Supplementary Information (SI) for ChemComm.

Facile Synthesis of CuOCoOOH Composite Electrocatalyst for Efficient Glucose Electrooxidation

Xia Chen, Weiqiang Fan, Jinhui Hao*, Weidong Shi*

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China.

E-mail: swd1978@ujs.edu.cn (W. D. Shi), jinhu1_hao@ujs.edu.cn (J. H. Hao).

1. Electrode preparation and electrochemical measurement

The CuOCoOOH electrocatalyst was directly electrodeposited on nickel foam (NF) by potentiostatic method. Firstly, NF (1 cm × 1 cm) was successively deal with ultrasonic in 1 M HCl, anhydrous ethanol and deionized water for 20 minutes, respectively. Secondly, 0.75 mmol $Cu(NO_3)_2\cdot5H_2O$ and 1.75 mmol $Co(NO_3)_2\cdot6H_2O$ were dissolved into 50 mL deionized water to form the electrolyte. After electrodeposited for 600 s at -1.2 V vs. Ag/AgCl, and then activated by cyclic voltammetry (CV) in 1 M KOH solution for 20 cycles, the CuOCoOOH electrocatalyst was acquired. The CuO_x and CoOOH electrocatalysts were synthesized using the similar process except that the electrolyte was containing 2.5 mmol $Cu(NO_3)_2\cdot5H_2O$ and 2.5 mmol $Co(NO_3)_2\cdot6H_2O$, respectively. The procedure of synthesis of $CuCo(OH)_4$ electrocatalyst was similar to that of CuOCoOOH which without activated by CV.

The electrochemical oxidation of glucose was conducted in a three-electrode cell at room temperature on CHI 760E electrochemical workstation. Glucose was dissolved in a solution of KOH (1.0 M) to form the electrolyte. The linear sweep voltammetry (LSV) curves were recorded with a scanning rate of 5 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) measurements were conducted over a frequency range of 10 mHz to 100 kHz. To evaluate the electrochemical active surface area (ECSA), CV measurements were taken across a potential window of 0.0 to 0.1 V relative to Hg/HgO, utilizing scan rates of 20, 40, 60, 80, and 100 mV s^{-1}. All tests were carried out in a 1.0 M KOH solution containing 0.1 M glucose. The EIS was performed at a fixed potential of 0.15 V vs. Hg/HgO. All potentials vs. Hg/HgO were recalculated to be relative to the reversible hydrogen electrode (RHE) using the equation (E_{RHE} = 0.098V + $E_{Hg/HgO}$ + 0.059V * pH).

2. Analysis of glucose oxidation products

To detect the oxidation products generated at the anode, high-performance liquid chromatography (HPLC, 1260 Infinity II, Agilent) was employed. A Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm × 9 μm) and a refractive index detector were used for the analysis. The mobile phase consisted of a diluted H_2SO_4 solution (5 mM), and the flow rate was maintained at 0.5 mL per minute throughout the detection process. The column temperature was kept at 35 °C using a column heater. Prior to detection, the pH of the sample was adjusted to below 7.0 using 1.0 M H_2SO_4. An injection volume of 20 μL was used for each test. By comparing the retention times with those of standard substances, glucose and its oxidation products were identified. Their concentrations were determined using calibration curves of standard substances, which were established using the external standard method.

3. Calculation formulas for GOR

The conversion of glucose ($\eta_{glucose}$), the yield (Y_P), selectivity (S_P), Faradaic efficiency (FE) and Energy Efficiency (EE) were calculated using the following formulas (1, 2, 3, 4, 5):

$$\eta_{glucose} = (1 - C_{glucose} / C_{0\text{-}glucose}) \times 100\% \qquad (1)$$

$$Y_P = C_P / C_{0\text{-}glucose} \times 100\% \qquad (2)$$

$$S_P = C_P / (C_{0\text{-}glucose} - C_{glucose}) \times 100\% \qquad (3)$$

$$FE = F \times N \times z / Q \times 100\% \qquad (4)$$

$$EE = FE \times E_{theo} / E_{actual} \times 100\% \qquad (5)$$

where $C_{0\text{-}glucose}$ and $C_{glucose}$ are the initial glucose concentration and the concentrations of glucose at different reaction times, respectively. And C_P is the concentration of glucose oxidation products at different reaction times. N is the product amount, z is the required amounts of electrons to convert one glucose molecule into product, F is the Faraday constant (96485 C/mol), Q is the total amount of charge passed through the electrochemical cell, $Q = J \times S \times t$, where J (A/cm^2) is the current density at a specific applied potential, *S* is the electrode area (cm^2) and *t* is the reaction time (seconds).

