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Low Overpotential and High Current CO₂ Reduction with Surface Reconstructed Cu Foam Electrodes

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Abstract

While recent reports have demonstrated that oxide-derived Cu-based electrodes exhibit high selectivity for CO₂ reduction at low overpotential, the low catalytic current density (<2 mA/cm² at -0.45 V vs. RHE) still largely limits its applications for large-scale fuel synthesis. Here we report an extremely high current density for CO₂ reduction at low overpotential using a Cu foam electrode prepared by air-oxidation and subsequent electroreduction. Apart from possessing three-dimensional (3D) open frameworks, the resulting Cu foam electrodes prepared at higher temperatures exhibit enhanced electrochemically active surface area and distinct surface structures. In particular, the Cu foam electrode prepared at 500°C exhibits an extremely high geometric current density of ~9.4 mA/cm² in CO₂-saturated 0.1 M KHCO₃ aqueous solution and achieving ~39% CO and ~23% HCOOH Faradaic efficiencies at -0.45 V vs. RHE. The high activity and significant selectivity enhancement are attributable to the formation of abundant grain-boundary supported active sites and preferable (100) and (111) facets as a result of reconstruction of Cu surface facets. This work demonstrates that the structural integration of Cu foam with open 3D frameworks and the favorable surface structures is a promising strategy to develop an advanced Cu electrocatalyst that can operate at high current density and low overpotential for CO₂ reduction.

Keywords

CO₂ reduction; Cu foam electrode; Surface reconstruction; High current density; Low overpotential

1. Introduction

Electrocatalytic reduction of CO_2 to produce value-added chemicals and fuels powered by renewable energy input has been pursuing as a promising route to mitigate the depletion of fossil fuels and increasing environmental problems [1-5]. One of the major challenges to practically utilize such a process is to rationally design and develop advanced electrocatalysts that are active, selective and stable for this reaction. Although several metal electrocatalysts have demonstrated sufficient capability for reducing CO_2 in aqueous solutions, most of them suffer from high cost associated with the use of noble metals [6-12], low energy efficiency due to the need of high overpotential to activate inert CO_2 molecules, and low selectivity owing to the competitive H_2O reduction [4,5]. Among various electrocatalysts investigated to date, copper (Cu) has been identified to be promising because of its low cost, and in particular its potential of catalyzing the formation of high quantity of hydrocarbons [13-15]. A moderate to high overpotential, however, is still required for polycrystalline Cu to reach an appreciable reaction rate for the production of CO and HCOOH (>0.5 V) and further reduced products of methane (CH_4) and ethylene (C_2H_4) (~ 1 V) [13,14]. Moreover, a mixture of major and minor products is commonly produced at higher overpotentials in both gas and liquid phases. It is obvious that the improvements in energy efficiency of CO_2 reduction reaction and in selectivity by increasing the yields of the target products are desired. To achieve above-mentioned targets on Cu based electrocatalysts, several strategies have been attempted, including the control of macrostructure [16-18], particle size [19,20], exposed surface facets [21-27], and forming alloys with secondary metals [28-34]. Among these studies, a novel and universal strategy was recently developed by Kanan and co-workers to produce nanostructured metal electrodes for highly efficient CO_2 reduction [35-39]. Instead of using metallic electrodes to reduce CO_2 directly, they started from

metal oxides to prepare highly active metal electrodes such as Cu, Au, Pb, and Sn with specific surface structures. This approach enabled the high activity and selectivity for CO₂ reduction at much lower overpotentials, compared to those for their metal counterparts. Impressively, oxide-derived Cu (OD-Cu) produced from Cu foil substrate can achieve a ~40% Faradaic efficiency (FE) towards CO with a total current density of 2.7 mA/cm² for aqueous CO₂ reduction at E = -0.5 V vs. reversible hydrogen electrode (RHE) [36]. More significantly, when OD-Cu was used as an electrocatalyst for CO electroreduction, multi-carbon oxygenates (ethanol, acetate and n-propanol) were produced at a FE up to 57%, with ethanol as the major product at modest potentials of -0.25 V to -0.5 V vs. RHE in alkaline solutions, albeit with low current density (~0.5 mA/cm²) [40]. Mechanistic studies have revealed that the formation of the metastable active sites that are supported by grain boundaries formed during metal oxide reduction is responsible for the catalytic properties [38,41,42]. In order to further enhance the selectivity of CO₂ reduction, dense Cu nanowires grown on Cu mesh show an enhanced CO selectivity as high as 60% at -0.3 V vs. RHE and 53% at -0.5 V vs. RHE, but again with low catalytic currents at 0.3 and 2.4 mA/cm², respectively [43]. Despite being generally more selective and active than their bulk counterparts owing to the high surface area as originated from the formation of Cu nanostructures, these modified Cu electrodes have failed to operate with high catalytic currents at low overpotentials. To largely enhance the electrocatalytic CO₂ efficiency of Cu catalysts, we report here the preparation of surface reconstructed three-dimensional (3D) Cu foam electrodes for CO₂ reduction. The Cu foam substrate provides the large surface areas for growing Cu oxides (Cu₂O and CuO) on its 3D skeleton and the resulting Cu catalysts after electrochemical reduction show high electrochemically active surface area and distinct surface structures compared with the pristine Cu foam, leading to significant improvement in the CO₂ reduction efficiency. The

