Electronic Supplementary Information

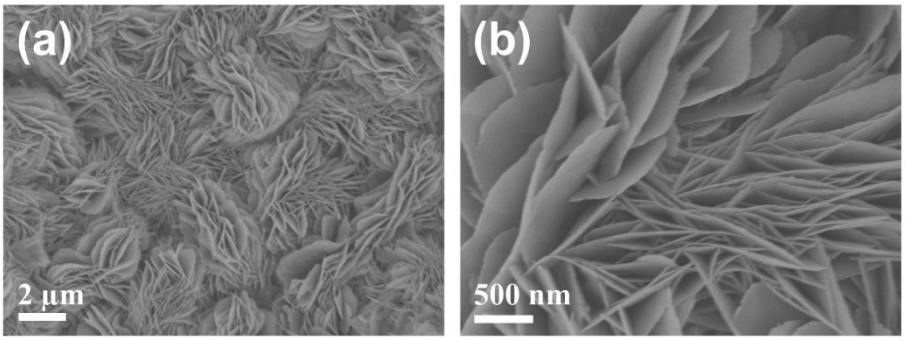

Fig. S1 SEM images of the NiRu-MOF/NF.

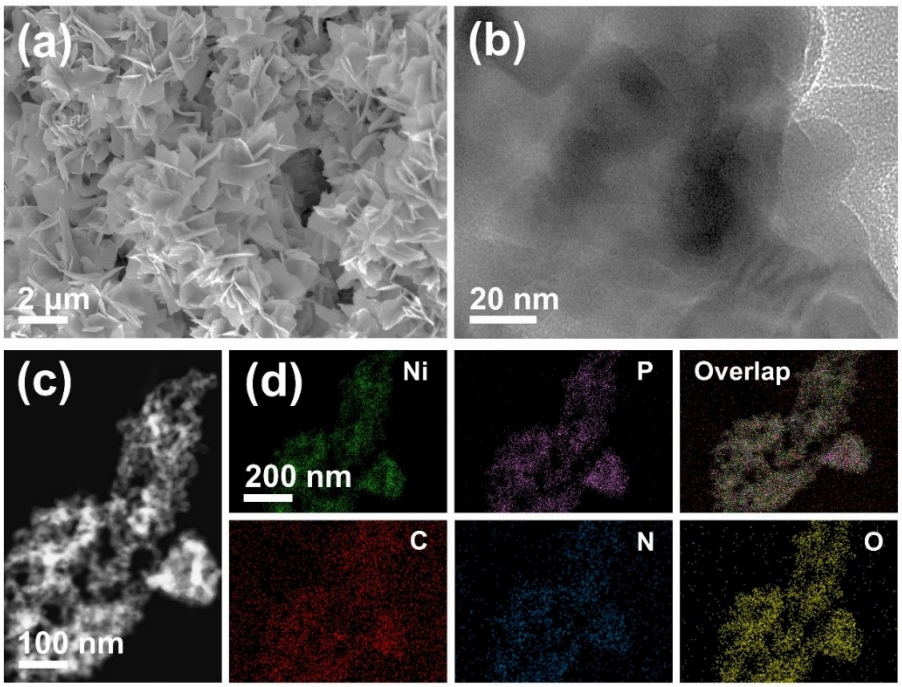

Fig. S2 (a) SEM image of the Ni_xP_y/N-C/NF. (b) TEM image, (c) HAADF-STEM image and (d) corresponding element mappings of the Ni_xP_y/N-C.

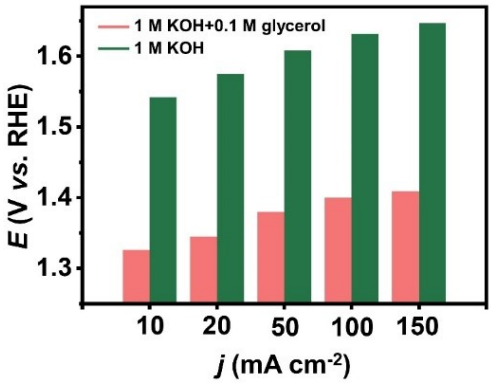

Fig. S3 Comparison of required applied potentials at different anodic current densities on the Ru-Ni_xP_y/N-C/NF electrode measured in 1 M KOH solution with and without 0.1 M glycerol.