4. Additional data and figures

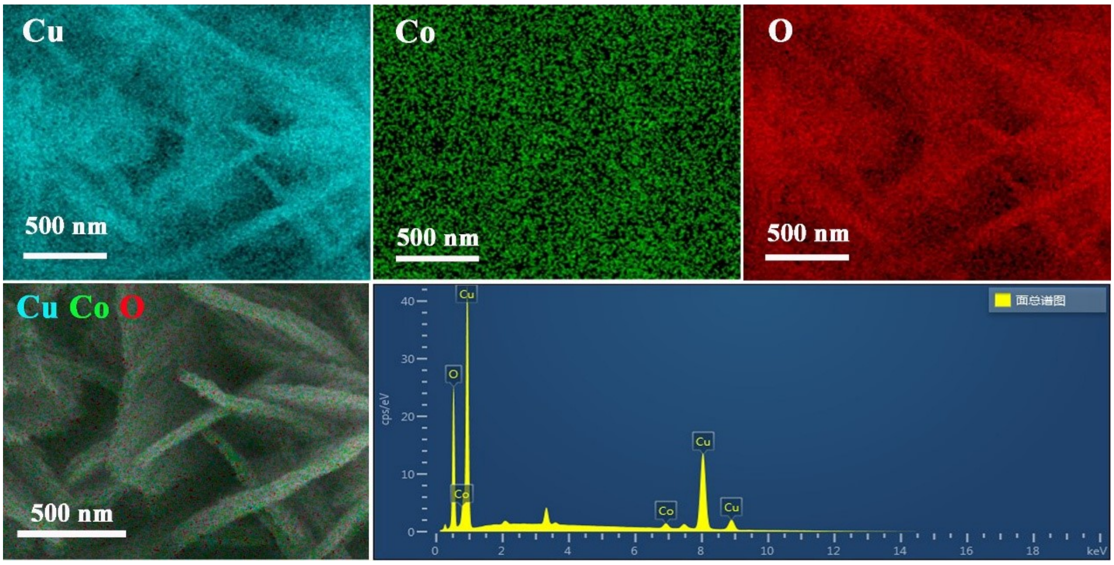

Fig. S1 SEM-EDS elemental mapping and spectrum of CuOCoOOH.

