Supplemental Information

Activation-oxidation on binary CuFe oxides for highly selective electrocatalytic oxidation of benzyl alcohol to benzaldehyde

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Experimental Section

Chemicals: The chemicals used in this work are Copper chloride ($CuCl_2 \cdot 2H_2O$, 99.9%), Ferrous sulfate **(**$FeSO_4 \cdot 7H_2O$, 99.9%), Ferric nitrate ($Fe (NO_3)_3 \cdot 9H_2O$, 99.9%), Sodium sulfite (Na_2SO_3, 99.9%), Sodium hydroxide (NaOH, 99.9%) and Potassium hydroxide (KOH, 99.9%), which were purchased from Aladdin Biological Technology. Benzyl alcohol (C_7H_7OH, 99.9%) was purchased from Energy Chemical. 2, 2, 6, 6-tetramethylpiperidine oxide (TEMPO，99%), Ethanol (C_2H_5OH, 99.9%) and Nafion solution (5wt%) were purchased from Sigma Aldrich. Hydrophilic carbon paper (TGP-H-060) was purchased from Toray Industries. All water used here is deionized water.

Preparation of Cu and Fe hydroxide precursors: We used double-droplet methods to get co-precipitated copper and iron hydroxides. 0.17 g $CuCl_2 \cdot 2H_2O$ and 1.67 g $FeSO_4 \cdot 7H_2O$ were dissolved in 30 mL H_2O as solution A, 0.6 g NaOH and 1.89 g Na_2SO_3 were dissolved in 30 mL H_2O as solution B. The precursors $CuCl_2 \cdot 2H_2O$ and $FeSO_4 \cdot 7H_2O$ were used in a molar ratio of 1:6 (Cu^{2+}: Fe^{2+}). Dripped A and B simultaneously into another beaker containing 50 mL H_2O, and observed the pH maintaining at about 8.5 while dripping. Stirred the solution for 4 hours at room temperature (the whole reaction process was passed through nitrogen) and the sample was washed with deionized water 3 times (centrifuge speed of 10000 r, 3 min) after the reaction. Then the precipitate was put into a vacuum freeze dryer for 12 hours to obtain a yellow-green powder, recorded as $CuFe(OH)_x$.

Preparation of CuFe bimetallic oxides： The yellow-green powder was put into a porcelain boat and calcined at 200℃ for 4 hours in 10% H_2/Ar mixture. The calcination was performed in a tube furnace under a 10% H_2/Ar (v/v) reducing atmosphere with a constant gas flow rate of 100 mL min^{-1}. The calcination temperature and time were varied to keep the heating rate at 10℃·min^{-1} to obtain $CuFeO_x$, and the effects of calcination temperature and time on the catalyst properties were also investigated.

Preparation of other samples： Solution A only have $CuCl_2 \cdot 2H_2O$ to get the comparison sample with Cu^{2+} as a precursor. Solution A only have $FeSO_4 \cdot 7H_2O$ to get the comparison sample with Fe^{2+} as a precursor. The subsequent procedure remained unchanged. Changed $FeSO_4 \cdot 7H_2O$ to $Fe(NO_3)_3 \cdot 9H_2O$ in solution A to get the comparison sample with Cu^{2+} and Fe^{3+} as precursors.

Characterizations： X-ray diffraction (XRD) tests were performed on a Rigaku D/max 2500 X-ray diffractometer with Cu Kα radiation. The range of 2θ was from 5° to 85° and the scanning speed was 5°·min^{-1}. The morphologies of the synthesized samples were characterized by scanning electron microscopy (SEM) on JEM 2100F. Characterization by transmission electron microscopy (TEM) were implemented by JEOL JEM 2100 and Cs-TEM FEI Titan G2, while samples were characterized by high-resolution transmission electron microscopy (HRTEM) using a double aberration-corrected field emission gun. The ESCALAB 250 was used to present X-ray photoelectron spectroscopy (XPS) tests on the catalysts.

Electrochemical performance tests： All tests were performed in a H-cell type electrolytic cell. In order to improve electrical conductivity and selectively, we added conductive carbon black and TEMPO.