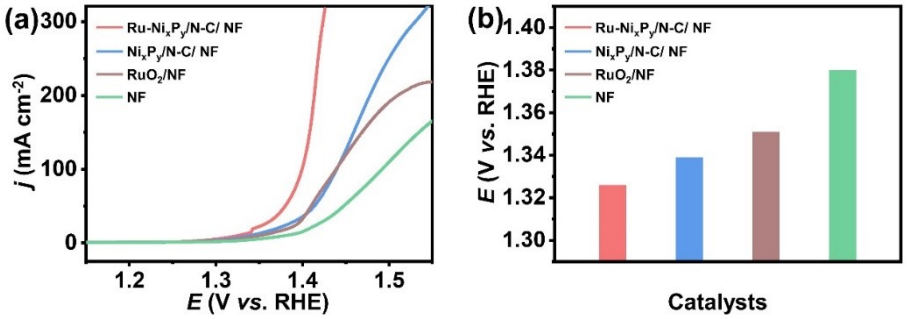

Fig. S4 (a) LSV curves measured in a 1.0 M KOH solution containing 0.1 M glycerol for Ru-Ni_xP_y/N-C/NF, Ni_xP_y/N-C /NF, RuO_2/NF and NF. (b) Comparison of required applied potentials at 10 mA cm^{-2} for various catalysts.

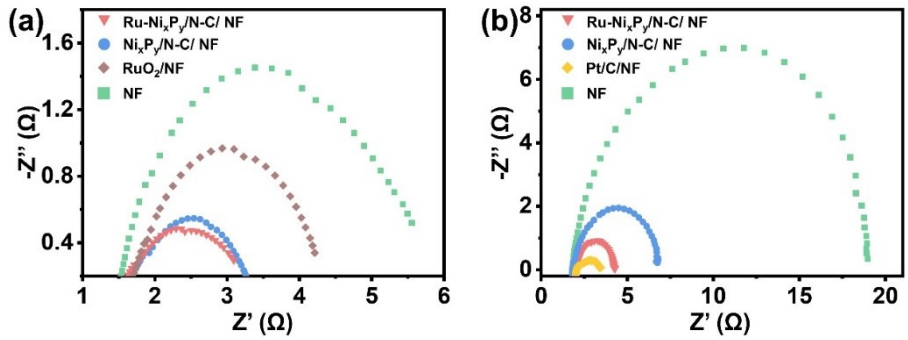

Fig. S5 Electrochemical impedance spectra of various catalysts in 1 M KOH solutions with and without 0.1 M glycerol and at different potentials: (a) 1.45 V (*vs.* RHE), with 0.1 M glycerol; (b) -0.20 V (*vs.* RHE), without glycerol.

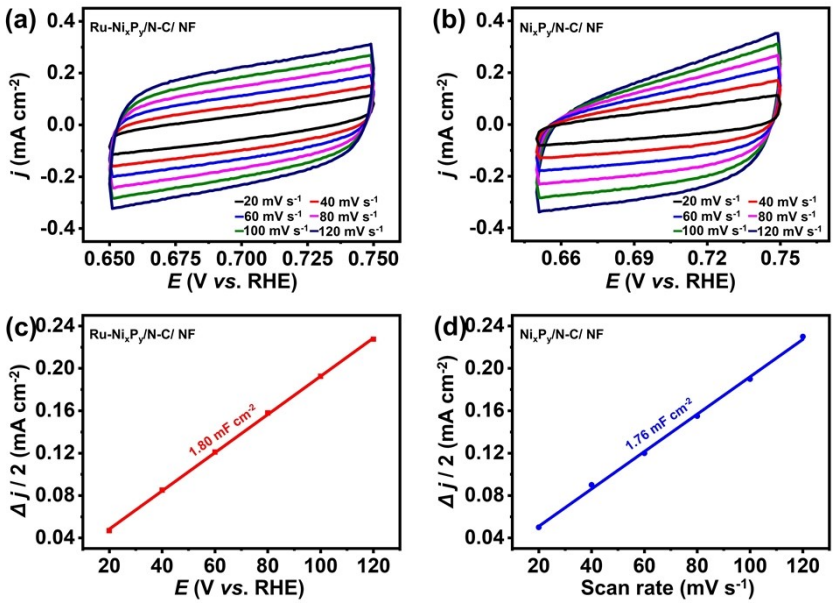

Fig. S6 Electrochemical C_{dl} measurements of (a) Ru-Ni_xP_y/N-C/NF and (b) Ni_xP_y/N-C/NF at scan rates of 20, 40, 60, 80, 100, and 120 mV s^{-1}. (c) Capacitance current density versus scan rate for (c) Ru-Ni_xP_y/N-C/NF and (d) Ni_xP_y/N-C/NF at 0.7 V (vs. RHE).