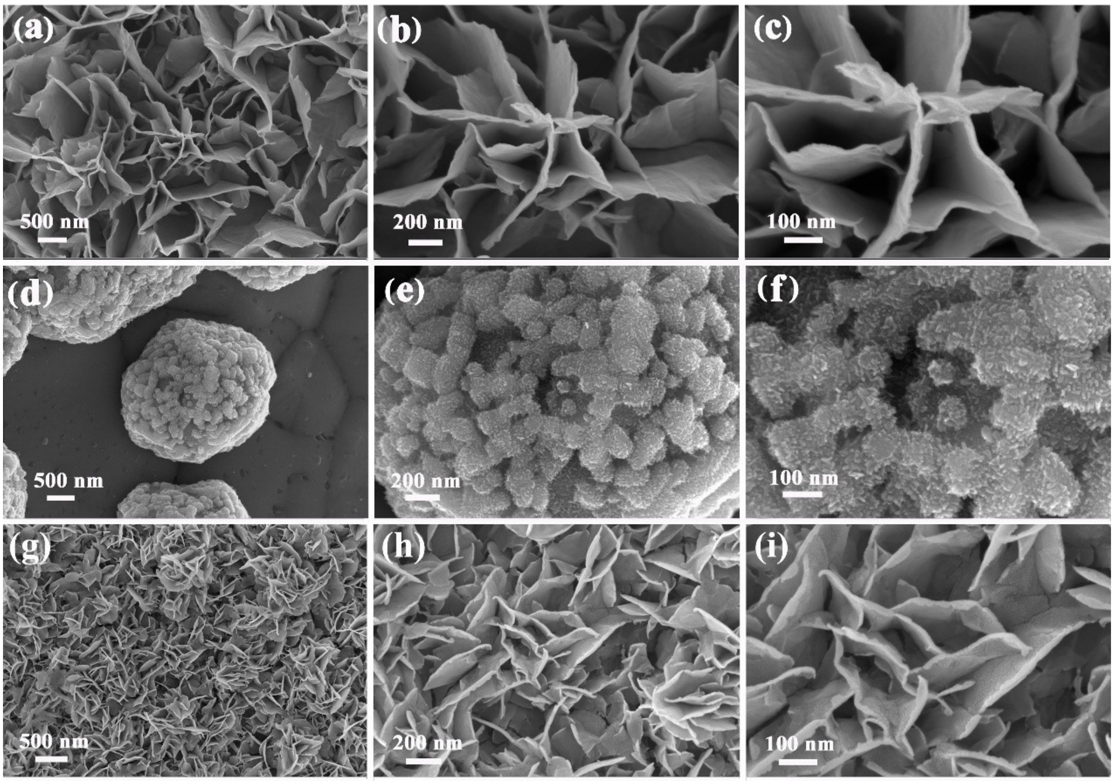

Fig. S2 SEM images of (a, b, c) CoOOH, (d, e, f) CuO_x and (g, h, i) $CuCo(OH)_4$ on NF.

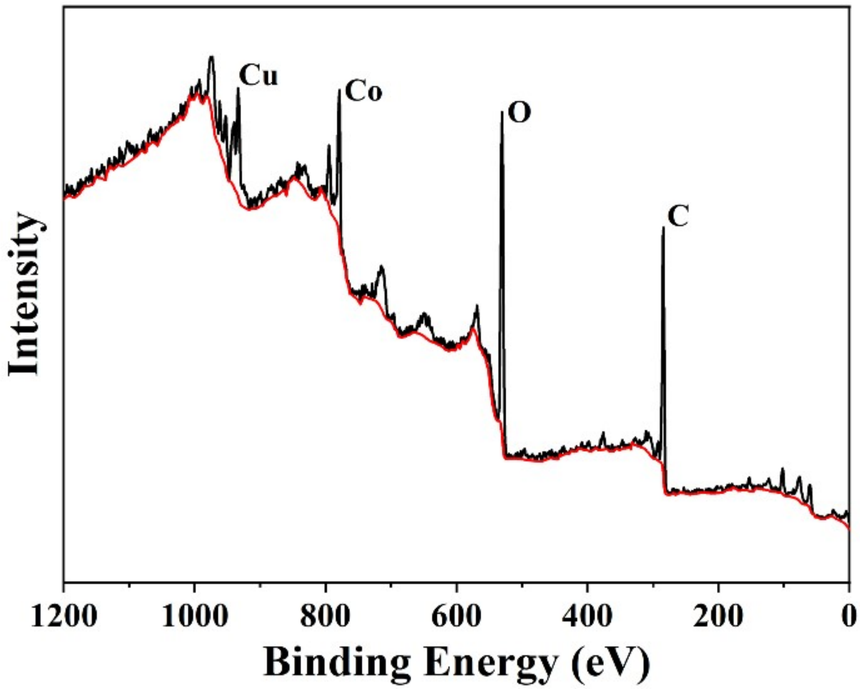

Fig. S3 The survey spectrum of Cu, Co, O, and C elements of CuOCoOOH.