Preparation of working electrode: ink consisted of 5 mg catalyst, 1 mg carbon black, 10 μL Nafion and 1 mL ethanol, which was ultrasonically homogenized and then dripped onto 1 × 1 cm^2 hydrophilic carbon paper, resulting in a catalyst loading of 5 mg cm^{-2}.The counter electrode was carbon rod, the reference electrode was Ag/AgCl and the electrolyte consisted of 1 M KOH with/without 0.1 M benzyl alcohol +0.8 mM TEMPO.

CV and LSV tests are used to determine the electrochemical activity of the catalyst. The working electrode was firstly activated in 1 M KOH for 20 revolutions with a sweep rate of 50 $mV\cdot s^{-1}$ and the potential range is -0.2 V ~ 0.8 V (vs. Ag/AgCl), changing the sweep rate to 5 $mV\cdot s^{-1}$ to obtain the CV and LSV curves of OER. Then change the electrolyte to run BAOR.

Electrochemical active surface area (ECSA) tests were all performed in 1 M KOH + 0.1 M benzyl alcohol +0.8 mM TEMPO electrolyte with a potential range of -0.1 V~ -0.05 V (vs. Ag/AgCl) and sweep speeds were 20 mV/s, 40 mV/s, 60 mV/s, 80 mV/s, and 100 mV/s, respectively. The CV curves at different sweep speeds were obtained by varying the scanning speed in non-Faraday section, which in turn got the double layer capacitor (C_{dl}) of the catalysts.

Electrochemical impedance spectroscopy (EIS) tests: The potential at a current density of 10 $mA\cdot cm^{-2}$ was selected as the test potential with a frequency of 10^5 Hz to 0.01 Hz and an amplitude of 5 mV.

Chronoamperometry (CA) test and Cyclic stability： These tests were all performed in 1 M KOH + 0.1 M benzyl alcohol +0.8 mM TEMPO electrolyte.

Tests of activation energy (E_a): Test temperatures were 35°C, 45°C, 55°C, 65°C, electrolyte consisted of 1 M KOH + 0.1 M benzyl alcohol + 0.8 mM TEMPO, sweep rate was 5 $mV\cdot s^{-1}$ and potential range was -0.2 V~0.8 V (vs. Ag/AgCl). The formula is $\text{Log } j = \text{Log } A - E_a/(2.3RT)$.

Product analysis: The electrolyte was 1 M KOH + 0.1 M benzyl alcohol +0.8 mM TEMPO, and the solution components were analyzed by gas chromatography after 7200 s at different potential. The reacted solution was extracted into 20 mL of dichloromethane, and 100 µL of light-yellow organic solution was obtained by spinning afterward. The electrolyte components were detected by using the differences in the boiling points of benzyl alcohol (204.7℃), benzaldehyde (179℃), and benzoic acid (249.2℃).

The quantitative analysis of benzyl alcohol (BA) and benzaldehyde (BAD) was performed on an Agilent 7890A gas chromatography system equipped with a flame ionization detector (FID) and a DB-WaxUI capillary column (5% phenyl polysiloxane, 30 m × 0.25 mm × 0.25 µm). High-purity nitrogen was used as the carrier gas at a constant flow rate of 1.5 mL min^{-1}. The injection volume was 0.5 µL with a split ratio of 20:1. The oven temperature program was optimized as follows: initial temperature of 60 °C held for 2 min, ramped to 180 °C at a rate of 20 °C min^{-1}, and then held at 180 °C for 3 min. The injector and detector temperatures were set at 220 °C and 250 °C, respectively.

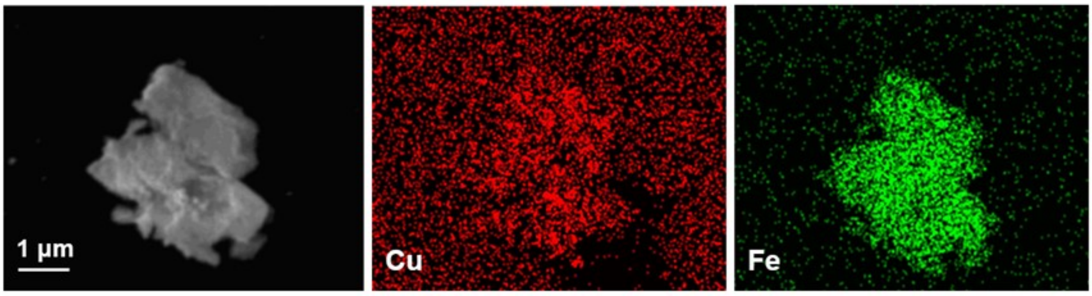

Fig. S1 Elemental mapping of CuFeO$_x$ catalyst (calcined at 200 °C for 4 h).

