Supporting Information

Facile Surface Reconstructions of Cobalt–Copper Phosphide Heterostructures Enable Efficient Electrocatalytic Glycerol Oxidation for Energy-Saving Hydrogen Evolution

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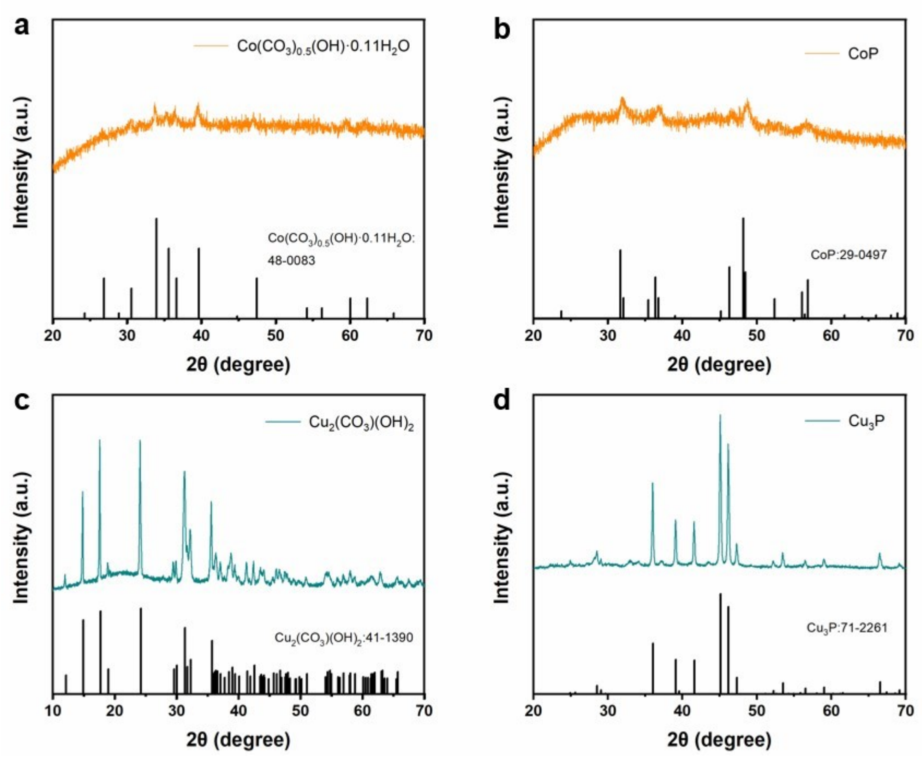

Fig. S1 XRD patterns of (a) $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$, (b) CoP, (c) $Cu_2(CO_3)(OH)_2$, and (d) Cu_3P.

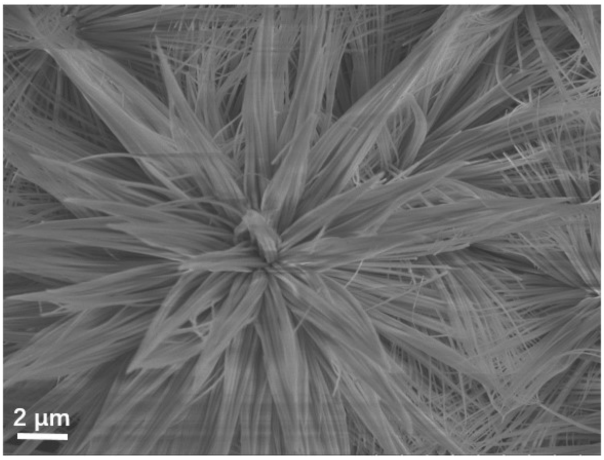

Fig. S2 SEM image of $(Co,Cu)_2CO_3(OH)_2$.

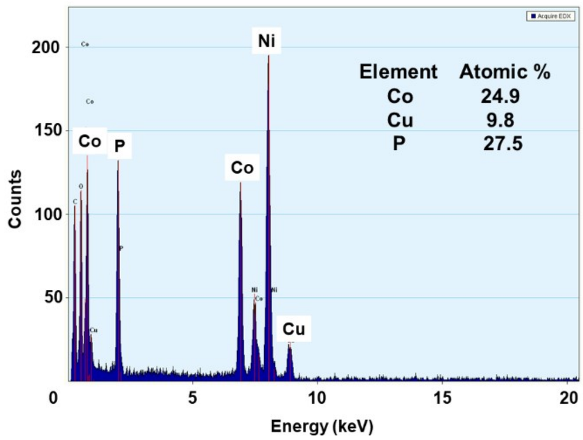

Fig. S3 EDS analysis and elemental quantification of CoP-Cu_3P.