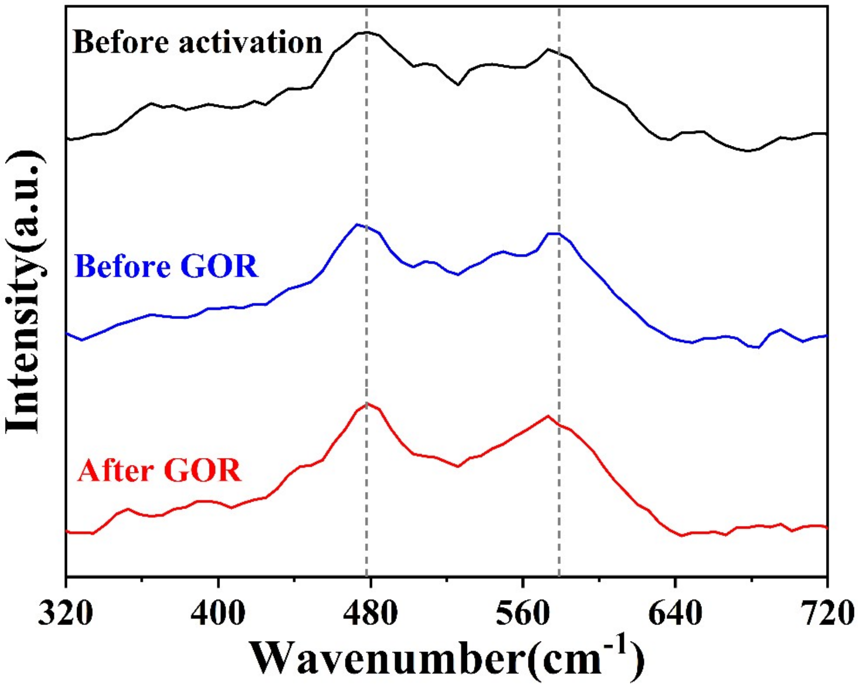

Fig. S4 In situ Raman spectroscopy of CuOCoOOH before activation, before and after GOR.

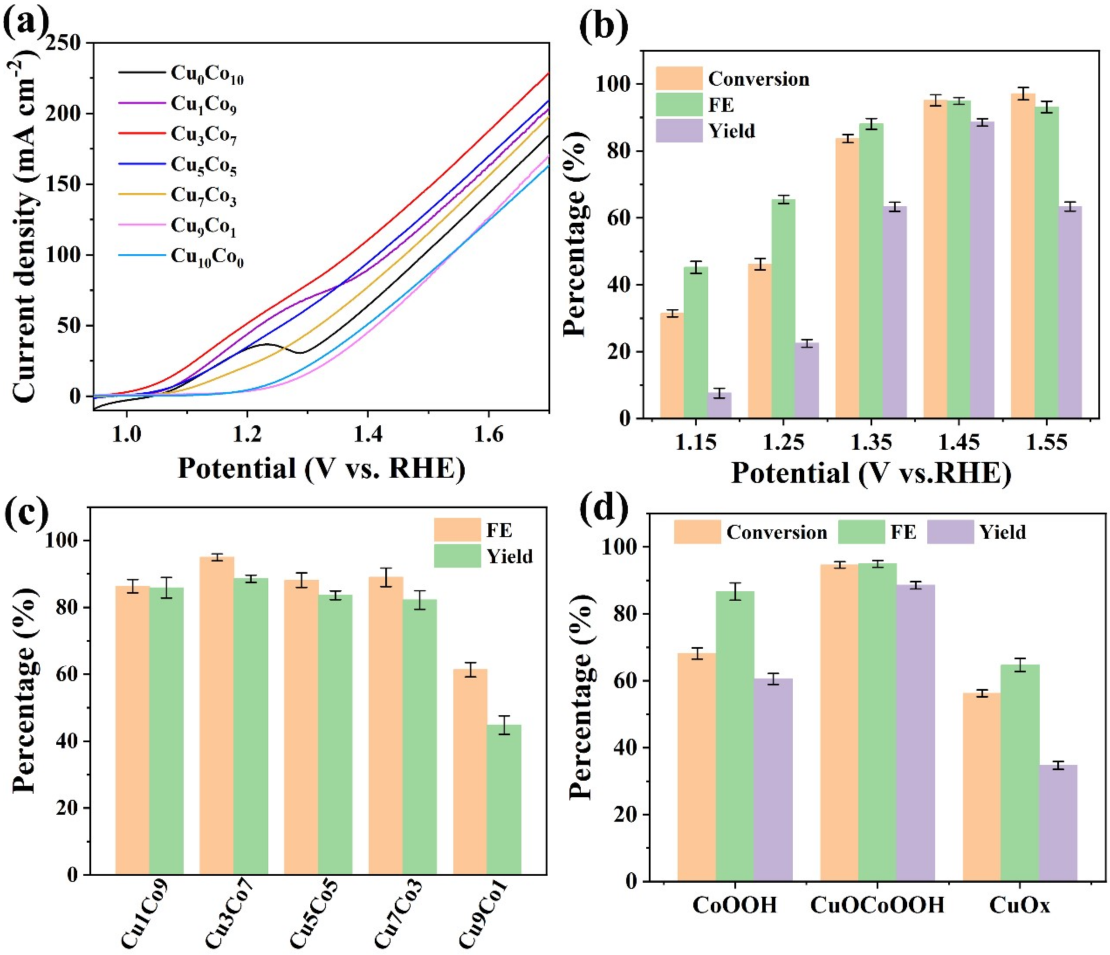

Fig. S5 (a)The polarization curves of electrocatalysts at different mole ratio between copper and cobalt in electrolyte. Performance after 2 h electrolysis: (b) by CuOCoOOH electrocatalyst. (c, d) at 1.45 V vs. RHE.

