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# Microwave-assisted hydrothermal synthesis of amino acid-loaded Cu<sub>2</sub>O hybrid particles for CO<sub>2</sub> reduction electrocatalysis†

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Amino acid-loaded Cu<sub>2</sub>O hybrid particles were synthesized *via* microwave-assisted hydrothermal reaction for efficient CO<sub>2</sub> reduction. The amino acid-loaded Cu<sub>2</sub>O particles exhibited different selectivities in the CO<sub>2</sub> electrolysis products depending on type of loaded amino acid. Notably, as compared to amino acid-unloaded Cu<sub>2</sub>O particles, the L-histidine-loaded Cu<sub>2</sub>O hybrid particles exhibited an improvement of faradaic efficiency to 18.5% toward ethylene production.

## 1 Introduction

The increasing concentration of carbon dioxide (CO<sub>2</sub>) in the atmosphere is a critical environmental issue, because of its significant contribution to global warming and climate change.<sup>1,2</sup> Efforts to mitigate CO<sub>2</sub> emissions have led to research on various strategies, including carbon capture and storage, utilization of renewable energy sources, and development of technologies for CO<sub>2</sub> conversion and utilization.<sup>3</sup> Among the researched CO<sub>2</sub> mitigation strategies, electrochemical CO<sub>2</sub> reduction has garnered substantial attention as a promising approach to reducing atmospheric CO<sub>2</sub> levels.<sup>4</sup> Electrochemical CO<sub>2</sub> reduction offers several advantages, including the ability to operate under mild conditions, the potential to integrate with renewable energy sources, and the possibility to produce a wide range of value-added products. However, the efficiency and selectivity of the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) process are highly dependent on the type of the used catalyst. To improve the product selectivity of CO<sub>2</sub> electrolysis, the competing hydrogen evolution reaction (HER) must be minimized or suppressed. Therefore, developing effective electrocatalysts that can efficiently convert CO<sub>2</sub> into desired products *via* electrolysis while minimizing the unwanted HER is crucial for advancing the CO<sub>2</sub> electrolysis technology.

Recent advances in the design of catalysts for the electrochemical CO<sub>2</sub> reduction have focused on improving their activity, selectivity, and stability. Various materials, including metals,<sup>5</sup> metal oxides,<sup>6</sup> metal-organic frameworks,<sup>7</sup> and molecular composites,<sup>8</sup> have been investigated for their potential to facilitate CO<sub>2</sub> reduction. Among the catalysts studied for CO<sub>2</sub> reduction, copper-based catalysts have been reported as the catalysts that facilitate CO<sub>2</sub> reduction to produce hydrocarbons and alcohols; however, high overpotentials and low product selectivity are the challenges associated with the use of copper-based catalysts.<sup>9</sup> Cuprous oxide (Cu<sub>2</sub>O) is a particularly promising catalyst for CO<sub>2</sub> electrolysis, as it facilitates the production of ethylene (C<sub>2</sub>H<sub>4</sub>), an important industrial chemical.<sup>10</sup> The selectivity of CO<sub>2</sub> electrolysis for producing the desired products depends on the adsorptive power of reaction intermediates, such as carbon monoxide (CO), on the catalyst.<sup>11</sup> To control the adsorptive power of reaction intermediates, controlled physicochemical modifications, such as alloying<sup>12</sup> and decorating inorganic catalysts using organic materials,<sup>13</sup> have been explored. Previously, we explored the performance of electrodeposited Cu loaded with different types of amino acids toward electrocatalytic CO<sub>2</sub>RR.<sup>14</sup> We tested the product selectivities of five different electrodeposited Cu-based catalysts during CO<sub>2</sub> electrolysis. The faradaic efficiency (FE) of methane (CH<sub>4</sub>) production *via* CO<sub>2</sub> electrolysis was found to depend on the type of amino acid loading in the electrodeposited Cu. The electrodeposited Cu without any amino acid produced CH<sub>4</sub> with an FE of 55.0%, and the electrodeposited Cu loading L-histidine, a type of imidazole-containing amino acid, produced CH<sub>4</sub> with an FE of 67.6%.<sup>14</sup> In conclusion, introducing organic components into inorganic catalysts is an effective strategy for improving their product selectivities during CO<sub>2</sub> electrolysis.

Hydrothermal synthesis is one of the promising methods for synthesizing functional materials because it can provide control over the crystal orientation, particle size, and particle shape by

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adjusting the synthesis temperature and reaction time, by changing material source and precursor concentrations, and by adding structure-directing agents (SDAs).<sup>15</sup> Furthermore, the reactions involved in hydrothermal synthesis can be accelerated by microwave radiation and homogeneous heating, resulting in synthesizing high-purity crystals.<sup>16</sup> In this study, we synthesized hybrid particles of Cu<sub>2</sub>O loading seven different amino acids (Fig. 1)—Glycine (Gly), L-lysine (Lys), L-glutamine (Gln), L-arginine (Arg), L-citrulline (Cit), L-histidine (His), or L-phenylalanine (Phe)—using a microwave-assisted hydrothermal method and evaluated their product selectivities during CO<sub>2</sub> electrolysis. Loading amino acids into Cu<sub>2</sub>O particles can be anticipated to alter the adsorption of reaction intermediates on their surfaces, affecting their product selectivities during CO<sub>2</sub> electrolysis.

## 2 Experimental

### 2.1 Materials

Copper (II) acetate (Cu(CH<sub>3</sub>COO)<sub>2</sub>, 97.0%, Wako), D(+)-glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, 98.0%, Wako), glycine (Gly, C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>, 99.0%, Wako), L-lysine (Lys, C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>, 95.0%, Wako), L-glutamine (Gln, C<sub>5</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>, 99.0%, Wako), L-arginine (Arg, C<sub>6</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>, 98.0%, Wako), L-citrulline (Cit, C<sub>6</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>, 97.0%), L-histidine (His, C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>, 98.0%, Wako), L-phenylalanine (Phe, C<sub>9</sub>H<sub>11</sub>NO<sub>2</sub>, 99.0%, Wako) and potassium hydrogen carbonate (KHCO<sub>3</sub>, 99.5%, Wako) were purchased and used as received without further purification. Structures of amino acids used in this research showed in Fig. 1.

