

Electronic Supplementary Information

High selectivity electrocatalytic reductive amination of α -keto acids to alanine over cuprous oxide nanowires

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1. Experimental section

1.1 Chemicals and materials

Pyruvate, glyoxylic acid, oxaloacetic acid, α -ketoglutaric acid, 3-methyl-2-ketobutanoic acid, 3-methyl-2-oxovaleric acid, 4-methyl-2-oxovaleric acid, 2-oxopentanoic acid, and hydroxylamine sulfate were purchased from Aladdin Reagent Company. H_2SO_4 (AR, $\geq 85\%$), NaOH (AR, 96%), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (AR, $\geq 98\%$), Na_2SO_4 (AR, 99%), acetone ($\text{C}_3\text{H}_6\text{O}$), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and DMSO- d_6 were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water (DW) made by laboratory. All chemicals were used without further purification.

1.2 Pre-treatment of Copper foam (CF)

The commercial copper foam (CF) was cut into $3 \times 3 \times 0.1 \text{ cm}^3$ slices. Then, it was sonicated for 15 min in HCl (3.0 M) and acetone solution. This was followed by rinsing with ethanol and deionized water. Finally, the CF was placed in a vacuum drying oven and dried at 60°C for 6 hours for use.

1.3 Preparation of $\text{Cu}_2\text{O}/\text{CF}$

1.3.1 Preparation of $\text{Cu}(\text{OH})_2/\text{CF}$

In typical preparation, 1.6 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 7 g of NaOH were dispersed in 70 mL of deionized water. was fully submerged in the solution and allowed to stand at room temperature for 60 minutes. The surface of the copper foam was uniformly coated with blue $\text{Cu}(\text{OH})_2$. After removal from the solution, the copper foam was rinsed with deionized water and ethanol, followed by drying in a vacuum oven at 60°C for 6 hours, resulting in the formation of the blue $\text{Cu}(\text{OH})_2/\text{CF}$.

1.3.2 Preparation of Cu₂O/CF

The as-prepared Cu(OH)₂/CF electrode was directly reduced in (5%) H₂/Ar atmosphere at 400 °C for 1 h to obtain the Cu₂O/CF electrode.

1.3 Catalysts characterization

The crystalline structures of samples were identified by the X-ray diffraction analysis (XRD, Philips X'pert PRO) using Ni filtered monochromatic CuK α 1 radiation (λ K α 1 = 1.5418 Å) at 40 kV and 40 mA. Scanning electron microscope (SEM) images of the sample were obtained using SU8020 (Hitachi, Japan) with an accelerating voltage of 10.0 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al K α 1, 2 monochromatized radiations at 1486.6 eV X-ray source. ¹H nuclear magnetic resonance (¹H NMR) was recorded on Bruker Ascend™ 400 (400 MHz).

1.4 *In-situ* attenuated total reflection surface-enhanced infrared adsorption spectroscopy (ATR-SEIRAS)

The in situ attenuated total reflection surface-enhanced infrared adsorption spectroscopy (ATR-SEIRAS) was performed on a FTIR spectrometer (Nicolet iS50, Thermo Scientific) equipped with an MCT-A detector with silicon as the prismatic window. First, a piece of Cu₂O/CF was pressed thin and placed on the surface of the silicon prism as a working electrode. The surface of the silicon prismatic had been chemically deposited with a gold film beforehand. The platinum mesh and Ag/AgCl electrode containing saturated KCl solution were used as the counter and reference electrodes, respectively. The 0.2 M Na₂SO₄ (pH = 6.5) solution was employed as the

electrolyte. Each infrared absorption spectrum was acquired by averaging 128 scans at a resolution of 4.0 cm^{-1} . The background spectrum of the catalyst electrode was acquired at an open-circuit voltage before each systemic measurement, and then the electrocatalytic synthesis of alanine was measured at -0.55 V vs. RHE potential for a long time.

1.5 Electrochemical measurements

All electrochemical measurements were performed on a CHI 760E electrochemical workstation (CH Instrumental Corporation, Shanghai, China) with a typical three electrode system, with $\text{Cu}_2\text{O}/\text{CF}$ ($1 \times 1\text{ cm}^2$) as the working electrode. An active area of 1 cm^2 was assumed to define the current density (scaled current data). The electrosynthesis of amino acids at a constant potential, an Ag/AgCl (in 3 M KCl solution) electrode was used as the reference electrode and a Pt wire was used as the counter electrode. All electrochemical measurements were performed with agitation. The electrolyte solution with a pH of $2.5 \sim 10.5$ was prepared with $0.2\text{ M Na}_2\text{SO}_4$ as the supporting electrolyte and the pH of the solution was adjusted by adding aqueous H_2SO_4 or NaOH .

Prior to testing, pyruvate and $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ were added to the electrolyte and stirred for 2 hours at room temperature to form a cathodic electrolyte (total volume 10 mL). The scan rate for linear scan voltammetry (LSV) was kept at 10 mV s^{-1} . The potentials were converted to RHE scale using the following Nernst equation: The measured potentials versus the reversible hydrogen electrode (RHE) were converted based on the following equation (1):

$$E_{(\text{RHE})} = E_{(\text{Ag}/\text{AgCl})} + 0.197 + 0.059 \times \text{pH} \quad (1)$$

1.6 Product analysis

The organic products in the amino acid electrosynthesis reaction were analyzed by ^1H NMR (Bruker Avance, 400 MHz) with solvent (water) suppression. The cathodic electrolyte (1 mL) after electrolysis was mixed with DMSO- d_6 (50 μL), and 200 μL of aqueous maleic acid (0.1 M) was added as an internal standard for ^1H NMR analysis. For quantitative analysis, the amount of analyte was calculated based on the area ratio of the analyte peak to the internal standard (maleic acid). The chemical shift of the expected product was determined by dissolving a certain amount of the standard chemical in the corresponding electrolyte after electrolysis.

The amount of amino acid was calculated by the equation (2):

$$n \text{ (}\mu\text{mol)} = \frac{m \times A_r \times 2}{A_s \times a} \times 10 \quad (2)$$

Where m is the number of moles of the internal standard (20 μmol), A_r is the peak area of the amino acid, A_s is the peak area of the internal standard, a is the number of H atoms of the characteristic peak of amino acid.

The yield rate of amino acid was calculated using the following equation (3):

$$\text{Yield (100\%)} = \frac{\text{moles of amino acid}}{\text{moles of the initial substrate}} \times 100\% \quad (3)$$

The faradaic efficiency of amino acid was calculated using the equation (4):

$$\text{Faraday efficiency} = \frac{n \times N \times F}{I \times t} \quad (4)$$

Where n is the number of moles of the product, N is the number of electrons obtained

from the reactant to the product, F is Faraday constant (96485 C mol^{-1}), I is the current, and t is the time.

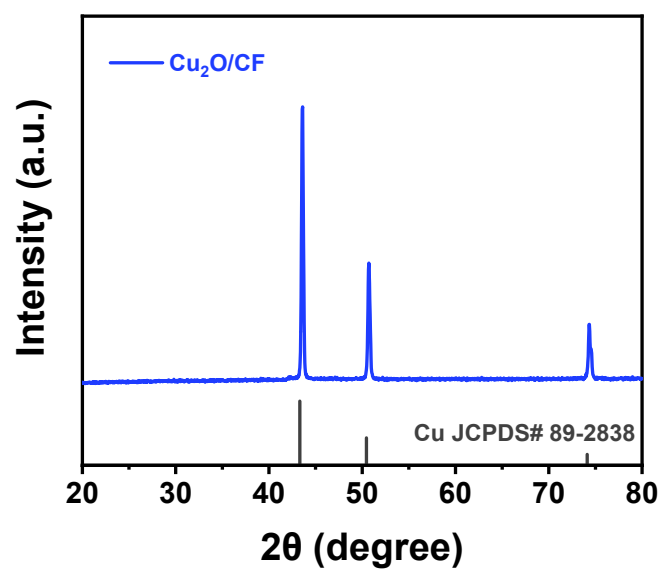


Fig. S1 XRD pattern of Cu₂O/CF.

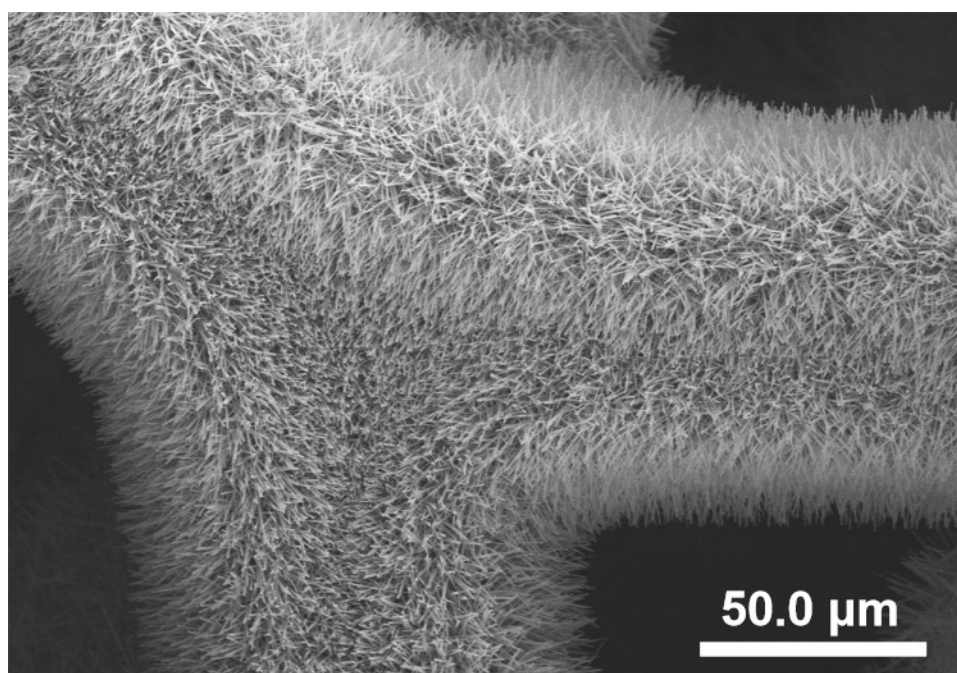


Fig. S2 SEM image of Cu(OH)₂/CF.

