

Electronic Supplementary Information

Efficient electrosynthesis of alanine from α -keto acids over self-supported electrocatalyst with superior activity

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1. Experimental section

1.1 Chemicals and materials

Pyruvic acid, glyoxylic acid, oxaloacetic acid, α -ketoglutaric acid, 3-methyl-2-ketobutanoic acid, 3-methyl-2-oxovaleric acid, 4-methyl-2-oxovaleric acid, 2-oxobutanoic acid, 2-oxopentanoic acid, 2-oxohexanoic acid, and hydroxylamine sulfate were purchased from Aladdin Reagent Company. H_2SO_4 (AR, $\geq 85\%$), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (AR, 98%), 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. Ti foil (0.025 mm thickness) was purchased from Toho Technical Service, Co., Ltd. Deionized water (DW) made by laboratory. All chemicals were used without further purification.

1.2 Preparation of Cu/Ti

The commercial Ti foil was cut into $1 \times 1.5 \text{ cm}^2$ slices. Then, it was polished with sandpaper to remove surface oxides. The polished Ti foil was ultrasonicated in acetone to remove surface oils. Cu/Ti was prepared by electrodeposition using a mixture of H_2SO_4 (0.5 mol L^{-1}) and CuSO_4 (0.04 mol L^{-1}) solution. The electrodeposition was carried out using a three-electrode system, in which a Ti sheet (the effective area of $1 \times 1 \text{ cm}^2$) was used as the working electrode, a Pt wire was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. The electrodeposition was carried out at the current density of 250 mA cm^{-2} for 300 s. The synthesized electrode was rinsed thoroughly with water and ethanol in turn and blown to dryness with nitrogen.

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 Cu K α radiation ($\lambda_{\text{K}\alpha 1} = 1.5418 \text{ \AA}$) 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 AscendTM 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 Cu/Ti was 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 Na_2SO_4 + 0.08 M pyruvate + 0.048 M $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$ 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 the measured potential ranges of the electrocatalytic process were -0.47 to -0.67 V (vs. RHE) with an interval of 0.05 V .

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 Cu/Ti ($1 \times 1\text{ cm}^2$) 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. A Na_2SO_4 (aq.) containing α -keto acids and $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$ was used as cathodic and anodic electrolyte solutions. The electrolytes with a pH of 0.53–8.54 were adjusted by adding aqueous H_2SO_4 or NaOH.

Prior to testing, pyruvic acid 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):

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

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.

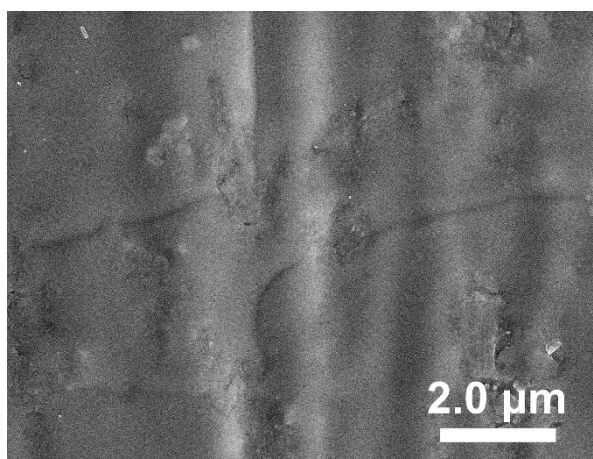


Fig. S1 SEM image of commercially available Ti foil.

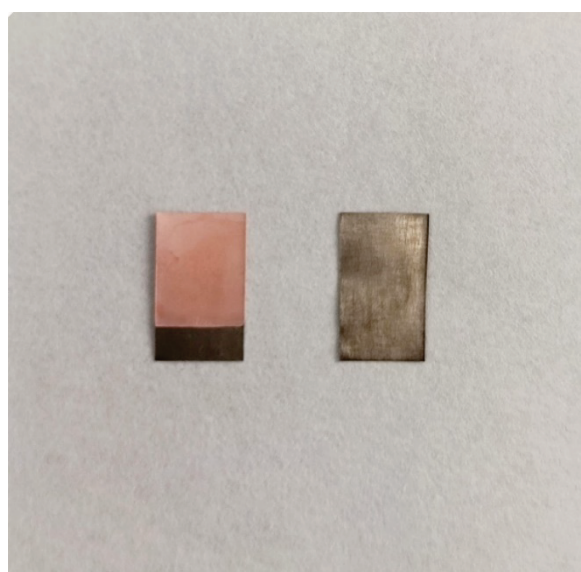


Fig. S2 The physical photographs of synthetic Cu/Ti self-supporting electrode.

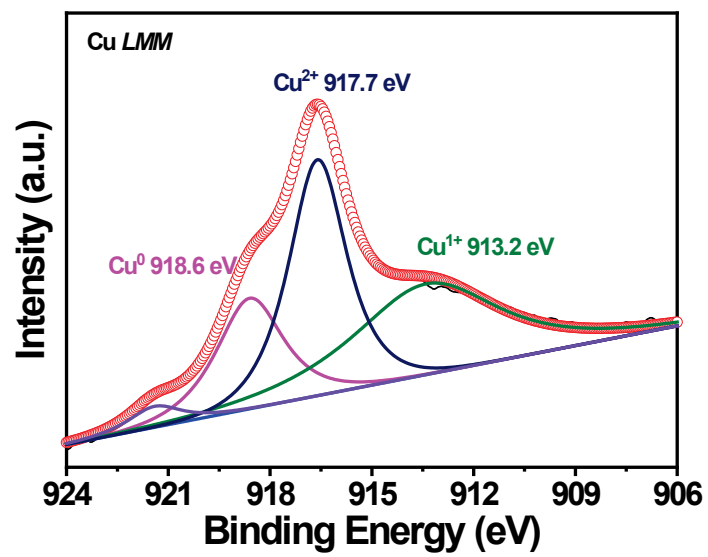


Fig. S3 High-resolution XPS spectrum of Cu *LMM* for Cu/Ti.

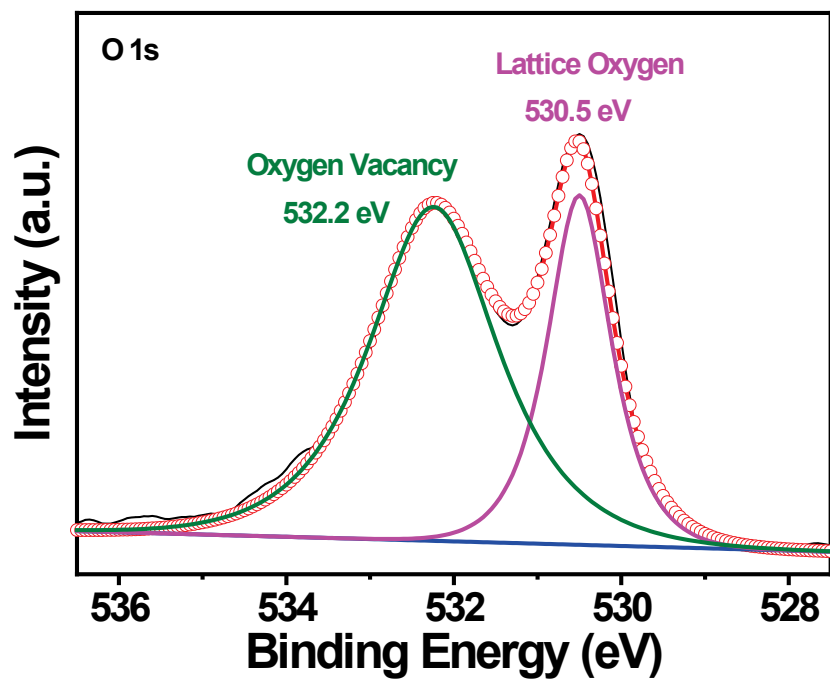


Fig. S4 High-resolution XPS spectrum of O 1s for Cu/Ti.

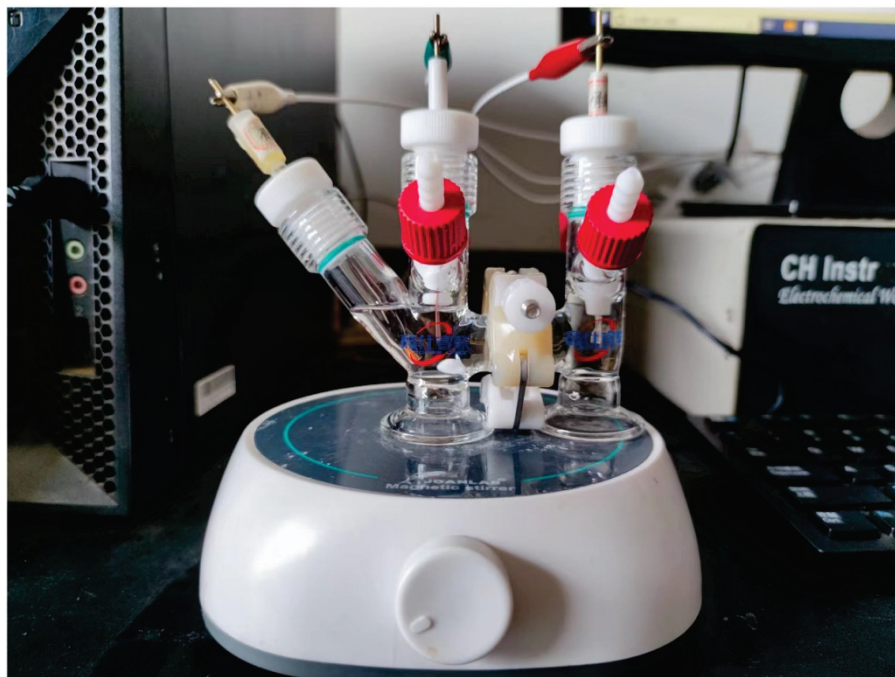


Fig. S5 Reaction setup for the electrochemical synthesis of amino acids over a Cu/Ti cathode.

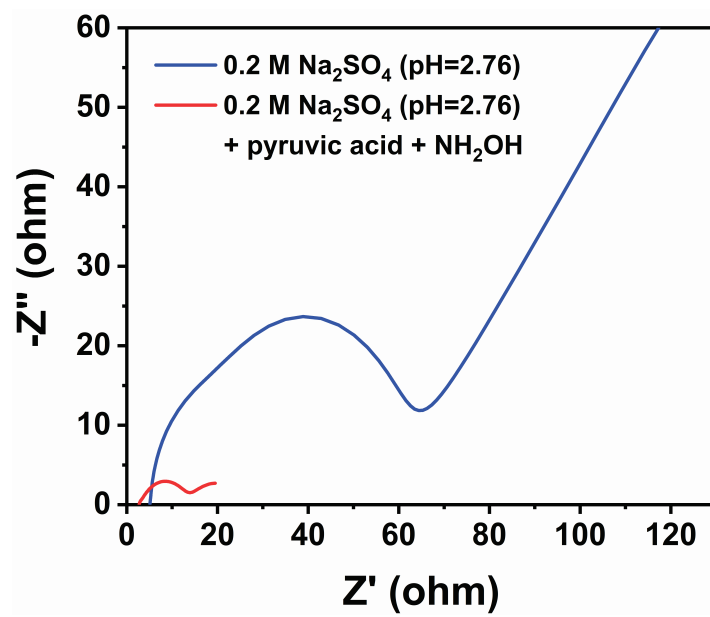


Fig. S6 The EIS spectra of Cu/Ti in different solutions.

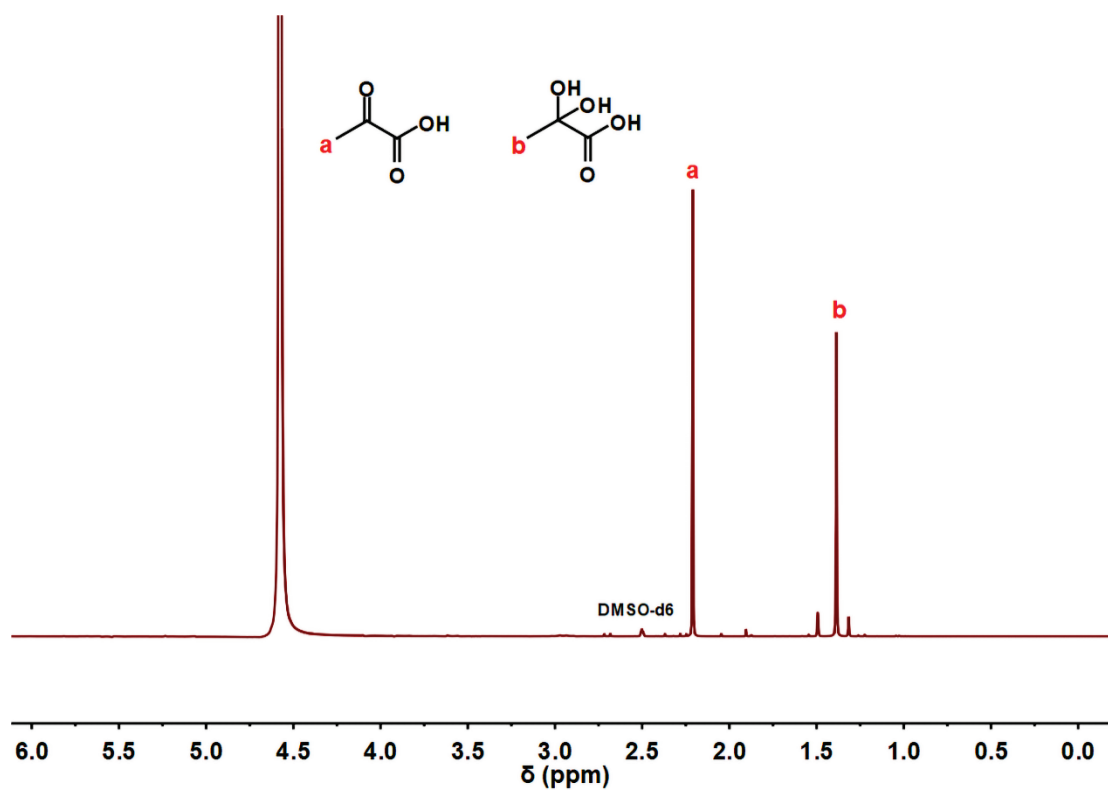


Fig. S7 ^1H NMR spectrum of commercial pyruvate and its hydrated diol-form dissolved in 0.2 M H_2SO_4 (aq).