### 2.2 Synthesis of amino acids-loaded Cu<sub>2</sub>O hybrid particles

Aqueous precursor solutions containing 0.2 mol dm<sup>-3</sup> Cu(CH<sub>3</sub>COO)<sub>2</sub>, 0.1 mmol dm<sup>-3</sup> D(+)-Glucose, and 5.0 mmol dm<sup>-3</sup> of amino acids was put in glass vial, set to a Biotage® Initiator + Robot Eight for a 2.45 GHz microwave radiation to

promote reaction at 130 °C for 10 min. The resulting samples were centrifugally separated at 4500 rpm for 10 min, washed with ultrapure water and ethanol each for 3 times, and dried in an oven at 60 °C for 12 h under vacuum condition.

### 2.3 Characterizations

The crystal structures were determined by X-ray diffraction (XRD) spectroscopy with a scan range of  $\theta$ – $2\theta$  scans using a RIGAKU Ultima IV X-ray diffractometer. The average crystallite size of the synthesized samples was calculated from the Cu<sub>2</sub>O (111) diffraction peak, the most intense of the four peaks, using the Scherrer equation eqn (1):

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where  $\tau$ ,  $K$ ,  $\lambda$ ,  $\beta$ , and  $\theta$  represent the average crystallite size, shape factor ( $\approx 0.9$ ), X-ray wavelength (CuK $\alpha \approx 1.54$  Å), full width at half maximum, and Bragg angle, respectively. Scanning electron microscopy (SEM) measurements were conducted using a JEOL JSM-IT100. The X-ray photoelectron spectroscopy (XPS) measurements were conducted using a PHI 5000 VersaProbe (ULVAC-PHI, Japan) with monochromatic Al K $\alpha$  X-rays (1486.6 eV). The X-ray irradiation output was set to 25 W at 15 kV. In this process, the peak calibration was performed using the binding energy of C1s, set at 284.6 eV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping images were acquired by energy dispersive X-ray spectroscopy (EDS) using a Talos F200X G2 (Thermo Fisher Scientific) equipped with ADF-STEM systems and operated at 200 kV. Thermogravimetric (TG) analysis was performed by DTG-60 SHIMADZU. BET specific surface area was measured on a BELSORP MAX analyzer (MicrotracBEL, Japan) under liquid N<sub>2</sub> temperature conditions (77 K). Prior to BET measurements, deaeration was conducted at 80 °C for 10 h. The loading density of amino acid ( $L$ , mol g<sup>-2</sup>) was calculated by weight reduction ( $\Delta m$ , g) from TG analysis, molecular weight ( $M$ , mol L<sup>-1</sup>), and specific surface area ( $S$ , m<sup>2</sup> g<sup>-1</sup>) from BET measurements following eqn (2).

$$L = \frac{\Delta m \times M}{S} \quad (2)$$

Fourier transform infrared (FT-IR) spectra were measured by SHIMADZU IRTracer-100 with attenuated total reflection (ATR) unit.

### 2.4 Preparation of electrodes

For electrochemical measurements, synthesized particles were processed into electrodes. The particles (10 mg) were sufficiently dispersed in methanol (500 mg, Wako 99.5%) with Nafion ionomer (80 mg, 5 wt%, Sigma-Aldrich) by using ultrasonic equipment. The resulting slurry was drop-casted onto carbon paper (CP, SGL carbon, SIGRACET®), then dried at 70 °C for 12 h under vacuum condition. Prior to drop-casted, the CP was cut into pieces measuring 10 × 20 mm. The projected area

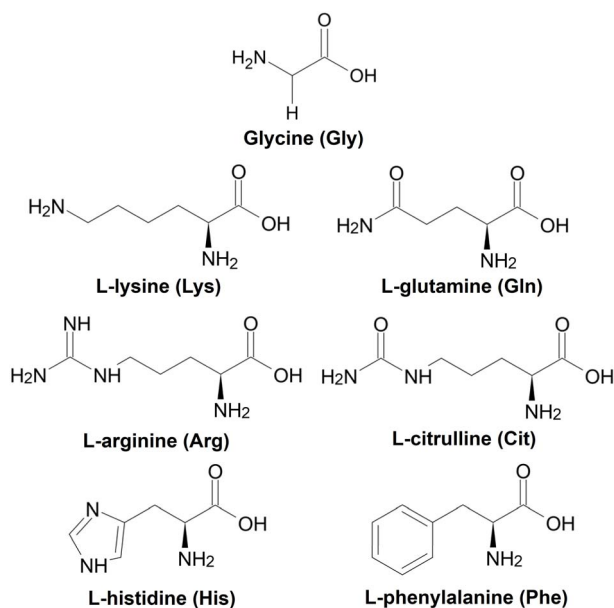


Fig. 1 Structures of the amino acids used in this study.



of the working electrode was confined to 1.0 cm<sup>2</sup>. This confinement was achieved using polyimide tape.

## 2.5 Electrochemical CO<sub>2</sub> reduction

The evaluation of the catalytic activities of electrochemical CO<sub>2</sub> reduction was conducted in a simple three electrodes H-type cells containing CO<sub>2</sub> saturated 13 mL aqueous KHCO<sub>3</sub> solution (pH ≈ 8.75) using an HZ-Pro S12 electrochemical measurement system (HOKUTO DENKO). For CO<sub>2</sub> saturating in electrolytic bath, the solution was continuously bubbled with highly pure CO<sub>2</sub> (99.995%) at a flow rate of 20 mL min<sup>-1</sup> for 20 min before conducting electrolysis. In the electrolytic cell, prepared each electrode, a silver–silver chloride (Ag/AgCl) electrode (3 mol dm<sup>-3</sup> KCl), and Pt wire were used as the working, reference, and counter electrodes, respectively. The cathode and anode were separated by anion exchanging membrane (ASTOM Corporation, NEOSEPTA AHA). The CO<sub>2</sub> electrolysis was conducted by constant potential electrolysis at -1.27 V vs. reversible hydrogen electrode (RHE) to ensure a charge of 3.0 C. The potential of vs. Ag/AgCl was converted to the RHE scale using eqn (3):

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + 0.208 \quad (3)$$

The gaseous products of CO<sub>2</sub> electrolysis, including CO<sub>2</sub> and H<sub>2</sub>, were analyzed using a gas chromatograph (GC) equipped with both a mass spectrometer (GCMS-QP2010 Ultra, SHIMADZU) and a thermal conductivity detector (GC-8AIT, SHIMADZU). 0.1 mL sample of the produced gas from the 12 mL headspace of the cell was extracted using a gas-tight syringe and then injected into the GC system for detailed compositional analysis. The CO<sub>2</sub> electrolysis products analysis was conducted at least three times in each condition.