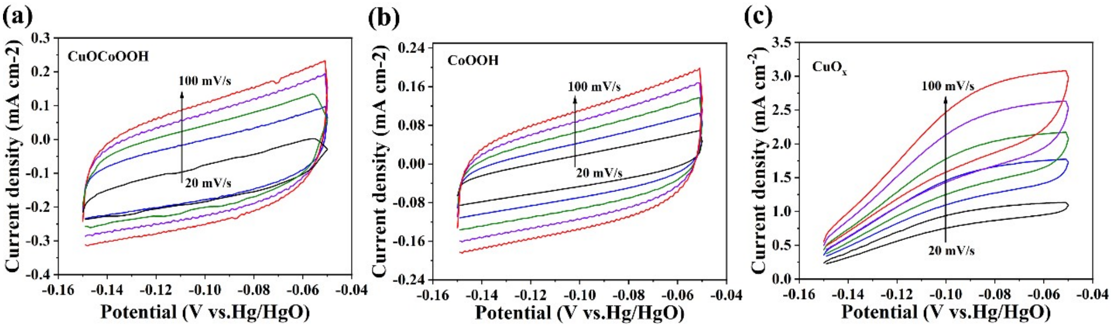

Fig. S6 Cyclic voltammogram curves of (a) CuOCoOOH, (b) CoOOH and (c) CuO_x in the double layer capacitive region at the scan rates of 20 mV s^{-1} to 100 mV s^{-1} in 1.0 M KOH with 0.1 M glucose.

