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Selective electro- or photo-reduction of carbon dioxide to formic acid using Cu-Zn alloy catalyst

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A copper-and-zinc (Cu-Zn) alloy material was synthesized using a vacuum sealing method, in which evaporated zinc was reacted with copper film or nanoparticles to form a homogeneous Cu-Zn alloy. This alloy was evaluated as an electrocatalyst and/or cocatalyst for photocatalysis to selectively reduce carbon dioxide to formic acid. Based on the optimised alloy composition, the Cu₅Zn₈ catalyst exhibited efficient electrochemical CO₂ reduction. Furthermore, we constructed a photoelectrochemical (PEC) three-electrode system, in which the Cu₅Zn₈ film functioned as the cathode for CO₂ reduction in the dark and strontium titanate (SrTiO₃) served as the photoanode for water oxidation. The PEC system also selectively reduced CO₂ to formic acid with a Faradaic efficiency of 79.11% under UV-light and the absence of an applied bias potential. SrTiO₃ particles decorated with nanoparticles of the Cu-Zn alloy also photocatalytically reduced CO₂ to formic acid under UV-light. Isotope trace analysis demonstrated that water served as the electron donor to produce oxygen and organic molecules under UV-light, similar to photosynthesis in plants. The Cu-Zn alloy material developed in the present study is composed of ubiquitous and safe materials, and can catalyse CO₂ conversion by means of various kinds of renewable energies.

1. Introduction

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The increasing emission of carbon dioxide (CO_2) into the atmosphere from the consumption of fossil fuels has become a global problem. The non-renewable nature of hydrocarbonbased fossil fuels necessitates the use of CO_2 -free energy sources like solar energy, wind power, and hydropower. The development of CO_2 -recycling systems based on such renewable energy sources is of growing importance to establish the desired carbon-neutral society. In particular, the rational design of high-performance catalysts is in critical demand to efficiently reduce CO_2 to valuable organic products for different renewable energy sources under moderate conditions through electrocatalysis, photoelectrocatalysis and/or photocatalysis.

The main products of CO₂ reduction in aqueous media are formic acid (HCOOH), carbon monoxide (CO), formaldehyde (HCHO), and methane (CH₄).¹⁻⁷ Among the possible CO₂ reduction products, HCOOH is highly desirable as it is widely used in the energy and chemical industries as a fuel and as a raw material for H₂ generation.⁸ HCOOH is also important for the production of various organic agents through thermal treatments or catalytic reactions,⁹ and can be used in agricultural and animal husbandry as a silage additive.¹⁰ At the industrial scale, HCOOH is mainly produced from methyl formate, which is synthesised from CH₃OH and CO in the presence of a strong salt base. However, this method requires a large excess of water and the disposal of accumulated by-products.¹¹ As the market for formic acid is estimated to exceed \$600 million by 2019,¹² it is highly desirable to develop clean and renewable HCOOH production processes based on CO₂ conversion with solar-, wind- and/or hydropower.

In previous studies, Ru complex catalysts were used for selective CO₂ reduction to HCOOH.³ Although high efficiency (Faradic efficiency over 70%) was achieved, the Ru-complex was precluded from broad use due to its high cost and complicated synthesis. To achieve low-cost and easy preparation, numerous types of metals and alloys were proposed as CO₂-reduction catalysts ¹³⁻²³ such as Zn^{24,25}, Cu²⁶⁻³⁴, Ag³⁵⁻³⁷, Au^{38,39}, Cu-Au⁴⁰, etc. These materials can catalyse CO₂ reduction owing to their delectron availability¹⁰ and low surface CO₂ adsorption strengths⁴¹. However, only a few metals can achieve selective CO2 to HCOOH conversion with low efficiency and high overpotential.⁴² It is known that different CO₂ reduction products are generated via different pathways depending on the balance of the adsorption strengths of reduction intermediates ($CO_2^{\bullet-}$ anion radicals and CO^{\bullet} radicals) on the catalyst surface.^{7,29,43-46} Thus we anticipated that the selective conversion of CO₂ to HCOOH can be realized by tuning the chemisorption strengths of the reduction intermediates on the

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catalyst surface through rational alloying of elemental metals with different adsorption abilities.