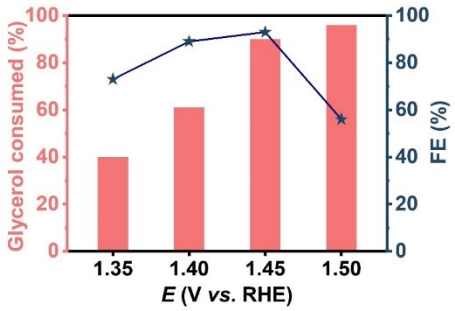

Fig. S7 Glycerol consumed and formate FE for Ru-Ni_xP_y/N-C/NF electrode at different potentials in a 1 M KOH solution containing 0.1 M glycerol.

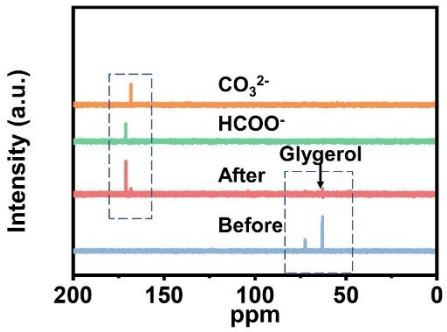

Fig. S8 The ^{13}C NMR spectra of the products of glycerol before and after 15 h of anodic oxidation, and the spectra of $HCOO^-$ and CO_3^{2-}.

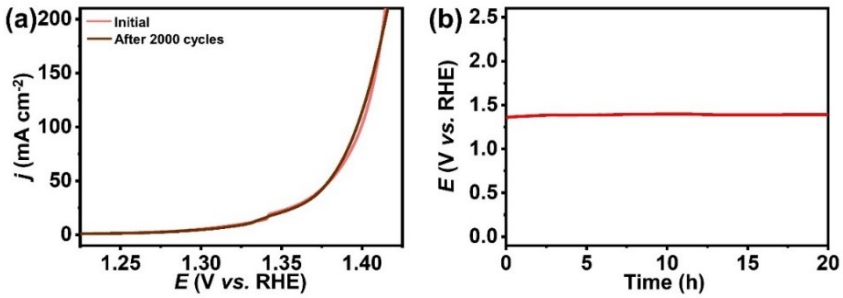

Fig. S9 (a) GOR polarization curves of Ru-Ni_xP_y/N-C/NF at initial and after 2000 cycles. A fresh 1 M KOH solution containing 0.1 M glycerol was used when reported the LSV plot of 2000th cycle. (b) The V-t curves of Ru-Ni_xP_y/N-C/NF measured at 10 mA cm^{-2} for 20 h (without iR compensation).

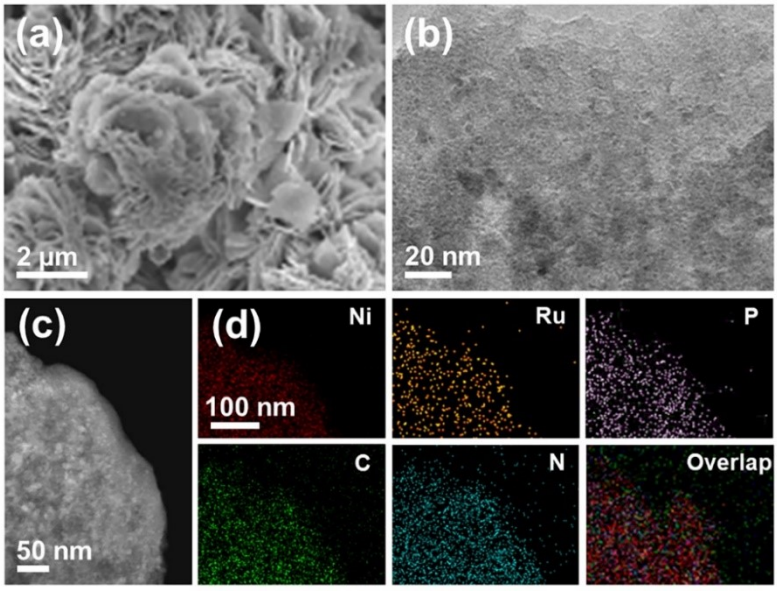

Fig. S10 (a) SEM of post-HER Ru-Ni_xP_y/N-C/NF. (b) TEM, (c) HAADF-STEM and (d) corresponding element mappings of the post-GOR Ru-Ni_xP_y/N-C.