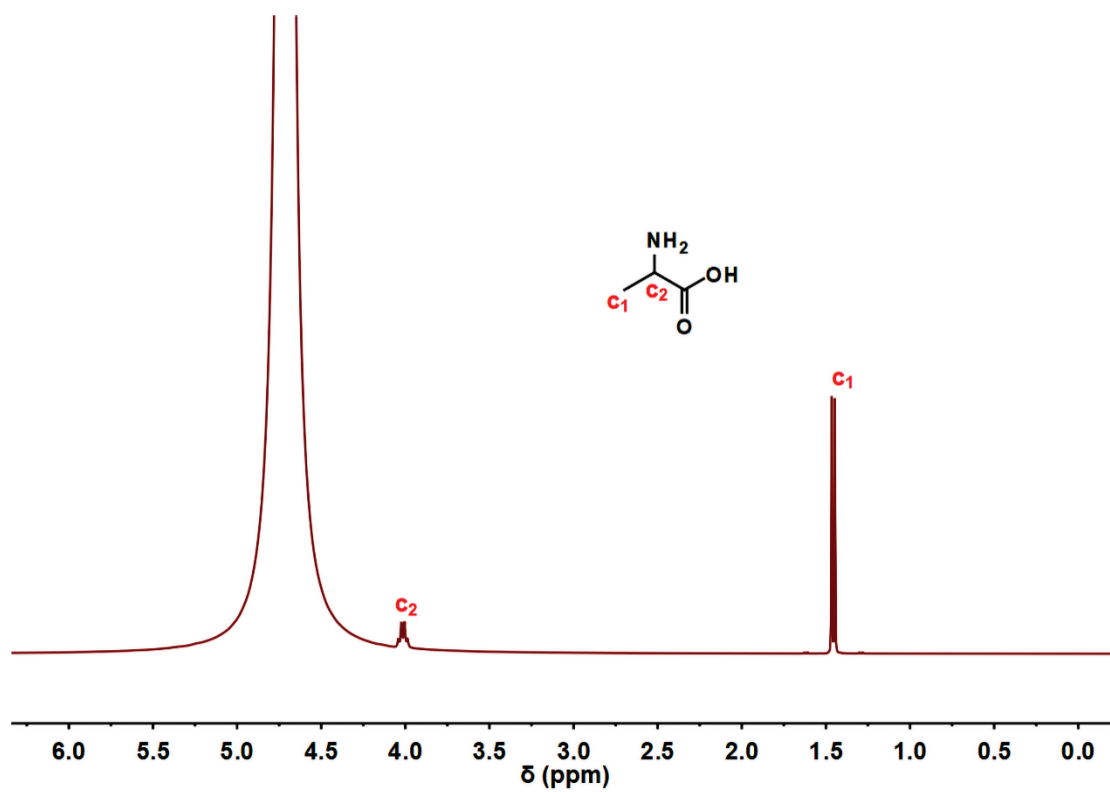


Fig. S8 ^1H NMR spectrum of commercial pyruvate dissolved in 0.2 M H_2SO_4 (aq).

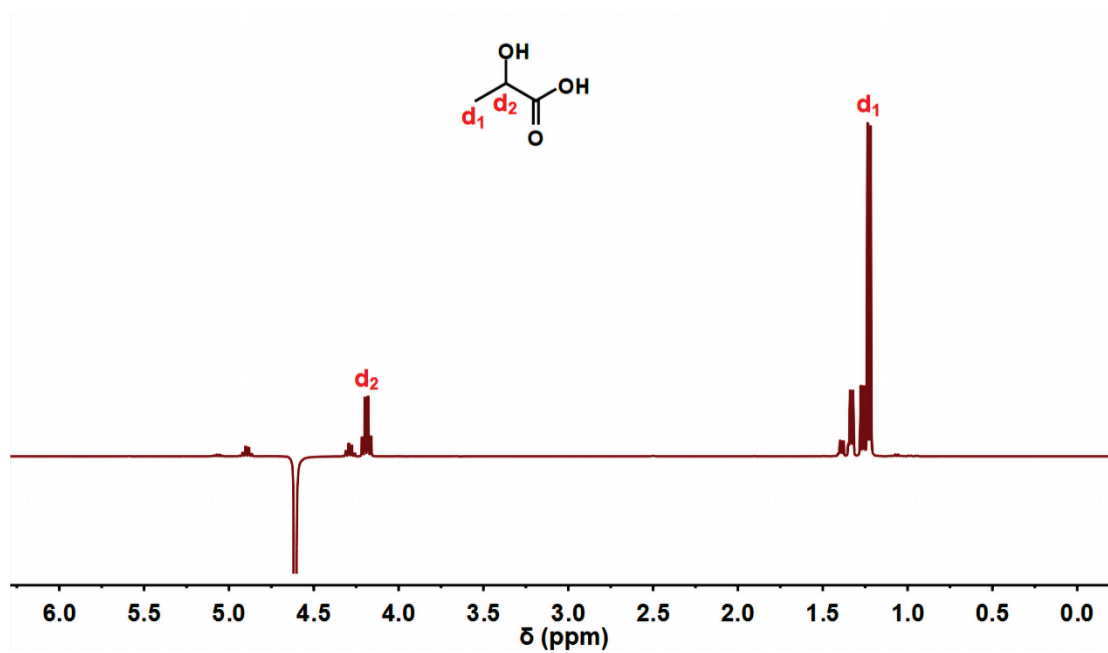


Fig. S9 ^1H NMR spectrum of commercial lactic acid dissolved in 0.2 M H_2SO_4 (aq).

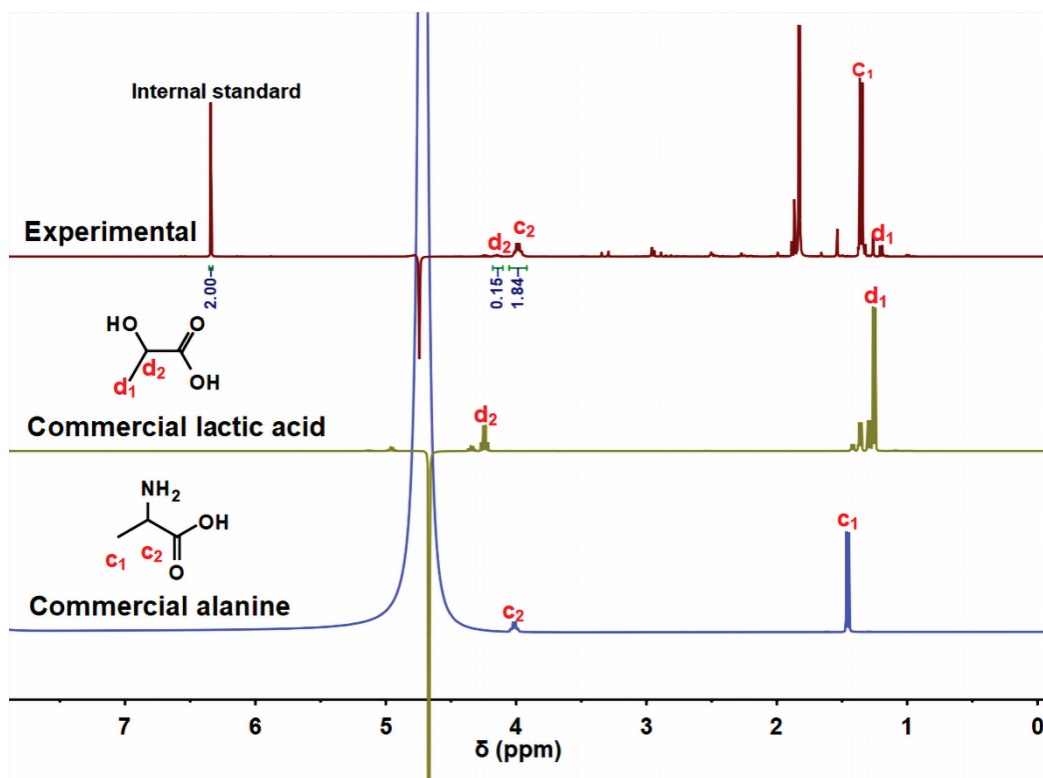


Fig. S10 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.57 V (vs. RHE) in 0.2 M H_2SO_4 ($\text{pH} = 0.53$) containing 160 mM pyruvate and 96 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

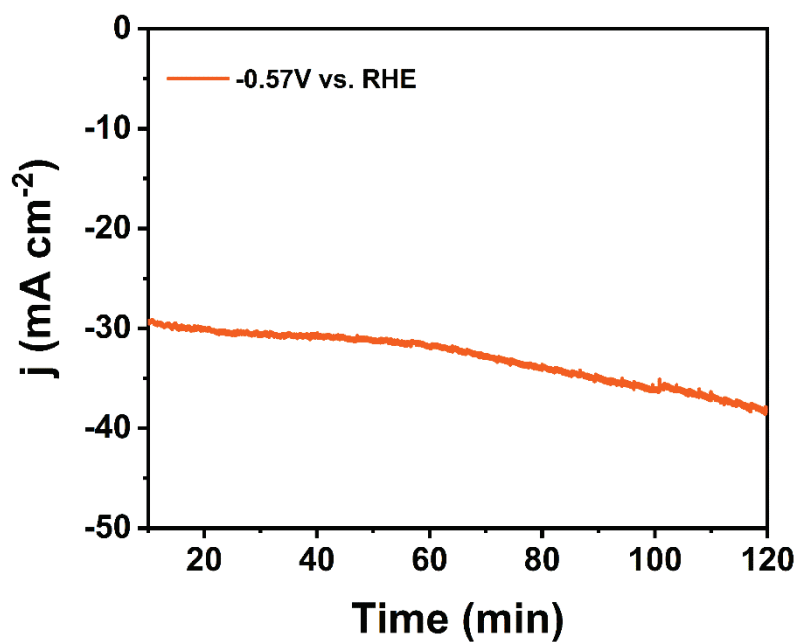


Fig. S11 The chronoamperometric curves of Cu/Ti at -0.57 V (vs. RHE) in 0.2 M H_2SO_4 ($\text{pH} = 0.53$) containing 160 mM pyruvate and 96 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

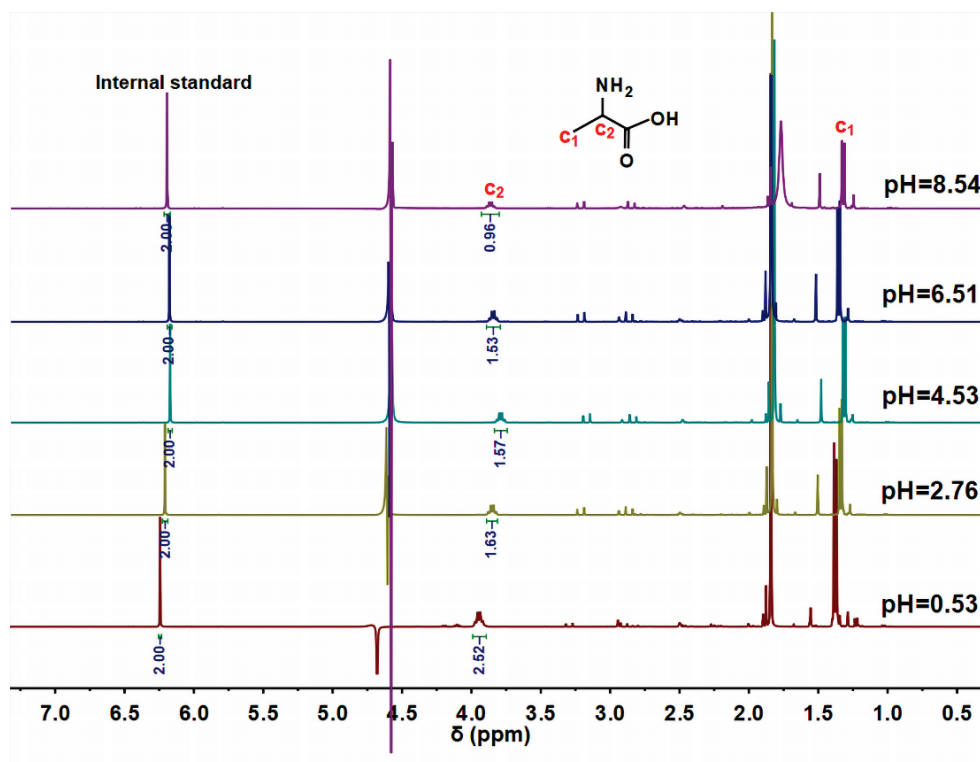


Fig. S12 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.57 V (vs. RHE) in different pH conditions. Reaction conditions: 10 mL 0.2 M H_2SO_4 (pH = 0.53) or 0.2 M Na_2SO_4 (pH = 2.76, 4.53, 6.51, 8.54) electrolyte containing 160 mM pyruvate and 96 mM $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$.

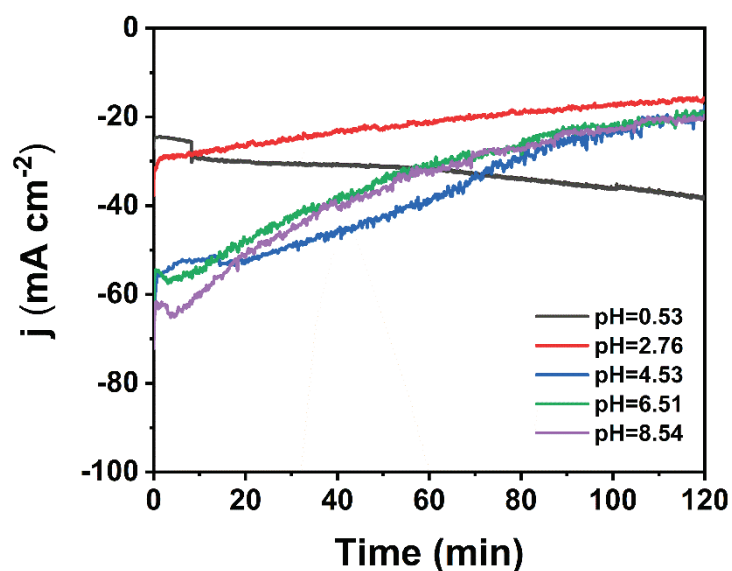


Fig. S13 The chronoamperometric curves of Cu/Ti at -0.57 V (vs. RHE) in 0.2 M H_2SO_4 (pH = 0.53) or 0.2 M Na_2SO_4 (pH = 2.76, 4.53, 6.51, 8.54) electrolyte containing 160 mM pyruvate and 96 mM $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$.

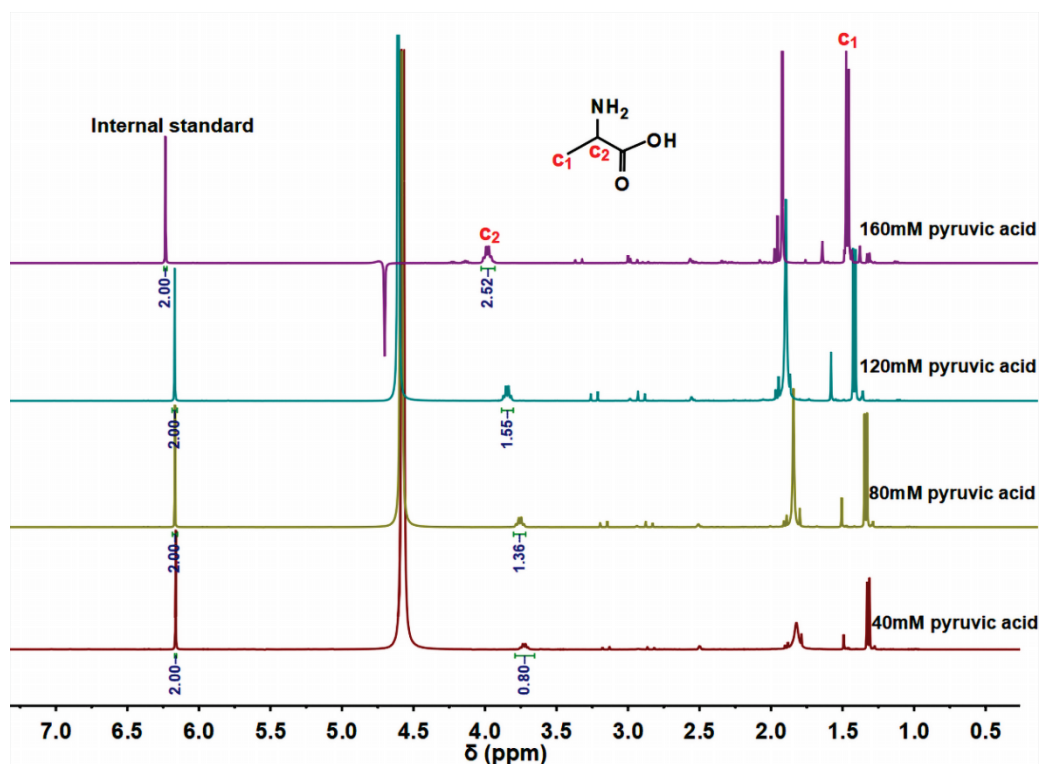


Fig. S14 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.57 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na_2SO_4 solution (pH = 2.76) containing different concentrations of pyruvate and 1.2 equiv. NH_2OH .