electrocatalytic CO₂ reduction in a CO₂ saturated 0.1 M KHCO₃ solution shows acatalytic current density of ~9.4 mA/cm² at -0.45 V vs. RHE, which is approximately one-order higher than that of pristine Cu foam. These results suggest that this type of catalyst is promising for large-scale CO₂ reduction with low energy consumption.

2. Experimental section

2.1 Materials

The copper foam (99.9999%, 0.3 mm thick), copper foil (99.9999%, 0.03 mm thick), Carbon dioxide (CO₂, 99.99%), Argon (Ar, 99.9999%), and Helium (99.999%) were used as received; A 0.1 M KHCO₃ (Sigma-Aldrich, 99.99% metals basis) solution was prepared with 18.2 MΩ deionized water from a Millipore system and used as the electrolyte. The pH value of the electrolyte saturated with CO₂ was determined to be 6.8.

2.2 Annealing Cu foam and Cu foil in air

For the air-oxidation of Cu foam, a piece of Cu foam (0.5×1.0 cm²) was first washed with 1 M HCl solution for several seconds to remove the native oxide layer. After rising with water and drying under a steam of Ar, Cu foam was subject to air-oxidation in a tubular CVD furnace under static air atmosphere conditions at different temperatures ranging from 120 to 500 °C for 2 h. Electrodes were then allowed to cool slowly to room temperature over several hours. For a comparison, flat Cu foil (1×1.5 cm²) was also subjected to heat-treatment in air under exactly same conditions as Cu foam.

2.3 Characterizations

Scanning electron microscopy (SEM) images were acquired with an FEI Quanta 600 Scanning Electron Microscope. X-ray diffraction (XRD) patterns were obtained with a BrukerD8Discover diffractometer Cu-Kα radiation from a Cu anode X-ray tube operated at 40 kV and 40 mA was

used as an X-ray source. X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu=1486.6$ eV) operating at 150 W, a multichannel plate and delay line detector under a vacuum of 1×10^{-9} mbar. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. Binding energies were referenced to the C1s peak (set at 284.8 eV) of the sp^2 hybridized (C=C) carbon from carbon tape. The Raman spectra were acquired using a 532-nm laser with a confocal microscope system (WITec Alpha300).

2.4 Electrochemical measurements

All the electrochemical experiments were carried out in an air-tight, glass frit-separated two compartment three-electrode electrochemical cell. A coiled platinum wire and an Ag/AgCl in saturated KCl were used as counter and reference electrodes, respectively. During the electrochemical experiments, the working and reference electrodes were separated from the counter electrode. Electrochemistry was carried out with an electrochemical impedance spectroscopy using a Biologic VMP-300 potentiostat. All the applied potentials are reported as reversible hydrogen electrode (RHE) potentials scale using $E(\text{vs. RHE})=E(\text{vs. Ag/AgCl})+0.210\text{ V}+0.0592\text{ V}\times 6.8$. Potentiostatic EIS was used to determine the uncompensated solution resistance (R_s) at open circuit potentials. The potentiostat compensated for 85% of the value of R_s and the last 15% was post-corrected to arrive at accurate potentials. For controlled potential electrolysis of CO₂, the cathodic compartment of the cell was degassed and saturated with CO₂ at $10\text{ mL}\cdot\text{min}^{-1}$ for at least 15 minutes. Annealed Cu foam or pristine Cu foam was used as the working electrode. During the electrolysis, CO₂ gas was continuously bubbled into the cathodic compartment at a rate of 10 mL/min. The eluent was delivered directly to the sampling loop of an on-line pre-calibrated gas chromatograph (Agilent 7890B) (H₂, CO, CH₄, C₂H₄, C₂H₆, CO₂),