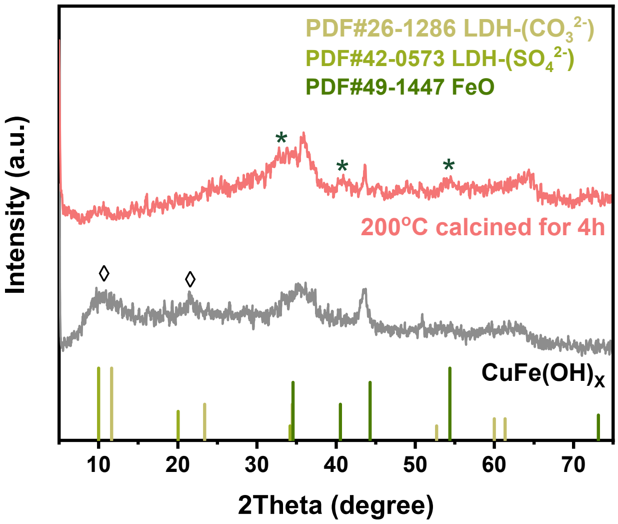

Fig. S2 XRD pattern of catalysts (a) before and (b) after calcination in H_2/Ar mixture atmosphere.

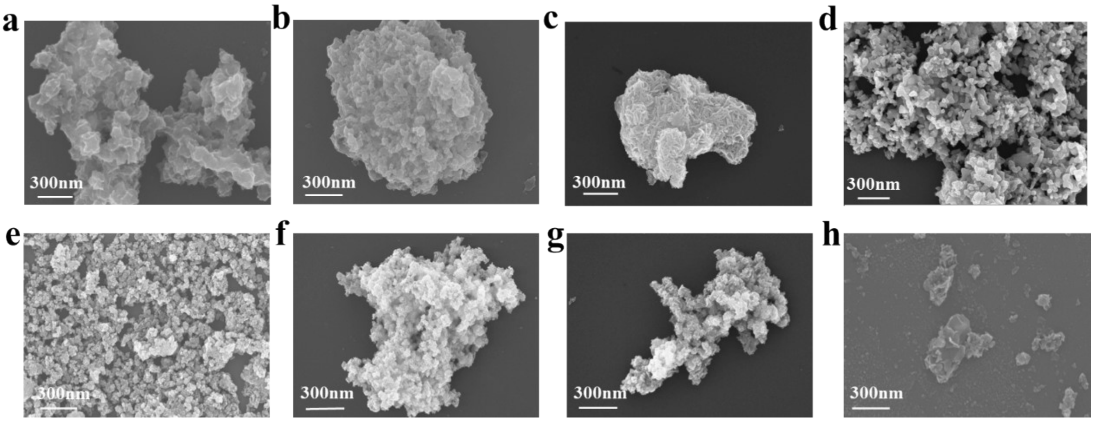

Fig. S3 SEM images of the catalysts of different calcination temperatures and times. (a) 100℃ 4 hours, (b) 200℃ 4 hours, (c) 300℃ 4 hours, (d) 400℃ 4 hours, (e) 200℃ 1 hours, (f) 200℃ 2 hours, (g) 200℃ 3 hours and (h) before calcination.