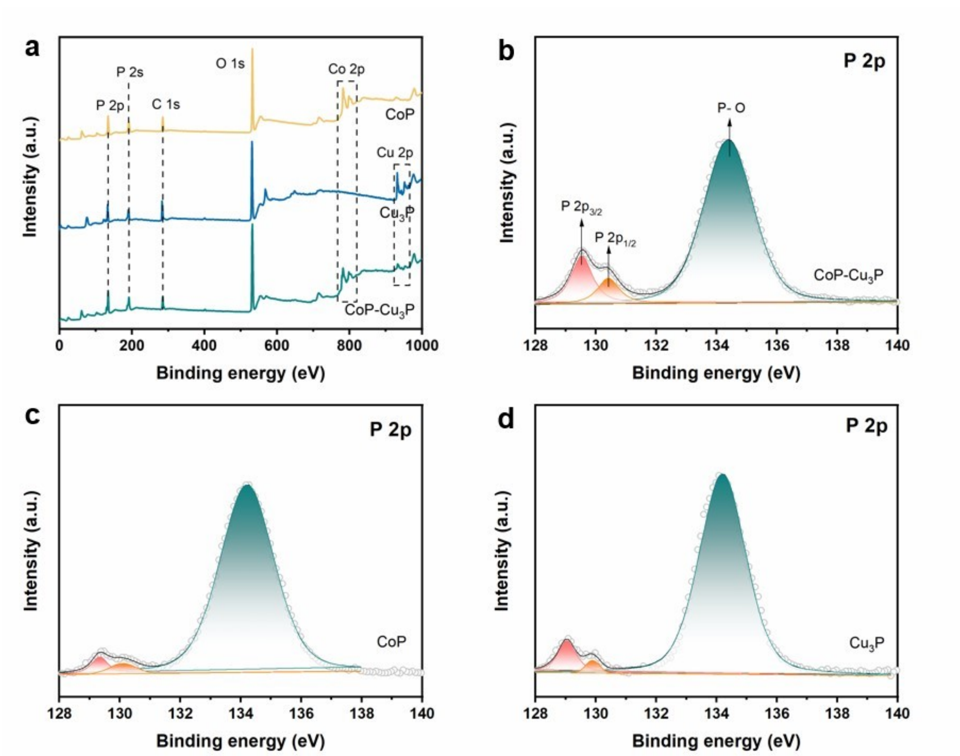

Fig. S4 (a) XPS survey scans of CoP, Cu_3P, and CoP-Cu_3P in the binding energy range of 0-1000 eV. High resolution P 2p XPS spectra of (b) CoP-Cu_3P, (c) CoP, and (d) Cu_3P.

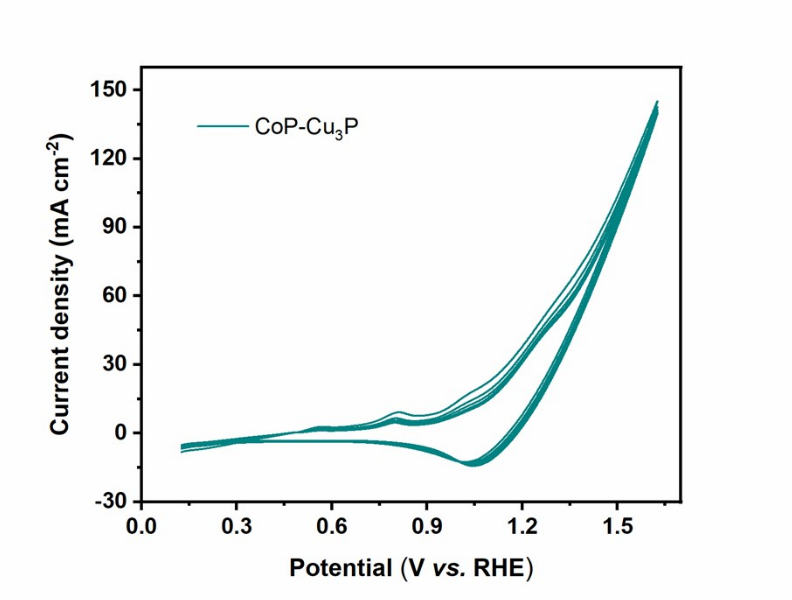

Fig. S5 CV curves in the potential range of 0.1-1.6 V versus RHE for CoP-Cu_3P, with a scan rate of 5 mV s^{-1}.