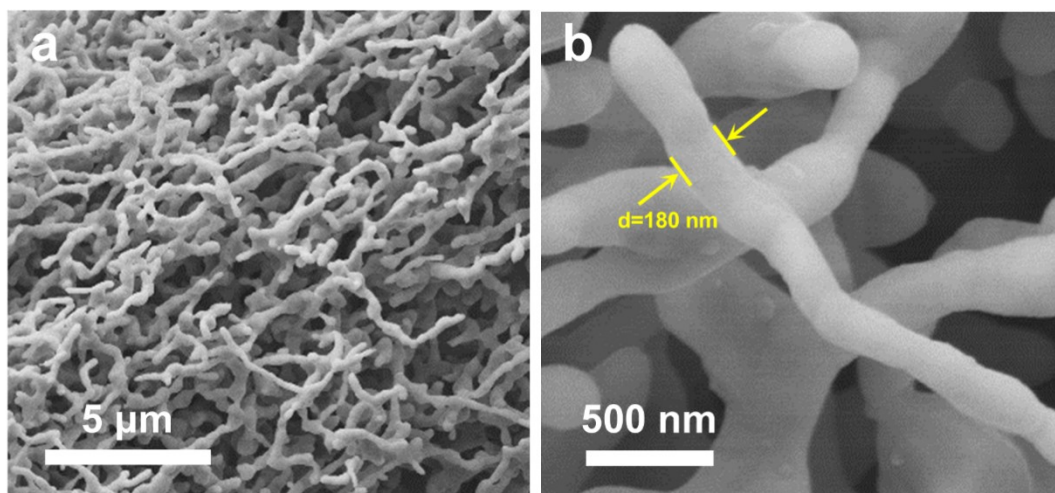


Fig. S3. SEM images of Cu₂O/CF.

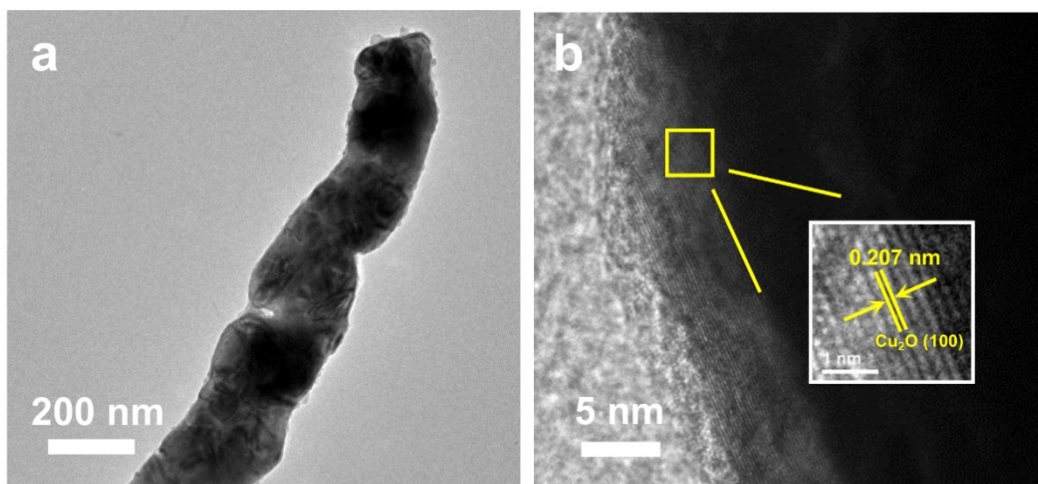


Fig. S4. (a) TEM and (b) HR-TEM images of $\text{Cu}_2\text{O}/\text{CF}$.

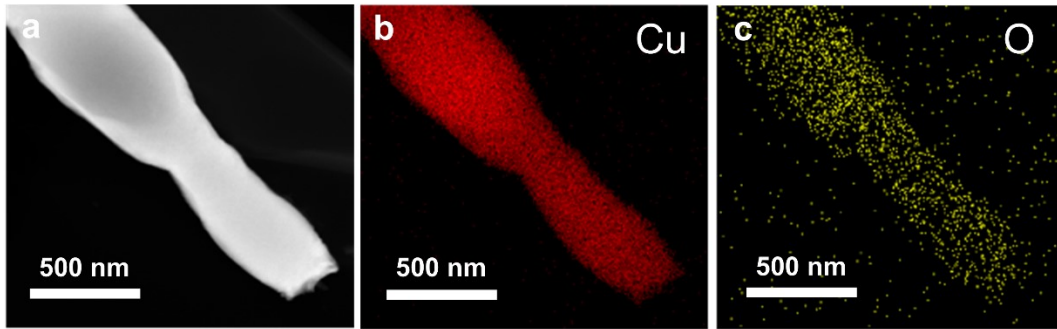


Fig. S5. EDS elemental mapping analysis results for Cu and O in $\text{Cu}_2\text{O}/\text{CF}$.

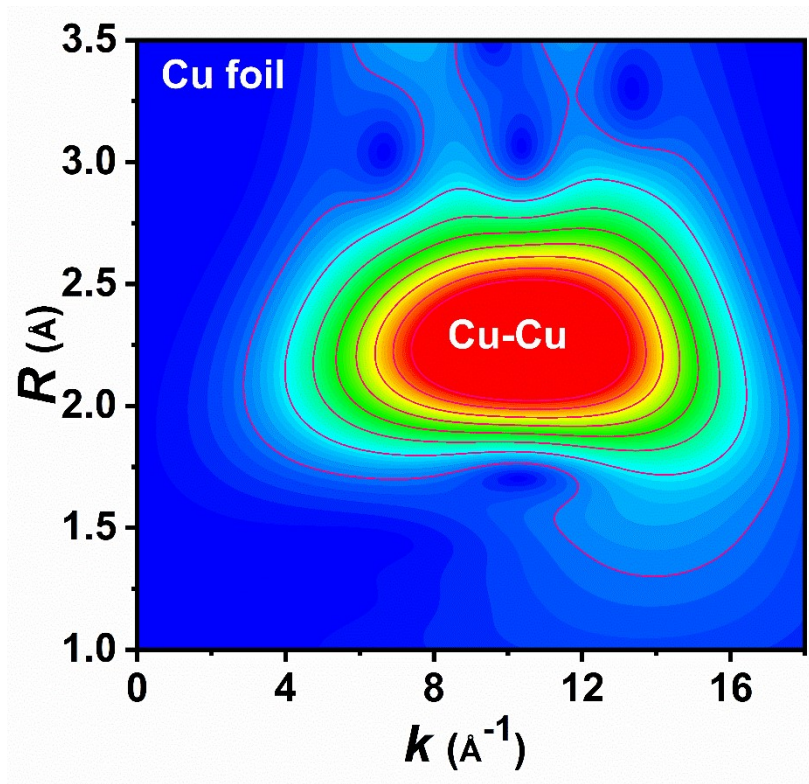


Fig. S6. Cu *K*-edge WT-EXAFS of Cu foil.

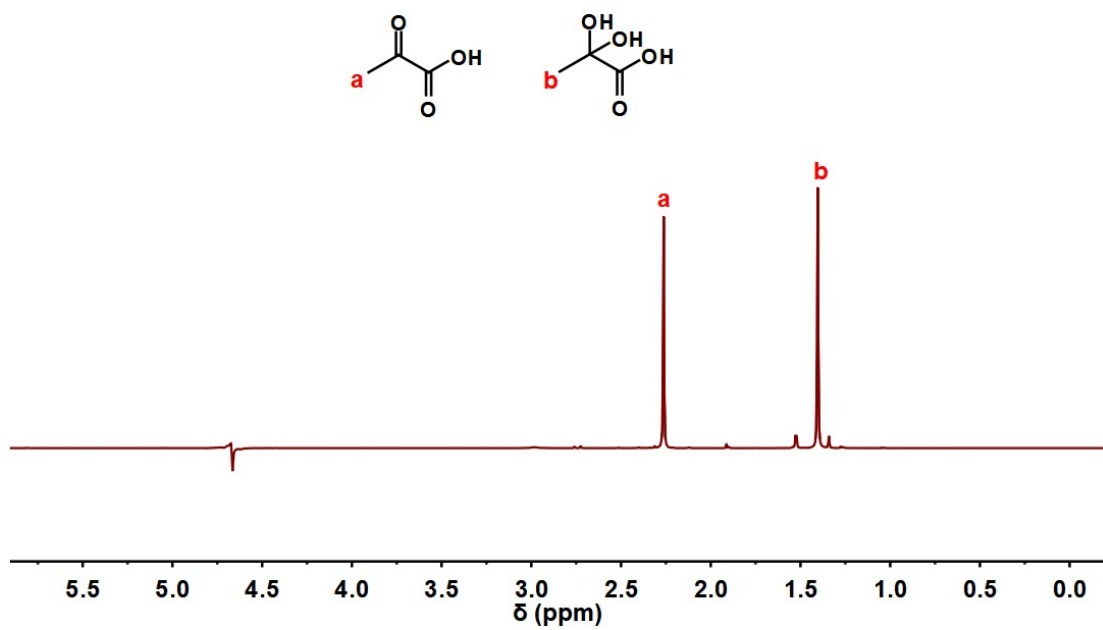


Fig. S7 ¹H NMR spectrum of commercial pyruvate and its hydrated diol-form dissolved in 0.2 M Na₂SO₄ (aq).

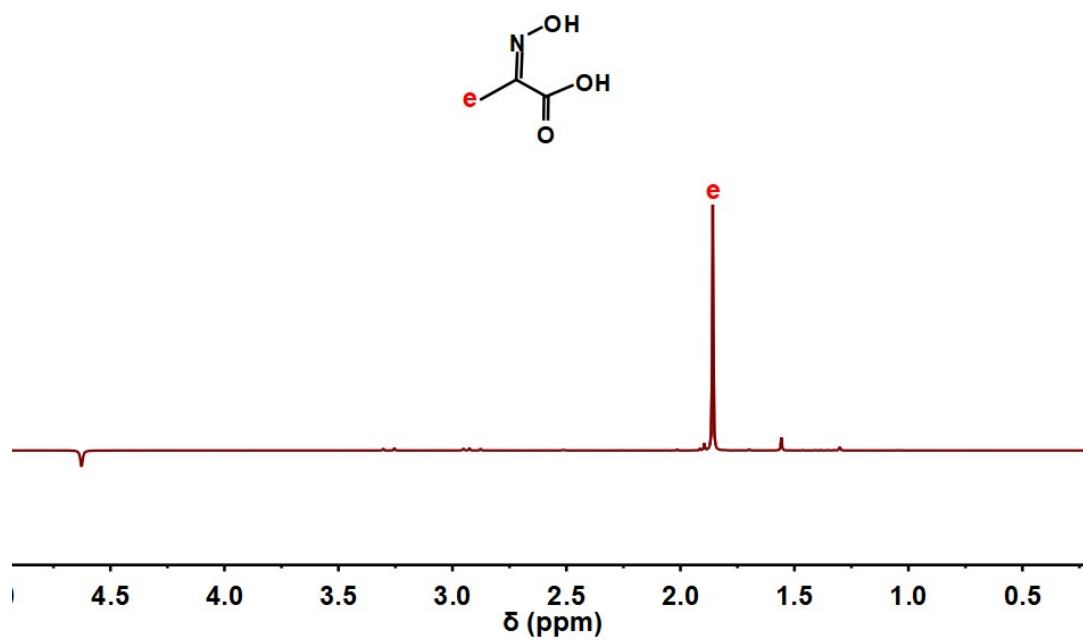


Fig. S8 ¹H NMR spectrum for 160 mM pyruvate with 96 mM (NH₂OH)₂·H₂SO₄, in 0.2 M Na₂SO₄ solution (pH = 6.5). The appearance of peak (e) was identified as oxime.