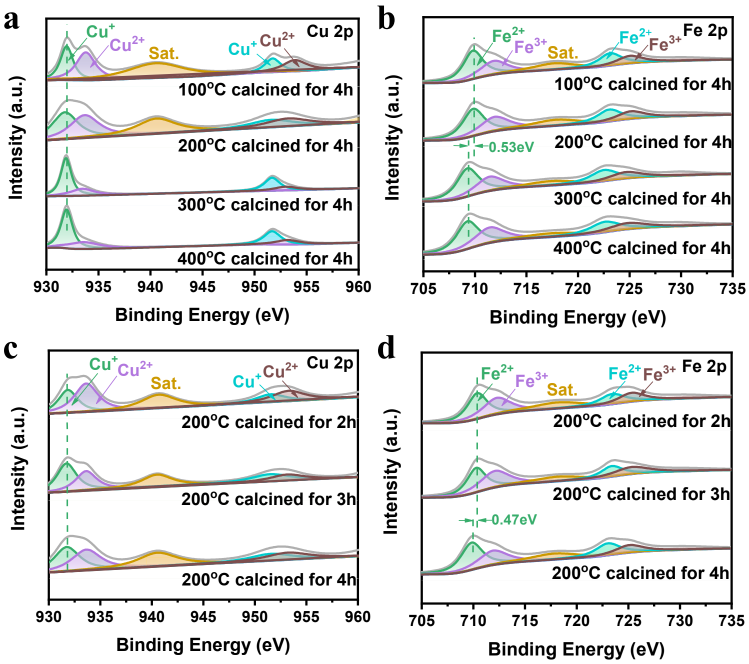

Fig. S4 XPS spectra of the catalysts with different (a-b) calcination temperatures and (c-d) calcination times.

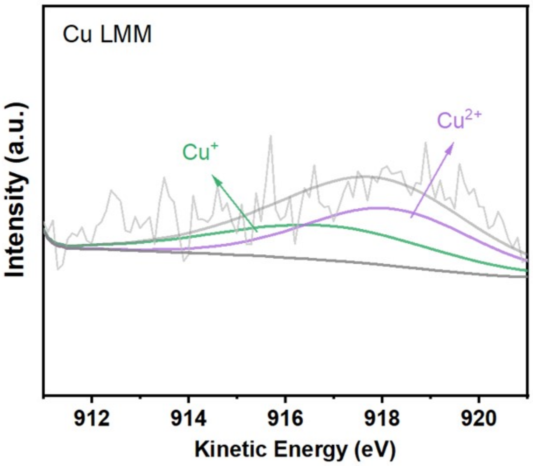

Fig. S5 Cu LMM Auger Electron Spectroscopy of the $CuFeO_x$ catalyst.

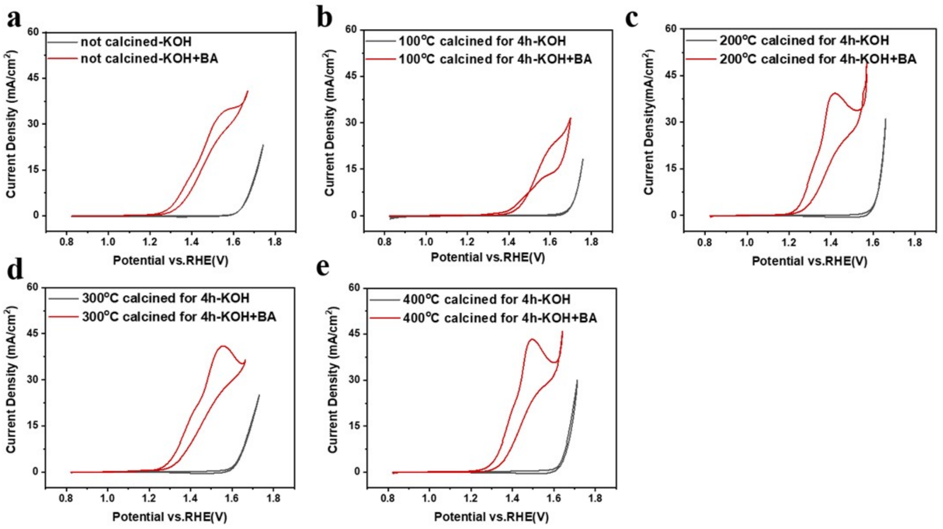

Fig. S6 CV curves of catalysts at different calcination temperatures in 1 M KOH + 0.1 M BA solution.