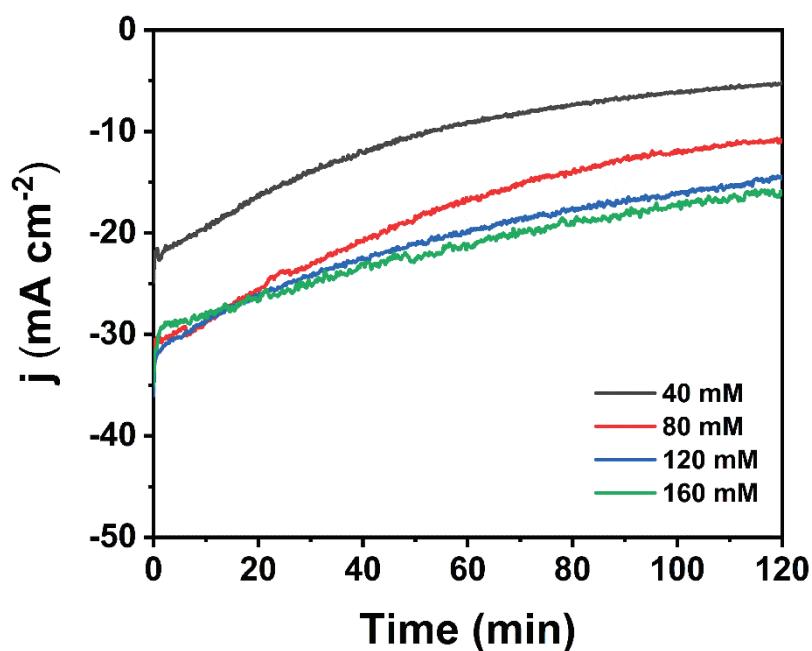


Fig. S15 The chronoamperometric curves of Cu/Ti at -0.57 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing different concentrations of pyruvate and 1.2 equiv. NH_2OH .

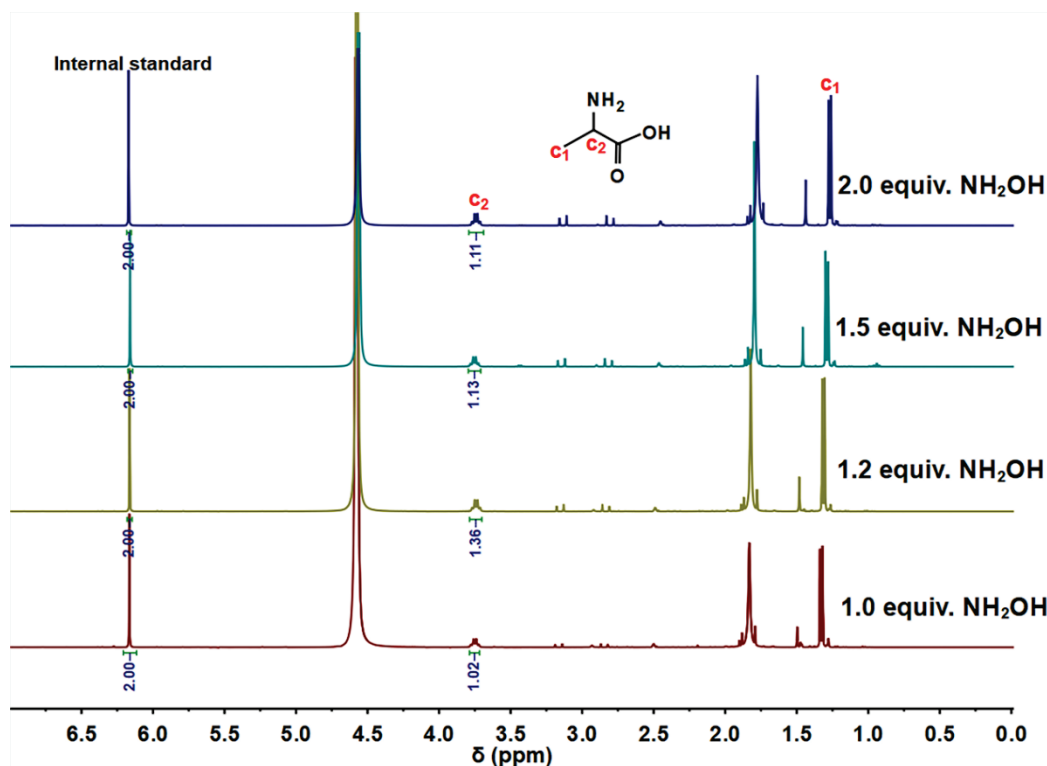


Fig. S16 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.57 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na_2SO_4 solution electrolyte (pH = 2.76) containing 80 mM pyruvate and different concentrations of $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

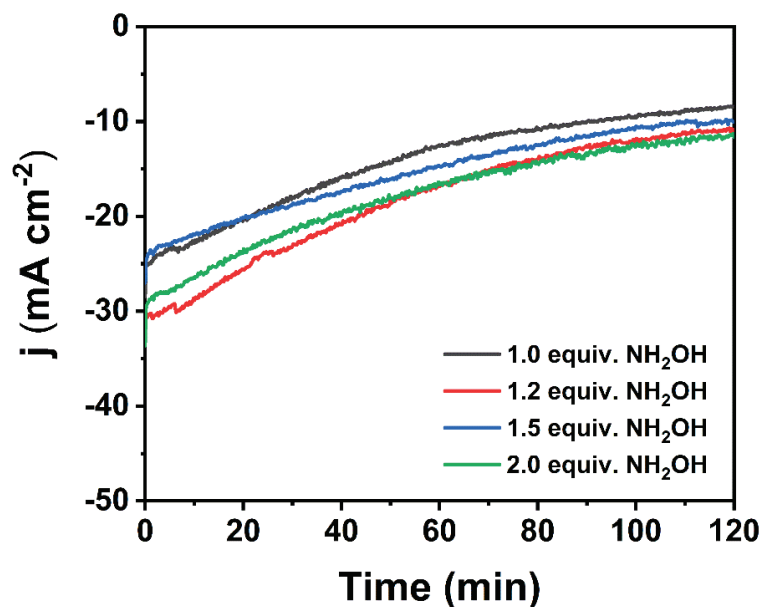


Fig. S17 The chronoamperometric curves of Cu/Ti at -0.57 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM pyruvate and different concentrations of $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

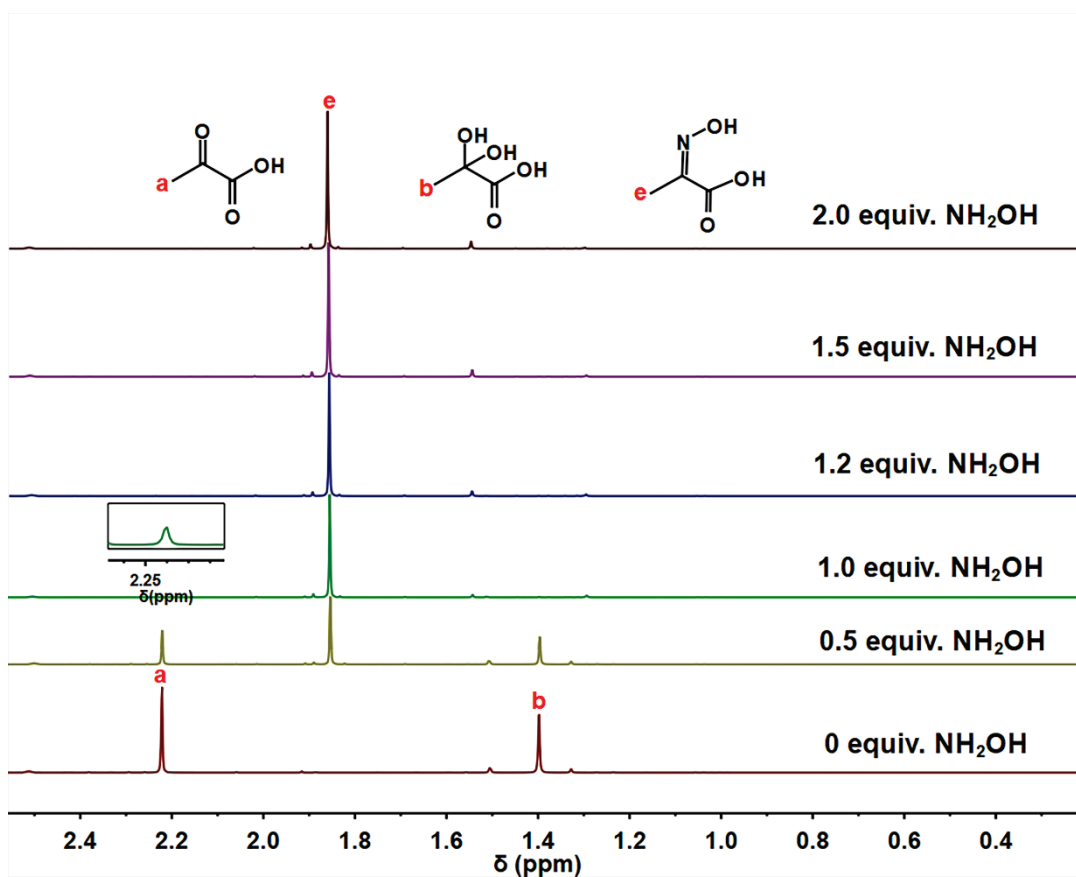


Fig. S18 ¹H NMR spectrum for 80 mM pyruvate without hydroxylamine, with 20 mM (NH₂OH)₂·H₂SO₄, 40 mM (NH₂OH)₂·H₂SO₄, 48 mM (NH₂OH)₂·H₂SO₄, 60 mM (NH₂OH)₂·H₂SO₄ and 80 mM (NH₂OH)₂·H₂SO₄ in 0.2 M Na₂SO₄ solution (pH = 2.76). The appearance of new peaks (e) was identified as oxime.

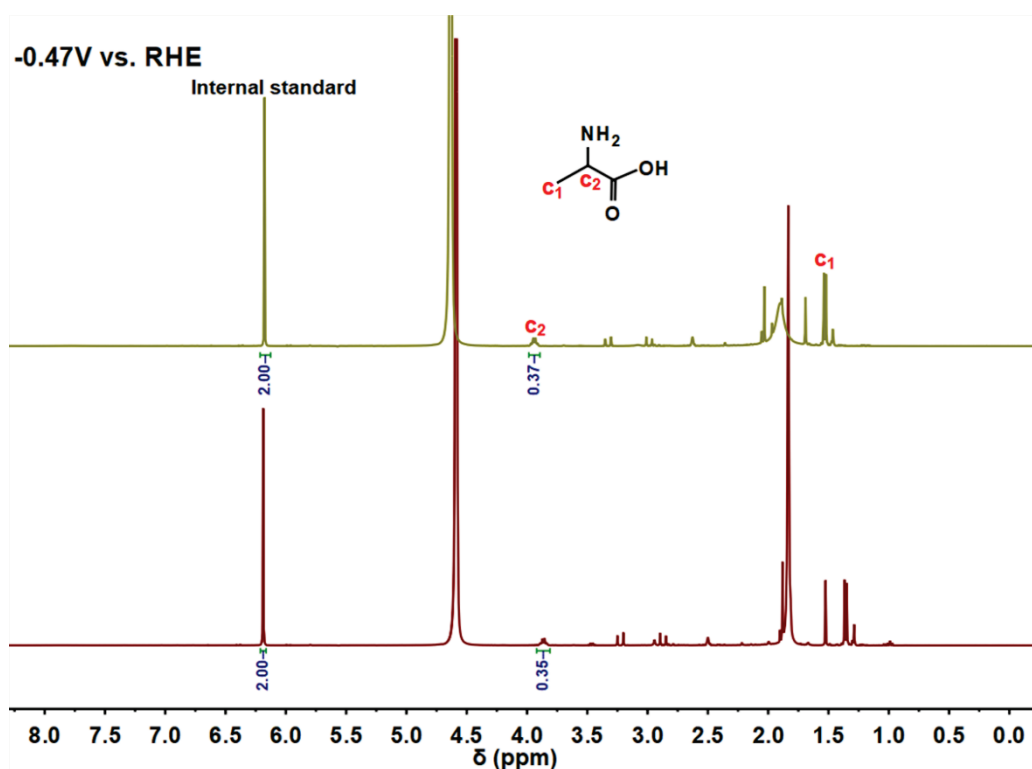


Fig. S19 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.47 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

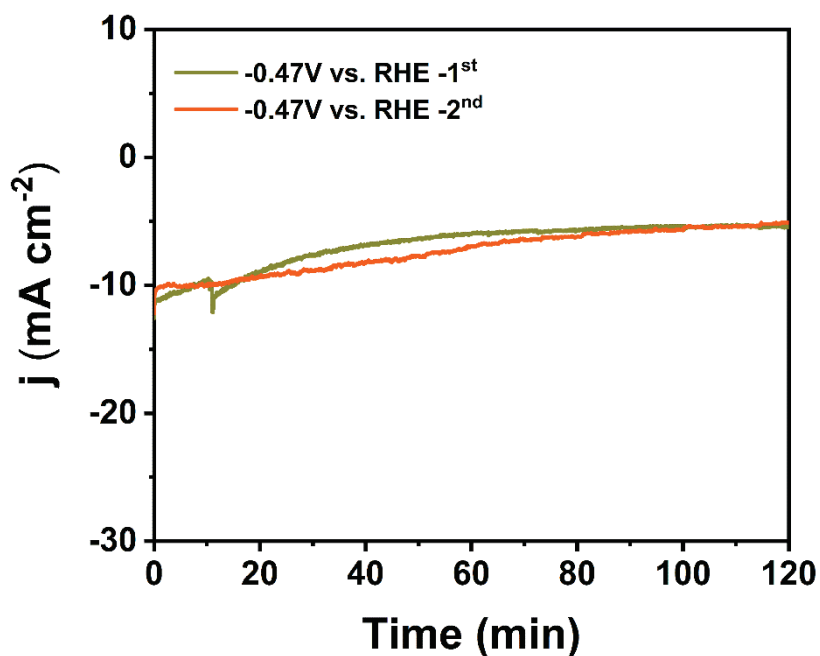


Fig. S20 The chronoamperometric curves of Cu/Ti at -0.47 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

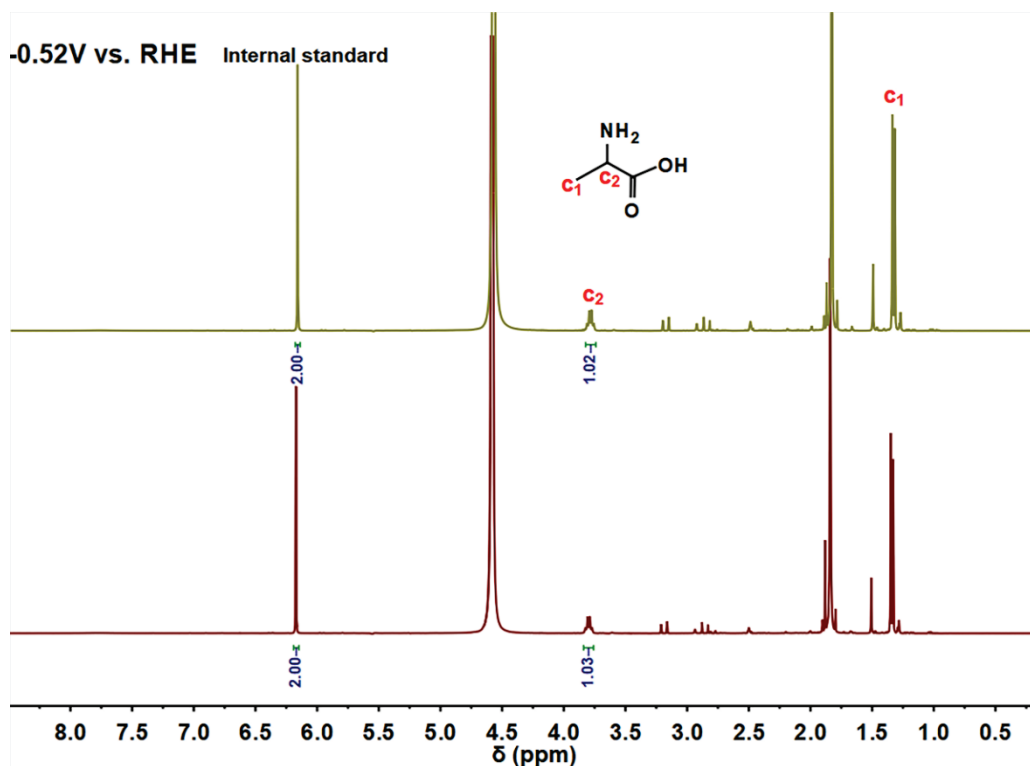


Fig. S21 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.52 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM pyruvate and 48mM $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$.