The faradaic efficiency (FE) of gaseous products were calculated by following eqn (4),

$$\text{FE}(\%) = \frac{n \times F \times z}{Q} \times 100 \quad (4)$$

in which  $n$ ,  $F$ ,  $z$ , and  $Q$  represents the amount of moles of the product (mol), the Faraday's constant (96 485 C mol<sup>-1</sup>), the number of electrons transferred per molecule of the product, and the total charge passed during the electrolysis (C), respectively.

## 3 Results and discussion

Gly has a standard amino acid structure, containing both carboxyl and amino groups. Lys, Arg, and His are basic amino acids, whereas Gln, Cit, and Phe are neutral amino acids with similar structures. The synthesis of powdered samples, irrespective of the presence or absence of amino acids, was achieved *via* a hydrothermal process using microwave radiation. Indian red-colored powder samples were obtained; however, an orange-colored powder was obtained when L-His was used. The difference in the observed colors of the particles can be attributed to their different of the particle sizes, as discussed later. XRD patterns of the Cu<sub>2</sub>O powders synthesized with different

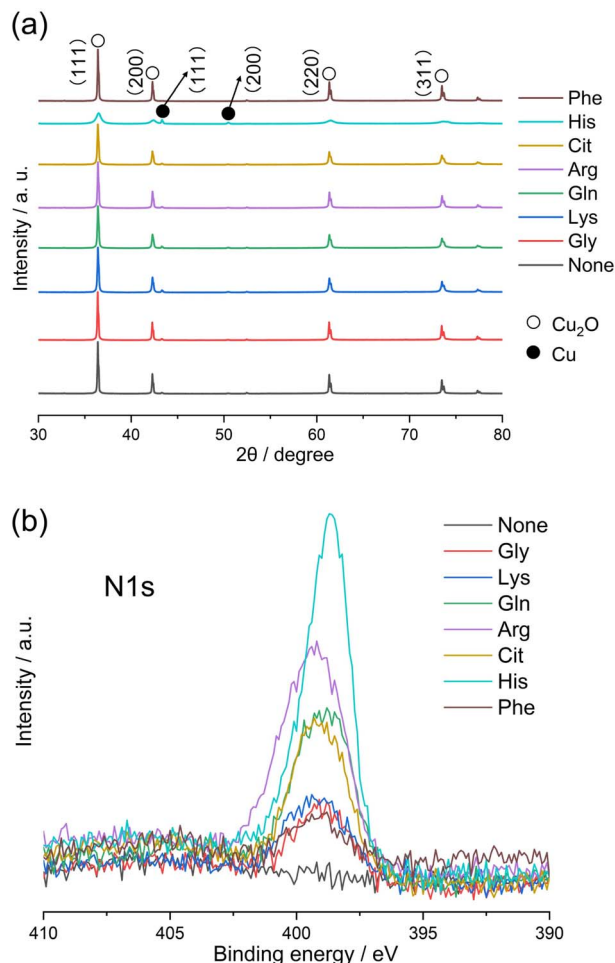


Fig. 2 (a) XRD patterns and (b) N1s core-level XPS spectra of the Cu<sub>2</sub>O particles synthesized with 5.0 mmol dm<sup>-3</sup> amino acids.

amino acids or without amino acids (hereafter referred to as None) are shown in Fig. 2a. The XRD patterns in Fig. 2a show peaks at approximately 36.4°, 42.3°, 61.4°, and 73.5°, corresponding to the (111), (200), (220), and (311) planes in Cu<sub>2</sub>O, respectively. XRD analysis also reveals the presence of low intensity peaks at 43.4° and 50.5°, attributed to the (111) and (200) planes in Cu, respectively (Fig. S1†). Note that His possesses an imidazole group and exhibits high electron-donating ability, functioning as a reducing agent.<sup>17</sup> In this experiment, the relatively stronger diffraction peak intensity exhibited by the His-loaded Cu<sub>2</sub>O particles can be attributed to the reducing property of His. The Cu<sub>2</sub>O particles synthesized with different amino acids, excluding those loaded with His, exhibit XRD patterns similar to that of None, with no observable changes attributable to the loaded amino acids. The presence of His in the Cu<sub>2</sub>O particles decreases the intensities and increases the widths of the Cu<sub>2</sub>O-related peaks. The average crystallite sizes in the synthesized Cu<sub>2</sub>O particles were calculated by applying the Scherrer equation on the (111) diffraction peak of Cu<sub>2</sub>O, and the results are shown in Fig. S2.† The crystallite sizes in None, Gly, and Phe are 916, 912, and 926 Å, respectively, which are almost identical. The crystallite size in Arg is 846 Å,





which is slightly smaller than that in None. The crystallite sizes in Lys, Gln, and Cit are 730, 713, and 734 Å, respectively, which are smaller than those in Arg. The crystallite size in His is 147 Å, which is the lowest value among all studied samples. To validate the loading of amino acids into Cu<sub>2</sub>O particles, N1s XPS spectra were measured for the Cu<sub>2</sub>O powders synthesized with different amino acids. Amino acid-loaded Cu<sub>2</sub>O hybrid particles should exhibit a peak in the N1s core-level XPS spectrum, indicating the loading of organic components. In Fig. 2b, no peaks can be observed in the N1s XPS spectrum corresponding to None, whereas a peak can be observed in the XPS spectra of the Cu<sub>2</sub>O particles synthesized with amino acids. The observed differences in the XPS peak shapes originate from the different functional groups present in the amino acids. Note that the functional groups (or side chain) of amino acids determine their chemical properties and how they interact with each other and their environment. Notably, the amino acids used in this study would not undergo decomposition while synthesizing Cu<sub>2</sub>O particles at a temperature of 130 °C because thermal decomposition of the utilized amino acids occurs in the temperature range of 185–280 °C.<sup>18</sup> The surface morphologies of the synthesized Cu<sub>2</sub>O particles were examined using SEM, and the results are shown in Fig. 3. SEM images show that None contains octahedron-shaped particles with sizes ranging from 3 to 5 μm (Fig. 3a), whereas Gly (Fig. 1b) and Phe (Fig. 3h) loaded