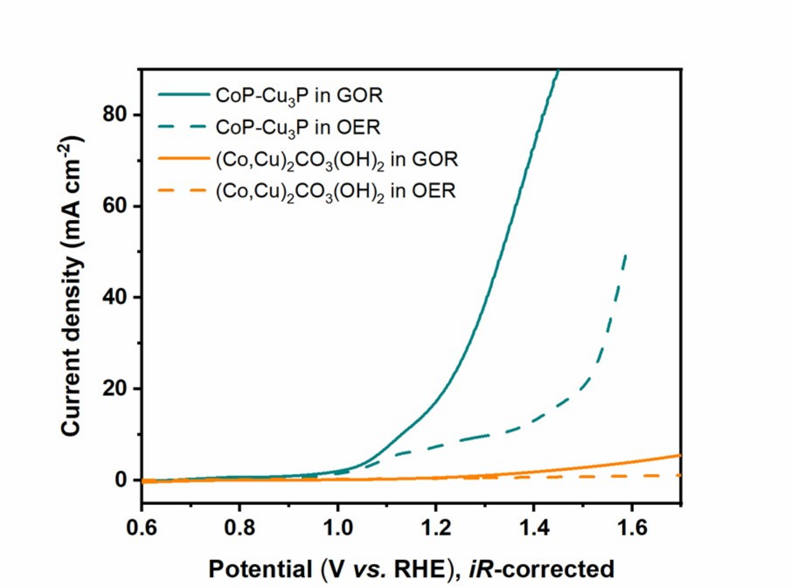

Fig. S6 LSV curves of CoP-Cu_3P and $(Co,Cu)_2CO_3(OH)_2$ grown on carbon cloth in 1 M KOH solution with (solid lines) and without (dashed lines) 0.1 M glycerol addition.

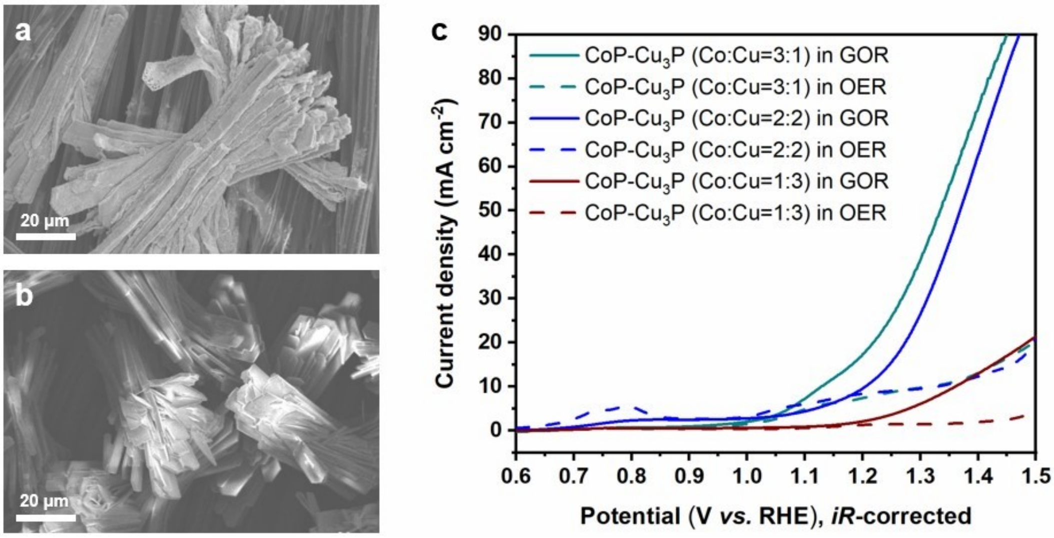

Fig. S7 SEM images of CoP-Cu_3P composites with different initial feeding Co:Cu ratio, (a) Co:Cu=2:2, (b) Co:Cu=1:3. (c) LSV curves of CoP-Cu_3P/CC with different Co:Cu ratio in CoP-Cu_3P composites, in 1 M KOH solution with (solid lines) and without (dashed lines) 0.1 M glycerol addition.

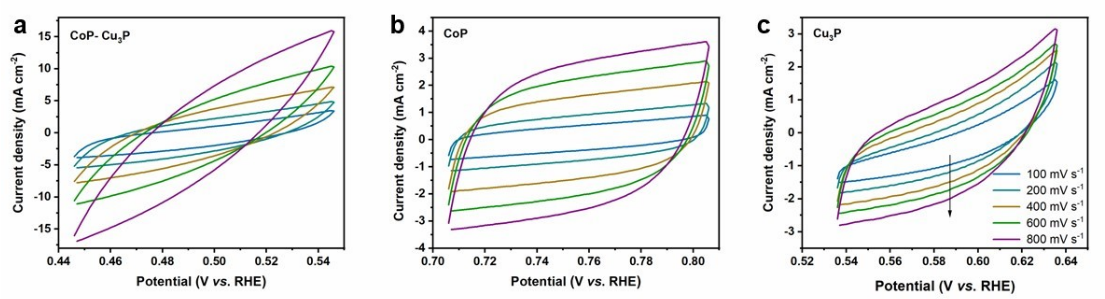

Fig. S8 Electrochemical capacitance measurements for various electrodes. CV were taken in a potential range with no Faradic processes for (a) CoP-Cu_3P, (b) CoP, and (c) Cu_3P.