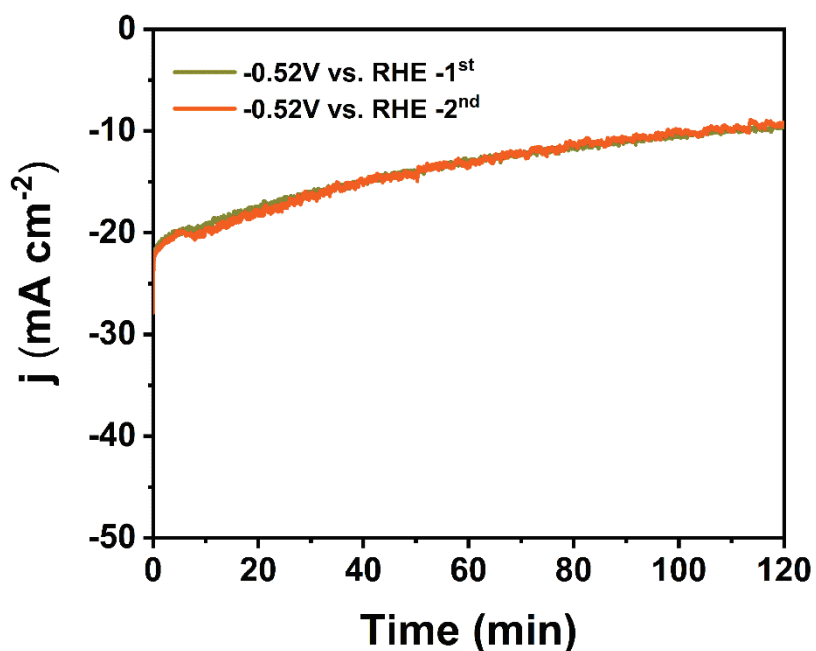


Fig. S22 The chronoamperometric curves of Cu/Ti at -0.52 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$.

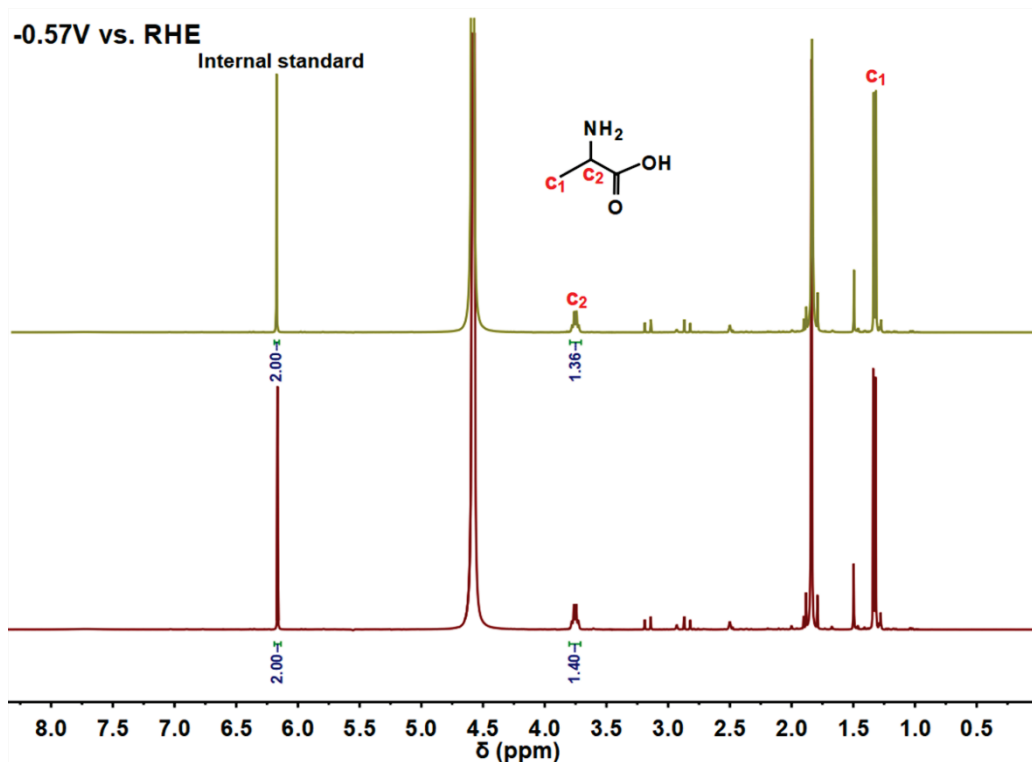


Fig. S23 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.57 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

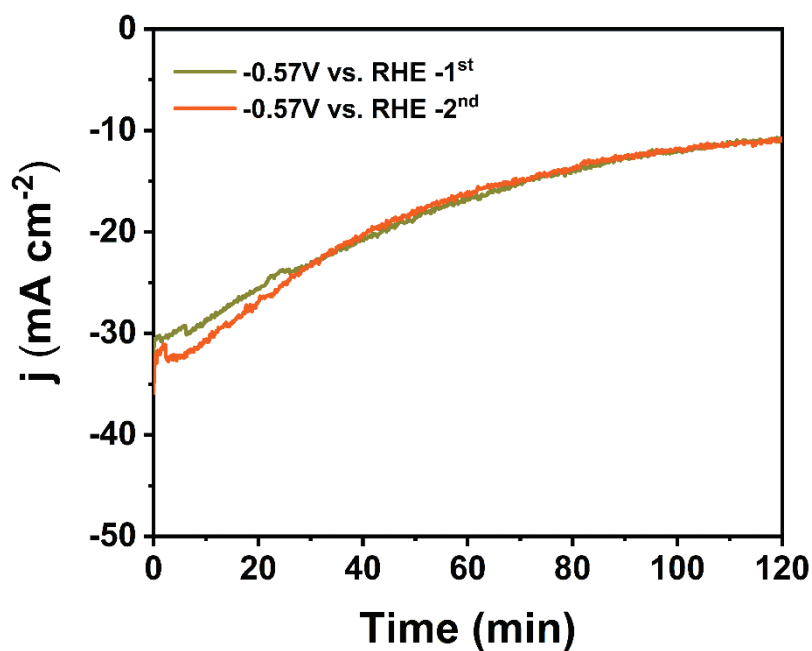


Fig. S24 The chronoamperometric curves of Cu/Ti at -0.57 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

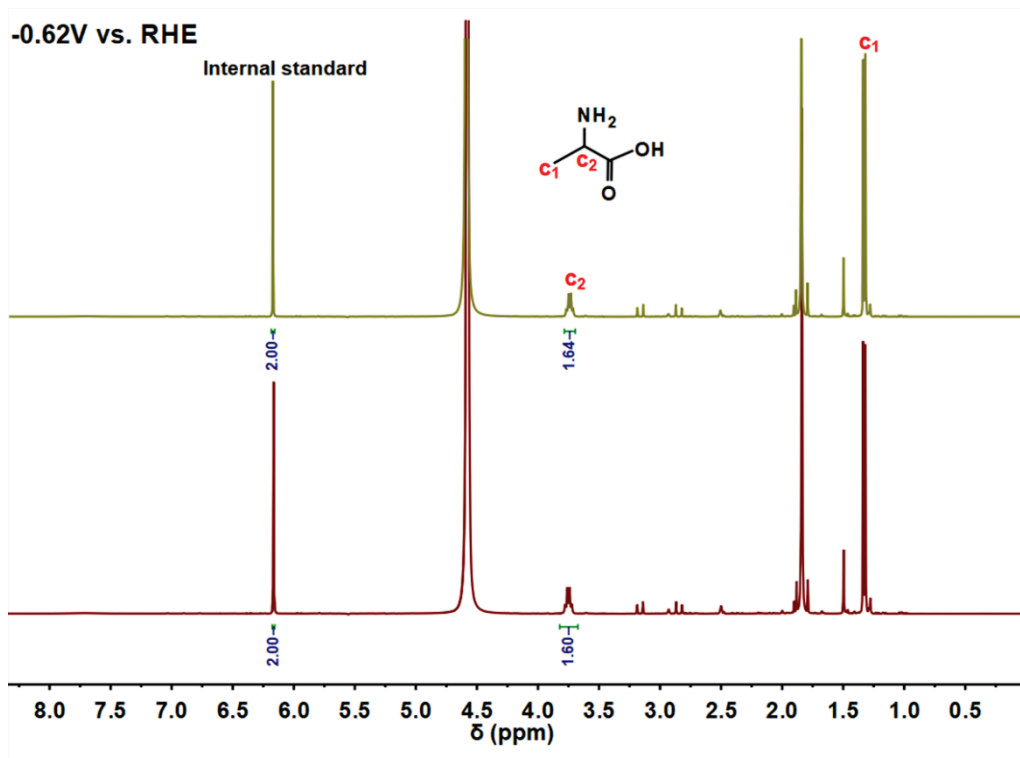


Fig. S25 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.62 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

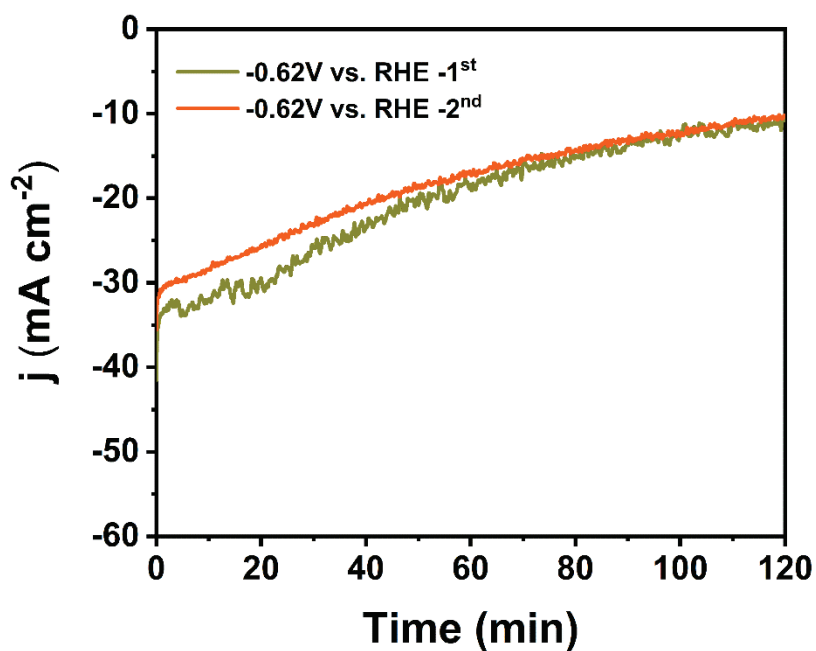


Fig. S26 The chronoamperometric curves of Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

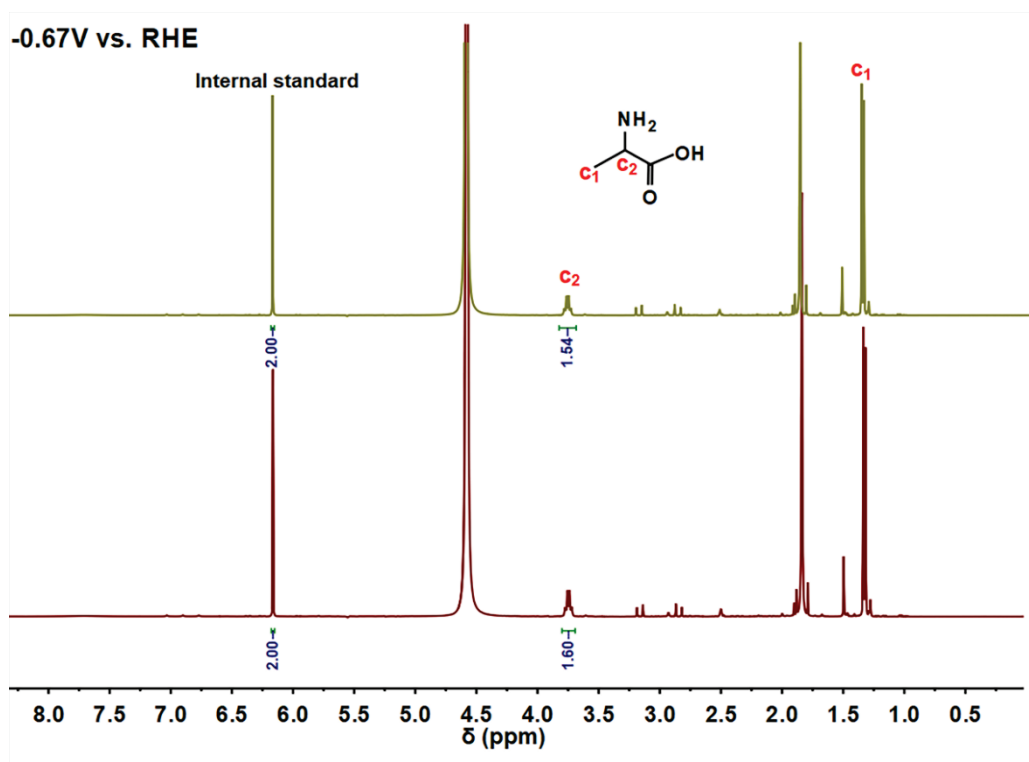


Fig. S27 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.67 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

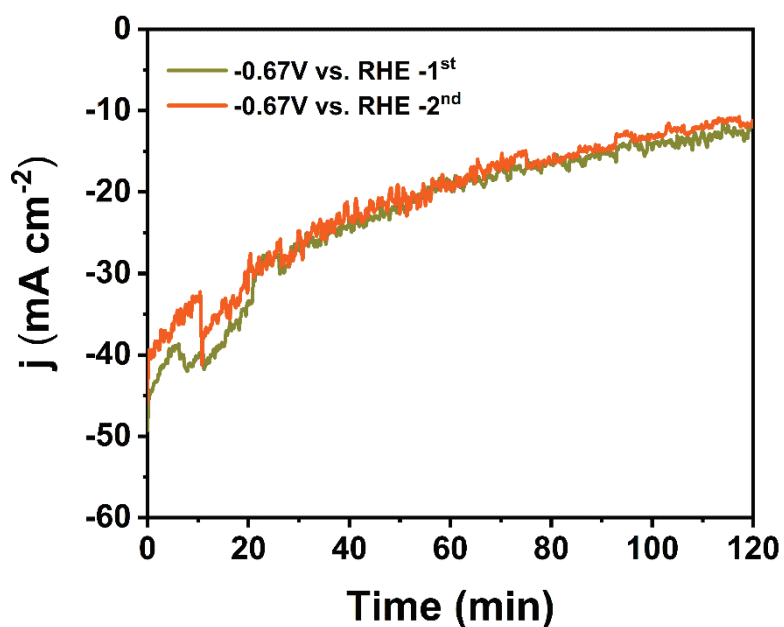


Fig. S28 The chronoamperometric curves of Cu/Ti at -0.67 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