Cu<sub>2</sub>O particles having morphologies similar to that of None. Lys (Fig. 3c), Gln (Fig. 3d), Arg (Fig. 3e), and Cit (Fig. 3f) loaded Cu<sub>2</sub>O particles exhibit slightly deformed shapes with rounded appearances, which are more pronounced for Cit and Arg loaded Cu<sub>2</sub>O particles. Notably, the shape of Cu<sub>2</sub>O particles changes by a relatively greater extent upon His loading. The His-loaded Cu<sub>2</sub>O hybrid particles exhibit a spherical shape, with a radius of approximately 1 μm (Fig. 3g).

The catalytic activity and product selectivity of the synthesized amino acid-loaded Cu<sub>2</sub>O hybrid particles during electrochemical CO<sub>2</sub>RR were evaluated. Initially, the linear sweep voltammogram (LSV) curves were obtained for the synthesized amino acid-loaded Cu<sub>2</sub>O electrocatalyst in a CO<sub>2</sub>-purged 0.5 mol dm<sup>-3</sup> aqueous KHCO<sub>3</sub> solution (pH ≈ 8.75), and the results are shown in Fig. 4a. During LSV measurements, no notable differences occur between the electrodes despite the different morphologies and particle sizes of the different amino acid-loaded Cu<sub>2</sub>O catalysts. In the LSV curves illustrated in Fig. 4a,

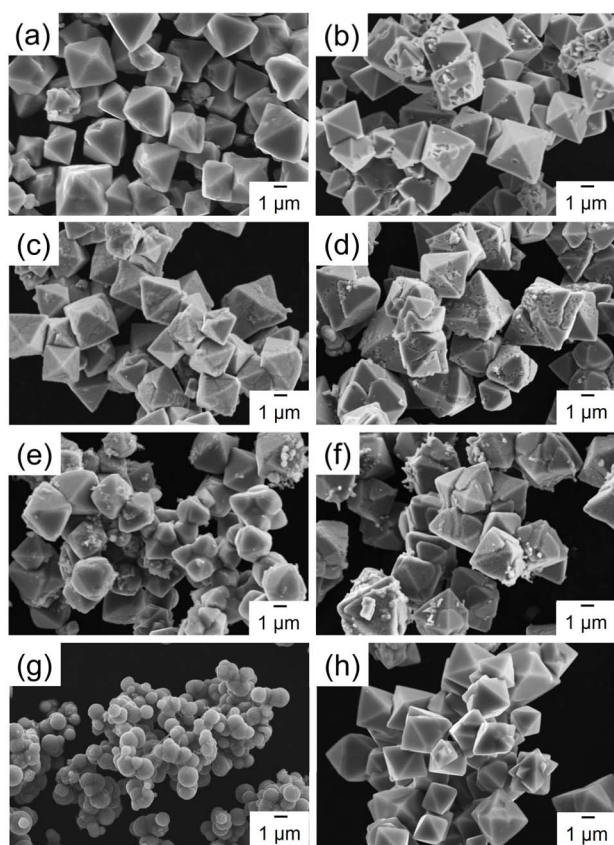


Fig. 3 SEM images of the Cu<sub>2</sub>O particles synthesized with 5.0 mmol dm<sup>-3</sup> amino acids: (a) None, (b) Gly, (c) Lys, (d) Gln, (e) Arg, (f) Cit, (g) His, and (h) Phe.

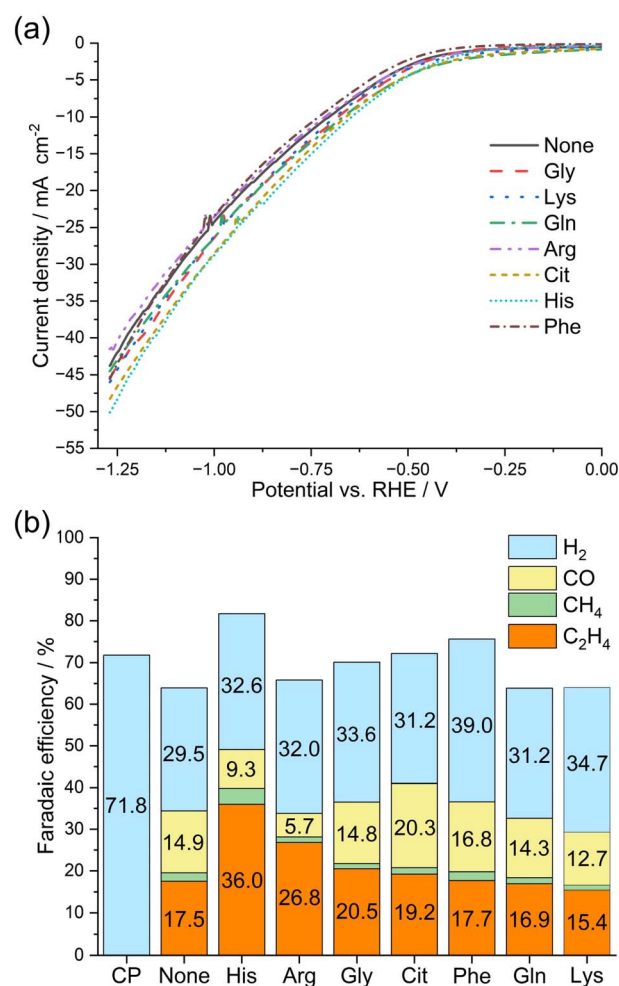


Fig. 4 (a) LSV curves of the Cu<sub>2</sub>O-based electrodes synthesized with 5.0 mmol dm<sup>-3</sup> amino acids at 10 mV s<sup>-1</sup> in a CO<sub>2</sub>-purged 0.5 mol dm<sup>-3</sup> aqueous KHCO<sub>3</sub> solution (pH ≈ 8.75). (b) FE values exhibited by the amino acid-loaded Cu<sub>2</sub>O-based electrodes toward gaseous products during CO<sub>2</sub> electrolysis under an applied potential of -1.27 V vs. RHE at 3.0 °C.