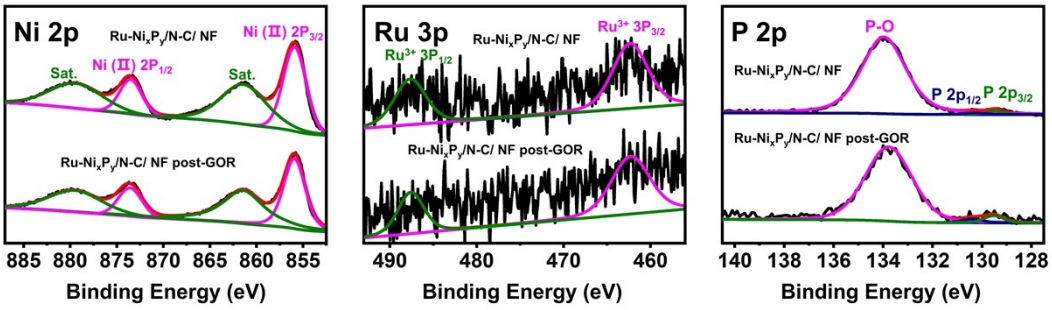

Fig. S11 (a) Ni 2p, (b) Ru 3p and (c) P 2p XPS spectra of fresh and post-GOR Ru-Ni_xP_y/N-C samples.

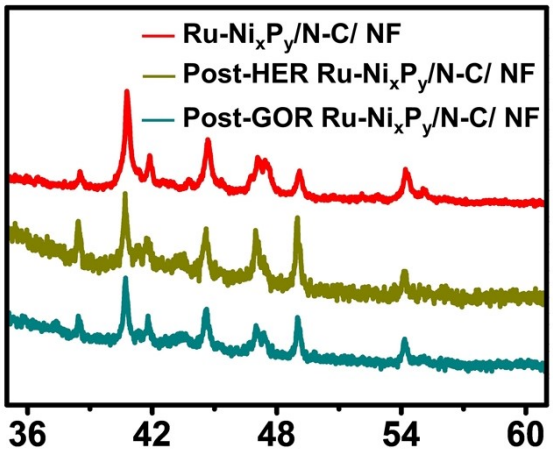

Fig. S12 XRD patterns of fresh, post-GOR and post-HER Ru-Ni_xP_y/N-C samples.

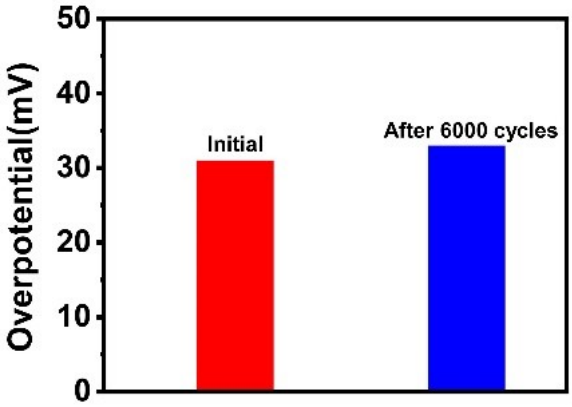

Fig. S13 Comparison of required overpotentials at a HER current density of 10 mA cm^{-2} for Ru-Ni_xP_y/N-C/NF before and after 6000 cycles.

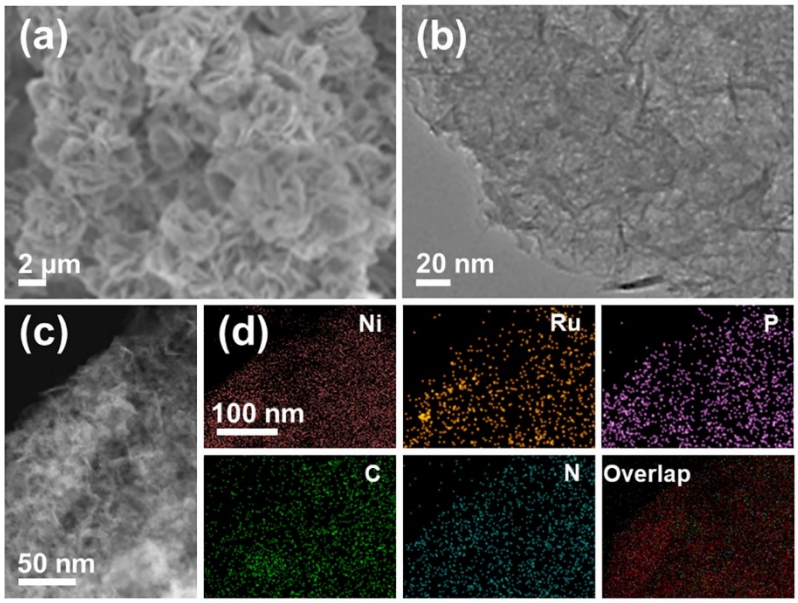

Fig. S14 (a) SEM of post-HER Ru-Ni_xP_y/N-C/NF. (b) TEM, (c) HAADF-STEM and (d) corresponding element mappings of the post-HER Ru-Ni_xP_y/N-C.