which was equipped with the following two channels: 1) two HayeSep Q columns and one 13X molecular sieves with a thermal conductivity detector using He as a carrier gas for CO₂, CO, CH₄, C₂H₄, and C₂H₆ analysis, and 2) one HayeSep Q and one 13x molecular sieves with a thermal conductivity detector using Ar as a carrier gas for H₂ analysis. The Faradaic efficiencies (FEs) of CO and H₂ were calculated from the volume concentration of gaseous products as below:

$$FE_j(\%) = \frac{2Fv_jGtp_0}{RT_0Q_{total} \times 10^6} \times 100\%$$

where v_j (vol%) is volume concentration of CO or H₂ in the exhaust gas from the electrochemical cell (GC data) at a given sampling time, G (ml/min) is gas flow rate at room temperature and ambient pressure, Q_{total} (C) is integrated charge passed during electrolysis (Chronoamperometry data), and t (min) is electrolysis time ($p_0=1.01 \times 10^5$ Pa, $T_0=269.2$ K, $F=96500$ C/mol, $R=8.314$ J/mol·K).

At the end of the electrolysis, the liquid product HCOOH was analyzed using a high-pressure liquid chromatography (HPLC, Agilent technologies) system equipped with Agilent 1200, 1260 and 1290 Infinity liquid chromatography technology. The FEs for CO and H₂ are average values and that for HCOOH is a cumulative value during the electrolysis. Induction period of 0.5 h for gas analyses was observed due to filling dead space of the reactor to the inlet of GC.

2.5 Determination of ECSAs and surface roughness factors

ECSAs and surface roughness factors for annealed Cu foam electrodes relative to pristine Cu foam were determined by measuring double layer capacitances by using cyclic voltammetry (CV) method [36]. CV experiments were performed in the same electrochemical cell as in bulk CO₂ electrolysis in 0.1 M HClO₄ electrolyte after the annealed Cu foam electrodes were electrochemically reduced in CO₂-saturated 0.1 M KHCO₃ solution at -0.45 V vs. RHE. CV curves were obtained within a potential range in which no faradaic processes were occurring, and

the geometric current density was plotted against the scan rate of the CV. The slope of the linear regression gives the capacitance.

2.6 Determination of exposed crystalline facets on Cu foam surfaces

The exposed surface facets on Cu foam electrodes were probed by investigating the electrosorption behaviors of O and OH species in alkaline solutions [51]. The CV was performed in 1 M KOH after the annealed Cu foam electrodes were electrochemically reduced in CO₂-saturated 0.1 M KHCO₃ solution at -0.45 V vs. RHE.

3. Results

3.1 Preparation of Cu foam-based electrocatalysts by thermal oxidation/electro-reduction methods

To prepare oxide-derived Cu (OD-Cu) electrocatalysts for CO₂ reduction, a two-step method involving the thermal oxidation and the subsequent electrochemical reduction was adopted [36,38,40,42]. Cu oxides were firstly grown on the Cu substrates by annealing in air. The subsequent reduction by cathodic polarization was performed under CO₂ electrolysis conditions. For the flat Cu foil substrate, due to its low exposed geometric surface area, the growth of Cu oxides on its surface is limited and ineffective. Hence, the electrochemical active surface area (ECSA) for the Cu foil after the Cu oxide reduction is limited, leading to the low catalytic current for CO₂ reduction. Moreover, the generated Cu oxides tend to detach from the flat substrate due to the large lattice mismatch between the underlying Cu substrate and obtained Cu oxides [44]. In the present study, a Cu foam with three-dimensional (3D) Cu skeletons was selected to prepare high surface area Cu catalysts for CO₂ reduction. Because of its 3D open frameworks with appropriate pore sizes, the catalytic sites are easily accessible by reactants and electrolytes. The formation of abundant active sites and distinct surface crystal structures largely

enhance the catalytic current densities (normalized by the projected geometrical area), resulting in an extremely low overpotential for CO₂ reduction. Such catalyst is beneficial for the electrochemical cell design aiming at low energy consumption.

3.2 Structural characterizations

Figure 1a shows the scanning electron microscopy (SEM) images for the pristine Cu foam, where the pores with the size of 200 to 600 μm are observed and the Cu grains of the skeletons are visible at a higher magnification. After removal of native oxide by washing with 1 M HCl_(aq), the Cu oxides were generated on Cu foam surfaces by air annealing at various temperatures ranging from 120 to 500 °C for 2 h. Figure S1a and Figure 1b show that the surface of Cu foam is slightly changed at 120 °C and some small particles start to develop at 200 °C. When the temperature is increased to 300 and 400 °C (Figure 1c and Figure S1b), the Cu foam surface becomes much rougher, indicating an appreciable change of the surface structures. The SEM images in Figure 1d and Figure S1c show that large numbers of flakes (~ 5 μm -thick) were formed after annealing at 500°C. Interestingly, the surface morphologies remain the same even after electrochemical reduction as shown in Figure 1e. It is also noted that reduction of Cu oxides was performed in the set-up and conditions for electrocatalytic reduction of CO₂ (i.e. in CO₂-saturated 0.1 M KHCO₃ aqueous solution at the potential of -0.45 V vs. RHE).