the current can be observed to rise at approximately  $-0.4$  V *vs.* RHE, and as the potential sweeps to negative, the current can be observed to decrease with almost identical slopes for all the investigated catalytic systems.  $\text{CO}_2$  electrolysis was conducted under a constant potential of  $-1.27$  V *vs.* RHE at  $3.0$  C in a  $\text{CO}_2$ -purged  $0.5$  mol  $\text{dm}^{-3}$  aqueous  $\text{KHCO}_3$  solution. The chronoamperograms that were measured during  $\text{CO}_2$  electrolysis and the FE values corresponding to the gaseous products obtained from  $\text{CO}_2$  electrolysis are presented in Figs. S3† and 4b, respectively. CP, which was prepared using a Nafion ionomer electrode and served as a reference, showed an electrolytic current of approximately  $-23$  mA  $\text{cm}^{-2}$ . The synthesized  $\text{Cu}_2\text{O}$  based electrodes shows higher current density than CP. Fig. 4b shows that all the synthesized  $\text{Cu}_2\text{O}$  electrocatalysis produced  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$  after  $\text{CO}_2$  electrolysis. Furthermore, Fig. 4b shows that all the synthesized amino acid-loaded  $\text{Cu}_2\text{O}$  electrocatalyst facilitate the electrochemical production of  $\text{H}_2$  with an FE of approximately 30% and exhibit an extremely low FE toward the electrochemical production of  $\text{CH}_4$ . Notably, the FE values exhibited by the synthesized amino acid-loaded  $\text{Cu}_2\text{O}$  electrocatalyst toward the production of  $\text{C}_2\text{H}_4$  are comparable to or higher than that exhibited by the None-based electrode (17.5%). The Gly, Cit, Phe, Gln, and Lys-based electrodes produced  $\text{C}_2\text{H}_4$  with FE values of 20.5, 19.2, 17.7, 16.9, and 15.4%, respectively, which are comparable to that obtained using the None-based electrode. Notably, the His and Arg-based electrodes facilitate the production of  $\text{C}_2\text{H}_4$  with high FE values of 36.0 and 26.8%, respectively. Especially, the His-based electrode facilitates the production of  $\text{C}_2\text{H}_4$  with an FE value, which is higher by 18.5% than that exhibited by the None-based electrode. The improvement observed in the production of  $\text{C}_2\text{H}_4$  demonstrated no correlation with the presence of Cu (Fig. S1†) or the average crystallite size (Fig. S2†) within the catalyst. The FE values exhibited by the electrodes toward  $\text{C}_2\text{H}_4$  production are not related to whether the loaded amino acids are basic or neutral, as the Lys-based electrode showed no improvement over the None-based electrode. The FE values toward CO production exhibited by the None, His, Arg, Gly, Cit, Phen, Gln, and Lys-based electrodes are 14.9, 9.3, 5.7, 14.8, 20.3, 16.8, 14.3, and 12.7%, respectively. The surface morphologies and XRD patterns of the electrodes fabricated using the  $\text{Cu}_2\text{O}$  particles synthesized with 0 and  $5.0$  mmol  $\text{dm}^{-3}$  His were examined before and after  $\text{CO}_2$  electrolysis (Fig. S4†). The XRD peak intensities can be observed to remain unchanged even after electrolysis (Fig. S4a†). The surface morphologies of the electrode can be also observed to remain unchanged even after electrolysis (Fig. S4b–e†). The results in Fig. S4,† confirm that the catalysts— $\text{Cu}_2\text{O}$  particles containing 0 and  $5.0$  mmol  $\text{dm}^{-3}$  His—on the fabricated electrodes remain unchanged during  $\text{CO}_2$  electrolysis. When using the His-loaded  $\text{Cu}_2\text{O}$  electrocatalysts, the enhanced selectivity of  $\text{CO}_2$  electrolysis toward  $\text{C}_2\text{H}_4$  formation can be associated with two plausible factors: (i) morphology and size control of  $\text{Cu}_2\text{O}$  particles; and (ii) the effect of loading His into  $\text{Cu}_2\text{O}$ . First, the morphology of  $\text{Cu}_2\text{O}$  particles changes from octahedral to spherical upon His loading, forming spherical-shaped His-loaded  $\text{Cu}_2\text{O}$  hybrid particles. In general, octahedral-shaped  $\text{Cu}_2\text{O}$  predominantly exposes the

(111) facet, which is known to facilitate proton adsorption and reduction, thereby resulting in the formation of formic acid and  $\text{CO}$ .<sup>19</sup> Notably, spherical-shaped His-loaded  $\text{Cu}_2\text{O}$  particles randomly expose various crystal facets across the surface. As a result, the reactivity tends to become uniform while, the selectivity for specific products decreases.<sup>19</sup> In addition, as the particle size decreases, the specific surface area increases, resulting in a larger surface area involved in the reaction. Therefore, the observed increase in the reaction rate can be anticipated to result from the high catalytic activity of His-loaded  $\text{Cu}_2\text{O}$  electrocatalysts, making it particularly useful for promoting CO production.<sup>20</sup> However, due to the presence of any defect sites, the reaction rate increases, but the selectivity would decrease.<sup>21</sup> As previously mentioned, during  $\text{CO}_2$  electrolysis for  $\text{C}_2\text{H}_4$  production, the generation of CO must occur first. Thus, the use of His-loaded  $\text{Cu}_2\text{O}$  electrocatalysts can be anticipated to improve CO generation by offering a larger surface due to the spherical shape of the particles and reduced particle size. Furthermore, loading His into  $\text{Cu}_2\text{O}$  particles contributed to stabilizing CO on the electrode, facilitating the production of  $\text{C}_2\text{H}_4$  instead of CO generation as the reaction progresses.