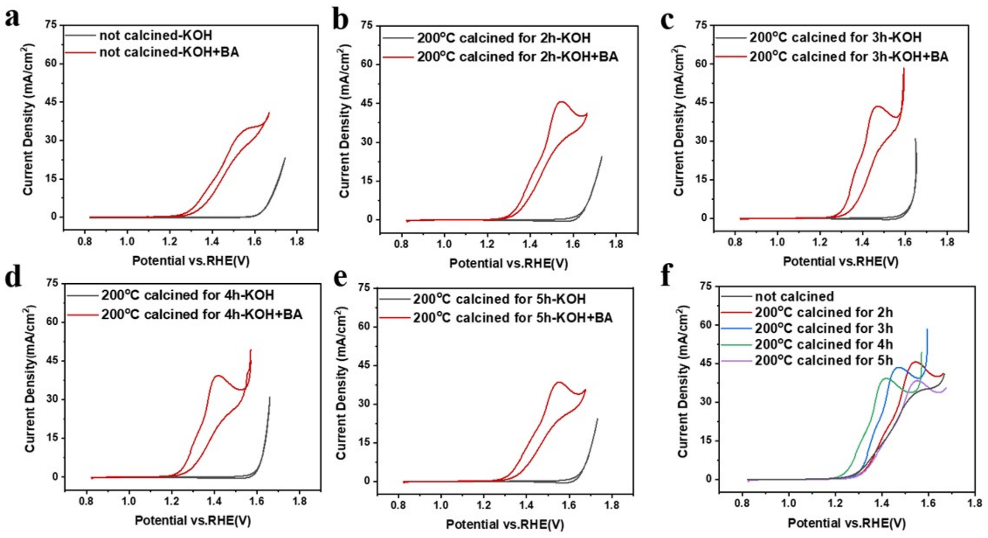

Fig. S7 CV curves of catalysts at different calcination time in 1 M KOH + 0.1 M BA solution.

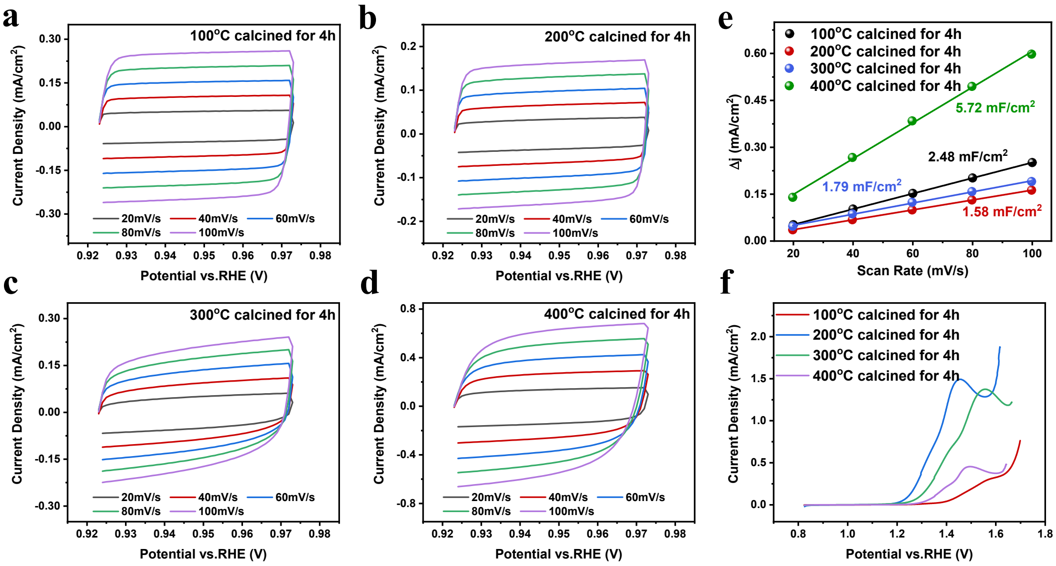

Fig. S8 (a-e) Electrochemical active surface area of catalysts at different calcination temperatures in KOH+BA solution. (f) LSV curves after ECSA-normalized.