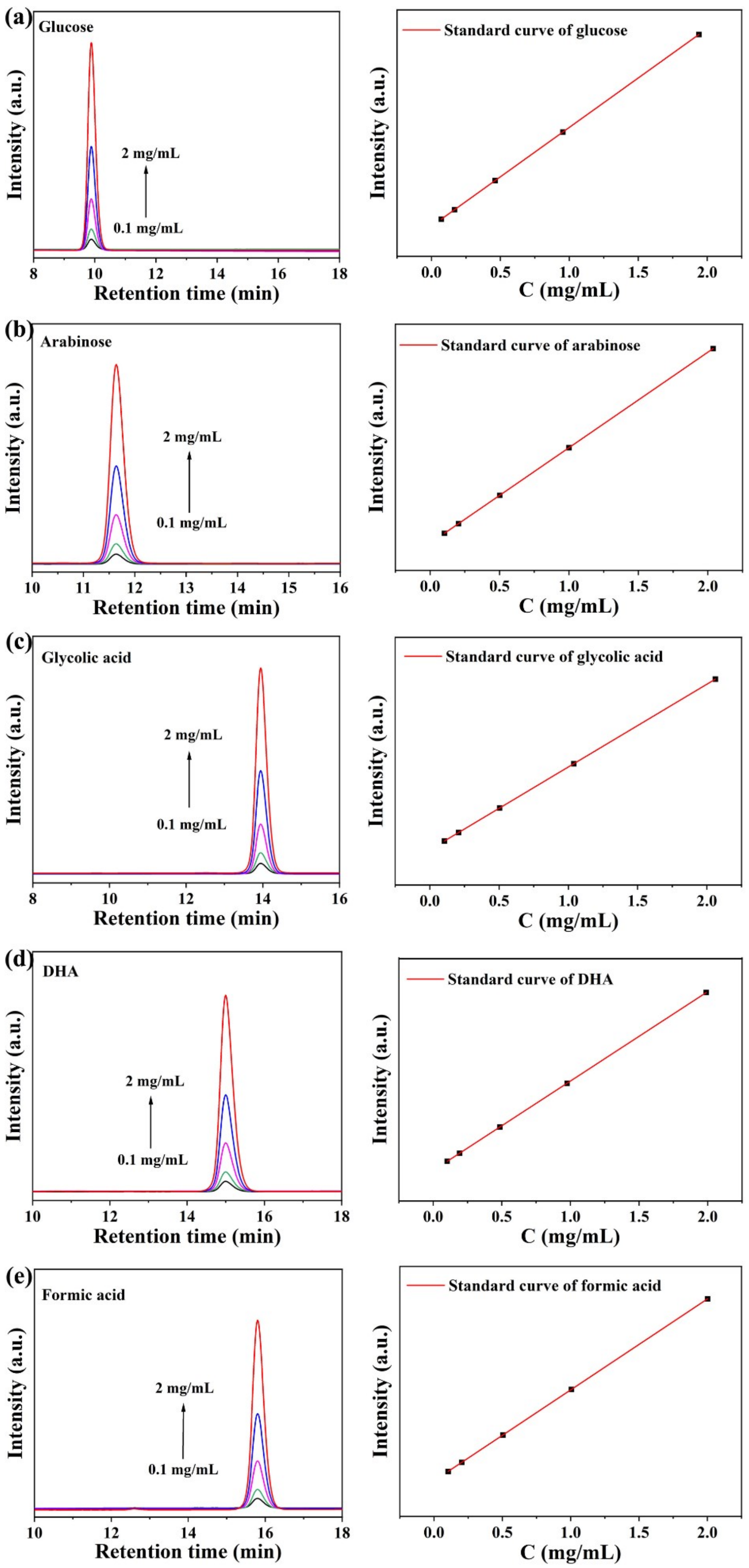

Fig. S7 The HPLC standard curves of glucose and corresponding products.

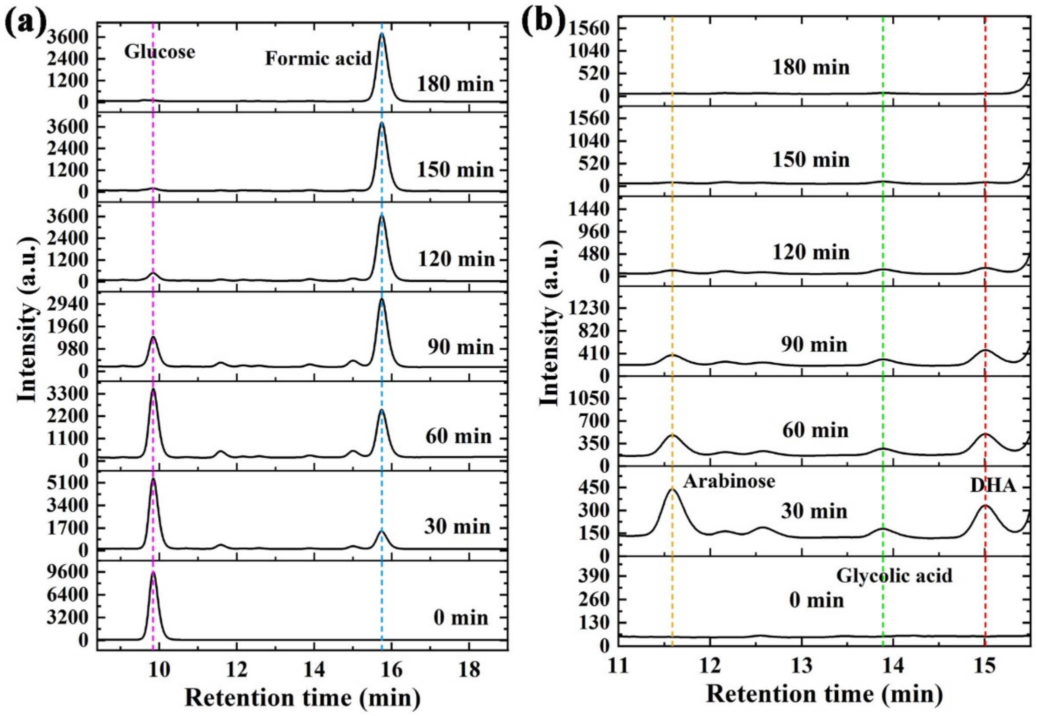

Fig. S8 HPLC chromatograms for (a) glucose and formic acid and (b) arabinose, glycolic acid and DHA at different retention times.

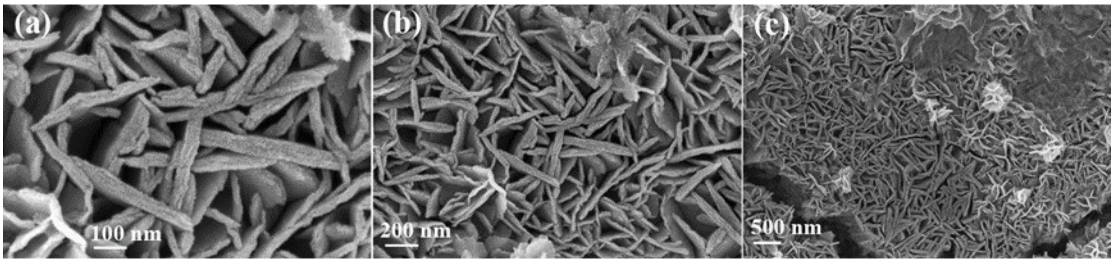

Fig. S9 SEM images of CuOCoOOH after five successive cycles GOR test.