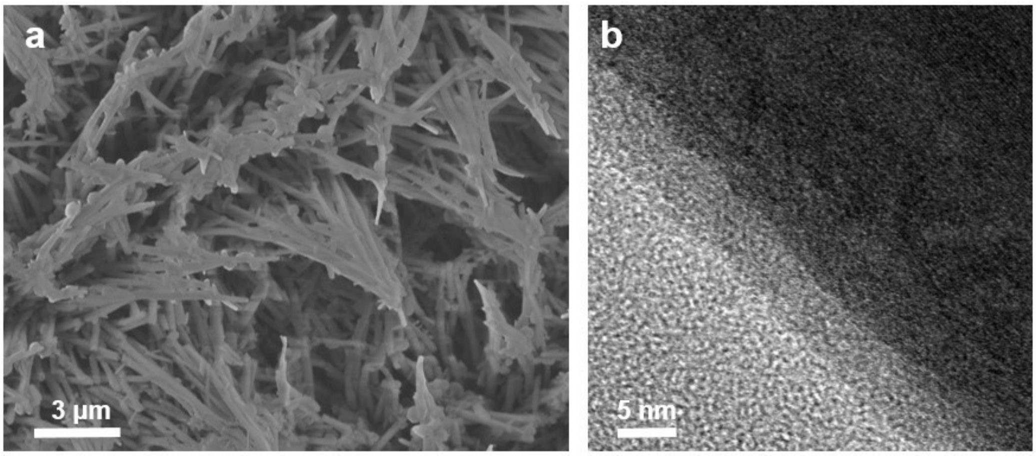

Fig. S9 (a) SEM and (b) TEM images of CoP-Cu_3P after GOR process.

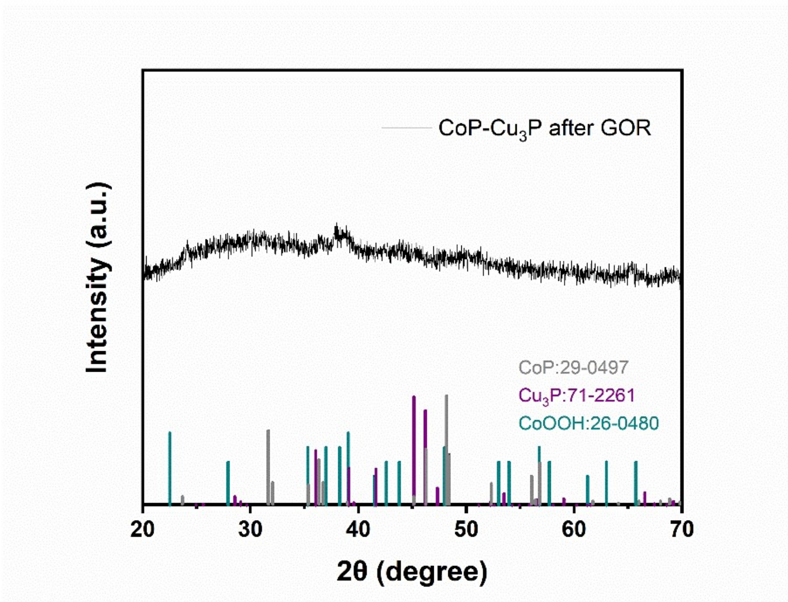

Fig. S10 XRD pattern of CoP-Cu_3P after GOR process.

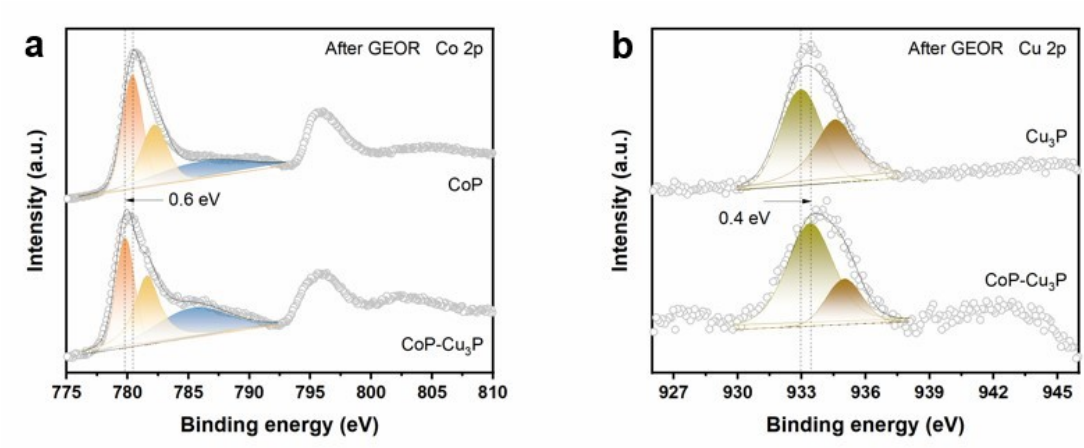

Fig. S11 (a) High resolution Co 2p XPS spectra of CoP and CoP-Cu_3P after GOR process. (b) High resolution Cu 2p XPS spectra of Cu_3P and CoP-Cu_3P after GOR process.