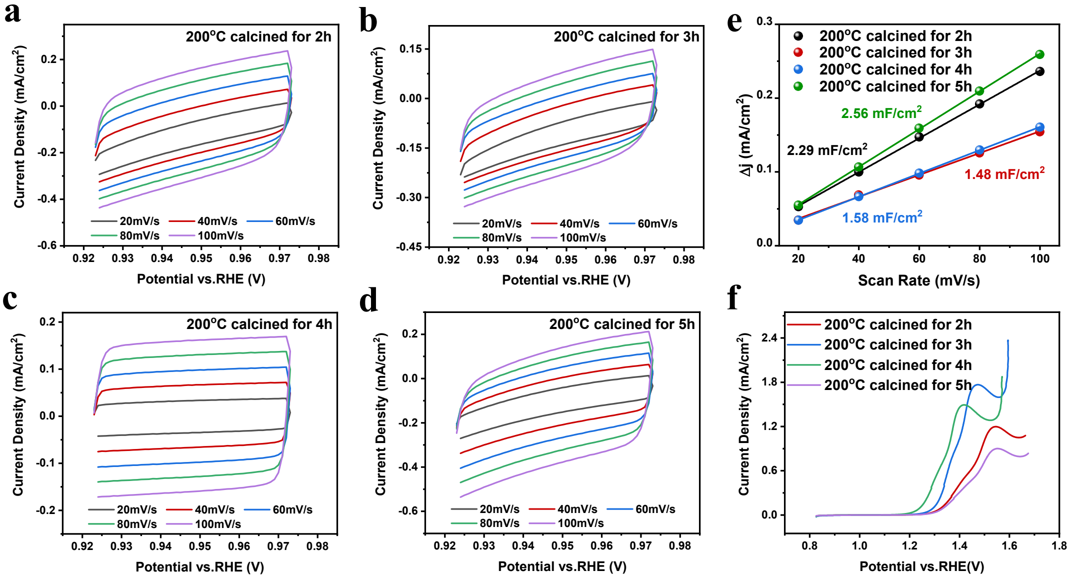

Fig. S9 (a-e) Electrochemical active surface area of catalysts at different calcination time in KOH+BA solution. (f) LSV curve after ECSA-normalized.

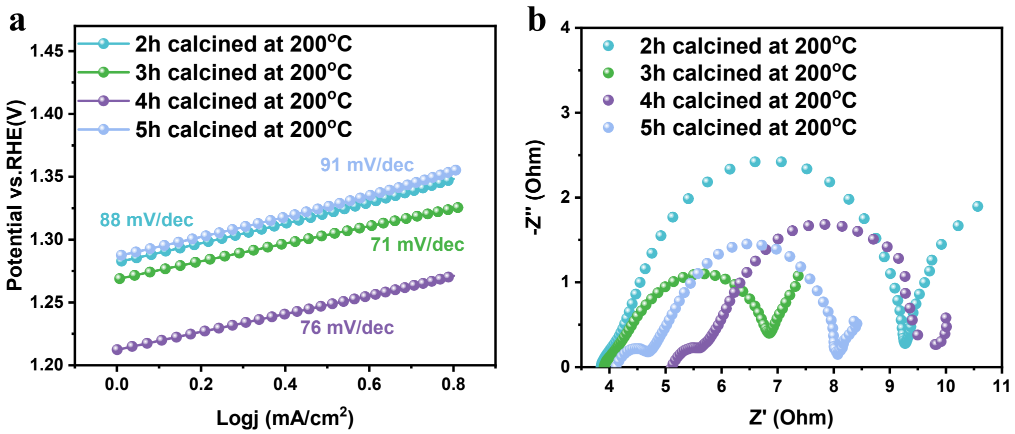

Fig. S10 (a) Tafel slopes and (b) EIS of catalysts at different calcination temperatures in 1 M KOH+ 0.1 M BA solution.

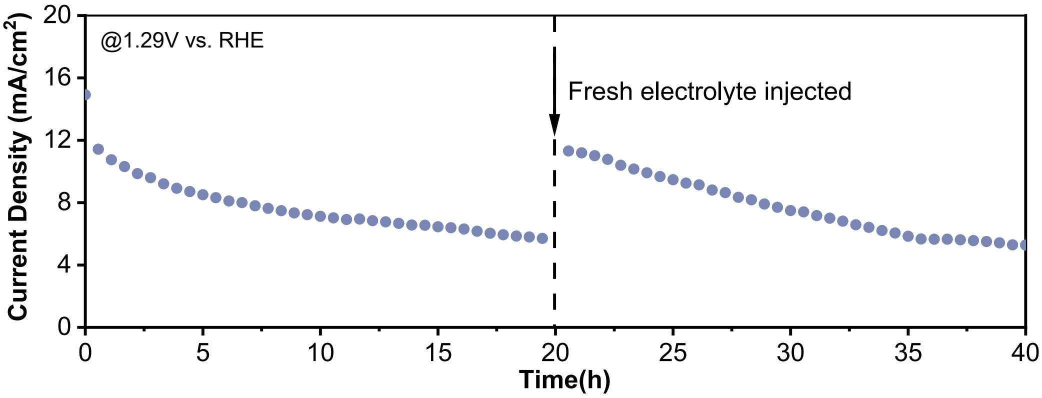

Fig. S11 Long-term CA results at 1.29 V vs. RHE.