Herein, we report that an alloy of Cu and Zn (Cu-Zn), which is historically called "*poor man's gold*" due to its abundance, nontoxicity, and brilliant finish, can selectively convert CO_2 to HCOOH in aqueous media at room temperature probably because the chemisorption strengths of $CO_2^{\bullet-}$ and CO^{\bullet} radicals were regulated to an ideal condition for the CO_2 to HCOOH conversion.

In previous studies, a Cu-Zn alloy electrode was reported to be used in electrocatalytic CO₂ reduction^{47,48} and a Cu-modified zinc oxide was reported to function as a CO₂ hydrogenation catalyst at high temperatures.49-51 However in this study, we have successfully materialized Cu-Zn alloy catalysts as film electrodes and SrTiO₃-supported nanoparticles for the electrochemical/photoelectrochemical reduction and photocatalytic conversion of CO₂. The CO₂ reduction activity of the Cu-Zn catalysts was firstly optimised by tuning the alloy composition of the film electrodes to Cu:Zn= 5:8 (Cu₅Zn₈). The Cu₅Zn₈ film catalyst further exhibited enhanced photoelectrochemical performance for the conversion of CO₂ to HCOOH under UV light when used as the cathode in photoelectrochemical cells (PEC) equipped with mesoporous SrTiO₃ photoanodes. It was finally demonstrated that Cu-Zn nanoparticle-loaded SrTiO3 can also serve as an efficient photocatalyst that selectively promotes the desired CO2-to-HCOOH conversion under UV irradiation.

2. Experimental and Evaluation

2.1 Preparation of Cu-Zn film electrodes

Titanium (Ti) metal sheets (99.5%, Nilaco Co.) were used as the substrate to fabricate electrodes. Pure Cu films with a thickness of 50 nm were sputtered onto the surface of the Ti sheets. These Cu-coated Ti sheets served as pure Cu electrodes in the control group. The prepared Cu-coated Ti sheets were placed in vacuum-sealed quartz ampoules with pure zinc (Zn) metal grains. The vacuum-sealed ampoules were then heated in an electric oven to temperatures higher than the melting point of Zn (> 419 °C at ambient pressure) such that the Cucoated Ti sheets were annealed in Zn vapour for 1 h to yield the Cu-Zn film electrodes. The Zn concentration of the Cu-Zn film electrode was controlled by tuning the Zn vapour pressure, which was dependent on the heating temperature.

2.2 Preparation of SrTiO₃ photoanodes

SrTiO₃ paste was prepared from commercial SrTiO₃ powder (ALDRICH, nanopowder, < 100 nm particle size, > 99.5% trace metal basis). Mesoporous SrTiO₃ films 8 µm thick were prepared on FTO glass substrates by screen-printing the SrTiO₃ paste over the surface, which were further annealed at 450 °C for 1 h to yield mesoporous SrTiO₃ electrodes. Exposed surface of the FTO substrate was covered with heat-resistant insulating tapes for an electrochemical measurement.

2.3 Preparation of Cu-Zn nanoparticle-loaded SrTiO₃ powder

Pure Cu nanoparticles were first deposited onto the surface of the SrTiO₃ powder to obtain Cu nanoparticle added SpTiO₃ powder. An aliquot (2 g) of SrTiO₃ powder was dispersed in 40 mL of distilled water that contained 5.28 mg of CuCl₂·2H₂O. This solution was stirred overnight in an Ar atmosphere and cooled in an ice bath. An adequate amount of NaBH₄ solution (> 0.61 mL of 1 M solution) was added to this solution to precipitate Cu nanoparticles. The obtained Cu nanoparticle-loaded SrTiO₃ powder was collected by centrifugation and dried under vacuum at 80 °C for 2 hours. The Cu nanoparticle-loaded SrTiO₃ powder was then vacuum-sealed in quartz ampoules with pure Zn grains and heated at elevated temperatures for 2 days to yield the desired Cu-Zn nanoparticle-loaded SrTiO₃ powder.

2.4 Electrochemical CO₂-reduction performance tests

The prepared Cu-Zn film electrodes, pure Pt plates, and Ag/AgCl electrodes were used as working, counter, and reference electrodes, respectively. Air-tight electrochemical cells were half filled with a 0.1 M aqueous solution of KHCO₃. The Cu-Zn film electrodes were cleaned by 10 cycles of repeated cyclic voltammetry in the electrolyte solution: starting bias (E₀)= -0.9 V, 1st operating bias (E₁) = -1.8 V, and 2nd operating bias (E₂)= -0.1 V, with slope 90 mV/sec. Either CO₂ or Ar gas was purged into this electrolyte solution prior to the performance test.