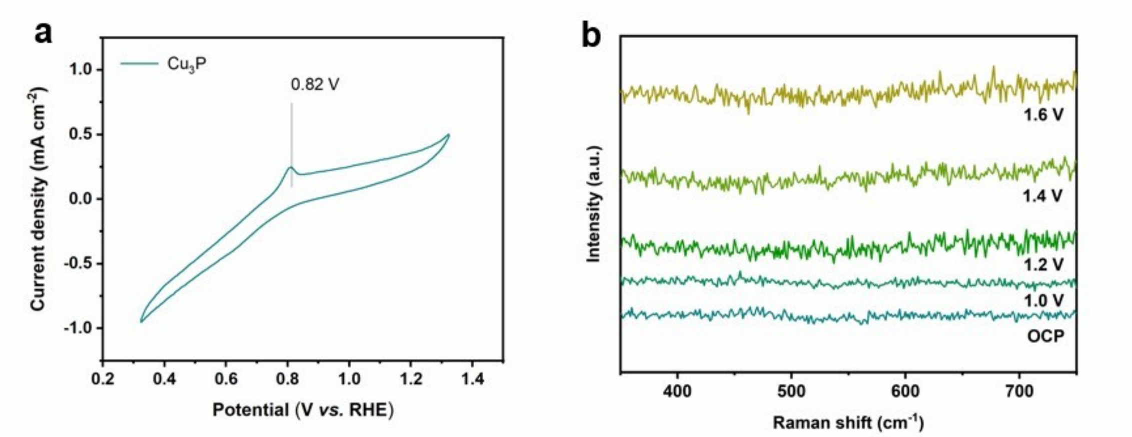

Fig. S12 (a) CV curve in the potential range of 0.3-1.3 V versus RHE for Cu_3P, with a scan rate of 5 mV s^{-1}. (b) In situ Raman spectra recorded on Cu_3P electrode at increasing applied potentials from OCP to 1.6 V.

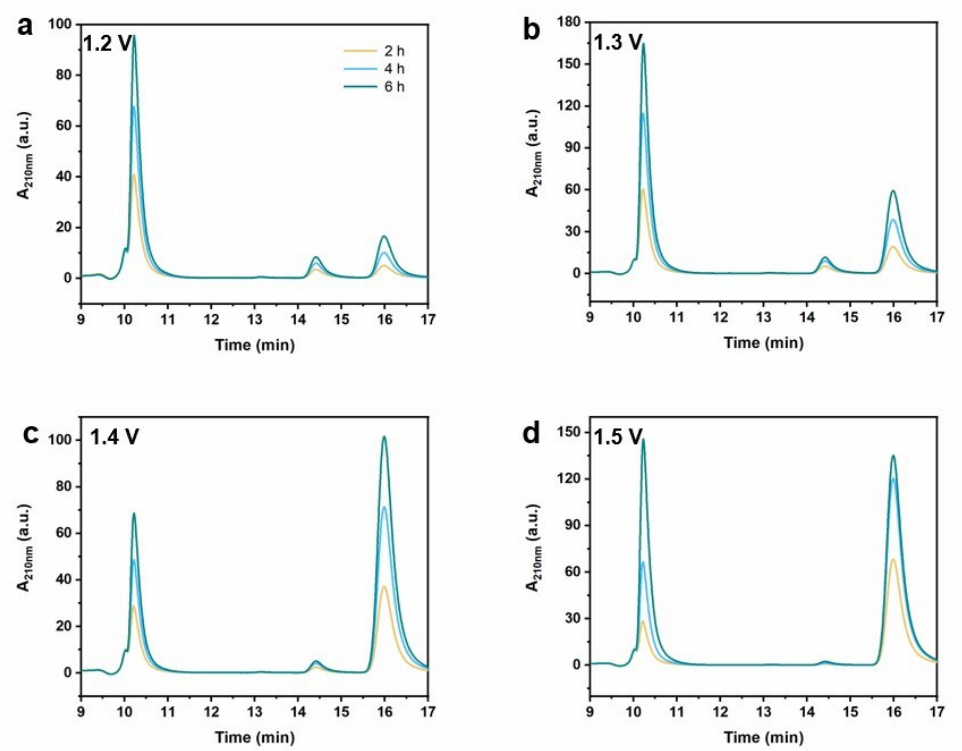

Fig. S13 HPLC chromatograms of collected solution products after GOR on CoP-Cu_3P at a constant potential of (a) 1.2 V, (b) 1.3 V, (c) 1.4 V, and (d) 1.5 V *vs.* RHE in 1 M KOH containing 0.1 M glycerol.