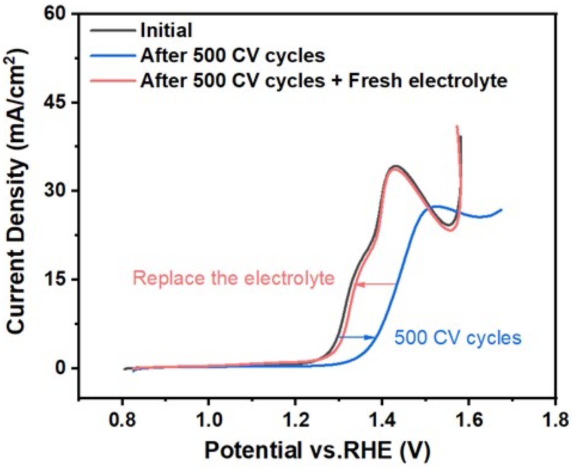

Fig. S12 LSV curves of the CuFeO$_x$ catalyst under different conditions: initial state, after the 500 CV cycles and after cycles with fresh electrolyte.

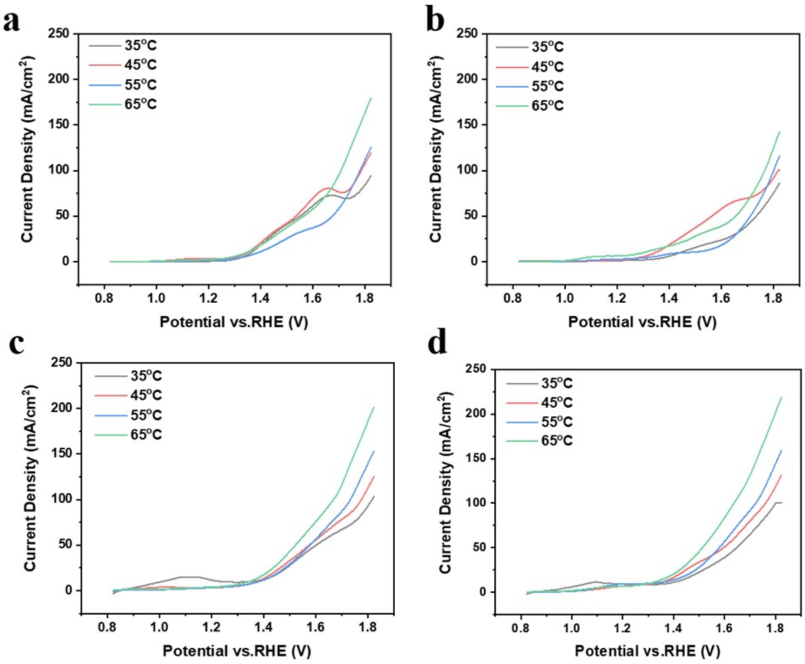

Fig. S13 (a) 100℃ for 4 hours, (b) 200℃ for 4 hours, (c) 300℃ for 4 hours and (d) 400℃ for 4 hours are the LSV curves of the calcined catalyst under different test temperatures.

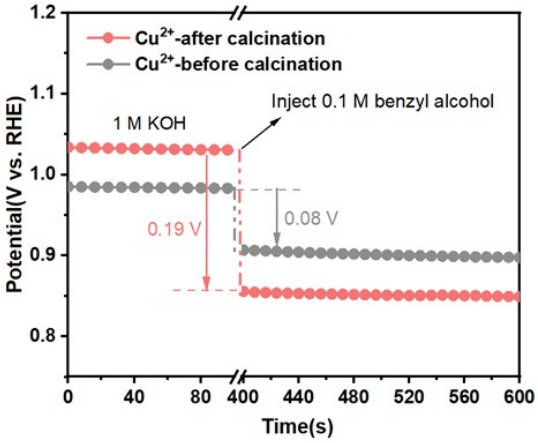

Fig. S14 OCP curves of Cu^{2+}-after calcination and Cu^{2+}-before calcination in 1 M KOH and 0.1 M benzyl alcohol injected subsequently.