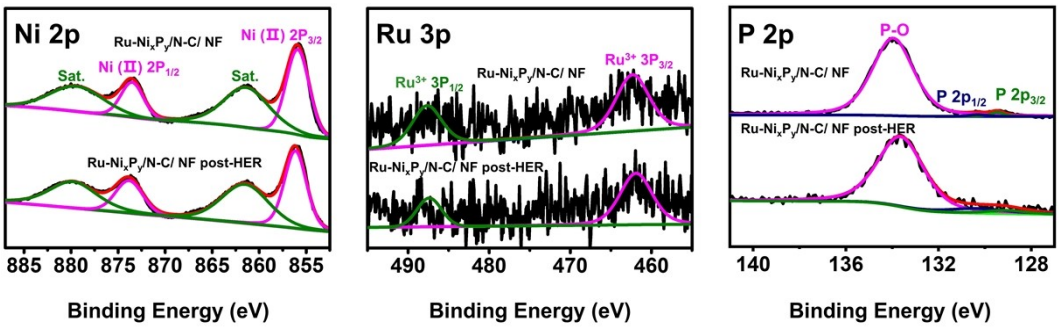

Fig. S15 (a) Ni 2p, (b) Ru 3p and (c) P 2p XPS spectra of fresh and post-HER Ru-Ni_xP_y/N-C samples.

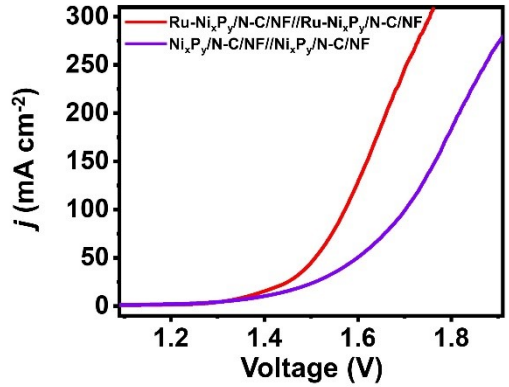

Fig. S16 LSV plots for Ru-Ni_xP_y/N-C/NF||Ru-Ni_xP_y/N-C/NF system and Ni_xP_y/N-C/NF||Ni_xP_y/N-C/NF in a 1 M KOH solution with 0.1 M glycerol.

Table S1. Comparison of the hydrogen evolution and organic electrosynthesis performance of our Ru-Ni_xP_y/N-C/NF||Ru-Ni_xP_y/N-C/NF system and other reported bifunctional catalyst-based co-electrolysis systems.

Bifunctional catalysts	**Electrolyte**	**Main anode product**	**Cell voltage at 10 mA cm^{-2} (V)**	**Ref.**
Ru-Ni_xP_y/N-C/NF	**1 M KOH+ 0.1 M glycerol**	**Formate**	**1.36**	**This work**
NC/Ni-Mo-N/NF	1.0 M KOH+ 0.1 M glycerol	Formate	1.38	1
Ni_3S_2/NF	1M KOH + 0.01 M 5-hydroxymethylfurfural	2,5-furandicarboxylic acid	1.46	2
Ni_2P-UNMs/NF	1 M KOH + 0.125 M benzylamine	Benzonitrile	1.41	3
NiIr-MOF/NF	1 M KOH +4 M methanol	Formate	1.39	4
$Ni(OH)_2$/NF	1 M KOH + 0.5 M methanol	Formate	1.52	5
$Ni_{0.33}Co_{0.67}(OH)_2$/NF	1 M KOH + 0.5 M methanol	Formate	1.5	6
Co_3S_4-NSs/Ni-F	1.0 M KOH + 0.5 M ethanol	Acetate	1.48	7
Co-Ni alloy	1 M KOH + 0.1 M glucose	Gluconolactone, gluconic	1.39	8
Co-S-P/CC	1.0 M KOH + 1.0 M ethanol	Acetic acid	1.63	9

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