2.5 Photoelectrochemical CO₂-reduction performance tests

An H-type glass cell was used for the photoelectrochemical CO2 reduction over the Cu-Zn film electrodes. The Cu-Zn film electrodes were used as the cathode, while the prepared mesoporous SrTiO₃ electrodes were used as the photoanode (see Figure S1 in the Supporting Information). The cathodic- and anodic sides of the glass cell were separated by a Nafion membrane. The electrolyte on the cathodic side was a CO2purged 0.1 M KHCO₃ solution and that on the anodic side was a 0.01 M NaOH solution containing 0.1 M KCl. During the performance tests, the anodic side was irradiated with UV light (Hg-Xe lamp (240-300nm), LA-410UV, Hayashi Ltd., see the spectrum of the light source in the Supporting Information (Figure S2)). The gaseous products in the headspace such as CH₄, CO, and H₂ were quantified with a gas chromatograph (BID, SHIMADZU). The liquid products in the electrolyte solution such as HCOOH were quantified with an ion chromatograph (SHIMADZU).

2.6 Photocatalytic CO₂-reduction performance tests

A 100 mg aliquot of the prepared Cu-Zn nanoparticle-loaded SrTiO₃ powder was dispersed in a CO₂-purged 0.1 M KHCO₃ solution that was contained in an air-tight glass reactor equipped with a quartz window. The same light source and chromatograph as mentioned above were used for the performance test. A rectangular quartz cell ($10 \times 10 \times 50 \text{ mm}^3$) was used for isotope tracing experiments. For the tracing of ¹³C, the Cu-Zn nanoparticle-loaded SrTiO₃ powders were dispersed in 1 mL of 0.1 M KH¹³CO₃ solution into which ¹³CO₂ gas was purged prior to irradiation. For the tracing of ¹⁸O, H₂¹⁸O was used as the solvent for the electrolytes. The gaseous products

were quantified with a gas chromatograph-mass spectrometer (GC-MS, SHIMADZU).

2.7 in situ Fourier transform infrared (FT-IR) spectroscopy analysis.

The *in situ* FT-IR spectra were measured using FTIR6100 (JASCO), the catalytic reaction was conducted in a gas-flow reactor with a quartz window (S.T. Japan), in which Cu-Zn nanoparticle-loaded SrTiO₃ powders were put in a porous ceramic cup. For pretreatment, pure Ar gas was introduced to the reactor at the flow rate of 100ml/min at 573K for 1 hour. Heater was only used for pretreatment. During the catalytic reaction, Ar gas or CO₂ gas were introduced into the reactor through bubbling of water to flow humid gas. UV light (Hg-Xe lamp (240-300nm), LA-410UV, Hayashi Ltd, was used as light source. The Cu nanoparticles loaded SrTiO₃ prepared according to the session 2.3 was also analyzed as a control group. The schematic illustration of the in situ FT-IR analysis was shown in our supporting information (Figure S3).

3. Results

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3.1. Characterisation



Fig. 1 HAXPES spectra of a) Cu 2p and b) Zn 2p core-levels in the Cu-Zn alloy electrode. The HAXPES spectra of pure copper and zinc are also shown. c) The XRD pattern of the Cu-Zn alloy electrode prepared at 500 °C. Ti metal sheet was used as the substrate. ACu_5Zn_8 (cubic); \blacksquare pure Ti

The prepared Cu-Zn film electrodes were characterised using hard X-ray photoelectron spectroscopy (HAXPES; hv = 5.95 keV) at the undulator beamline BL15XU⁵² of SPring-8 as shown in Fig. 1a and 1b. The Cu 2p and Zn 2p peak positions for the Cu-Zn film electrode (Cu:Zn=5:8, see Fig. 2 and the corresponding paragraph) were different from those for pure Cu and Zn metals, indicating that the Cu-Zn film was neither pure Cu nor Zn, but an alloy of Cu and Zn. Figure 1c shows the X-ray diffraction (XRD) profile of the same Cu-Zn film electrode. The reflection peaks at 35.97, 37.89, 43.23, and 62.96° correspond to the (222), (321), (330), and (600) reflections of the atomically ordered Cu₅Zn₈ alloy (cubic), which is consistent with the expected chemical composition of the Cu-Zn film, Cu:Zn=5:8. As discussed in the next section, this Cu₅Zn₈ film electrode exhibited significantly enhanced electrochemical CO₂ reduction.