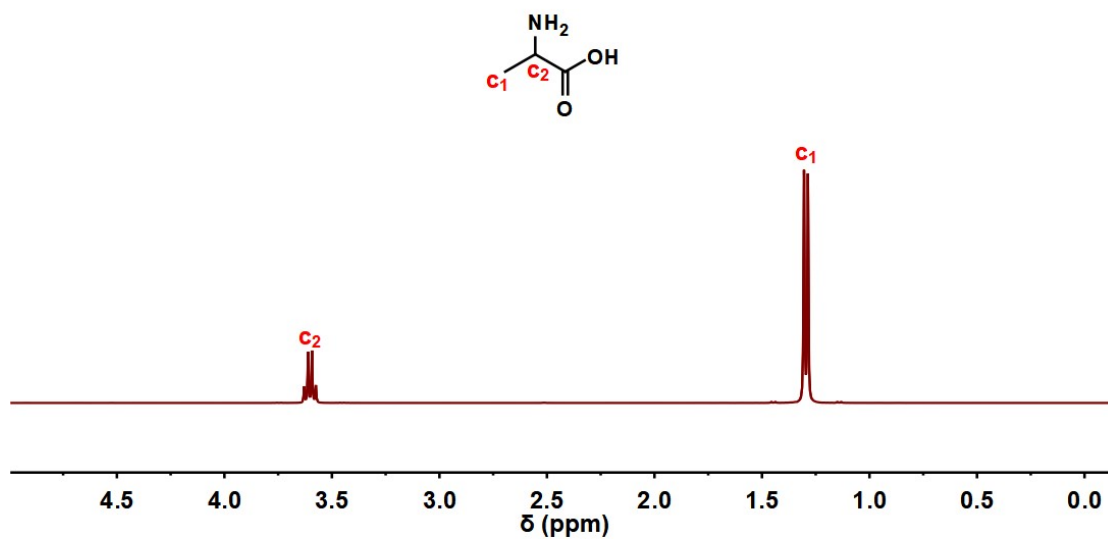


Fig. S9 ¹H NMR spectrum of commercial alanine dissolved in 0.2 M Na₂SO₄ (aq).

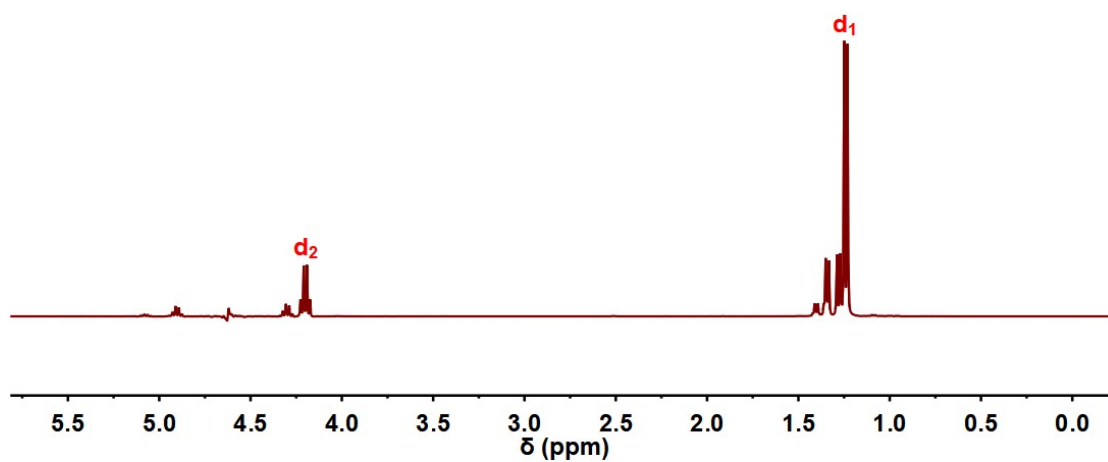
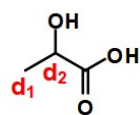


Fig. S10 ^1H NMR spectrum of commercial lactic acid dissolved in 0.2 M Na_2SO_4 (aq).

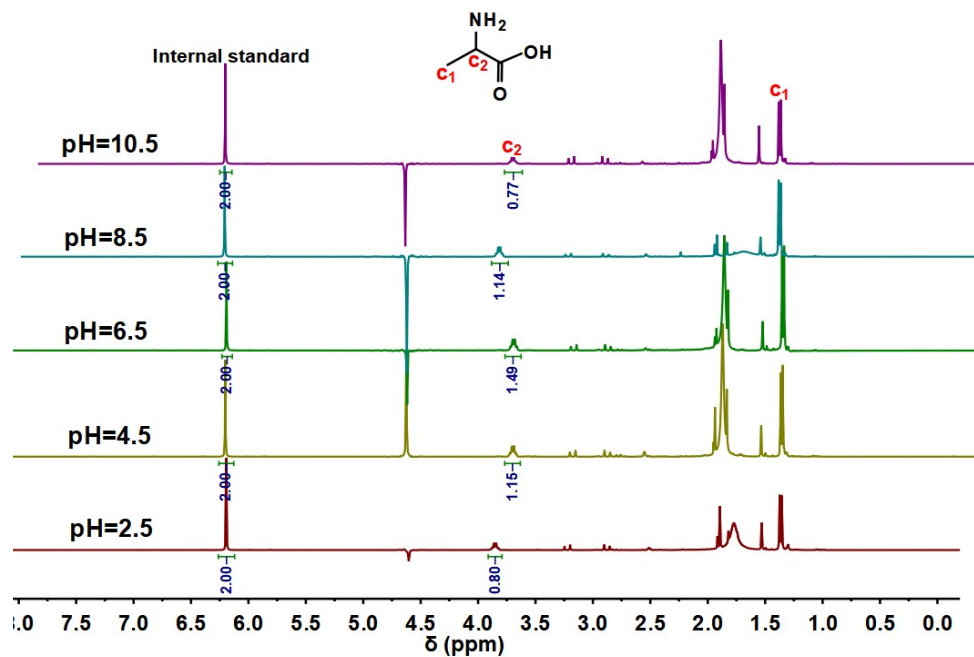


Fig. S11 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.6 V (vs. RHE) in different pH conditions. Reaction conditions: 10 mL 0.2 M Na_2SO_4 (pH = 2.5, 4.5, 6.5, 8.5, 10.5) electrolyte containing 160 mM pyruvate and 96 mM $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$.

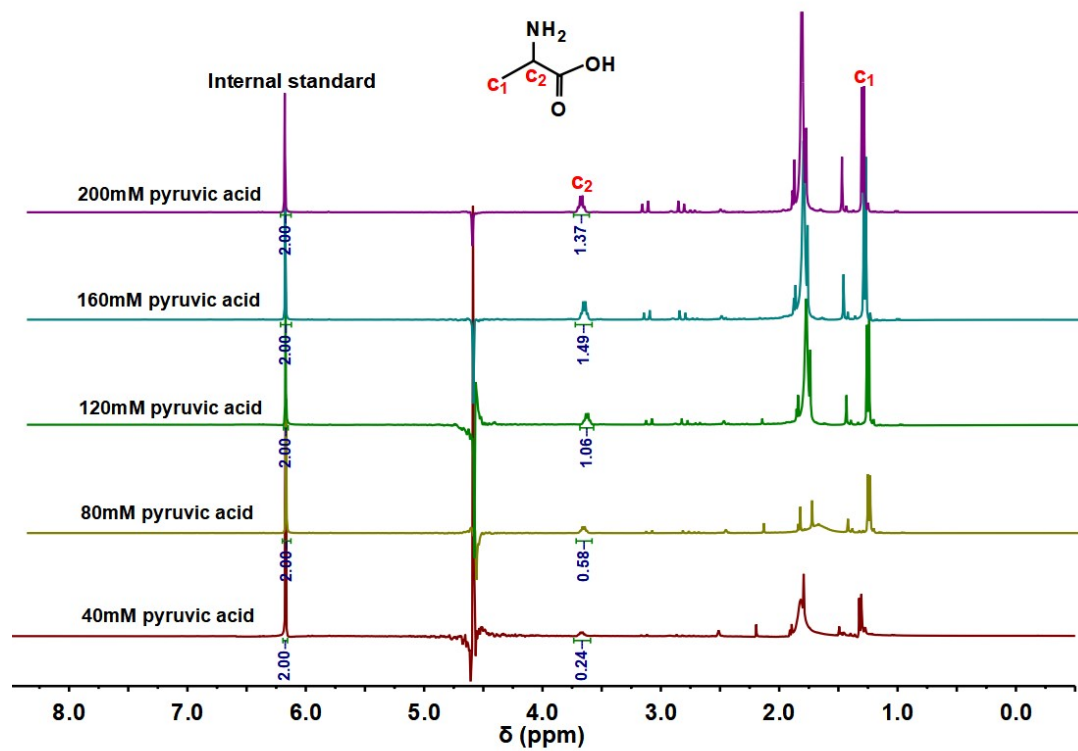


Fig. S12 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.60 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na_2SO_4 solution (pH = 6.5) containing different concentrations of pyruvate and 96 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

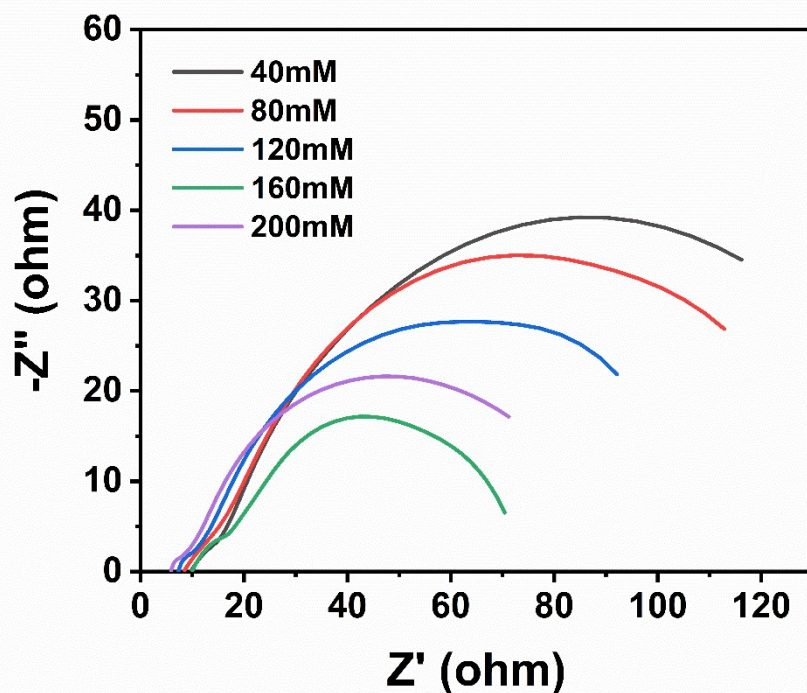


Fig. S13 The electrochemical impedance spectra of Cu₂O/CF at different concentrations.