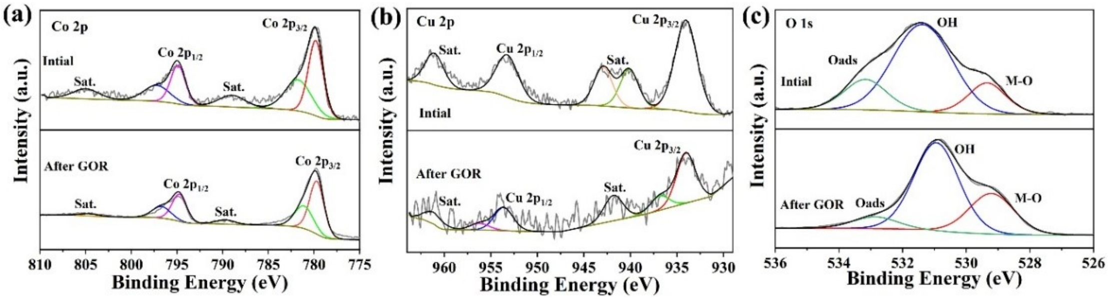

Fig. S10 High-resolution XPS of (a) Co 2p, (b) Cu 2p and (c) O 1s spectra of CuOCoOOH after five successive cycles GOR test.

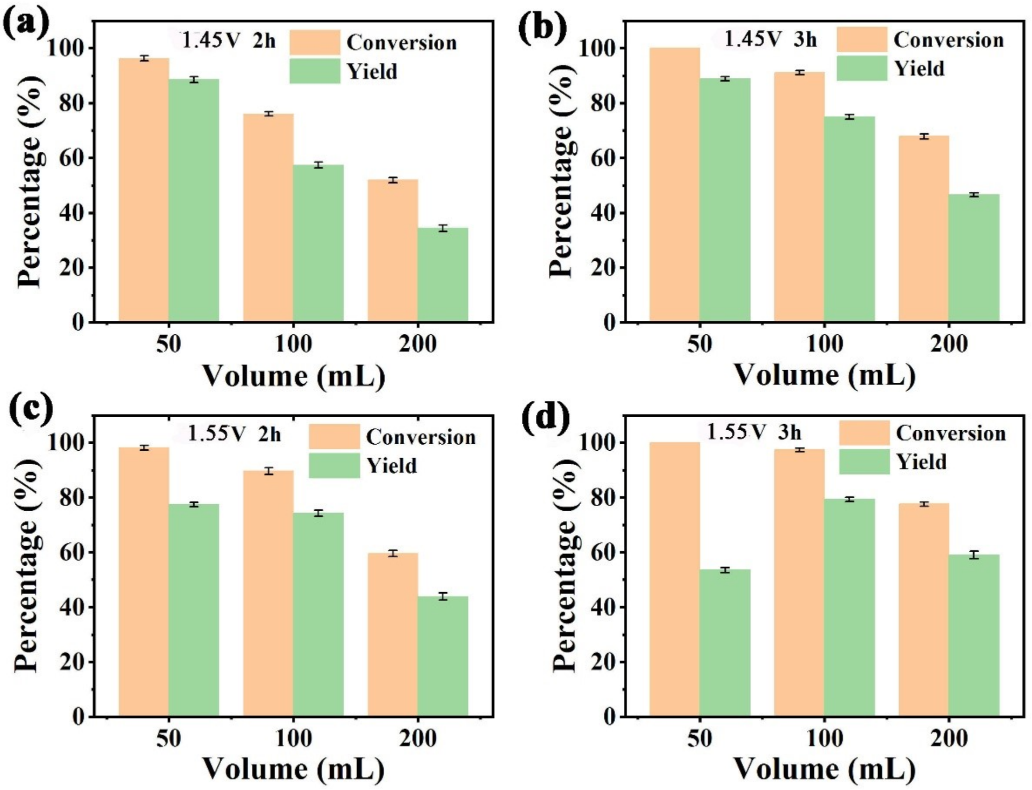

Fig. S11 Glucose conversion (%) and formic acid yield (%) at different potential and electrolysis time, (a) 1.45 V, 2h. (b) 1.45 V, 3h. (c)1.55 V, 2h. (d) 1.55 V, 3h.