The synthesized His-loaded  $\text{Cu}_2\text{O}$  hybrid particles, which exhibited the highest selectivity toward  $\text{C}_2\text{H}_4$  production among the studied catalyst and a dramatically different morphology compared to that of None, were further examined. To investigate the effect of His concentration in the synthesizing precursor of  $\text{Cu}_2\text{O}$  on the production and selectivity during  $\text{CO}_2$  electrolysis, the concentrations of His were varied from 0, 2.0, 5.0, 10.0, and  $20.0$  mmol  $\text{dm}^{-3}$ . The concentration of 0 mmol  $\text{dm}^{-3}$  refers to the None. As the concentration of His increases, the intensity of the  $\text{Cu}_2\text{O}$ -related XRD peak decreases, the peak becomes broader (Fig. S5a†), and the average crystallite size decreases (Fig. S5b†). The SEM images demonstrating surface morphologies, along with HAADF-STEM images and EDS mappings of  $\text{Cu}_2\text{O}$  particles synthesized with different concentrations of His are illustrated in Fig. 5. The shape of the  $\text{Cu}_2\text{O}$  particles clearly changes from octahedral (Fig. 5a) to spherical after adding  $2.0$  mmol  $\text{dm}^{-3}$  His (Fig. 5d). Furthermore, HAADF-STEM images demonstrate that the particle size decreases as the concentrations of His increases up to  $10.0$  mmol  $\text{dm}^{-3}$  (Fig. 5k) and remains the same or becomes slightly larger at  $20.0$  mmol  $\text{dm}^{-3}$  (Fig. 5n). The particle size reaches approximately  $200$  nm for His concentrations below  $10.0$  mmol  $\text{dm}^{-3}$ . Certain amino acids function as capping agents in metal nanoparticle synthesis, enhancing dispersion and contributing to stabilization. Additionally, previous reports suggest that increasing the concentration of amino acids leads to smaller metal nanoparticle sizes.<sup>17</sup> A similar phenomenon can be anticipated to occur during the synthesis of amino acid-loaded  $\text{Cu}_2\text{O}$  particles in this study. The correlation between particle size and specific surface area was confirmed *via* BET analysis. The specific surface area values of His-loaded  $\text{Cu}_2\text{O}$  particles synthesized with 0, 2.0, 5.0, 10.0, and  $20.0$  mmol  $\text{dm}^{-3}$  His show 0.33, 1.11, 3.17, 4.74, and  $3.39$   $\text{m}^2$   $\text{g}^{-1}$ , respectively. These results demonstrated that a decrease in particle size leads to an increase in specific surface area (Fig. 6a). The presence

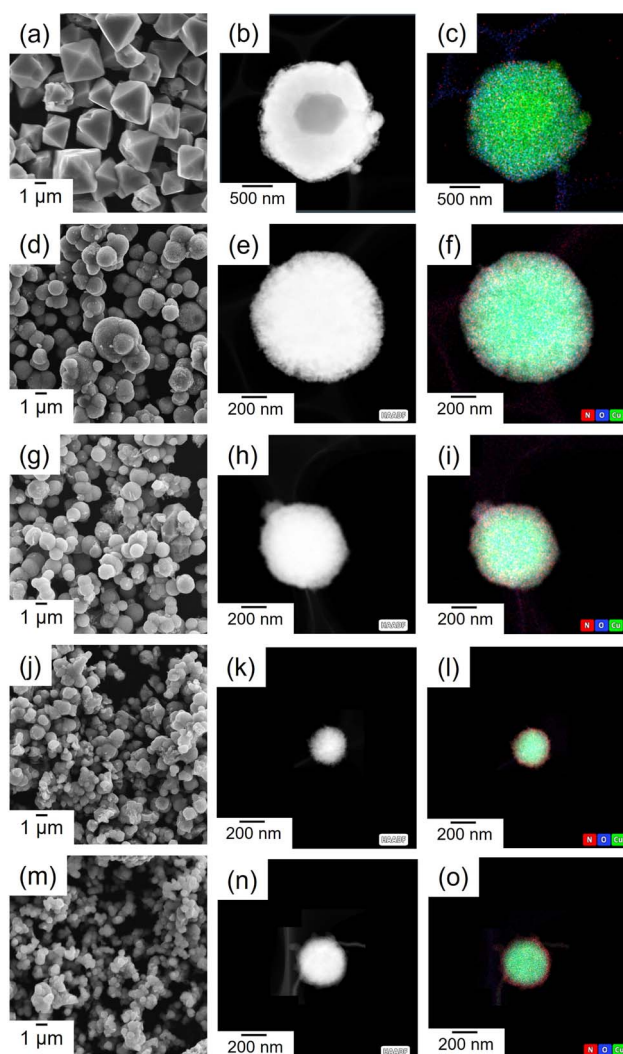


Fig. 5 SEM images, HAADF-STEM images, and EDS mappings (Cu: green, O: blue, N: red) of the  $\text{Cu}_2\text{O}$  particles synthesized with (a–c) 0, (d–f) 2.0, (g–i) 5.0, (j–l) 10.0, and (m–o) 20.0  $\text{mmol dm}^{-3}$  His.

of N atoms can be observed in the EDS maps obtained from the synthesized His-loaded  $\text{Cu}_2\text{O}$  powders. Indeed, the presence of N atoms cannot be observed in the EDS maps obtained from 0  $\text{mmol dm}^{-3}$  His. The presence or absence of N atoms can be clearly observed by comparing the EDS spectra of  $\text{Cu}_2\text{O}$  particles synthesized with 0  $\text{mmol dm}^{-3}$  and 10.0  $\text{mmol dm}^{-3}$  His (Fig. S6†). In the EDS maps shown in Fig. 3f, i, l, and o, N atoms are primarily present on the surface of  $\text{Cu}_2\text{O}$  particles, and the intensity of the N-related signal increases with the concentration of His. Thermogravimetric (TG) analysis demonstrated that the weight loss increased upon adding up to 10.0  $\text{mmol dm}^{-3}$  of His and remains almost constant upon adding His at concentrations 10.0 and 20.0  $\text{mmol dm}^{-3}$  (Fig. S7†). Based on the weight loss and specific surface area of each particle, His loading density of His-loaded  $\text{Cu}_2\text{O}$  particles synthesized with 0, 2.0, 5.0, 10.0, and 20.0  $\text{mmol dm}^{-3}$  were calculated as 0, 3.62, 2.07, 2.72, and 3.81  $\text{mol g}^{-1}$ , respectively (Fig. 6b). The loading density of His did not exhibit any direct correlation with