To gain insights for the chemical structure change of Cu foam surface with various annealing temperatures, Raman spectroscopy was adopted to probe the surface bonding of the Cu foam. Figure 2a suggests that the Cu₂O phase (characteristics peaks at 97, 147, and 217 cm^{-1}) [45] is obtained after annealing at 120°C and the higher oxidation state, CuO (peaks at 297, 345, and 629 cm^{-1}) [46], is observed when the temperature is higher than 200 °C. Hence, the surface morphology change observed in SEM is strongly related to the formation of Cu₂O and/or CuO

structures on Cu foam. Since the penetration depth of visible laser (532 nm) used for Raman spectroscopy is short, X-ray diffraction (XRD) was used to reveal the crystal structure of the Cu foams after annealing. Figure 2b displays the XRD profiles for the Cu foams after annealed at different temperatures, which suggest that the formation of Cu_2O ($2\theta = 29.6, 36.5, 42.3, 53.5, 61.4, 73.4, 77.4^\circ$, JCPDS card No. 03-0898) and CuO ($2\theta = 35.6, 38.8, 48.7, 53.4, 58.1, 66.3, 68.2, 72.2, 75.1^\circ$, JCPDS card No. 03-0867) becomes appreciable only when the temperature is higher than 300°C . The interior of Cu foam skeleton still remains as metallic Cu (as indicated by the diffraction peaks ($2\theta = 43.4, 50.6, 74.2^\circ$, JCPDS card No. 03-1051) even when annealing temperature is as high as 500°C . Interestingly, after electrochemical reduction, the flakes (Cu_2O - and CuO -rich crystals) formed on the 500°C -annealed Cu foam electrode remain the same in morphologies but they were completely reduced to Cu crystals. The overall effect of annealing in air plus electrochemical reduction actually creates high-surface-area Cu crystals on the Cu-foam. To further confirm the conversion of Cu oxides to Cu, the corresponding X-ray photoelectron spectroscopy (XPS) was performed. Figure 2c reveals that the surface of pristine Cu foam is mainly Cu^0 state and the Cu^{2+} (binding energy 933.75 eV, 953.74 eV) and Cu^+ (binding energy 932.6, 952.4 eV) appear after 500°C annealing in air (also see the Cu LMM auger spectra in Figure S2) [47]. After electrochemical reduction at -0.45 V vs. RHE in CO_2 saturated 0.1 M KHCO_3 solution, the peaks associated with Cu^{2+} and Cu^{1+} in the spectra totally vanished, indicating that the $\text{CuO/Cu}_2\text{O}$ layer can be completely reduced during the CO_2 electrolysis and only the metallic Cu^0 surface is responsible for the observed activity for CO_2 reduction (vide infra).

3.3 Electrocatalytic reduction of CO_2

Electrocatalytic reduction of CO₂ was conducted in a CO₂-saturated 0.1 M KHCO₃ aqueous solution (pH 6.8) using an electrolysis cell with the cathode and anode compartments separated by a glass frit. The gas- and liquid-phase products were analyzed by a multichannel gas chromatography equipped with two TCD detectors and a high-pressure liquid chromatography (HPLC) (see experimental section for details). Figure S3 in Supporting Information shows the variations of several performance indices including total geometric current density (j_{gcd}) vs. time, the FE of CO vs. time and the overall FE of HCOOH on pristine and annealed Cu foam electrodes at -0.45 V vs. RHE, from which the average FEs for major products and the steady-state j_{gcd} were extracted and summarized in Figures 3a and 3b. The j_{gcd} for all samples stays high in the beginning and then gradually decreases to a steady value, and the initial high current is due to the reduction of Cu oxides to Cu. Hence, the charge quantity (Q) required to reduce the Cu oxides for each sample should be related to the amounts of Cu₂O and CuO on Cu foams. Specifically, the time to reach a stable j_{gcd} value of ~ 1.0 mA/cm² for the pristine Cu foam electrode is shorter than 8 min since only a layer of thin native Cu oxide exists. The FE for CO and HCOOH is smaller than 1.5% and 5%, respectively, and the major product is H₂ ($\sim 90\%$) from the competing H₂O reduction [14,15]. Annealing Cu foam at 120°C shows negligible effects on both FEs and j_{gcd} . The electrode annealed at 200 °C exhibits an initial j_{gcd} of 20 mA/cm² (around 8 min) for the reduction of CuO/Cu₂O layer and it subsequently reaches a stable value of ~ 2.9 mA/cm². The average FE for CO is enhanced to 4% along with an obvious decrease in FE of H₂; the overall FE for HCOOH is 10.8%. For the Cu foam annealed at 300 °C and 400 °C, its j_{gcd} reaches a steady value of ~ 4.2 and 7.7 mA/cm², respectively. The FE for CO is enhanced to 17% and 27%, respectively. However, the FE for HCOOH remains almost unchanged at 10~14% with the annealing temperature ranging from 200 to 400 °C, albeit with a