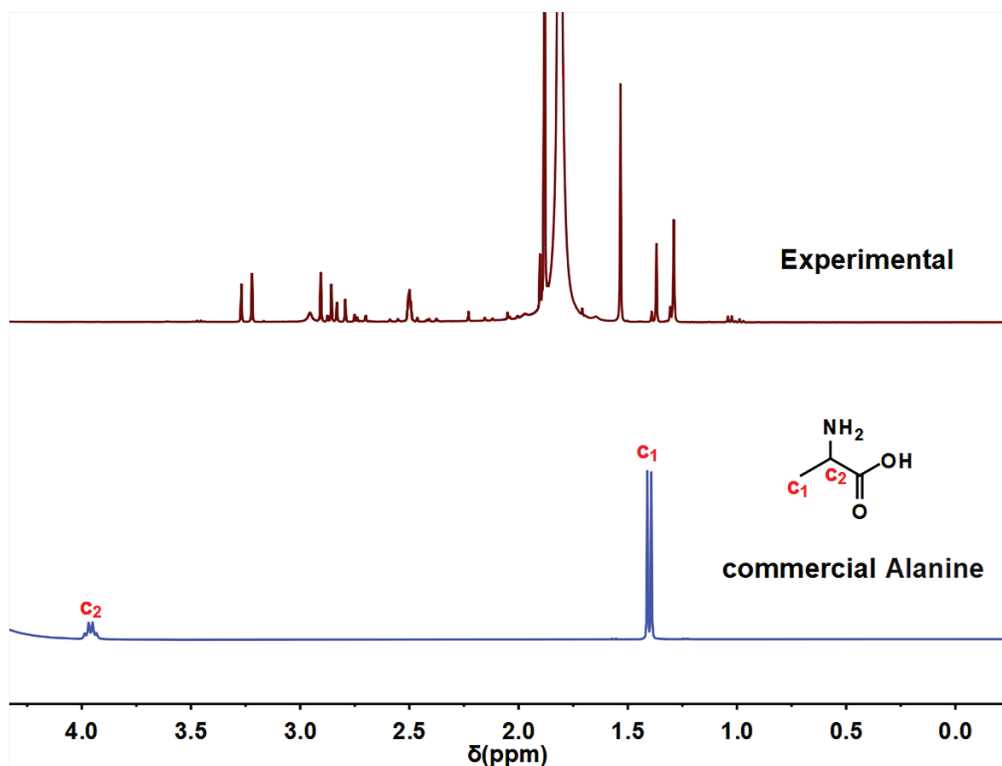


Fig. S29 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at open circuit voltage (OCV). Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

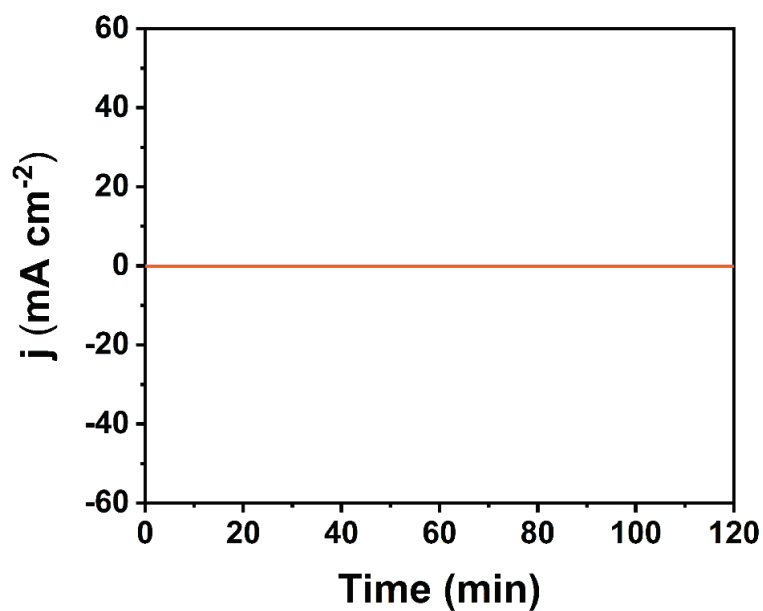


Fig. S30 The chronoamperometric curves of Cu/Ti at open circuit voltage (OCV) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

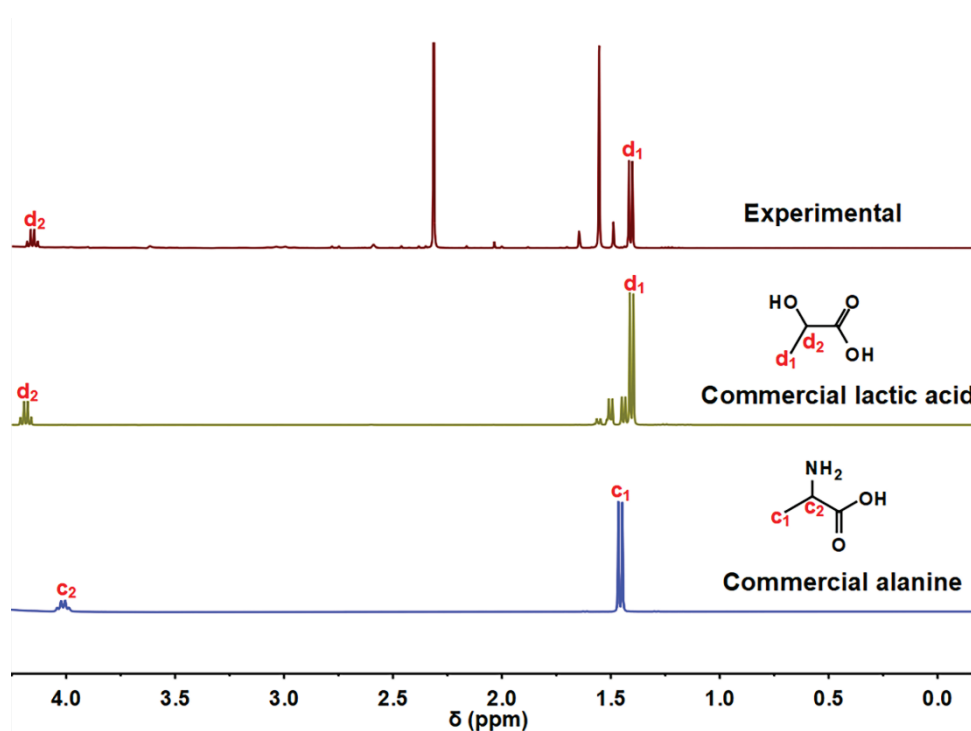


Fig. S31 ¹H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine at -0.62 V (vs. RHE). Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 2.76) containing 80 mM pyruvate (without NH₂OH).

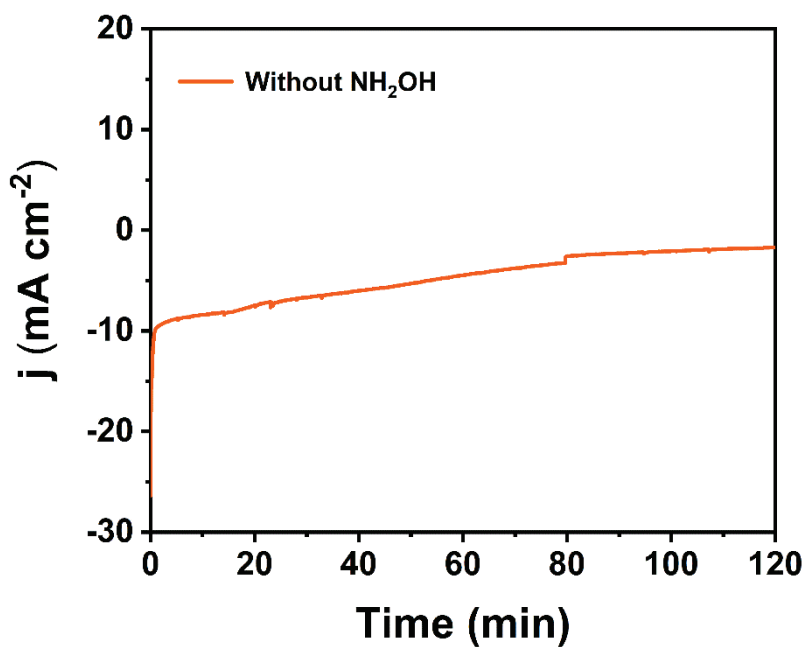


Fig. S32 The chronoamperometric curves of Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na₂SO₄ solution (pH = 2.76) electrolyte containing 80 mM pyruvate (without NH₂OH).

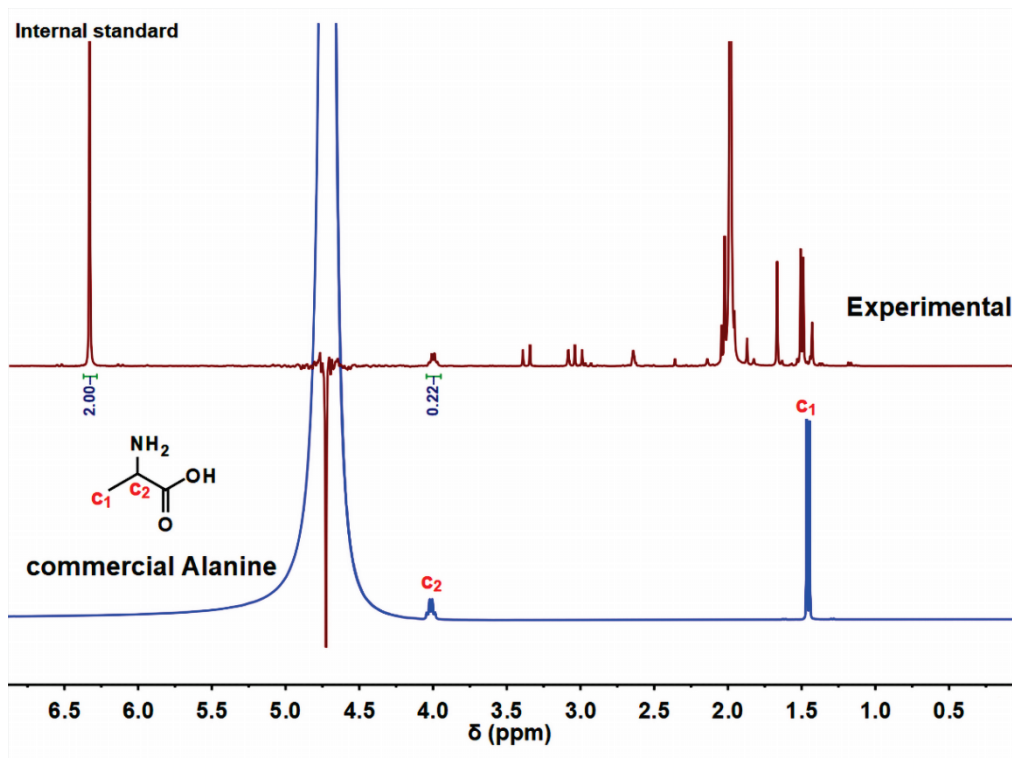


Fig. S33 ¹H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of alanine on Ti electrode. Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 2.76) containing 80mM pyruvate and 48 mM (NH₂OH)₂·H₂SO₄.

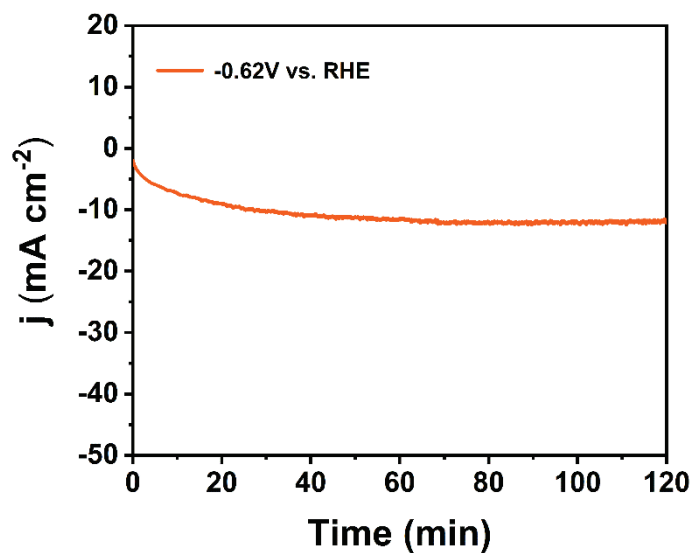


Fig. S34 The chronoamperometric curves of Ti at -0.62 V (vs. RHE) in 0.2 M Na₂SO₄ solution (pH = 2.76) electrolyte containing 80 mM pyruvate and 48 mM (NH₂OH)₂·H₂SO₄.

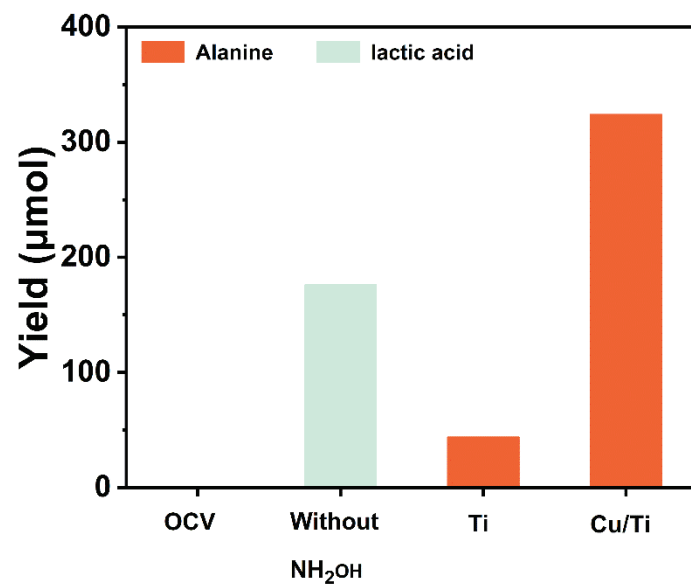


Fig. S35 The yield of alanine and lactic acid under different test conditions with Cu/Ti and control specimens.