As shown in **Fig. S13**, the impedance reduced with the increase of pyruvate concentration, and the impedance decreased to the lowest when the pyruvate concentration reached 160 mM, indicating that 160 mM is more favorable for the electrode reaction. When the pyruvate concentration increases to 200 mM, as a large organic molecule, the high concentration of pyruvate tends to cover the active sites on the Cu₂O/CF surface, resulting in an increase in impedance. Therefore, the yield of alanine decreased when the pyruvate concentration was higher than 160 mM.

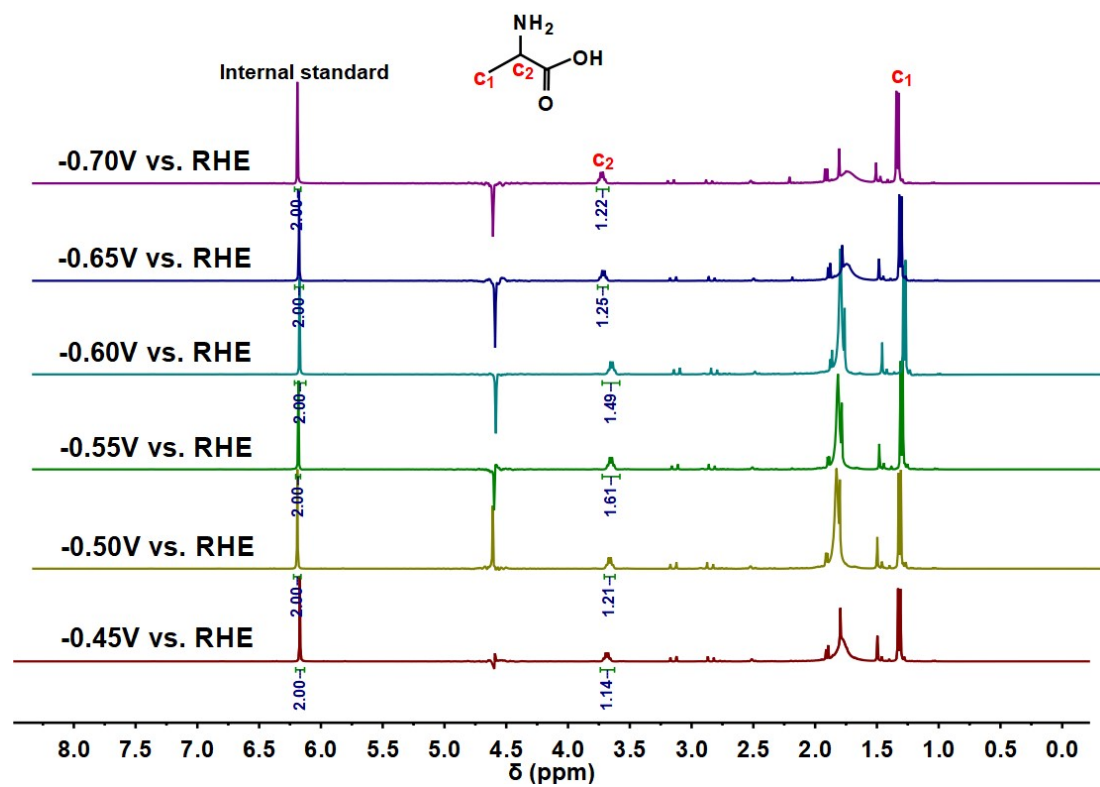


Fig. S14 ^1H NMR spectra of the electrolyte after 2 h in electrocatalytic synthesis of different potential. Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 6.5) containing 160 mM pyruvate and 96 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

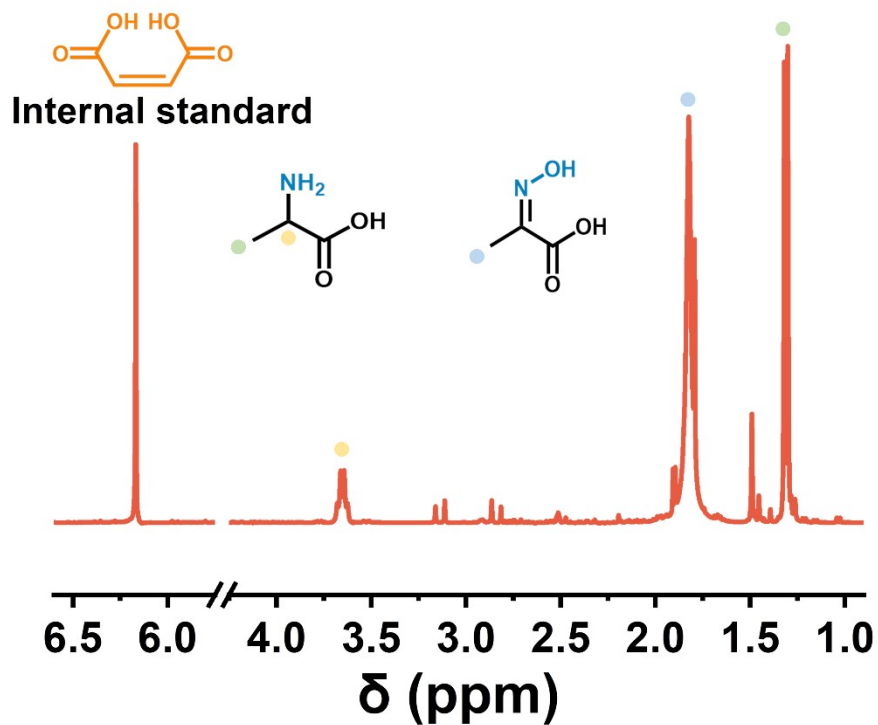


Fig. S15 ^1H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of alanine at -0.55 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 6.5) containing 160 mM pyruvate and 96 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

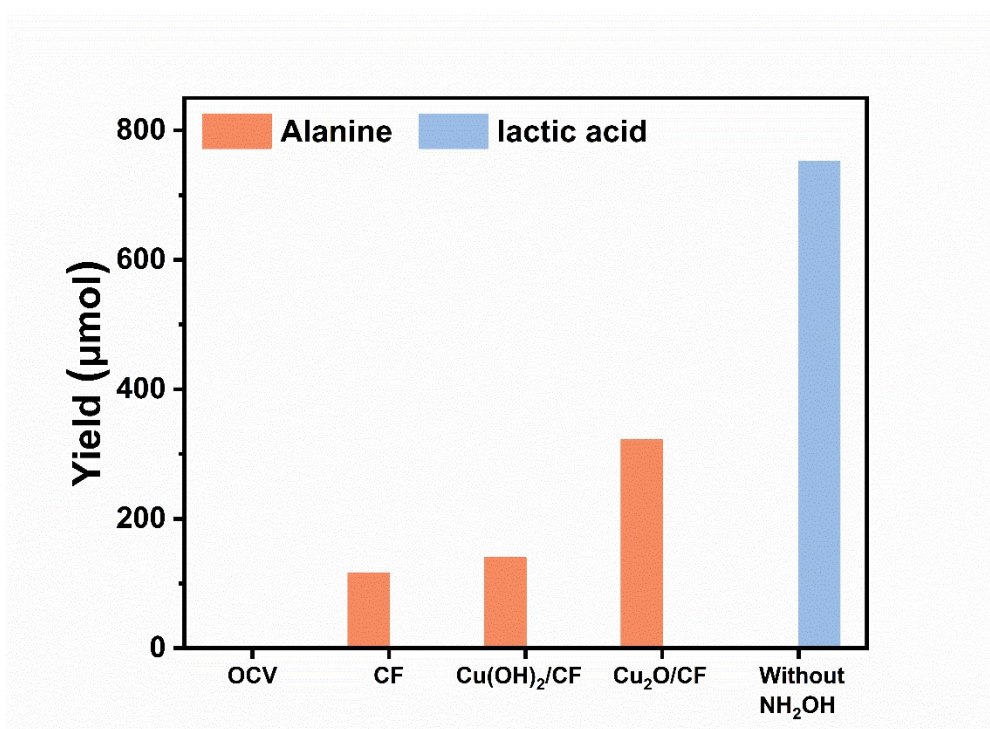


Fig. S16 The yield of products under different test conditions with Cu₂O/CF and control specimens.

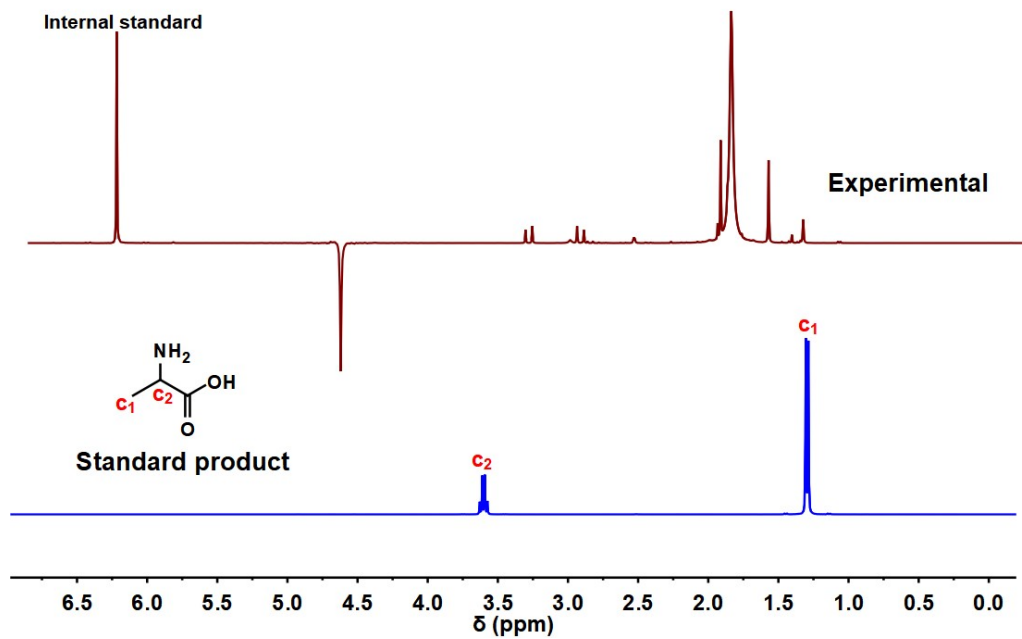


Fig. S17 ¹H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of alanine on Cu₂O/CF at open circuit voltage (OCV). Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 6.5) containing 160 mM pyruvate and 96 mM (NH₂OH)₂·H₂SO₄.

