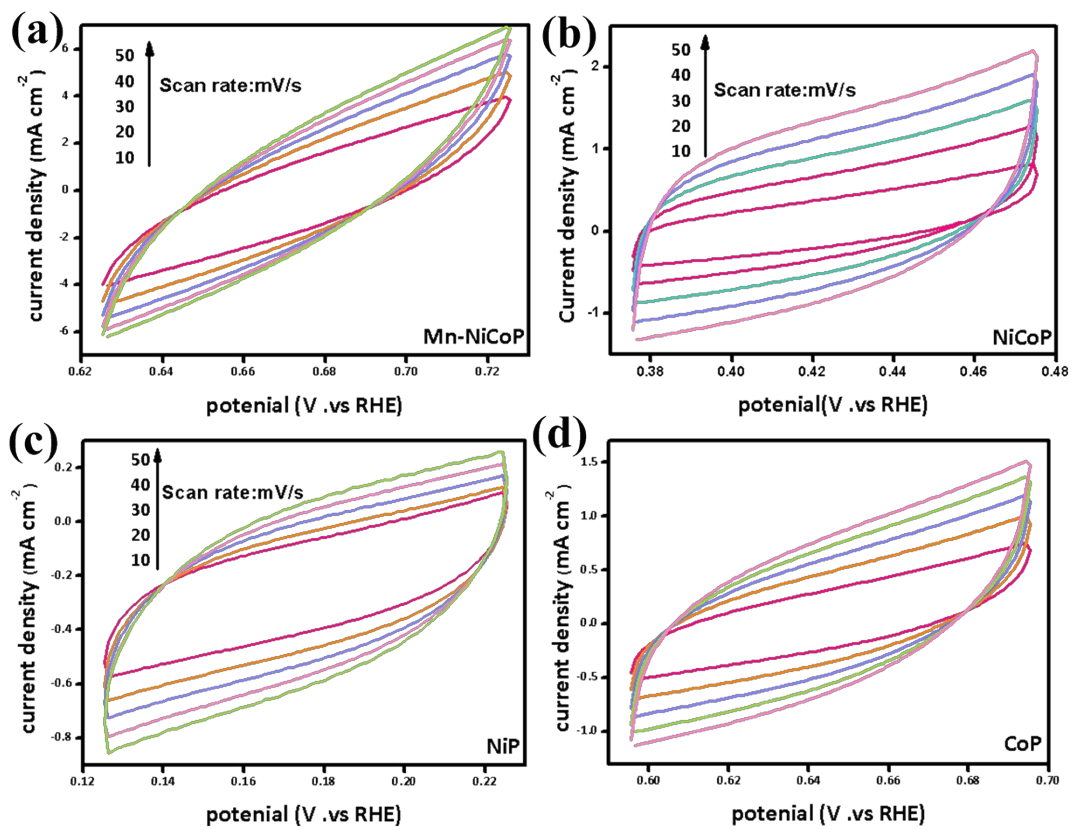
Fig. S6. XPS survey spectra of Mn-NiCoP/NF in (a) Ni 2p region (b) CoP 2p region (c) Mn 2p region and (d) P 2p region after long-term HER test.



**Fig. S7.** The polarization curves of MnCl<sub>2</sub>/Co(NO<sub>3</sub>)<sub>2</sub> solutions with molar ratios of 1:10, 1:5, 1:2 and 1:1 were tested in 1.0 M KOH solution.



**Fig. S8.** Difference between anodic and cathodic current density plotted against scan rate of Mn-NiCoP, NiCoP, NiP and CoP electrocatalysts.



**Fig. S9.** CV images within scan rate of 10~50 mV/s of Mn-NiCoP, NiCoP, NiP and CoP electrocatalysts.