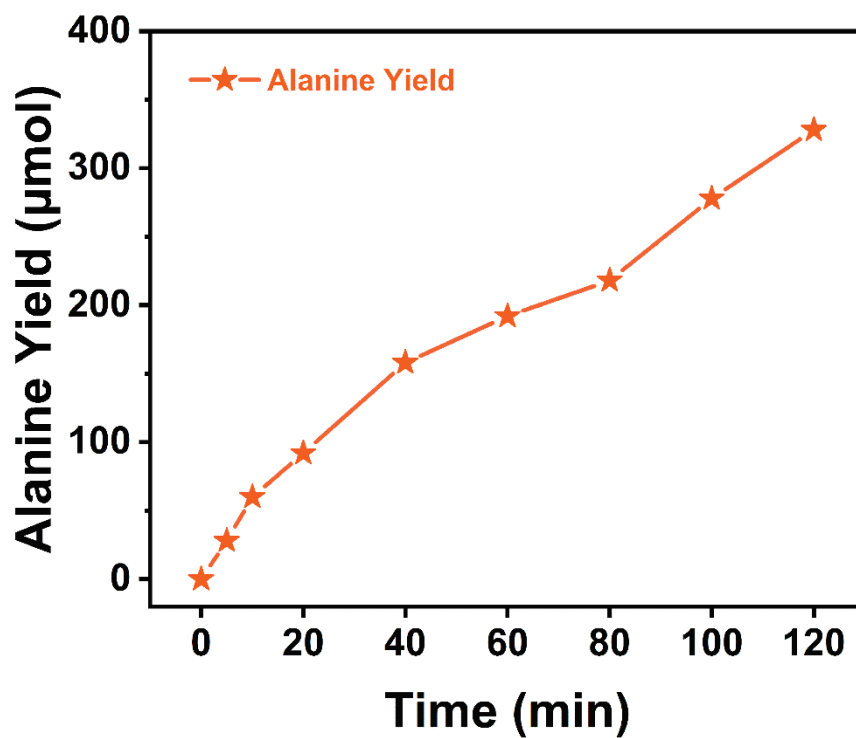


Fig. S36 Distribution of alanine yield over time alanine yield for Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na_2SO_4 solution ($\text{pH} = 2.76$) electrolyte containing 80 mM pyruvate and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

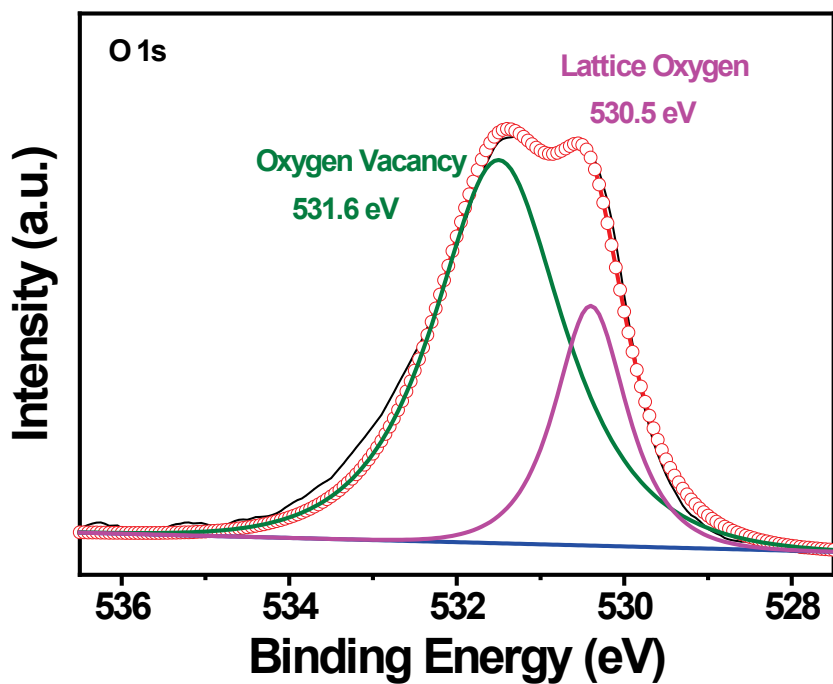
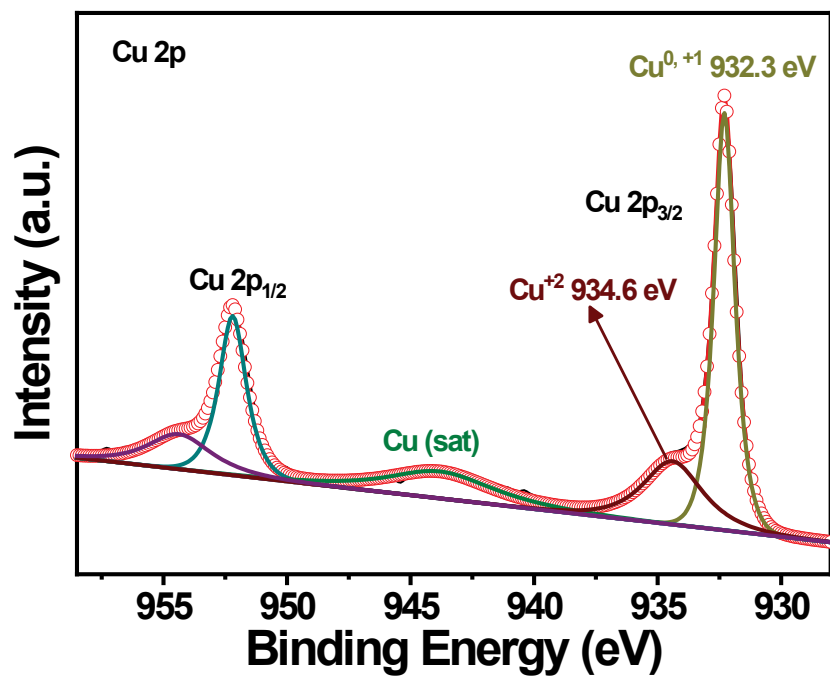


Fig. S37 High-resolution XPS spectrum of Cu 2p, O 1s for Cu/Ti after measured at -0.62V (vs. RHE)

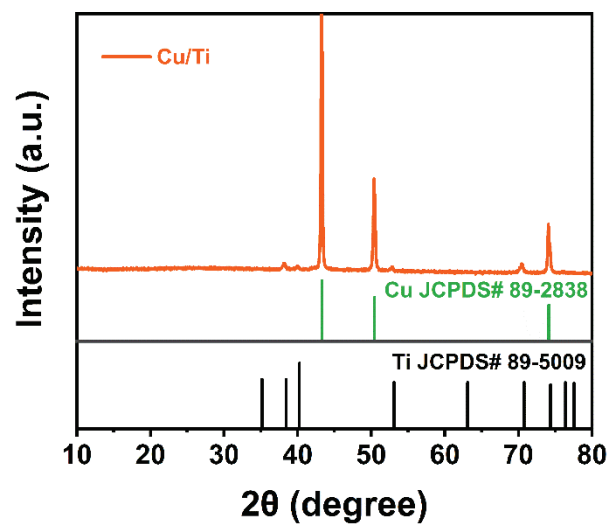


Fig. S38 XRD pattern of Cu/Ti after measured at -0.62 V (vs. RHE).

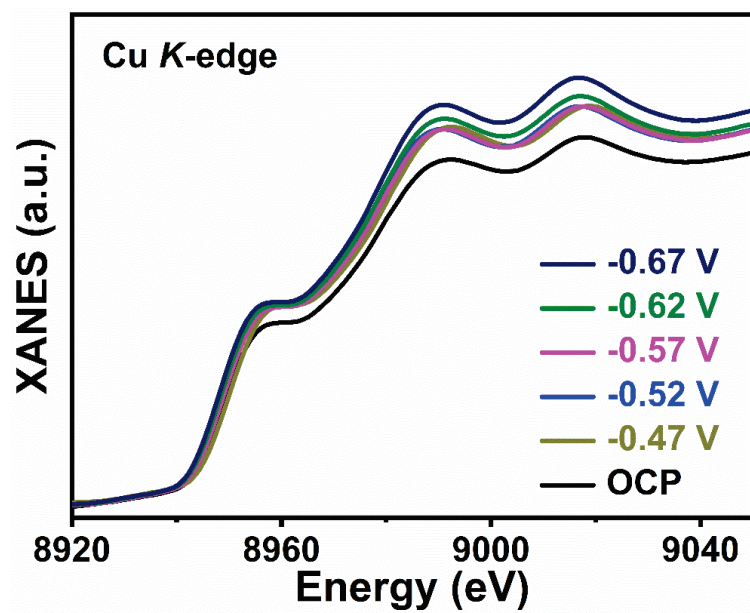


Fig. S39 *In-situ* Cu K-edge XANES spectra.

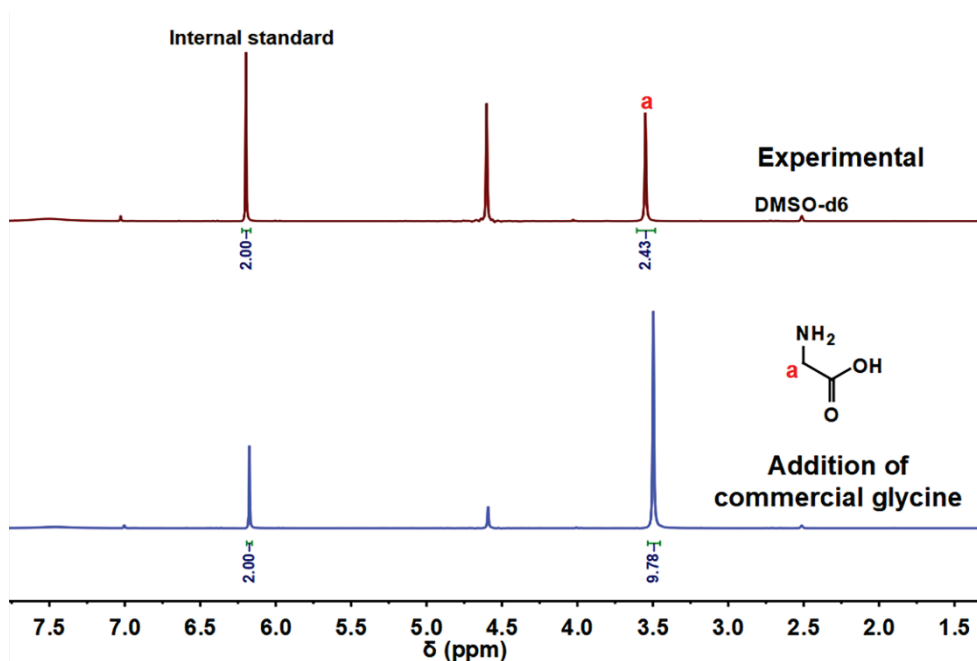


Fig. S40 ¹H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of glycine and electrolyte with standard glycine product. Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 2.76) containing 80 mM glyoxylic acid and 48 mM (NH₂OH)₂·H₂SO₄, applied potential at -0.62 V (vs. RHE).

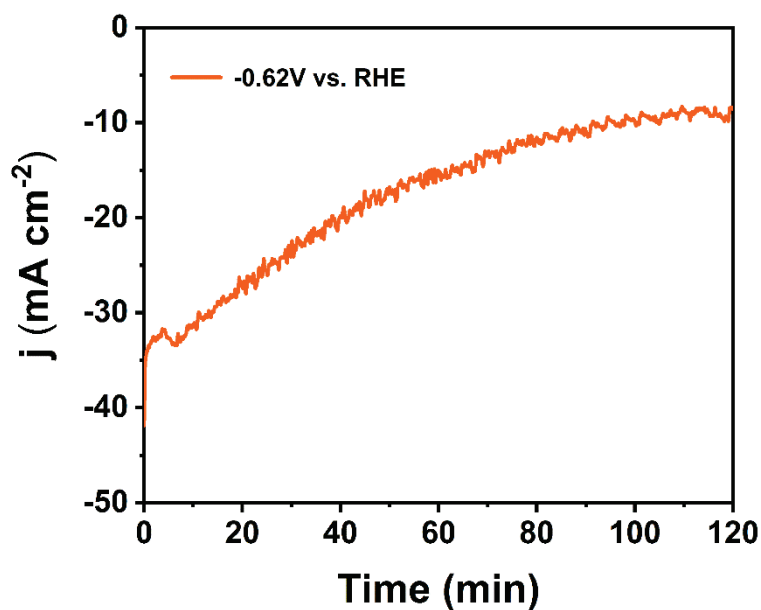


Fig. S41 The chronoamperometric curves of Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na₂SO₄ solution (pH = 2.76) electrolyte containing 80 mM glyoxylic acid and 48 mM (NH₂OH)₂·H₂SO₄.

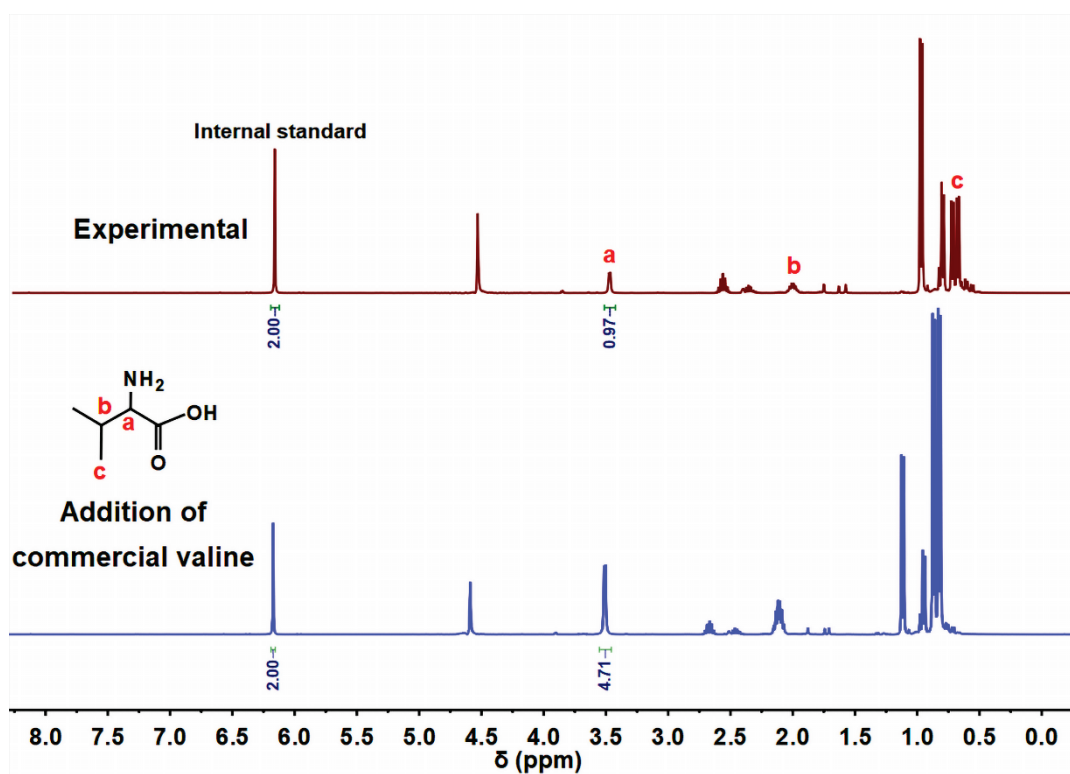


Fig. S42 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of valine and electrolyte with standard valine product. Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM 3-methyl-2-ketobutanoic acid and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$, applied potential at -0.62 V (vs. RHE).