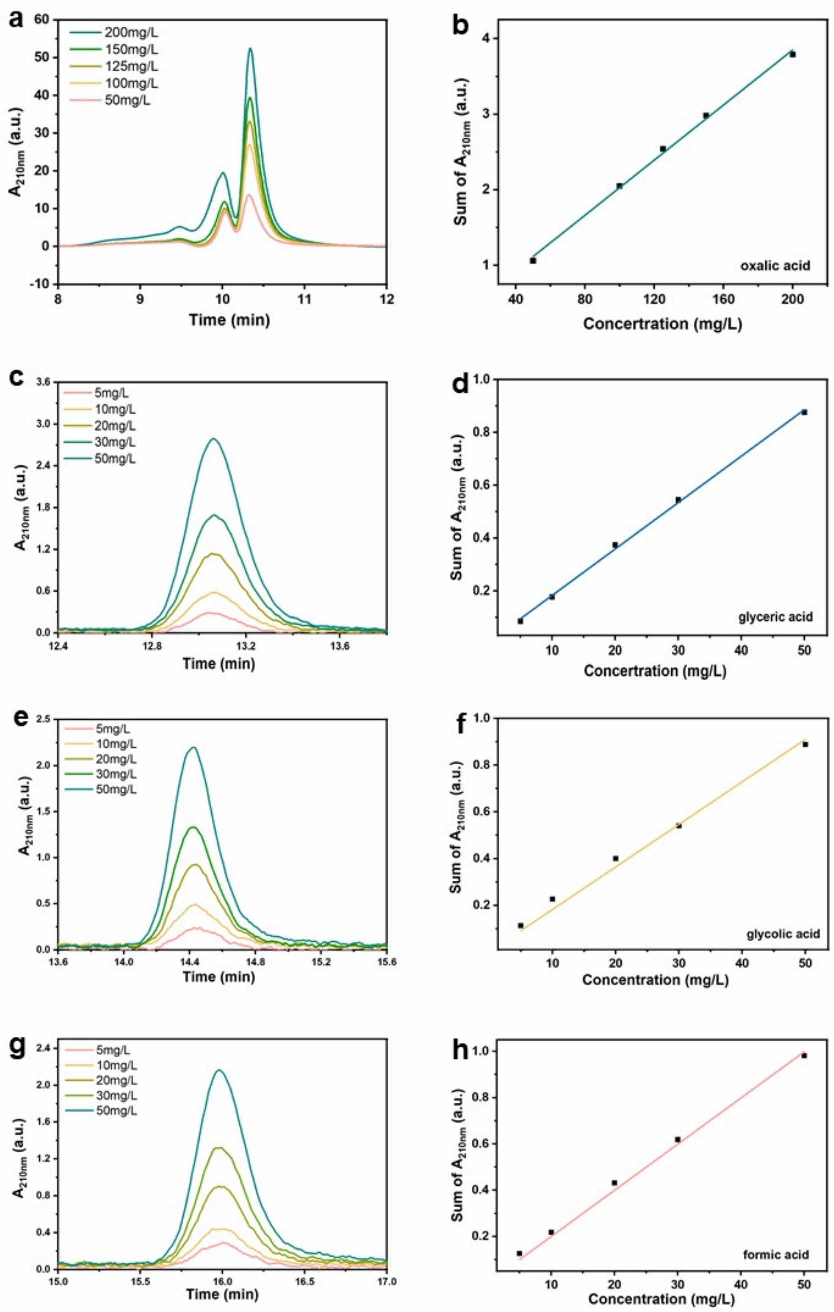

Fig. S14 The HPLC chromatograms of standard chemicals with known concentrations (left column) and the obtained calibration curves (right column): (a, b) oxalic acid, (c, d) glyceric acid, (e, f) glycolic acid, and (g, h) formic acid.