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Linear sweep voltammetry (LSV) curves of the prepared Cu-Zn electrode under CO₂ and Ar purging are shown in Fig. 2. Pure Cu and Zn electrodes were also evaluated as control groups. The onset potential of the Cu-Zn electrode was found to be -0.65 V vs. Ag/AgCl at the lowest, which was markedly lower than those of pure Cu (-1.0 V vs. Ag/AgCl) and Zn (-1.2 V vs. Ag/AgCl). The atomic ratio of Cu-Zn in the alloys was controlled by varying the annealing temperature under vacuum, as described in the experimental section. Specifically, with increasing heating temperature, the Zn concentration in the Cu-Zn electrode also increased. Figure 2d shows the influence of the Zn concentration in the Cu-Zn alloy electrode on the onset potential for CO2 reduction. The onset potential was lowest at a Zn concentration of ~60 atom%. The Zn concentrations in Figure 2d were determined using X-ray fluorescence (XRF) elemental analysis (raw data shown in Table S1 in the Supporting Information), and the optimised Zn concentration of ~60% was consistent with the crystal structure (Cu₅Zn₈) determined by XRD (Figure 1c).



Fig. 2 Linear sweep voltammetry (LSV) curves of a) Cu_5Zn_8 alloy electrode, b) pure Cu, and c) pure Zn. The onset potential for CO_2 reduction at the Cu-Zn electrode as a function of Zn atomic ratio is also shown (d).

The reaction products generated by the Cu₅Zn₈ electrode, pure Cu electrode, and pure Zn electrode under different bias potentials are also shown in Fig. 3. Notably, the scales of the vertical axis for the Cu₅Zn₈ electrode and pure Zn electrode are about 10 times larger than that for the pure Cu electrode. The amount of HCOOH generated at the Cu₅Zn₈ alloy electrode was markedly higher than that produced at the pure Cu electrode (< 0.03 µmol), which generated CH₄ and CO as the main reaction products. The Cu₅Zn₈ alloy electrode also generated more HCOOH than the pure Zn electrode (< 1 µmol). Specifically, under -1.0 V vs. Ag/AgCl, the selectivity of the Cu₅Zn₈ alloy for HCOOH generation was obviously better than pure Cu or pure Zn, as shown in Fig. 3d. It is noted that the Faradaic efficiency of the Cu₅Zn₈ alloy for HCOOH generation was 71.11% at a bias

application of -1.0 V vs. Ag/AgCl. The CO₂ to HCOOH conversion efficiency of the Cu₅Zn₈ alloy catalyst was higher than that of the previously reported Cu-Zn alloy electrocatalysts.^{47,48}

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Fig. 3 Products generated by a) Cu₃Zn₈ electrode, b) pure Cu electrode, and c) pure Zn electrode in electrochemical cells under different applied bias potentials for 1 h. Bias potentials were applied from -0.6 to -1.4 V vs. Ag/AgCl. d) The CO₂ reduction product distribution generated at Cu₃Zn₈ electrode, pure Cu electrode, and pure Zn electrode under -1.0 V vs. Ag/AgCl.

3.3 Photoelectrochemical CO₂ reduction

We constructed a photoelectrochemical (PEC) cell, in which the Cu₅Zn₈ electrode served as the cathode for CO₂ reduction and SrTiO₃ was used as a photoanode for oxygen production from water (Figure S1). When the SrTiO₃ photoanode was irradiated with UV light, water was oxidised at the anode by the photogenerated holes in the valence band of SrTiO₃, whereas the excited electrons were transferred to the cathodic Cu₅Zn₈ electrode and used for CO₂ reduction. The production of HCOOH at the cathodic side under rest potential conditions (without any bias application) is shown in Fig. 4. The amount of HCOOH generated by the Cu₅Zn₈ electrode was markedly higher than those by the pure Cu- or Zn electrodes, which were consistent with the results of electrochemical CO₂ reduction shown in Fig. 3.