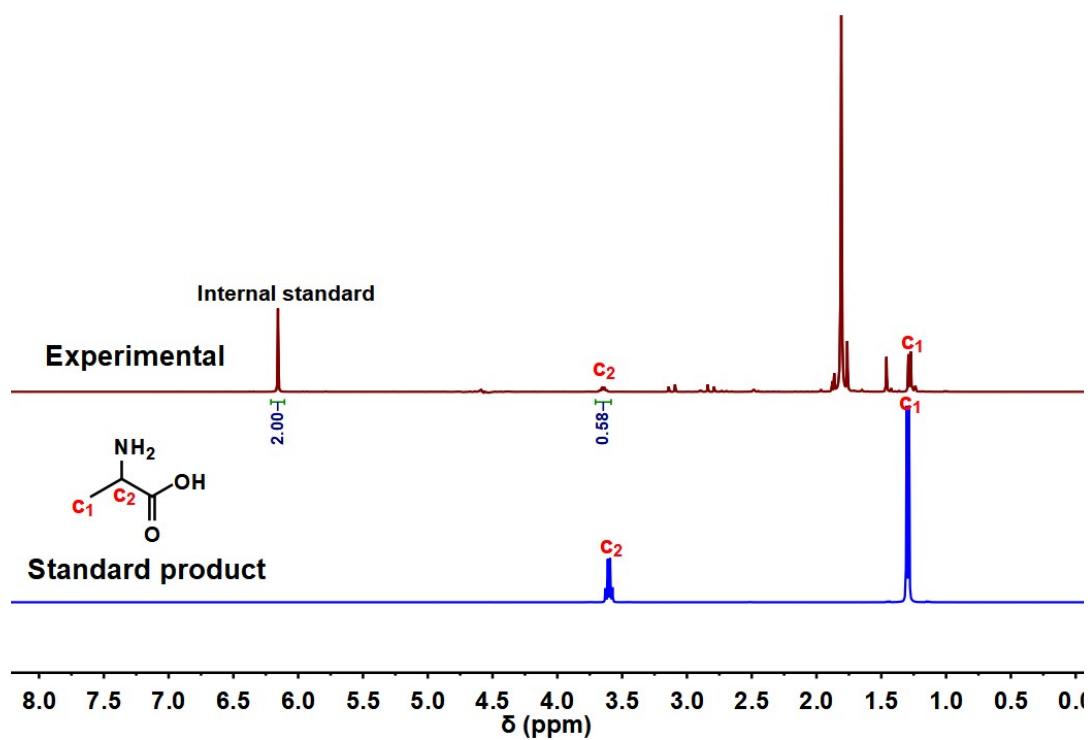


Fig. S18 ¹H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of alanine on copper foam at -0.55 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 6.5) containing 160 mM pyruvate and 96 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

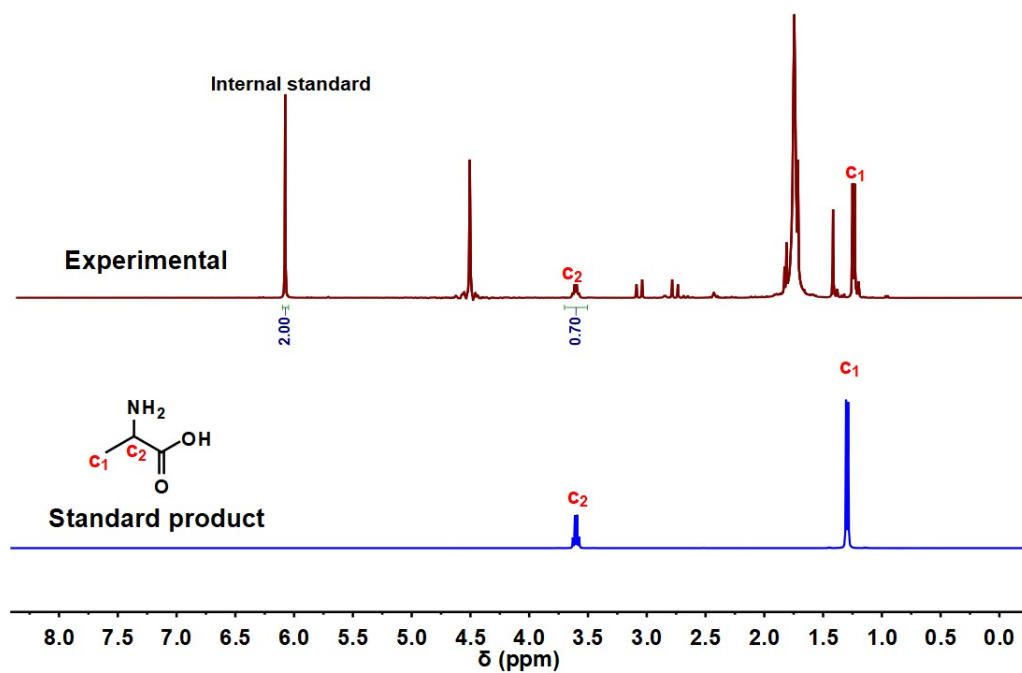


Fig. S19 ¹H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of alanine on Cu(OH)₂/CF at -0.55 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 6.5) containing 160 mM pyruvate and 96 mM (NH₂OH)₂·H₂SO₄.

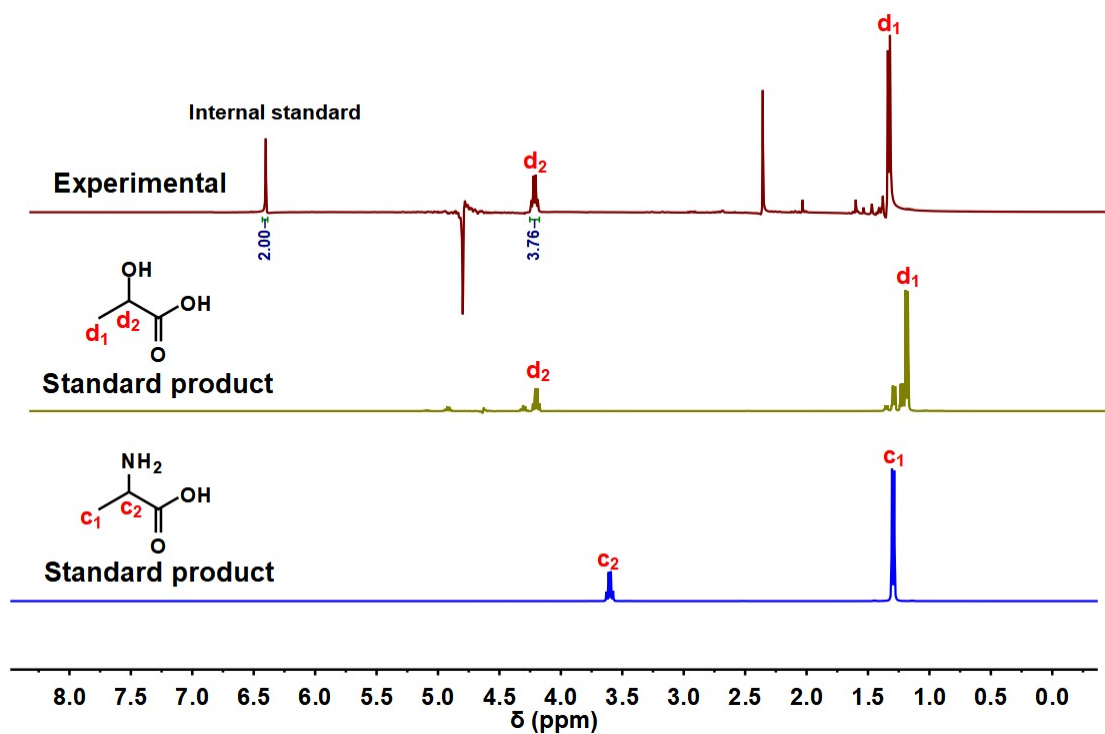


Fig. S20 ¹H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of alanine on Cu₂O/CF at -0.55 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 6.5) containing 160 mM pyruvate (without NH₂OH).

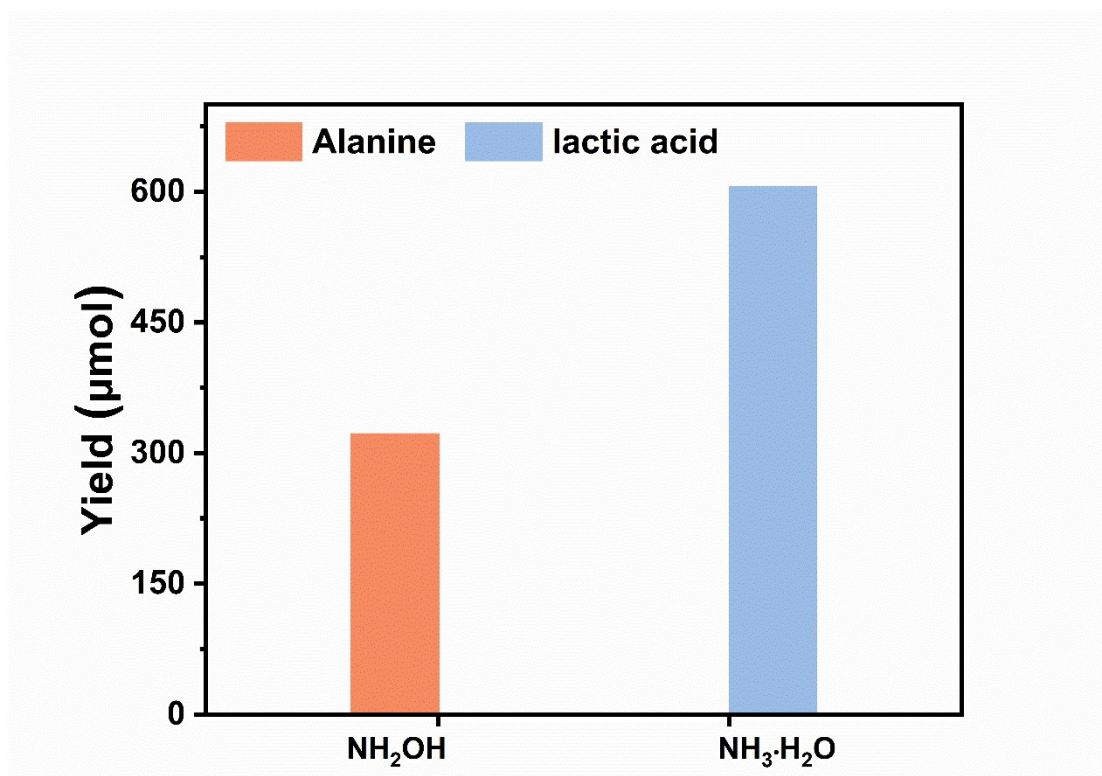


Fig. S21 The yield of products under different nitrogen sources with $\text{Cu}_2\text{O}/\text{CF}$.