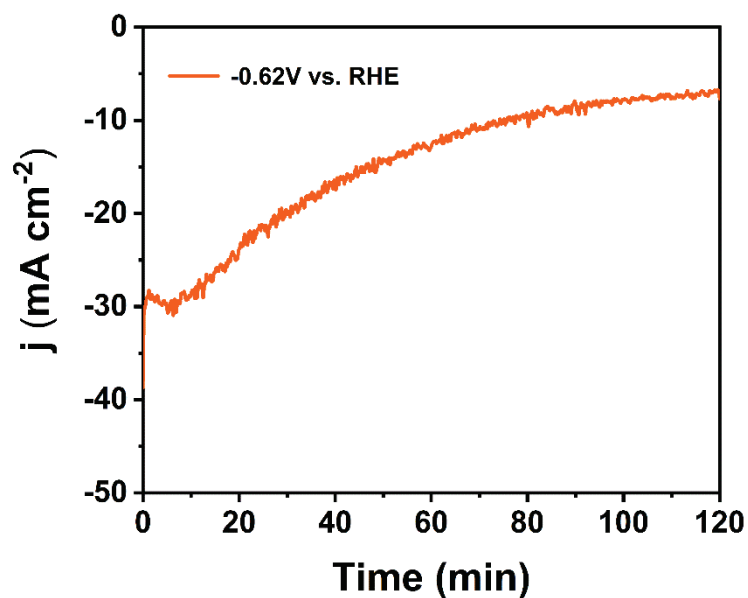


Fig. S43 The chronoamperometric curves of Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80mM 3-methyl-2-ketobutanoic acid and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

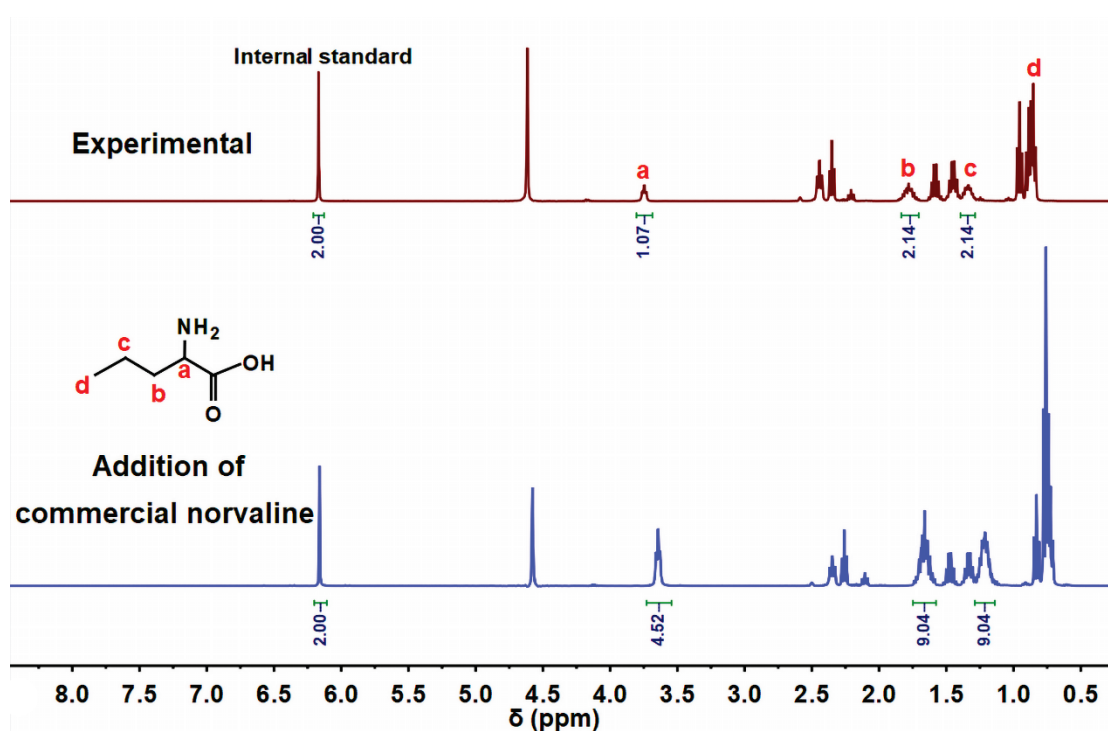


Fig. S44 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of norvaline and electrolyte with standard norvaline product. Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM 2-oxopentanoic acid and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$, applied potential at -0.62 V (vs. RHE).

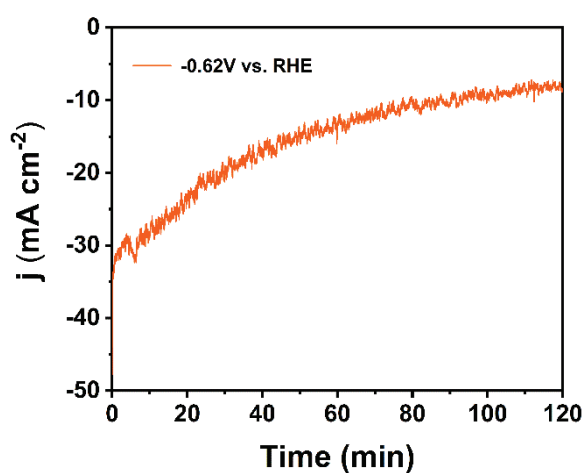


Fig. S45 The chronoamperometric curves of Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM 2-oxopentanoic acid and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

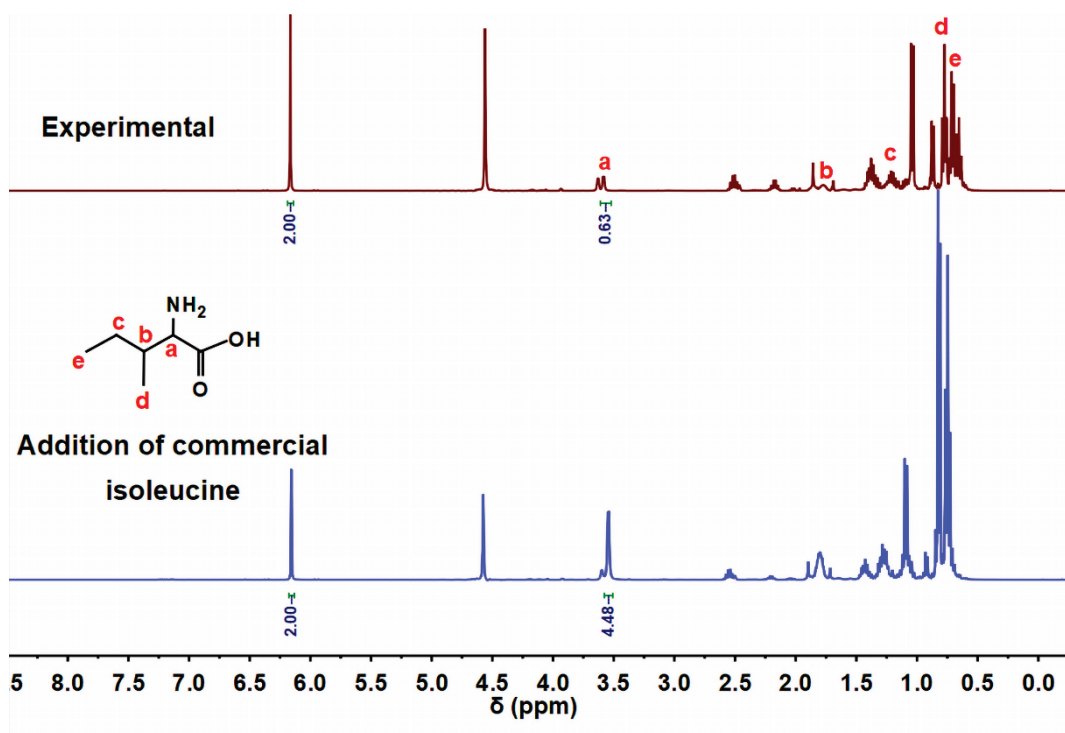


Fig. S46 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of isoleucine and electrolyte with standard isoleucine product. Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM 3-methyl-2-oxovaleric acid and 48 mM $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$, applied potential at -0.62 V (vs. RHE).

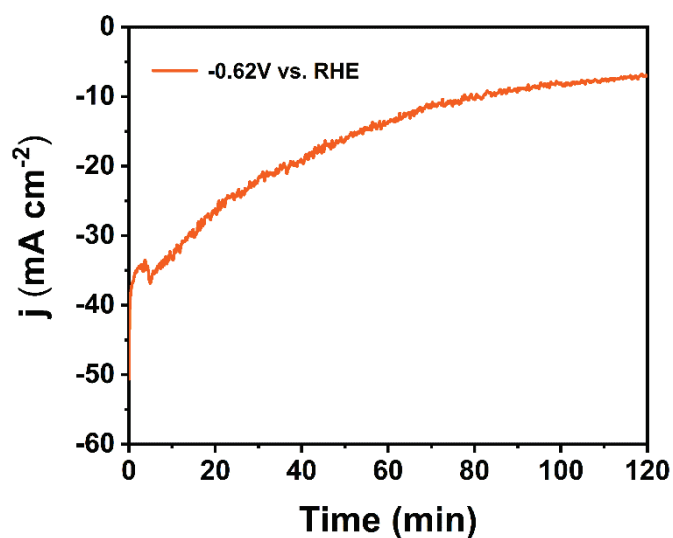


Fig. S47 The chronoamperometric curves of Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM 3-methyl-2-oxovaleric acid and 48 mM $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$.

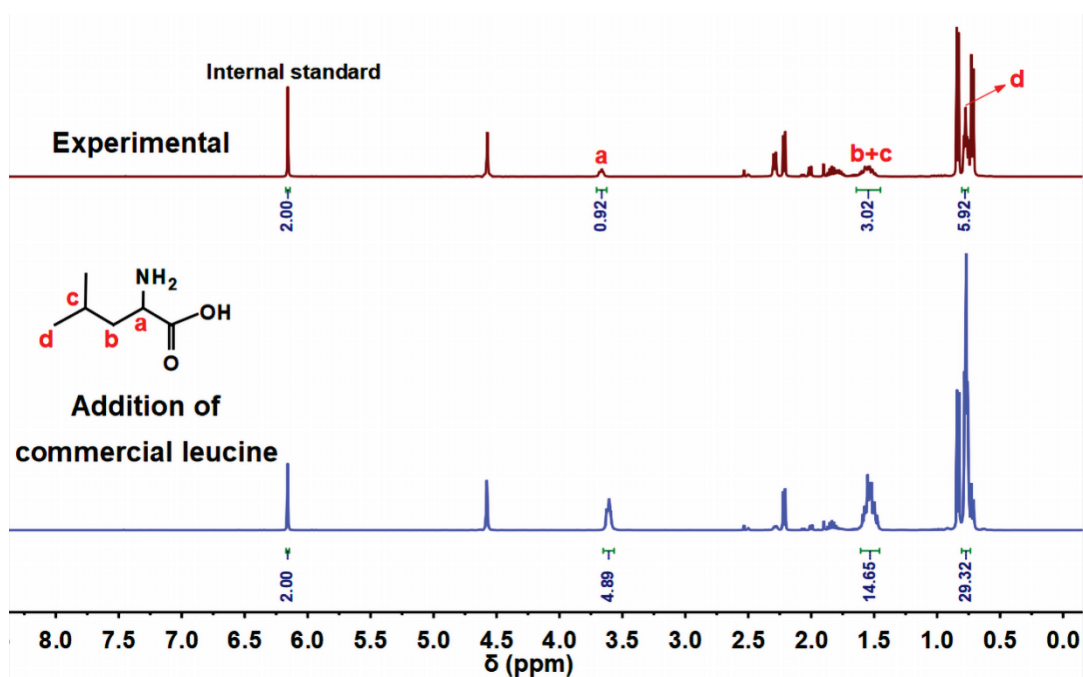


Fig. S48 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of leucine and electrolyte with standard leucine product. Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM 4-methyl-2-oxovaleric acid and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$, applied potential at -0.62 V (vs. RHE).

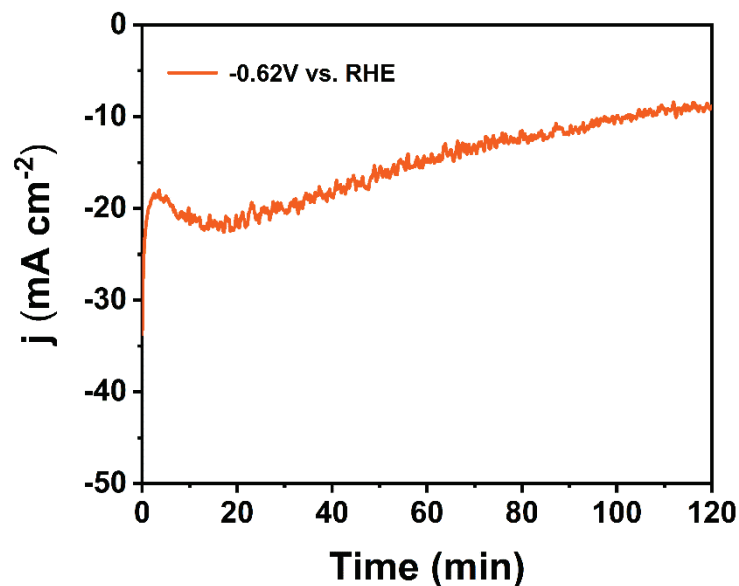


Fig. S49 The chronoamperometric curves of Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM 4-methyl-2-oxovaleric acid and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

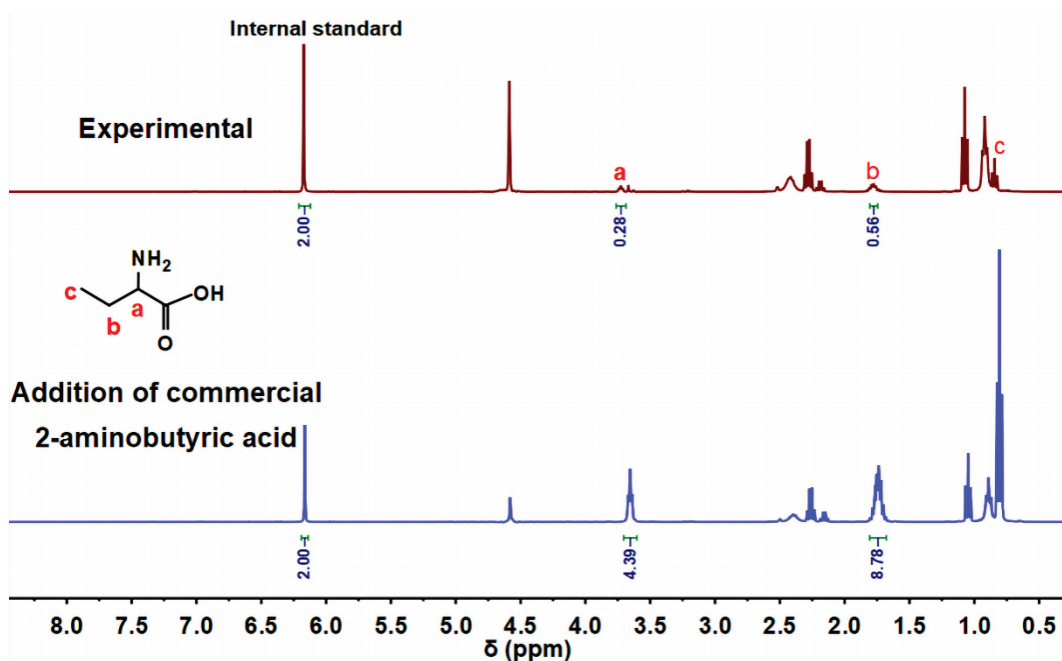


Fig. S50 ¹H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of 2-aminobutyric acid and electrolyte with standard 2-aminobutyric acid product. Reaction conditions: 10 mL 0.2 M Na₂SO₄ electrolyte (pH = 2.76) containing 80 mM 2-oxobutanoic acid and 48 mM (NH₂OH)₂·H₂SO₄, applied potential at -0.62 V (vs. RHE).

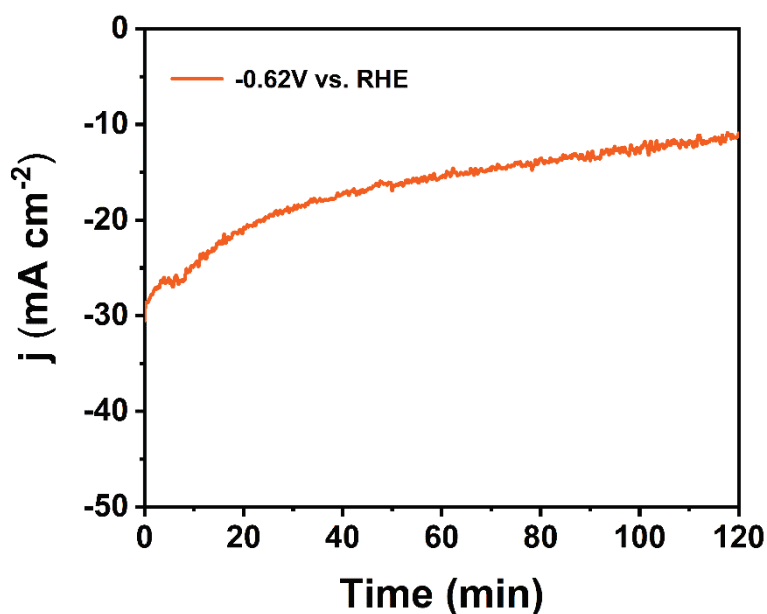


Fig. S51 The Chronoamperometric curves of Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na₂SO₄ solution (pH = 2.76) electrolyte containing 80 mM 2-oxobutanoic acid and 48 mM (NH₂OH)₂·H₂SO₄.