Fig. 4 Amount of HCOOH produced by a PEC cell equipped with a Cu_3Zn_8 electrode as the cathode and CO_2 -purged 0.1 M KHCO₃ as the electrolyte. PEC cells equipped with a pure Cu cathode and a pure Zn cathode in CO_2 -purged 0.1 M KHCO₃ (electrolyte) were used as controls.

We also conducted the photoelectrochemical performance test under argon (Ar) gas at the cathodic side as a control experiment (see Figure S4 in the Supporting Information). The C1 molecule production was quite limited, while H₂ production was significant with Ar bubbling. These results indicate that C1 molecules are produced by CO2 reduction on our Cu5Zn8 electrode. In addition to the HCOOH shown in Figure 4, other gaseous products such as CO, CH₄, and H₂ in the headspace of the reactor were quantified and are shown in our supporting information (Figure S5). Based on these data, we estimated the Faradaic efficiency for HCOOH production of the Cu₅Zn₈ cathode combined with a SrTiO₃ photoanode. It is noteworthy that the Faradaic efficiency of HCOOH production was as high as 79.11%, which is markedly higher than those of pure Cu (28.54%) or Zn (47.68%). In the case of pure Zn, hydrogen was mainly produced through water splitting and only limited CO2 reduction activity was observed. The Cu₅Zn₈ electrode also had excellent stability, with the turnover number (TON) for CO2 reduction reaching 1458.9, which was twice of that of pure Cu (731.3) under the same experimental conditions. The quantum efficiency of photoelectrochemical CO2 reduction by the Cu-Zn electrode was 0.13%.

3.4 Photocatalytic CO₂ reduction by Cu-Zn nanoparticle-loaded SrTiO₃ powder

Cu-Zn nanoparticle-loaded SrTiO₃ powder was prepared using a similar vacuum annealing method to that used for film fabrication, as mentioned in the experimental section. The prepared Cu-Zn nanoparticle-loaded SrTiO₃ powder was characterized by TEM, XPS, and UV-visible optical absorption, and the results are shown in Fig. 5. As can be seen in the TEM image, the Cu-Zn nanoparticles were approximately 3-5 nm in diameter and uniformly distributed on the SrTiO₃ surface. The deposition of alloy nanoparticles was also confirmed by UVvisible spectra, which absorbed visible light photons according to their metallic plasmon absorptions. The spectral shift observed in the XPS spectra demonstrated that the Cu Published on 10 April 2017. Downloaded by University of Newcastle on 11/04/2017 09:48:58.

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nanoparticles were successfully converted to Cu-Zn alloy nanoparticles.



Fig. 5 a) the TEM image of the Cu-Zn alloy nanoparticle-loaded SrTiO₃ nanopowder, b) the XPS Cu 2p and Zn 2p spectra of the Cu-Zn alloy nanoparticle-loaded SrTiO₃ nanopowder, compared with that of pure Cu and pure Zn. Measurement condition: 10 cycles, 3 repetitions, one step = 0.15 eV, 40 ms. c) The UV-Visible spectra of pure SrTiO₃ (STO), Cu nanoparticle-loaded SrTiO₃, Zn nanoparticle-loaded SrTiO₃, and the Cu-Zn alloy nanoparticle-loaded SrTiO₃.

Under UV irradiation of the Cu-Zn nanoparticle-loaded SrTiO₃ powder, CO₂ was mainly converted to HCOOH, whereas CH₄ and CO productions were limited (Fig. 6). A negligible amount of hydrogen was detected in the reactor headspace, indicating that the Cu-Zn co-catalyst was highly selective for CO₂ reduction. Oxygen production through water oxidation would be proceeded by photogenerated holes in SrTiO₃, but oxygen molecules that cannot be ignored already existed in the head space of our reactor and/or were adsorbed on the surface of the photocatalyst powder as H₂O₂ molecules.⁵³ Therefore, we tried to prove that the water molecule was an electron donor using isotope trace analysis,3,54 as shown in the Supporting Information (Figure S6). When $H_2^{18}O$ was used as the aqueous electrolyte solution, ${}^{18}O_2$ (m/z=36) generation was detected. This result strongly suggests that water molecules served as the electron donor in our photocatalyst system, which is consistent with photosynthesis in natural plants. We also analysed the gasphase products in the headspace under ${}^{13}CO_2$ (m/z = 45) isotope bubbling with light irradiation. As a result, gas phase 13 CO (m/z= 29) was detected, indicating that the extracted electrons from water molecules would be excited into the conduction band of SrTiO₃, and these excited electrons react with CO₂ to produce fuel molecules.