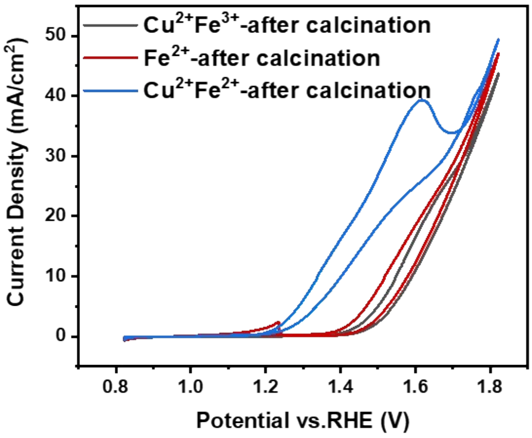

Fig. S15 Comparison of benzyl alcohol oxidation performance of three catalysts.

Table S1 The ICP data after the stability test.

Dissolved Elements	Content (mg/L)
Cu	1.17
Fe	0.06

Table S2 Activity and selectivity of different anode catalysts.

Catalysts	Electrolyte	Voltage/ Current, Time	Conversion	Selectivity	η (10 mA·cm^{-2})	Reference
CuFeO$_x$	**1.0 M KOH + 0.1 M BA**	**1.8 V, 120 min**	**41.57%**	**99.9% (benzaldehyde)**	**1.29 V**	**This work**
Ni$_3$Co$_1$-LDH/NF	1.5 M K$_2$CO$_3$+0.1M BA	1.6V, 180 min	91%	58% (benzaldehyde)	——	Journal of Electroanalytical Chemistry 996 (2025) 119410
PA-NF	1.0 M KOH + 1.0 mmol BA	1.4 V, 120 min	99.9%	88.3% (benzaldehyde)	1.31 V	ACS Catal. 2023, 13, 400-406
Commercial NF	1.0 M KOH + 1.0 mmol BA	1.4 V, 120 min	9.6%	78.1% (benzaldehyde)	1.67 V	ACS Catal. 2023, 13, 400-406
Cu-LPOMs@PPAR	0.25 mmol BA + 7 mg n-Bu$_4$NBF$_4$ + 3.0 mL CH$_3$CN	3.0 V, 480 min	——	75% (benzaldehyde)	——	Molecules 2023, 28, 6460
NiAl-LDH	1.0 M KOH + 10 mM BA	1.55 V ——	12%	38% (benzaldehyde)	1.81 V	Nanoscale, 2023, 15, 11867–11874
Au$_{1+n}$-NiAl-LDH	1.0 M KOH + 10 mM BA	1.55 V ——	32.5%	91% (benzaldehyde)	1.65 V	Nanoscale, 2023, 15, 11867–11874
Ru-NPs@NCNTs	1.0 M KOH + 0.5 mmol BA	1.60 V ——	——	99.9% (benzaldehyde)	1.19 V	ACS Appl. Mater. Interfaces 2022, 14, 1452–1459
CuO-NRs	1.0 M KOH + 10 mM BA	1.35 V, 120 min	90%	99% (benzaldehyde)	1.45 V	ACS Sustainable Chem. Eng. 2021, 9, 11855–11861
Fe/Co200	1.0M KOH + 15 mM BA	20 mA·cm^{-2}, 120 min	25%	66.7% (benzaldehyde)	1.42 V	ACS Energy Lett. 2018, 3, 1854-1860
0.2-WO-N/NF	1.0 M KOH+0.1M BA	1.87 V, 240 min	99.66%	99.74% (benzoic acid)	——	Molecules 2024, 29, 3734.
FeCoNiAlMo/CNT	1.0 M KOH + 0.2 M BA	10 mA·cm^{-2}, 720 min	46%	92% (benzoic acid)	1.38 V	Adv. Funct. Mater. 2023, 2311611
NiFeO$_x$	1 M NaOH + 0.2 M BA	25 mA·cm^{-2}, 300 min	99.2%	100% (benzoic acid)	1.41 V	Adv. Energy Mater. 2021, 11, 2101858
1.0 h-Ni(OH)$_2$	1.0 M KOH + 40 mM BA	20 mA·cm^{-2}, 132 min	99.9%	99.3% (benzoic acid)	1.39 V	Green Chem., 2019, 21, 578-588
Mo-Ni/MnO$_2$/NF	1.0 M KOH + 10 mM BA	1.35 V, 240 min	99%	99% (benzoic acid)	1.34 V	J. Mater. Chem. A, 2019, 7, 16501-16507
hp-Ni	1.0 M KOH + 10 mM BA	1.423 V, 1080 min	99.0%	100% (benzoic acid)	1.35 V	ACS Catal., 2017, 7, 4564-4570