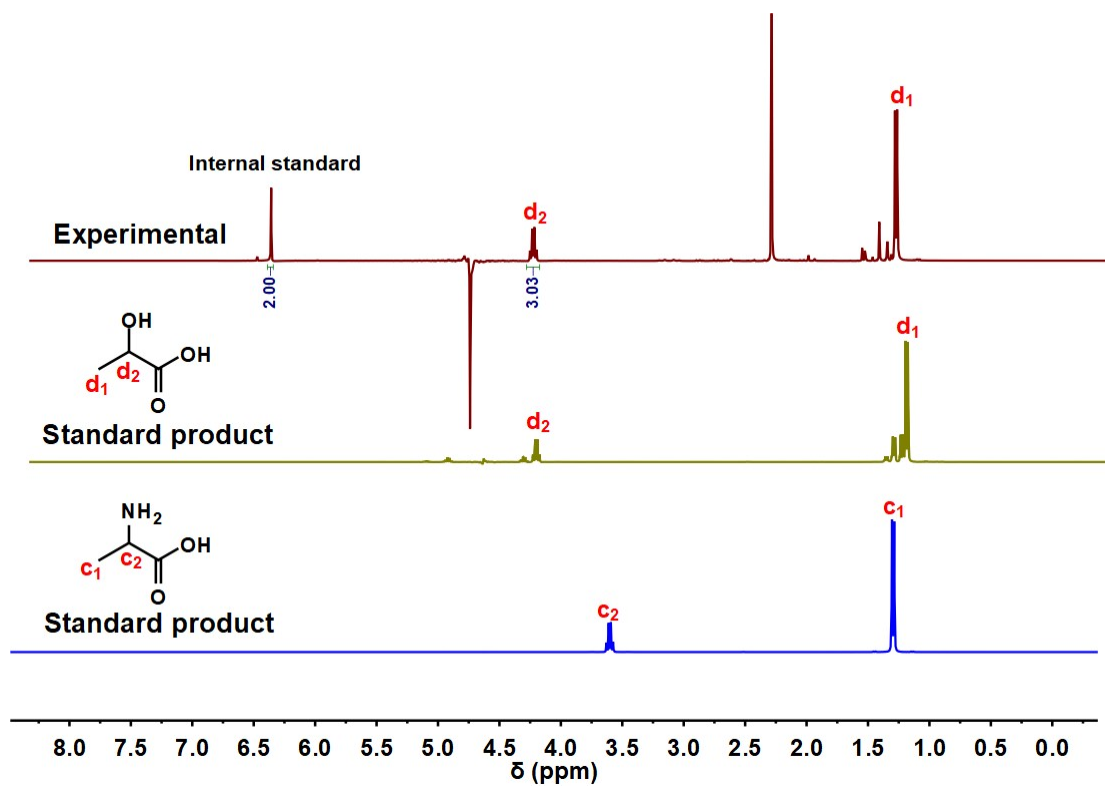


Fig. S22 ¹H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of alanine on Cu₂O/CF at -0.55 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 6.5) containing 160 mM pyruvate and 192 mM NH₃·H₂O.

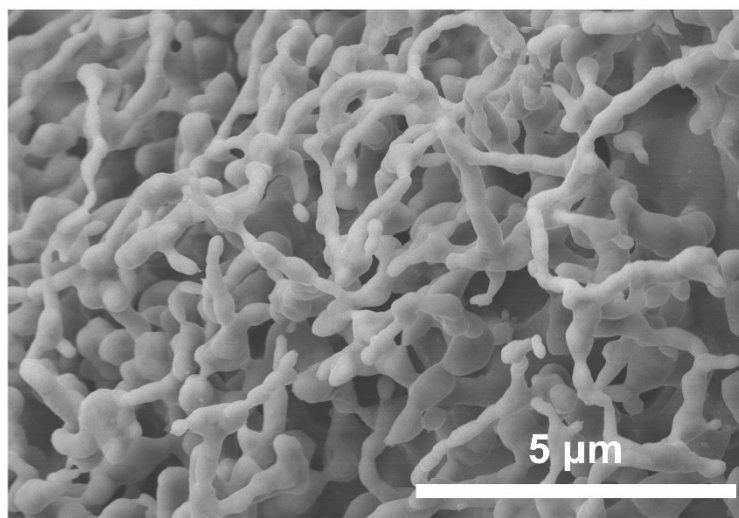


Fig. S23 SEM for Cu₂O/CF after measured at -0.55V (vs. RHE)

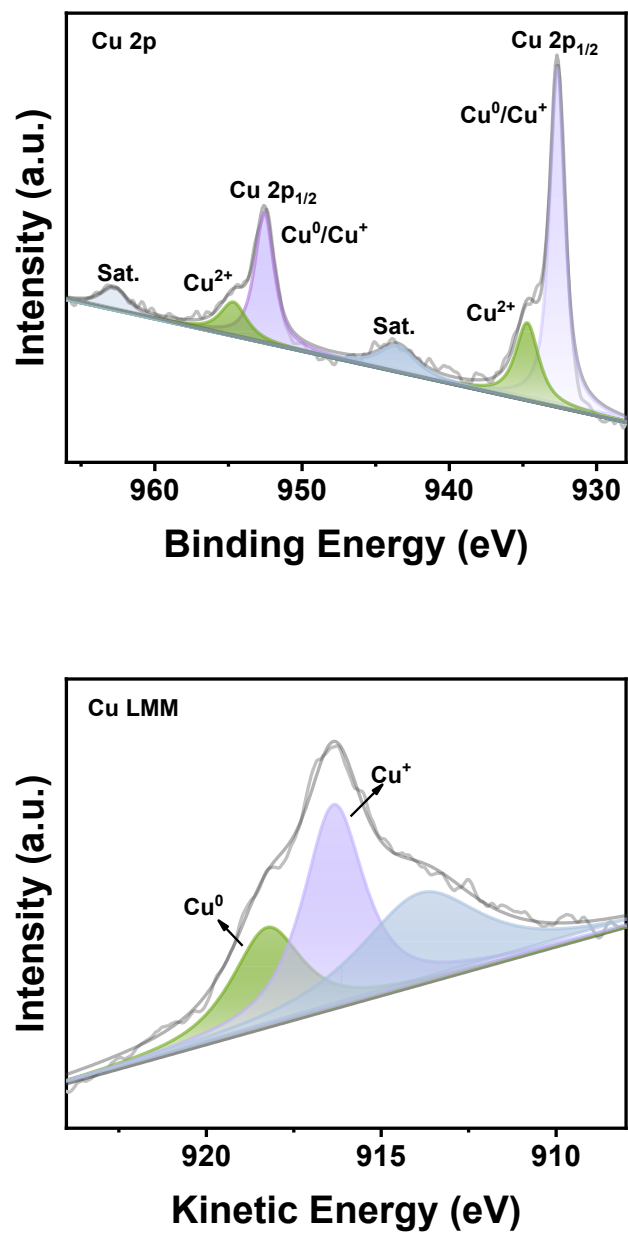


Fig. S24 High-resolution XPS spectrum of Cu 2p and Cu LMM for Cu₂O/CF after measured at -0.55V (vs. RHE)

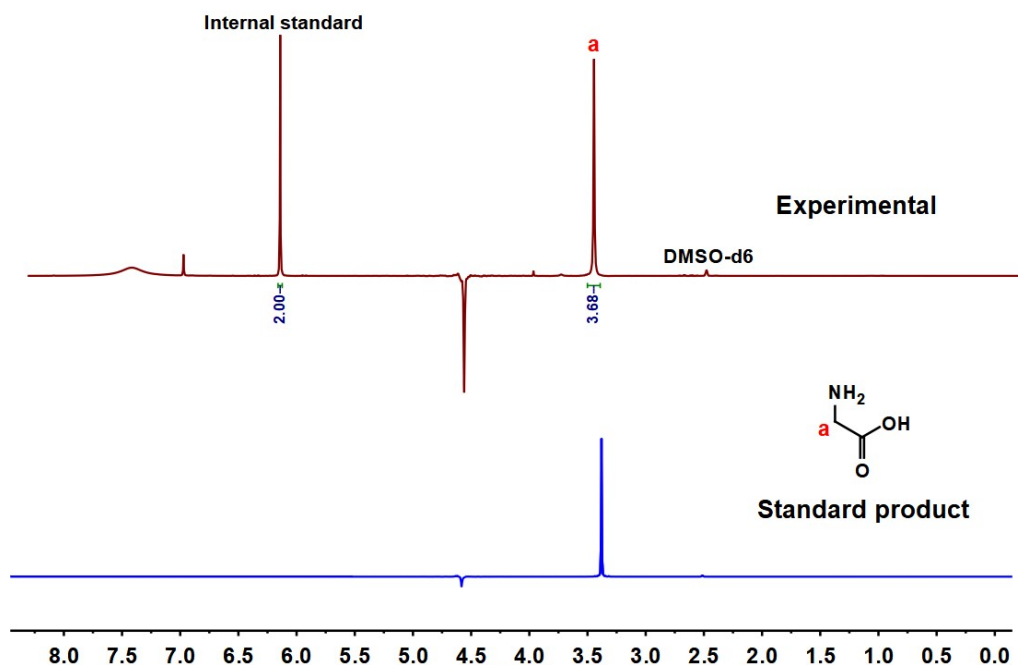


Fig. S25 ^1H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of glycine and electrolyte with standard glycine product. Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 6.5) containing 160 mM glyoxylic acid and 96 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$, applied potential at -0.55 V (vs. RHE).