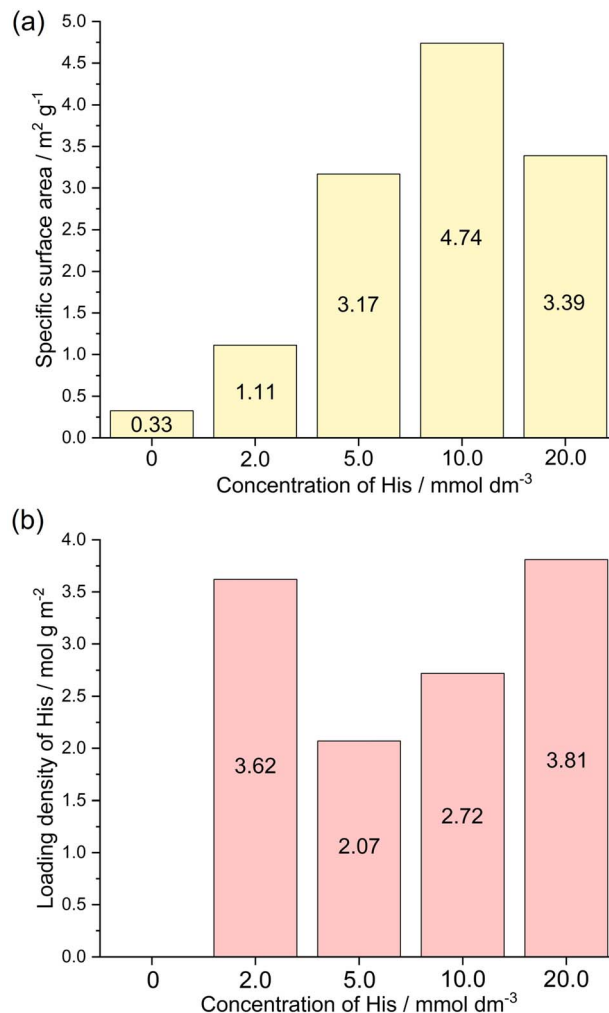


Fig. 6 (a) Specific surface area and (b) calculated loading density of the  $\text{Cu}_2\text{O}$  particles synthesized with 0, 2.0, 5.0, 10.0, and 20.0  $\text{mmol dm}^{-3}$  His.

the concentration of His added to the precursor. The loading density of His decreases at 5.0  $\text{mmol dm}^{-3}$  and increases thereafter. FT-IR spectra of the His-loaded  $\text{Cu}_2\text{O}$  particles and a commercial His powder are shown in Fig. S8†. The incorporation of His to obtain the His-loaded  $\text{Cu}_2\text{O}$  powders results in two new FT-IR peaks at approximately 1000 and 1500  $\text{cm}^{-1}$  (indicated using yellow dashed circles in Fig. S8†), possibly originating from the loaded His. The FT-IR peak at approximately 600  $\text{cm}^{-1}$  can be attributed to  $\text{Cu}_2\text{O}$  (black dashed circle in Fig. S8†). For checking whether  $\text{Cu}_2\text{O}$  particles can simply adsorb His on their surfaces, a soaking test was conducted by immersing None in a 10.0  $\text{mmol dm}^{-3}$  aqueous solution of His for 60 min. Fig. S9† illustrates the FT-IR spectra recorded on the  $\text{Cu}_2\text{O}$  particles before and after the soaking His aqueous solutions. In Fig. S9,† peaks at approximately 1000 and 1500  $\text{cm}^{-1}$  are absent, confirming that the observed new peaks in the FT-IR spectrum of His-loaded  $\text{Cu}_2\text{O}$  hybrid particles originate from His loading (Fig. S8†). In conclusion, His does not simply adsorb onto the surfaces of  $\text{Cu}_2\text{O}$  particles by just soaking His





solutions. The amino acid loaded-Cu<sub>2</sub>O hybrid particles can only be obtained by adding amino acids to the precursor solution used for Cu<sub>2</sub>O synthesis.

Fig. 7a illustrates the calculated FE values toward the formation of gaseous products during CO<sub>2</sub> electrolysis in the presence of the His-loaded Cu<sub>2</sub>O electrocatalyst synthesized with 0, 2.0, 5.0, 10.0, and 20.0 mmol dm<sup>-3</sup> of His at -1.27 V vs. RHE in a CO<sub>2</sub>-purged 0.5 mol dm<sup>-3</sup> aqueous KHCO<sub>3</sub> solution (pH ≈ 8.75). Fig. 7a shows that the FE value toward C<sub>2</sub>H<sub>4</sub> production increases from 17.5% (for unloaded Cu<sub>2</sub>O) to 27.2% (for His loaded-Cu<sub>2</sub>O), even for the electrode based on Cu<sub>2</sub>O synthesized with 2.0 mmol dm<sup>-3</sup> His. The FE value toward C<sub>2</sub>H<sub>4</sub> production further increases to 36.0% for the synthesized with 5.0 mmol dm<sup>-3</sup> His. However, for synthesized with 10.0 mmol dm<sup>-3</sup> His, H<sub>2</sub> production becomes dominant, decreasing the FE value toward C<sub>2</sub>H<sub>4</sub>