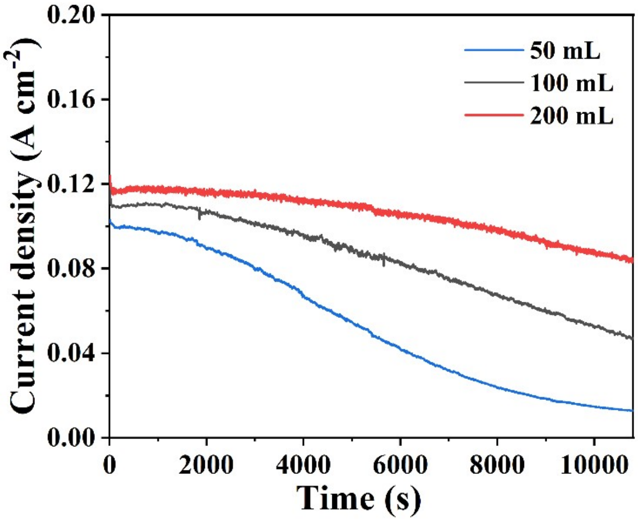

Fig. S12 I-t curves of 1×, 2× and 4× scale-up experiments at 1.45 V vs. RHE.

Table S1. Comparison of the CuOCoOOH catalyst with the other non-precious catalysts for electrooxidation of glucose to formic acid.

Catalyst	**Electrolyte**	**Products**	**Glucose conversion rate (%)**	**Selectivity of formic acid (%)**	**Yield of formic acid (%)**	**FE (%)**	**t (h)**	**Ref.**
NiCuO	1.0 M KOH	Formic acid, Glycolic acid	100	93.3	77.2	94.6	9	36
CuCoP/NF	1.0 M KOH	Formic acid, arabinose, glyceric acid, glycolic acid etc.	/	93.0	79.4	85.1	10	37
NiCoO-NS/NF	1.0 M KOH	Formic acid	95.56	~70	67.94	72.0	3	38
W,P-NiFeOOH/NF	1.0 M KOH	Formic acid	98.0	/	85.2	94.3	8	39
Cr,S-NiFe/NF	1.0 M KOH	Formic acid, oxalate, acetate, glycerate, ethanolate	99.0	86.5	81.3	94.1	24	40
NCO-CFP	1.0 M KOH	Formate, carbonate	~100	/	/	84	10	41
NiO/$NiCo_2O_4$/NF	1.0 M KOH	Formic acid, lactic acid	/	~94	72.0	/	12	42
Ni aerogel	1.0 M KOH	Fructose, arabinose, erythrose, glycolic acid, formic acid	94.9	/	83.5	90.0	/	43
NiCoP/NF	1.0 M KOH	Gluconate, glycerate, glycollate, oxalate, formate	~100	/	85.2	82.0	/	44
CuOCoOOH	1.0 M KOH	Formic acid	100	98.7	88.27	95.2	3	This work

Table S2. The number of electrons transferred to generate the products from glucose.

Compound	Reaction equation	Electron transfer number[a]
Glucose	-	-
Arabinose	$C_6H_{12}O_6 + 3OH^- \rightarrow C_5H_{10}O_5 + HCOO^- + 2H_2O + 2e^-$	2
Glycolic acid	$C_6H_{12}O_6 + 9OH^- \rightarrow 3CH_2OHCOO^- + 6H_2O + 6e^-$	2
1,3-dihydroxyacetone	$C_6H_{12}O_6 + 2OH^- \rightarrow 2C_3H_6O_3 + 2H_2O + 2e^-$	1
Formic acid	$C_6H_{12}O_6 + 18OH^- \rightarrow 6HCOO^- + 12H_2O + 12e^-$	2

[a] The electron transfer number refers to the electron transfer in circuit for producing one product molecule from glucose, which was calculated based on the average oxidation number of glucose and product.

Table S3. The comparison between 1×, 2× and 4× scale-up experiments by electrolysis for 3 h at 1.45V vs. RHE.

Magnification Factor	Initial current density (mA/cm²)	Total Charge (C)	Total FE (%)	EE (%)
1×	101.9	574.8	95.20	3.28
2×	112.7	909.4	90.41	3.12
4×	120.2	1140.6	88.19	3.04