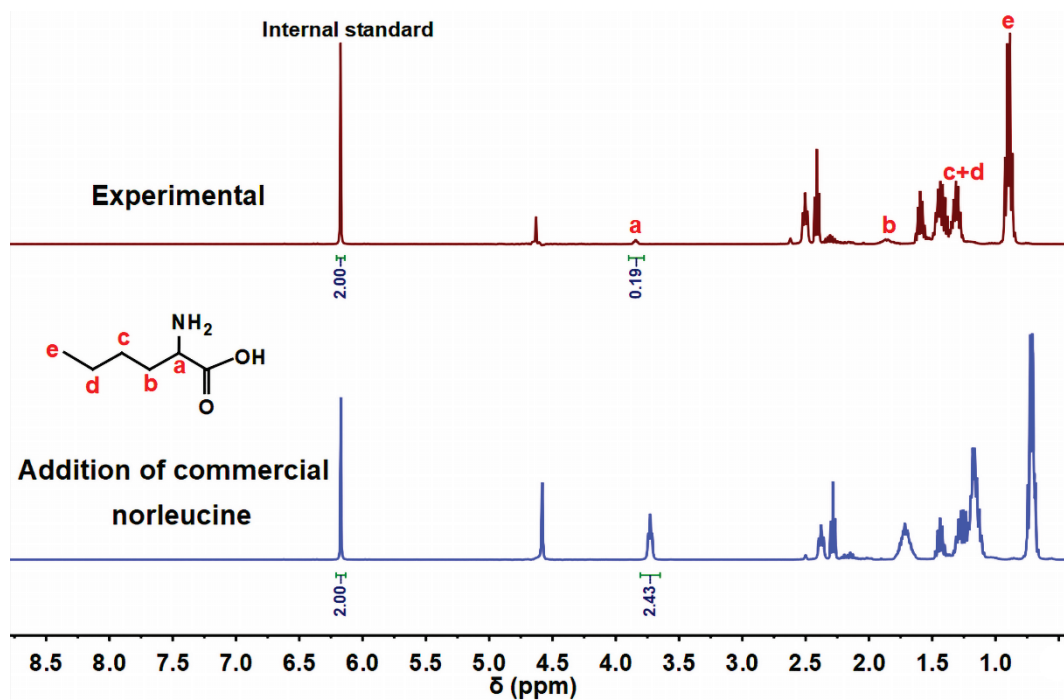


Fig. S52 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of norleucine and electrolyte with standard norleucine acid product. Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM 2-oxohexanoic acid and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$, applied potential at -0.62 V (vs. RHE).

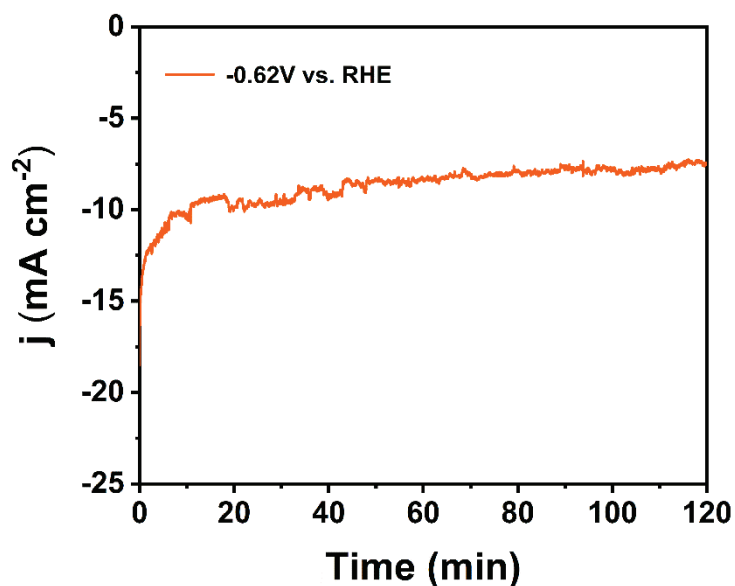


Fig. S53 The chronoamperometric curves of Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM 2-oxohexanoic acid and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

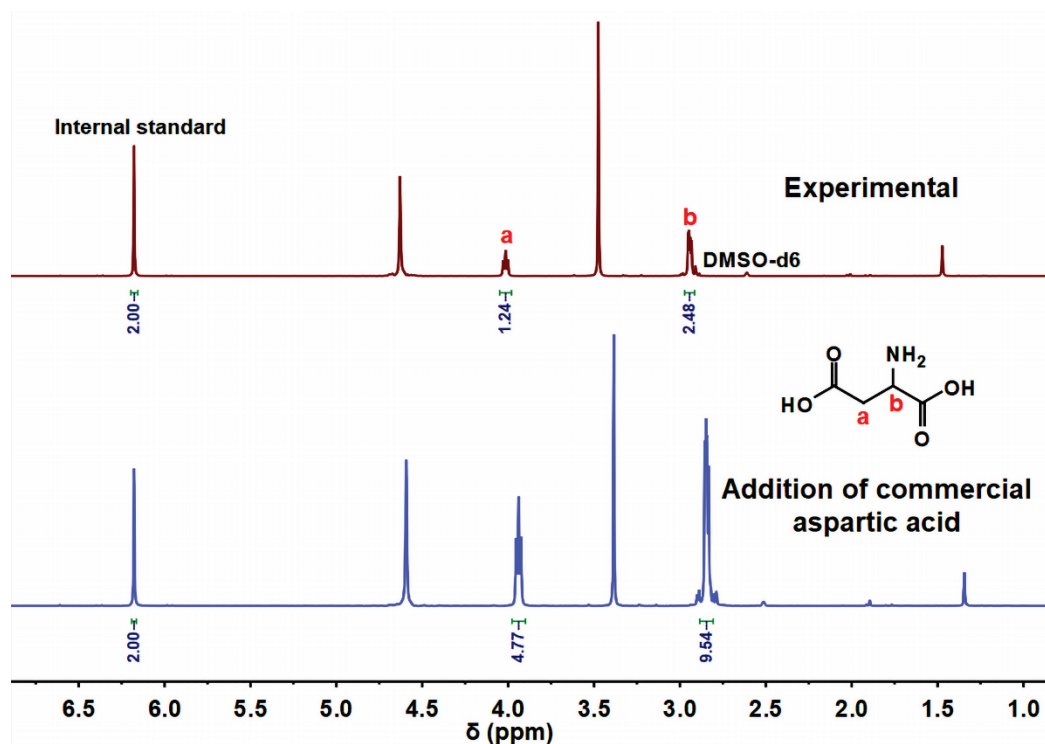


Fig. S54 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of aspartic acid and electrolyte with standard aspartic acid product. Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM oxaloacetic acid and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$, applied potential at -0.62 V (vs. RHE).

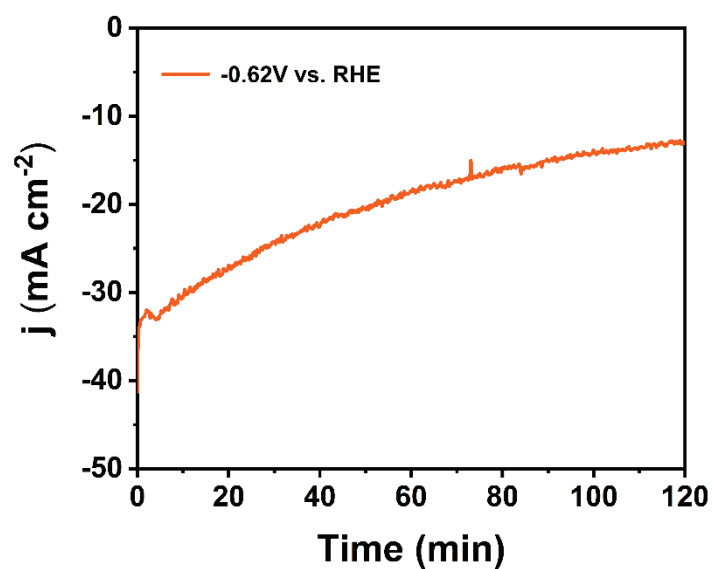


Fig. S55 The chronoamperometric curves of Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM oxaloacetic acid and 48 mM $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$.

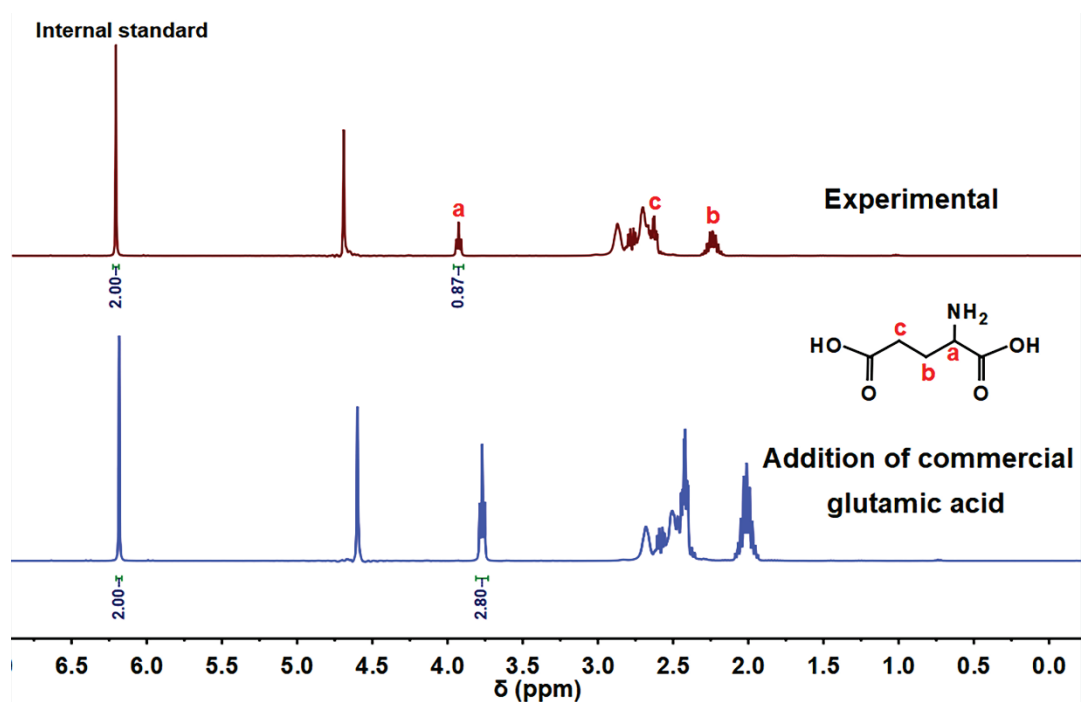


Fig. S56 ^1H NMR spectrum of electrolyte after 2 h electrocatalytic synthesis of glutamic acid and electrolyte with standard glutamic acid product. Reaction conditions: 10 mL 0.2 M Na_2SO_4 electrolyte (pH = 2.76) containing 80 mM α -ketoglutaric acid and 48 mM $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$, applied potential at -0.62 V (vs. RHE).

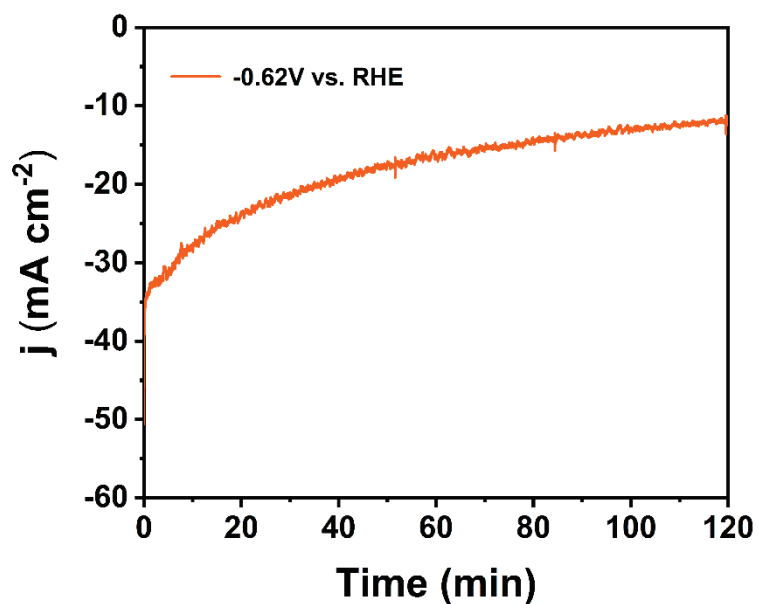


Fig. S57 The chronoamperometric curves of Cu/Ti at -0.62 V (vs. RHE) in 0.2 M Na_2SO_4 solution (pH = 2.76) electrolyte containing 80 mM α -ketoglutaric acid and 48 mM $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$.

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

	PH	Pyruvic acid conc.(mM)	NH ₂ OH amount (equiv. to pyruvic acid)	E (V vs RHE)	Yield (μmol)	Conv. (%)	FE (%)
a	0.63	160	1.2	-0.57	368.0	24.9	61.0
a	2.76	160	1.2	-0.57	326.0	20.4	80.7
a	4.53	160	1.2	-0.57	320.0	20.0	47.9
a	6.51	160	1.2	-0.57	374.0	23.4	59.1
a	8.54	160	1.2	-0.57	286.0	17.9	40.8
b	2.76	40	1.2	-0.57	160.0	40.0	80.2
b	2.76	80	1.2	-0.57	272.0	34.0	80.1
b	2.76	120	1.2	-0.57	310.0	25.8	79.7
b	2.76	160	1.2	-0.57	326.0	20.4	80.7
c	2.76	80	1.0	-0.57	204.0	25.5	76.4
c	2.76	80	1.2	-0.57	272.0	34	80.1
c	2.76	80	1.5	-0.57	226.0	28.3	78.6
c	2.76	80	2.0	-0.57	222.0	27.8	67.0
d	2.76	80	1.2	-0.47	72.0	9.0	55.1
d	2.76	80	1.2	-0.52	205.0	25.7	80.0
d	2.76	80	1.2	-0.57	276.0	34.5	80.7
d	2.76	80	1.2	-0.62	324.0	40.5	90.5
d	2.76	80	1.2	-0.67	312.0	39.1	77.4

Table S2. List of control experiments.









Entry	N-source	α -keto acids	E (V vs.RHE)	Time (h)	Product
1	—	pyruvate	-0.62	2	No product
2	NH ₂ OH	pyruvate	OCV	2	No product
3	NH ₂ OH	pyruvate	-0.62	2	Alanine

Reaction conditions: Cu/Ti as catalyst, 10 mL of 0.2 M Na₂SO₄ electrolyte (pH = 2.76) containing 80 mM pyruvate.

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, $\text{pH} = 2.76$.

Entry	E (V vs RHE)	C_{sub} (mM)	Substrate	Product	Yield (μmol)	Conv. (%)	FE (%)
1	-0.62	80			324.0	40.5	90.5
2	-0.62	80			243.0	30.4	74.1
3	-0.62	80			194.0	24.3	69.8
4	-0.62	80			214.0	26.8	73.5
5	-0.62	80			222.0	27.8	72.2
6	-0.62	80			184.0	23	64.8
7	-0.62	80			248.0	31	65.8
8	-0.62	80			174.0	21.8	51.3
9	-0.62	80			56.0	7.0	18.1
10	-0.62	80			38.0	4.8	23.4

Table S4. Comparison of Cu/Ti and other electrocatalysts in the electrocatalytic synthesis of pyruvate.

Substrate	C _{sub} (mM)	Nitrogen sources	Electrodes	Time (h)	product	Yield (μ mol)	FE
	80	(NH ₂ OH) ₂ H ₂ SO ₄	Cu/Ti	2		324.0	90.5
	20	NO	AD-Fe/NC	6		67.8	13.7
	20	(NH ₂ OH) ₂ H ₂ SO ₄	TiO ₂ /Ti mash	2		—	99
	—	NH ₃ /NH ₄ Cl	Hg	—		—	58