production to 22.0%, which further decreases to 18.0% for the synthesized with 20.0 mmol dm<sup>-3</sup> His. Based on Fig. 6b, the amount of His loading onto Cu<sub>2</sub>O particles can be considered to have a stronger effect on C<sub>2</sub>H<sub>4</sub> selectivity than the loading density of His. Excessive loading organics to electrode can be anticipated to completely cover the particle surface, inhibiting CO<sub>2</sub> electrolysis. Fig. 7b illustrates the dependence of the FE values toward various products on the potential of the His-loaded Cu<sub>2</sub>O electrocatalyst synthesized with 5.0 mmol dm<sup>-3</sup> His during CO<sub>2</sub> electrolysis. At a potential of -0.87 V vs. RHE, C<sub>2</sub>H<sub>4</sub> is not produced, and H<sub>2</sub> is predominantly generated with an FE of 57.2%. As the potential changes to -1.07 V vs. RHE, C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> are produced with FE values of 17.4 and 50.6%, respectively. At a more negative potential of -1.27 V vs. RHE, C<sub>2</sub>H<sub>4</sub> is produced with an increased FE of 36.0%, and H<sub>2</sub> is produced with a reduced FE of 32.6%. However, at a more negative potential of -1.47 V vs. RHE, C<sub>2</sub>H<sub>4</sub> is produced with a decreased FE of 29.5%, and H<sub>2</sub> is produced with an increased FE of 37.4%, indicating that at an excessively negative potential, the competing HER dominates over the CO<sub>2</sub>RR. For simply checking the stability of the His-loaded Cu<sub>2</sub>O electrode synthesized with 5.0 mmol dm<sup>-3</sup> His, CO<sub>2</sub> electrolysis was conducted for 1800 s. In Fig. S11,<sup>†</sup> the chronoamperogram obtained during electrolysis demonstrates no sudden fluctuations in current and no catalytic detachment during or after electrolysis. We are currently undergoing not only an appropriate durability test by gas diffusion electrolysis with an online gas chromatogram but also computational science for understanding catalytic mechanisms on His-loaded Cu<sub>2</sub>O electrocatalysis during CO<sub>2</sub> electrolysis.

## 4 Conclusions

In summary, we synthesized different amino acid-loaded Cu<sub>2</sub>O hybrid particles *via* microwave-assisted hydrothermal synthesis and evaluated their selectivities toward the formation of gaseous products during CO<sub>2</sub> electrolysis. The amino acids were loaded into the Cu<sub>2</sub>O particles during synthesis. Notably, the His-loaded Cu<sub>2</sub>O hybrid particles exhibited a unique behaviour in which the particle shape changed drastically, with the particles exhibiting a significant reduction in their size. Furthermore, the His-loaded Cu<sub>2</sub>O based electrocatalysts synthesized with 5.0 mmol dm<sup>-3</sup> His demonstrated an 18.5% increment compared to His-unloaded Cu<sub>2</sub>O toward C<sub>2</sub>H<sub>4</sub> production during CO<sub>2</sub> electrolysis. The loading of amino acids to Cu<sub>2</sub>O particles improved product selectivity, confirming that the proposed synthetic system is an effective catalyst for performing CO<sub>2</sub> electrolysis.

## Data availability

The data supporting this article have been included as part of the ESI.<sup>†</sup>

## Author contributions

Y. Tsuda: conceptualization, data curation, funding acquisition, methodology, resources, supervision, writing – original draft,

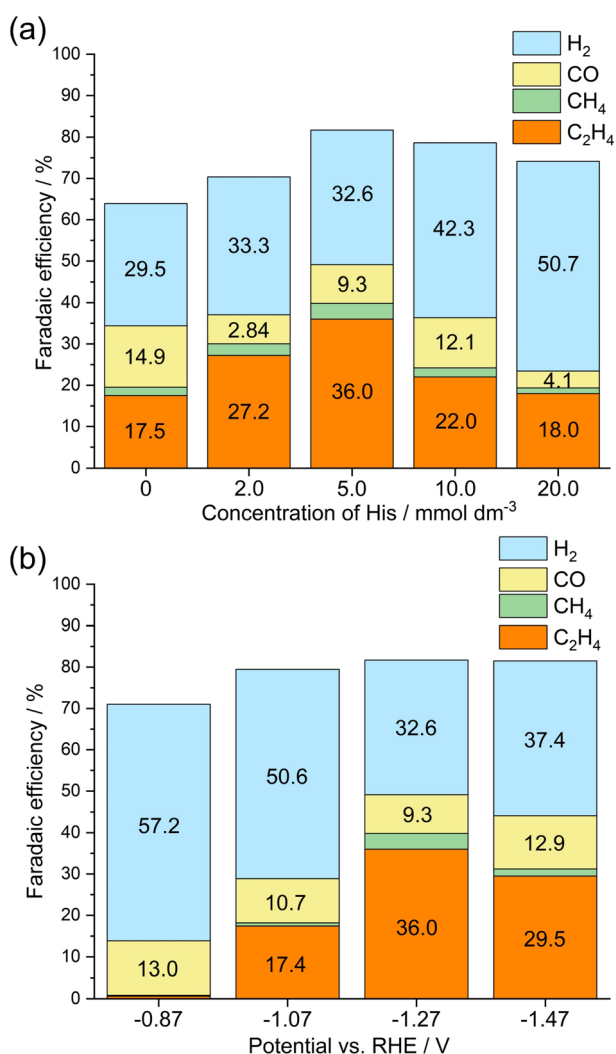


Fig. 7 (a) FE as a function of His concentration exhibited by the His-loaded Cu<sub>2</sub>O electrocatalysis toward gaseous products during CO<sub>2</sub> electrolysis under an applied potential of -1.27 V vs. RHE. (b) FE as a function of electrode potential exhibited by the His-loaded Cu<sub>2</sub>O electrocatalysis synthesized with 5.0 mmol dm<sup>-3</sup> His toward gaseous products during CO<sub>2</sub> electrolysis at 3.0 C in a CO<sub>2</sub>-purged 0.5 mol dm<sup>-3</sup> aqueous KHCO<sub>3</sub> solution (pH ≈ 8.75).



writing – review & editing; M. Irizawa: investigation, methodology; S. Fukuma: investigation, writing – review & editing; M. Kato: investigation, writing – review & editing; T. Gunji: investigation, writing – review & editing; K. Yoshii: investigation, writing–review & editing; N. Takeichi: funding acquisition, supervision, resources.

## Conflicts of interest

There are no conflicts to declare.

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