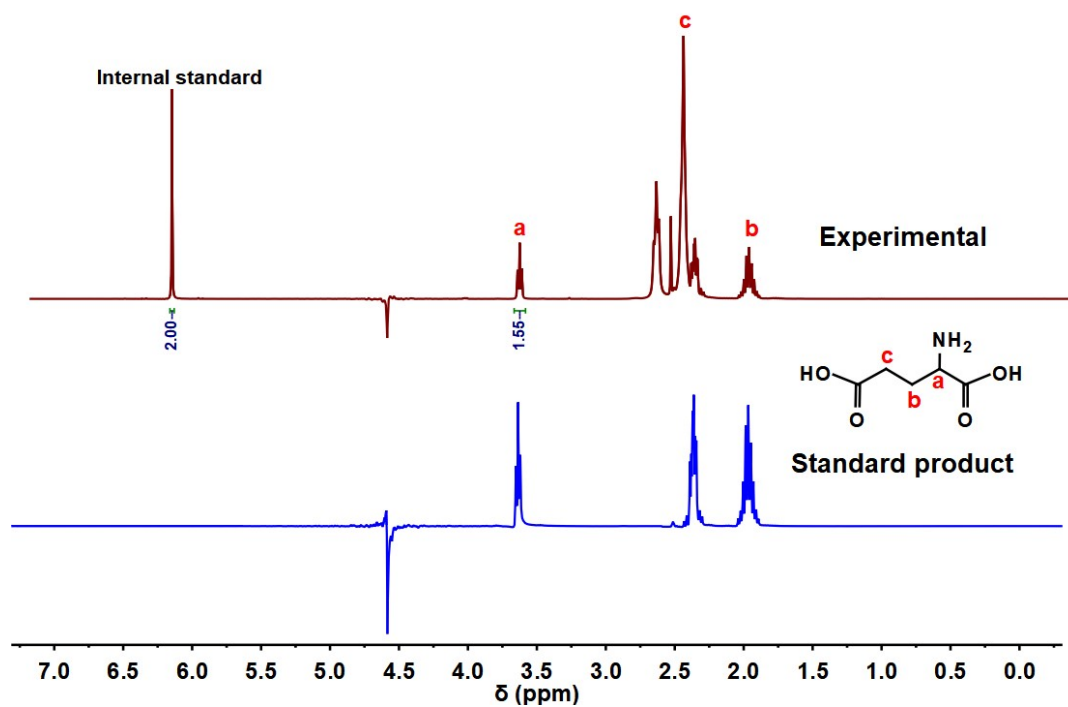


Fig. S26 ¹H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of glutamic acid and electrolyte with standard glutamic acid product. Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 6.5) containing 160 mM α-ketoglutaric acid and 96 mM (NH₂OH)₂·H₂SO₄, applied potential at -0.62 V (vs. RHE).

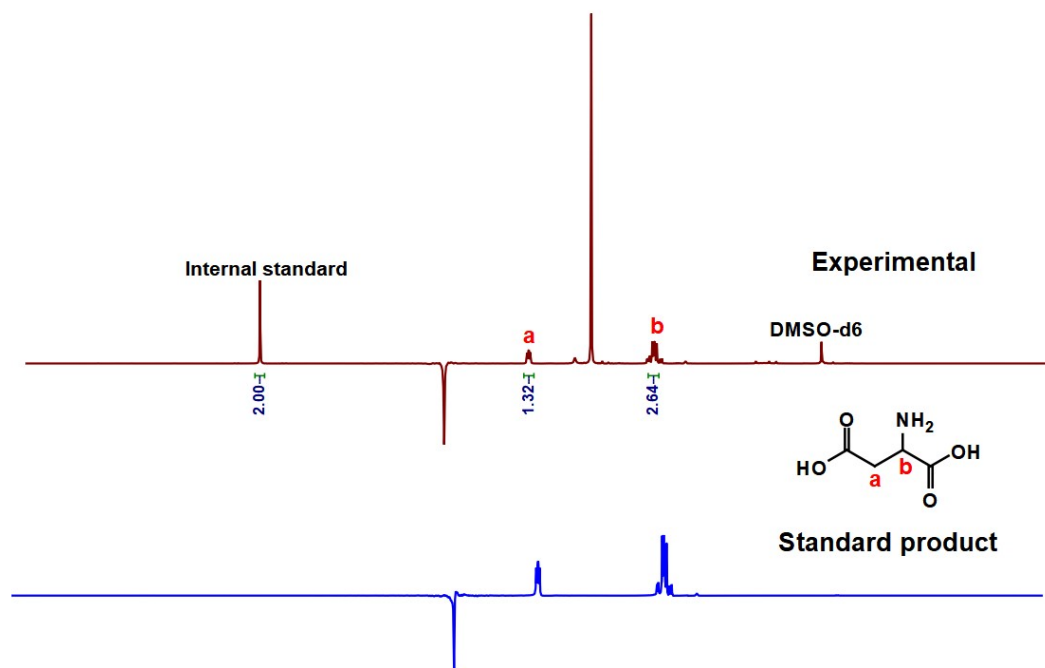


Fig. S27 ¹H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of aspartic acid and electrolyte with standard aspartic acid product. Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 6.5) containing 160 mM oxaloacetic acid and 96 mM (NH₂OH)₂·H₂SO₄, applied potential at -0.55 V (vs. RHE).

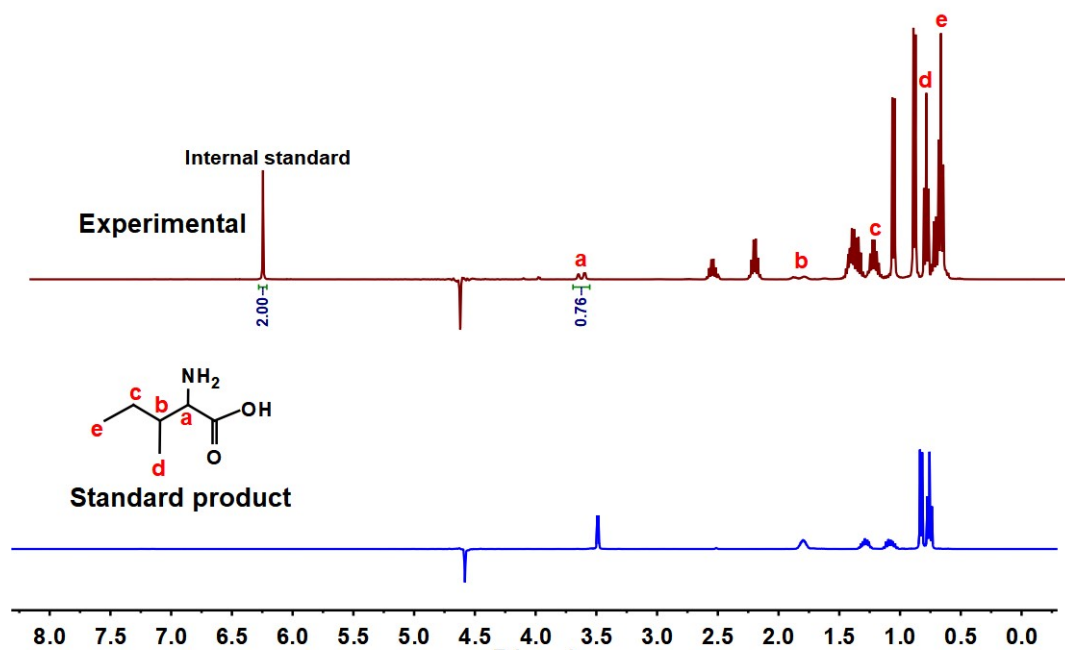


Fig. S28 ¹H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of isoleucine and electrolyte with standard isoleucine product. Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 6.5) containing 160 mM 3-methyl-2-oxovaleric acid and 96 mM (NH₂OH)₂·H₂SO₄, applied potential at -0.55 V (vs. RHE).

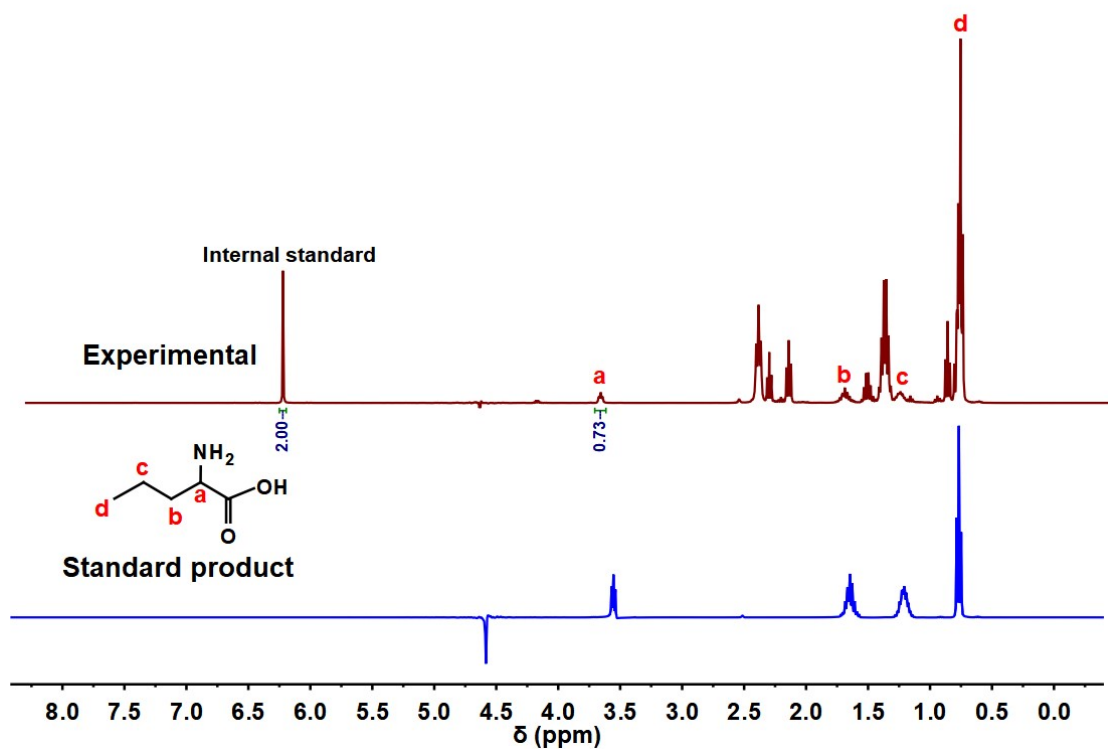


Fig. S29 ^1H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of norvaline and electrolyte with standard norvaline product. Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 6.5) containing 160 mM 2-oxopentanoic acid and 96 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$, applied potential at -0.55 V (vs. RHE).