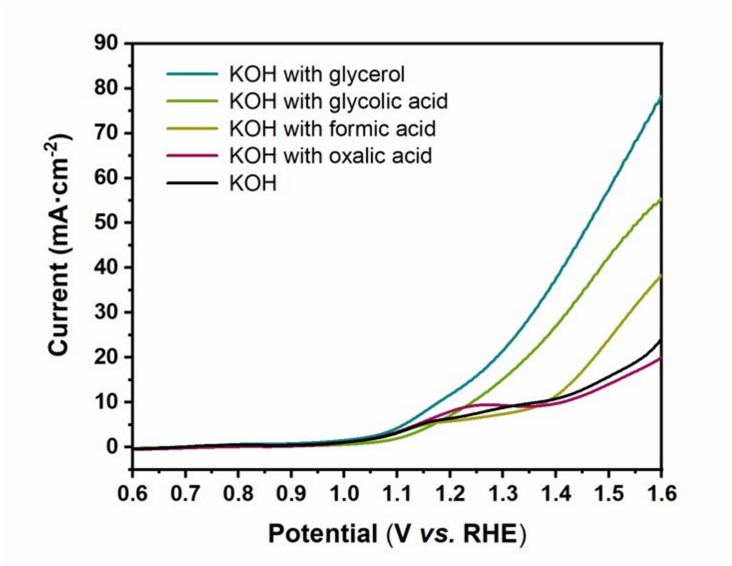

Fig. S15 LSV curves of CoP-Cu_3P/CC in 1 M KOH solution with GOR intermediate products (oxalic acid, glycolic acid, and formic acid).

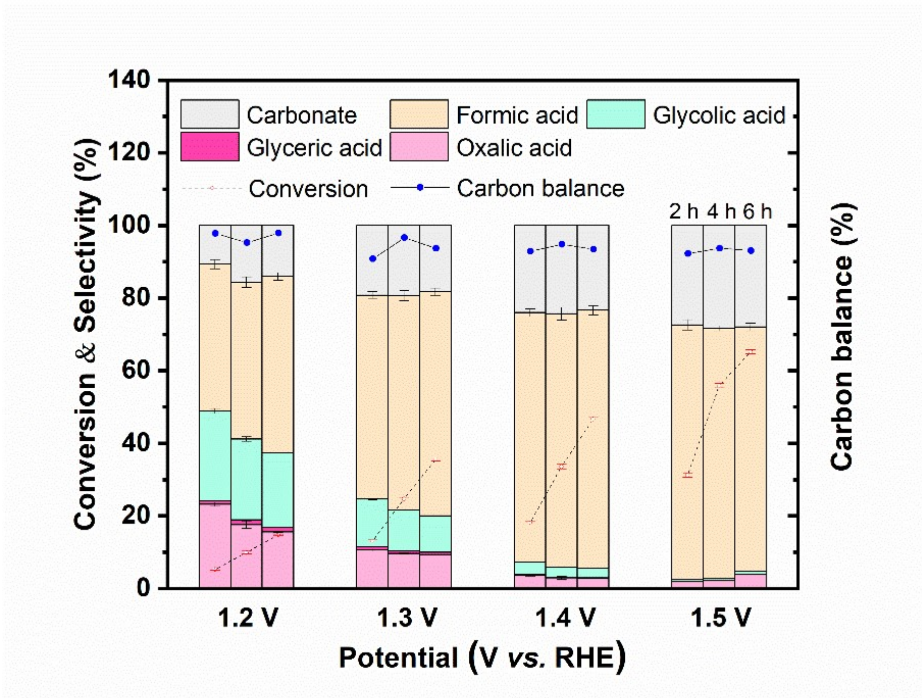

Fig. S16 The glycerol conversion, oxidation products selectivity, and carbon balance at different time points and applied potentials (1 M KOH, 0.1 M glycerol).

The glycerol conversion, selectivity of the product and carbon balance are calculated by the following equations:

$$Glycerol\ conversion = \frac{n_{converted\ glycerol}}{n_{initial\ glycerol}} \times 100\%$$

$$Selectivity_{product} = \frac{n_{product}}{n_{total}} \times 100\%$$

$$Carbon\ balance = \frac{3n_{C3} + 2n_{C2} + n_{C1} + 3n_{final\ glycerol}}{3n_{initial\ glycerol}} \times 100\%$$

where $n_{product}$ indicates the moles of the product, n_{total} denotes the moles of the total product, $n_{initial\ glycerol}$, $n_{converted\ glycerol}$, and $n_{finial\ glycerol}$ are the initial, converted, and final moles of glycerol, n_{C1}, n_{C2}, and n_{C3} are the moles of C1, C2, and C3 products, respectively.