According to the XPS analysis of the Cu-Zn nanoparticlesloaded $SrTiO_3$ powder collected after the CO₂ reduction, as shown in the supporting information (Figure S7), there was no valence change of Cu and Zn during the reaction, indicating that our catalyst was stable under photon irradiation in aqueous media. The TON for the CO₂ reduction of the particulate system was 11.46, which is lower than that of the Cu-Zn thin film electrode system under the same experimental conditions. Even though the two materials were prepared using the same vacuum annealing method, the Zn concentration of the Cu-Zh nanoparticles was higher than that of the Cu-Zn electrode (Table S2). The XRD pattern of Cu-Zn nanoparticles loaded SrTiO₃ (5%wt) also proved that pure Zn exists (Figure S8 supporting information). In the case of the particulate system, Zn vapour would be directly loaded on the surface of SrTiO₃ without reacting with Cu during annealing. The present modification method with Cu-Zn nanoparticles is facile and applicable to various light harvesting materials to enhance their photocatalytic CO₂ reduction activity.



Fig. 6 Photocatalytic CO_ reduction by Cu-Zn alloy nanoparticle-loaded STO powders. HCOOH, CH_4, CO, and H_2 were generated.

4. Discussion

The high selectivity of the Cu-Zn alloy electrode toward HCOOH generation can be explained based on the relationship between CO₂ reduction pathways and the state of the catalyst surface. Among numerous studies on CO₂ reduction pathways,14, 43, 44, 55 most papers suggest that the formation of HCOOH is initiated by a CO2⁻ radical formed near or weakly adsorbed on the catalyst surface.^{5,42,56} As shown in Figure 7, when the catalyst surface has weak adsorption for CO₂•- anion radicals, one electron would transfer to CO₂ and CO₂•- radicals would be predominantly formed in a state where the C atom is available for hydrogenation, leading to the generation of HCOO⁻. The Zn surface has very weak adsorption strength for $CO_2^{\bullet-}$ anion radicals; thus, during CO_2 reduction, CO_2 is converted into HCOO⁻ as the main reaction product. However, due to this weak adsorption strength, proton reduction (water splitting) competes with CO₂ reduction in aqueous electrolytes, and the selectivity of zinc for CO₂ reduction is quite low.^{10,14}

In contrast, when the catalyst surface has high adsorption strength for the $CO_2^{\bullet-}$ anion radical, the radical formed on the metal surface is stabilized by *d*-electron back donation and would be subsequently converted to the CO[•] radical. If the adsorption strength for the CO[•] radical is weak, the radical would desorb from the metal surface, resulting in the production of CO. In contrast, if the adsorption strength is appropriately strong to stabilize the CO[•] radical on the catalyst surface, the radical is further converted to CH₄ and/or CH₃OH. Notably, if the adsorption strength is sufficiently strong, the metal surface will be occupied by the CO[•] radical, leading to

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deactivation of the catalyst. In the case of Cu and Cu oxides, although the CO₂ reduction properties were previously reported,^{26,28,34,57-61} their adsorption and desorption strength with CO₂ was so strong that the CO₂ radicals can be adsorbed on the Cu surface,⁶² causing the generation of CH₄ and/or CH₃OH.

By combining Cu with Zn at the atomic scale, the surface adsorption and desorption would take place at the interface between Cu and Zn in the alloy compound. Specifically, the adsorption strength for both the CO₂^{•-} anion radical and CO[•] radical decreased, and thus, HCOOH was mainly generated as a CO₂ reduction product. By combining Cu and Zn at the atomic scale in an alloy, high selectivity for HCOOH formation and suppression of hydrogen production were achieved. This proposal is also supported by computational study on the free binding energies of hydrogen and *COOH of intermetallic alloys including CuZn alloy⁶³. In the present study, in situ FT-IR analysis was operated to verify our proposal, as shown in the supporting information (Figure S9), in humid CO2 under UV irradiation, bidentate surface carbonate were recognized in the case of Cu-Zn nanoparticles loaded SrTiO₃ powders while monodentate surface carbonate was detected from Cu nanoparticles loaded SrTiO₃ powders. These results provide a plausible explanation for the high selectivity of HCOOH generation of Cu-Zn catalyst.