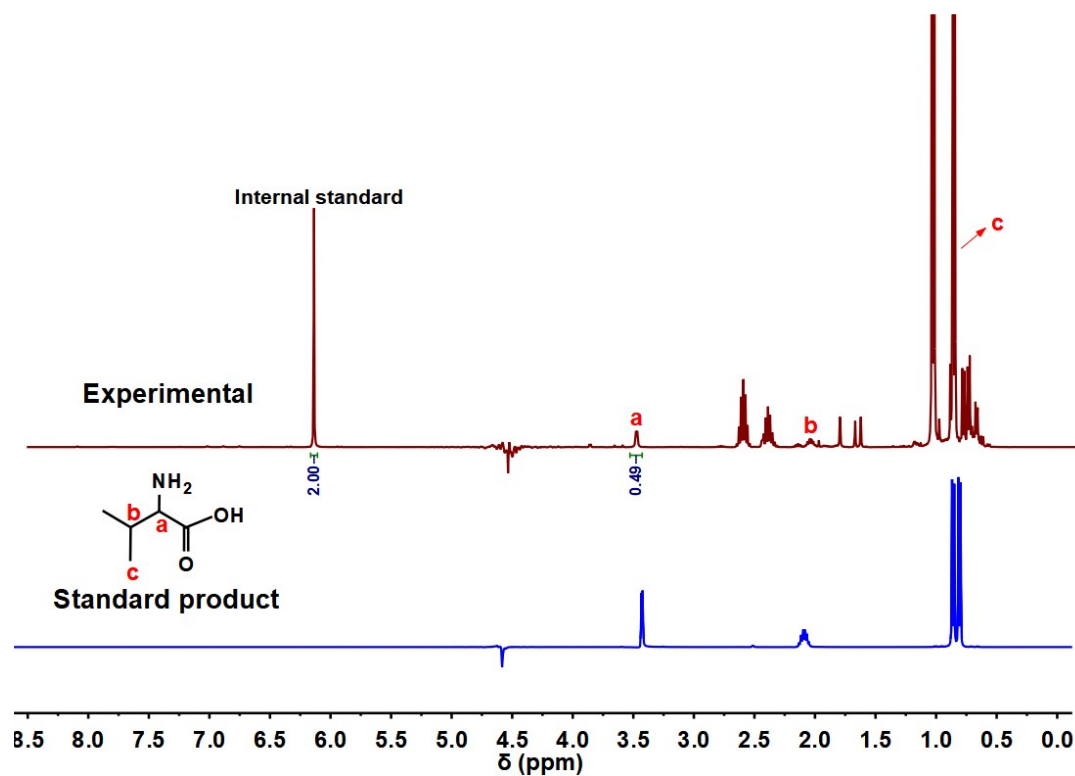


Fig. S30 ¹H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of valine and electrolyte with standard valine product. Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 6.5) containing 160 mM 3-methyl-2-ketobutanoic acid and 96 mM (NH₂OH)₂·H₂SO₄, applied potential at -0.55 V (vs. RHE).

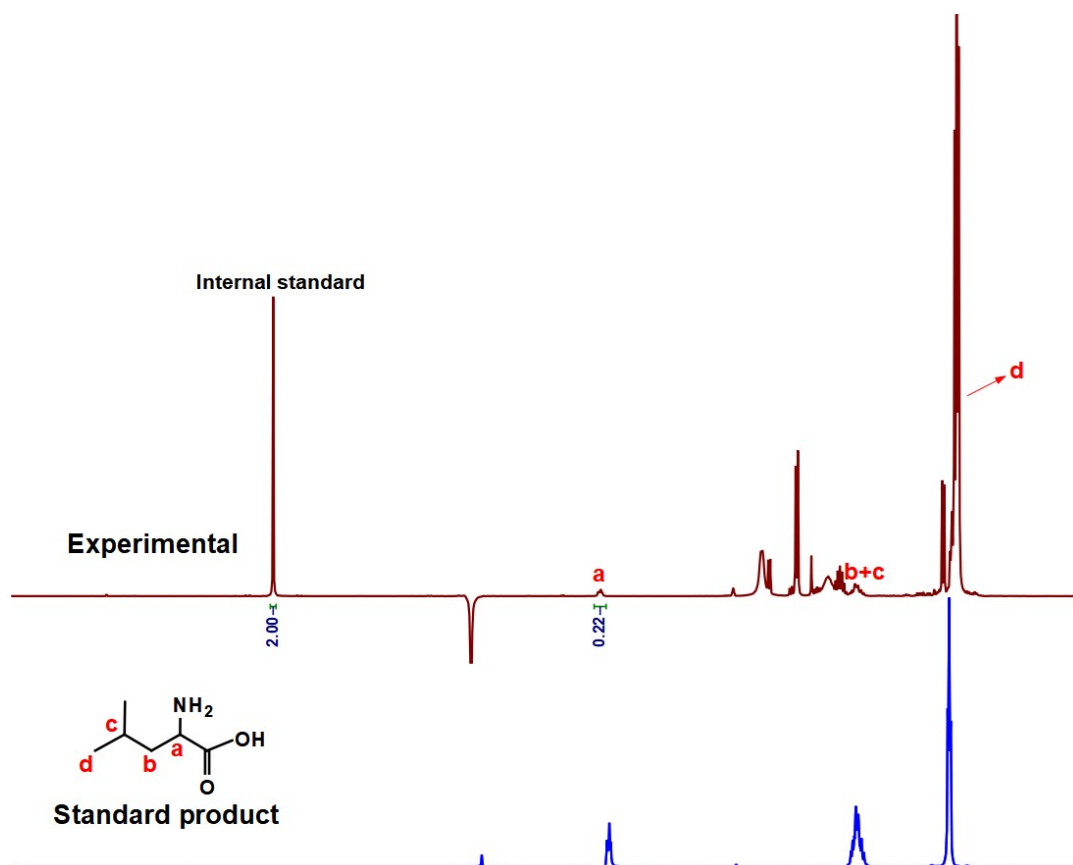


Fig. S31 ¹H NMR spectrum of electrolyte after 2 h in electrocatalytic synthesis of leucine and electrolyte with standard leucine product. Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 6.5) containing 160 mM 4-methyl-2-oxovaleric acid and 96 mM (NH₂OH)₂·H₂SO₄, applied potential at -0.55 V (vs. RHE).

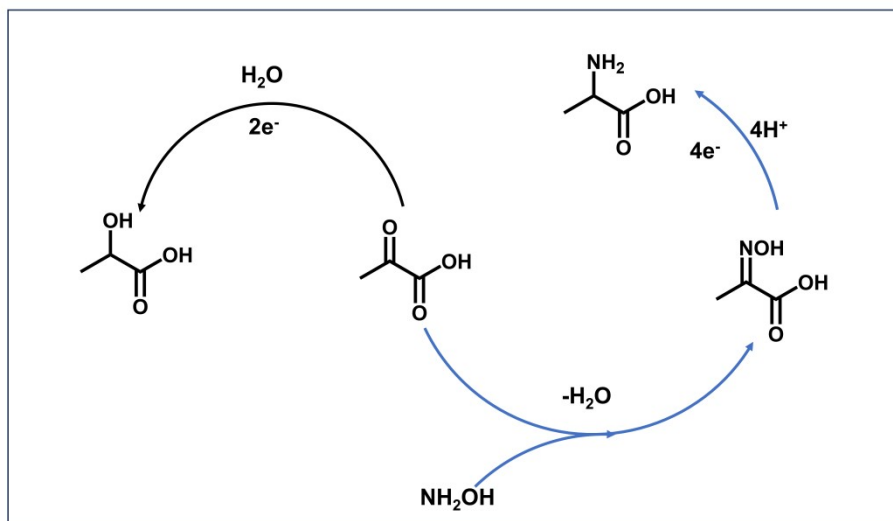














Fig. S32 The proposed reaction pathway for the electrocatalytic synthesis of alanine from pyruvate and NH_2OH (The blue line).

Table S1. Electrochemical reduction of pyruvate at various (a) pH values, (b) pyruvate concentrations, (c) NH₂OH amounts, (d) potentials.

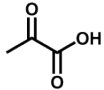
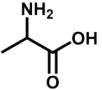
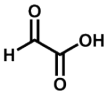
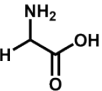
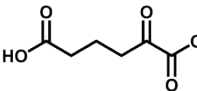
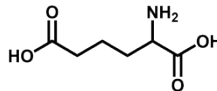
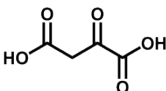
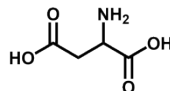
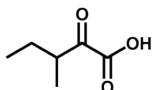
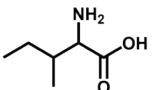
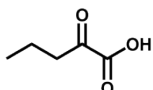
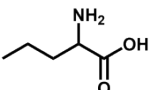
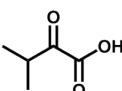
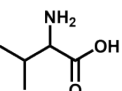
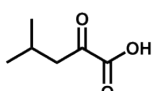
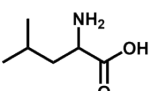
	pH	Pyruvate conc. (mM)	NH ₂ OH amount (equiv. to pyruvate)	E (V vs RHE)	Yield (μ mol)	FE (%)
a	2.5	160	1.2	-0.60	160.0	22.6
a	4.5	160	1.2	-0.60	239.2	25.2
a	6.5	160	1.2	-0.60	298.0	30.8
a	8.5	160	1.2	-0.60	228.0	23.0
a	10.5	160	1.2	-0.60	154.0	14.8
b	6.5	40	1.2	-0.60	48.0	19.1
b	6.5	80	1.2	-0.60	116.0	22.6
b	6.5	120	1.2	-0.60	212.0	28.1
b	6.5	160	1.2	-0.60	298.0	30.8
b	6.5	200	1.2	-0.60	274.0	21.0
c	6.5	160	1.2	-0.45	228.0	22.8
c	6.5	160	1.2	-0.50	242.0	21.9
c	6.5	160	1.2	-0.55	322.0	33.8
c	6.5	160	1.2	-0.60	298.0	30.8
c	6.5	160	1.2	-0.65	250.0	22.7
c	6.5	160	1.2	-0.70	244.0	19.5

Table S2. Comparison of Cu₂O/CF and other electrocatalysts in the electrocatalytic synthesis of alanine.

Substrate	C _{sub} (mM)	Nitrogen sources	Electrodes	Time (h)	product	Yield (μmol)	FE (%)	Sel. (%)
	160	NH ₂ OH	Cu ₂ O/CF	2		322.0	33.8	100
	20	NO	AD-Fe/NC	6		67.8	13.7	11.3
	50	NO ₃ ⁻	Pd ₁ Cu ₁ NBW _S	*10		—	—	*58.6
	200	NO ₃ ⁻	CoPc/CNT	*1.1		*453	61.2	*64.0
	10	¹⁵ NO ₂ ⁻	NF	8		*182	10.0	91.0
	160	NH ₂ OH	TiO ₂ /Ti mash	2		—	99.5	*100

*: Calculated from article data

Table S3. Electrosynthesis of various amino acids from corresponding α -keto acids and NH_2OH . The following conditions are identical for all the electrochemical reactions; 1.2 equiv. to α -keto acid for NH_2OH amount, $\text{pH} = 6.5$.

Entry	E (V vs RHE)	C_{sub} (mM)	Substrate	Product	Yield (μmol)	FE (%)
1	-0.55	160			322.0	33.8
2	-0.55	160			368.0	38.8
3	-0.55	160			310.0	22.0
4	-0.55	160			264.0	17.7
5	-0.55	160			152.0	16.5
6	-0.55	160			146.0	15.7
7	-0.55	160			98.0	14.9
8	-0.55	160			44.0	8.5