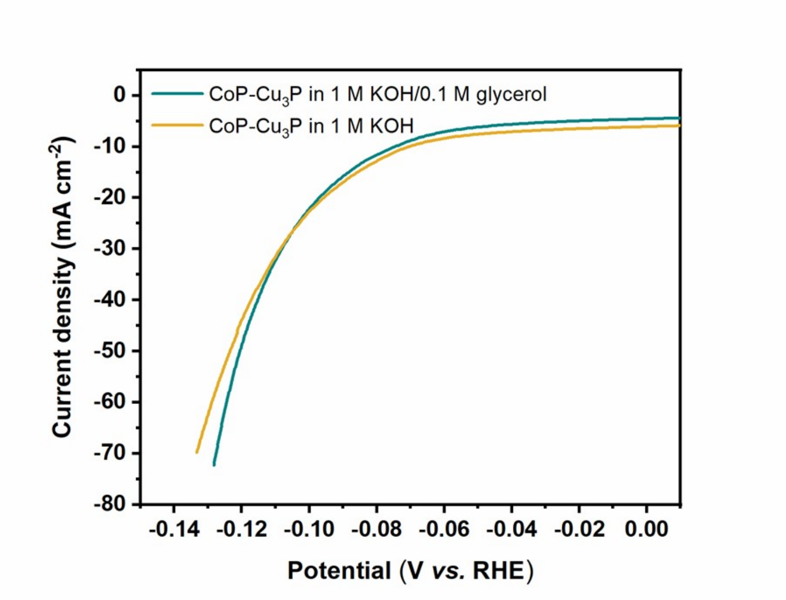

Fig. S17 LSV curves of CoP-Cu_3P/CC in 1 M KOH solution with (cyan) and without (yellow) 0.1 M glycerol addition.

Table S1. Comparison of the GOR acitivity between $CoP-Cu_3P/CC$ and some other electrocatalysts in the recent literature reports.

Anodic catalyst	Electrolyte	Applied potential at 10 mA cm^{-2} (V)	Ref.
$CoP-Cu_3P/CC$	1 M KOH + 0.1 M glycerol	1.13	This work
$CuCo_2O_4$	0.1 M KOH + 0.1 M glycerol	1.30	[1]
CuCo-oxide	0.1 M KOH + 0.1 M glycerol	1.25	[2]
$(Cu_{1-x}Co_x)_2CO_3(OH)_2$	1 M KOH + 0.1 M glycerol	>1.4	[3]
NiO_x/MWCNTs	1 M KOH + 1 M glycerol	1.31	[4]
Ni-Mo-N/CFC	1 M KOH + 0.1 M glycerol	1.30	[5]
Ni-Mo-N/NF	1 M KOH + 0.1 M glycerol	1.16	[6]
$CoMoO_4$	1 M KOH + 0.1 M glycerol	1.239	[7]
HEA-CoNiCuMnMo	1 M KOH + 0.1 M glycerol	1.25	[8]
CoNi hydroxide	1 M KOH + 0.1 M glycerol	1.35 V @100 mA cm^{-2}	[9]
NiV LDH	1 M KOH + 0.1 M glycerol	1.23	[10]

Table S2. Comparison of the chemical-assisted hydrogen evolution reaction performance between the CoP-Cu_3P/CC||CoP-Cu_3P/CC and some other reported systems.

Anodic catalyst	Cathodic catalyst	Electrolyte	Cell voltage at 10 mA cm^{-2} (V)	Ref.
CoP-Cu_3P/CC	CoP-Cu_3P/CC	1 M KOH + 0.1 M glycerol	1.21	This work
Ni-Mo-N/CFC	Ni-Mo-N/CFC	1 M KOH + 0.1 M glycerol	1.36	[5]
NC/Ni-Mo-N/NF	NC/Ni-Mo-N/NF	1 M KOH + 0.1 M glycerol	1.38	[6]
HEA-CoNiCuMnMo	RhIr/Ti	1 M KOH + 0.1 M glycerol||0.5 M H_2SO_4	0.55	[8]
NiV LDH	P-NiV LDH	1 M KOH + 0.1 M glycerol	1.25	[10]
Ni_3N-$Ni_{0.2}Mo_{0.8}N$/CC	Ni_3N-$Ni_{0.2}Mo_{0.8}N$/CC	1 M KOH + 0.1 M glycerol	1.40	[11]
MnO_2	Pt/C	0.005 M H_2SO_4 + 0.2 M glycerol	1.36	[12]
Ni_2P-CoP/NF	Ni_2P-CoP/NF	1 M KOH + 0.5 M methanol	1.3	[13]
Ni_2P	F-β-FeOOH	1 M KOH + 0.33 M ethanol	1.46	[14]
Co-S-P/CC	Co-S-P/CC	1 M KOH + 1 M ethanol	1.63	[15]
$NiFeO_x$-NF	$NiFeN_x$-NF	1 M KOH + 0.1 M glucose	1.39 @100 mA cm^{-2}	[16]
Co-Ni alloy	Co-Ni alloy	1 M KOH + 0.1 M glucose	1.39	[17]
NiS@Ni_3S_2/$NiMoO_4$	NiS@Ni_3S_2/$NiMoO_4$	1 M KOH + 0.5 M urea	1.40	[18]
CoS_2 NA/Ti	CoS_2 NA/Ti	1 M KOH + 0.3 M urea	1.59	[19]

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