1. Free CO₂⁻ radicals near the catalyst surface..

$$0=C=0 \xrightarrow{e^{-}} 0 \xrightarrow{c} 0 \xrightarrow{H_20} 0 \xrightarrow{c} 0 \xrightarrow{e^{-}} 0 \xrightarrow$$

2. CO_2^{-} radicals weakly adsorbed on the catalyst surface.

$$0=C=0 \xrightarrow{e^{-}} \underbrace{0}_{H_{2}} \xrightarrow{C_{H_{2}}} \underbrace{0}_{H_{2}} \xrightarrow{H_{2}} \underbrace{0}_{H_{2}} \xrightarrow{O^{-}} \underbrace{0}_{H_{2}} \xrightarrow{O^{+}} \underbrace{O^{+}} \xrightarrow{O^{+}} \underbrace{O^{+}} \xrightarrow{O^{+}} \underbrace{O^{+}} \xrightarrow{O^{+}} \xrightarrow{O^{+}} \underbrace{O^{+}} \xrightarrow{O^{+}} \xrightarrow{O^{+}} \underbrace{O^{+}} \xrightarrow{O^{+}} \underbrace{O^{+}} \xrightarrow{O^{+}} \underbrace{O^{+}} \xrightarrow{O^{+}} \xrightarrow{O^{+}} \underbrace{O^{+}} \xrightarrow{O^{+}} \underbrace{O^{+}} \xrightarrow{O^{+}} \xrightarrow{O^{+}} \underbrace{O^{+}} \xrightarrow{O^{+}} \xrightarrow{O^{+}} \xrightarrow{O^{+}} \xrightarrow{O^{+}} \xrightarrow{O^{+}} \xrightarrow{O^{+}} \xrightarrow{O^$$

3. Strong CO₂ radicals adsorption strength on the catalyst surface.

$$O = C = O \longrightarrow O \xrightarrow{O} O \xrightarrow{H_2O} O \xrightarrow{OH^-} O \xrightarrow{O$$

* A. Weak CO radical adsorption strength

B. Strong CO radical adsorption strength. C. the CO radical adsorption strength is too strong

Fig. 7 The speculated pathways for CO₂ reduction.

5. Conclusions

The Cu-Zn alloy catalyst developed here was prepared from abundant and environmentally friendly materials, and exhibited high conversion efficiency for the reduction of CO_2 to organic molecules, particularly HCOOH. The Cu-Zn alloy catalyst can be used as an electrode for electrochemical CO_2 reduction, or combined with a photoanode for photoelectrochemical reactions. The Faradaic efficiency of converting CO_2 to HCOOH was as high as 79.11% in the photoelectrochemical cell, demonstrating that the catalyst had high selectivity, toward HCOOH generation. The Cu-Zn electrode also had excellent stability with the turnover number (TON) for CO₂ reduction reaching 1458.9, which was twice that of pure Cu (731.3). The quantum efficiency of the photoelectrochemical CO₂ reduction by the Cu-Zn electrode was 0.13%. In addition, we also achieved nanoparticlisation of the Cu-Zn alloy catalyst. When the Cu-Zn nanoparticles were loaded onto the surface of SrTiO₃, the photocatalytic reduction of CO2 reduction was promoted under UV-light. We demonstrated that the Cu-Zn alloy catalyst exhibited high efficiency, stability, and selectivity for CO₂ reduction in the electrode system as well as the particulate photocatalyst. The ability to selectively regulate CO₂ reduction using the Cu-Zn alloy catalyst described here may prompt the development of new types of alloy catalysts with high selectivity for CO₂ reduction.

Author Contributions

GY acquired all experimental data and wrote the manuscript in discussion with all co-authors. HA and NR established the synthesis method of the Cu-Zn alloy catalyst. NR, HA, and SU conducted the XPS measurements. NS and AY provided important suggestions on the electrochemical analyses. MM and HA conducted the study and wrote the manuscript.

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