significant increase in the surface Cu flakes. Notably, the Cu foam annealed at 500 °C presents an extremely high and stable j_{gcd} value of 9.4 mA/cm², which is one-order of magnitude higher than that of the pristine Cu foam and the value is much higher than previously reported values for annealed Cu foil and mesh (Table S1). The electrode can also produce CO with ~39% FE and HCOOH with 23% FE as well as hydrocarbons (CH₄, C₂H₄) with FE of <5%. Furthermore, the FE for CO is stable throughout the CO₂ reduction processes. For a comparison, the flat Cu foil (thickness, ~30 μm) was subjected to heat-treatment in air and their electrocatalytic activities for CO₂ reduction were evaluated under similar catalytic conditions as the Cu foam. Since the Cu foil was fully oxidized at 500 °C and too fragile to be fabricated as an electrode, the annealing temperature for Cu foil was selected to be 120 to 400 °C. In contrast to the Cu foam, the SEM images (Figure S4) of annealed Cu foil reveal a growth of a dense Cu oxide layer at lower temperatures and eventually ~12 μm-nanorods of Cu₂O/CuO (Figure S5) with 100~500 nm diameters were grown on the Cu foil surface at 400 °C. The Cu nanorods formed by electrochemical reduction remain intact on the surface, consistent with the previous reports [35]. While for the Cu materials annealed at lower temperatures (120 °C, 200 °C), Cu foil and Cu foam show comparable current density and total selectivity for CO+HCOOH production, at the high annealing temperature, significantly higher catalytic current densities (2~6 times of those of Cu foil) were observed for Cu foam (Figure S6). It is obvious that the Cu foam is a promising substrate to develop a high-efficient electrocatalyst that can operate at high current density with low energy consumption for large-scale CO₂ reduction.

4. Discussions

As shown above, it is clear that the high catalytic current density for CO₂ reduction over annealed Cu foams is closely related to the formation of Cu surface structures, which is connected to the charge quantity Q required for CuO/Cu₂O reduction. The inset in Figure 3b plots the obtained j_{gcd} for each Cu foam electrode as a function of the Q extracted from the Figure S3, where the Q is obtained by integrating current-time curve before each sample reach a steady j_{gcd} . The approximate linear relationship suggests that the surface structures of Cu formed by electroreduction play a key role in CO₂ reduction, and the enhanced catalytic activity and FE come from the increased number of active sites. It is known that the double layer capacitance (DLC) obtained with the cyclic voltammetry (CV) method (Figure S7 and Table S2) is a good index for the electrochemically active surface area (ECSA) [48,49]. Figure 3c shows that the DLC is positively correlated with the Q , suggesting that the number of surface active sites increases with the quantity of the Cu crystals derived from Cu oxides. This result also clearly indicates that the larger j_{gcd} for CO₂ reduction stems from the enhanced ECSA, which can be anticipated since the CO₂ reduction seems to be dominated by the surface Cu structures. In order to further shed light on the higher intrinsic activity of annealed Cu foams, the FEs for CO and HCOOH production were plotted against Q in Figure 3d. The FE of CO increases linearly with the Q , while the FE of HCOOH increases with the Q in the beginning but the increase slows down at a higher Q . These results further confirm that the formation of a threshold quantity of the Cu oxides is essential to prepare a Cu foam electrode with high ECSA, which leads to a high catalytic current and a high selectivity towards CO₂ reduction [36].

Furthermore, the 500 °C-annealed Cu foam electrode is also efficient to selectively reduce CO₂ at a much lower overpotential. The plot of j_{gcd} vs. applied potential in Figure 4a reveals that the j_{gcd} of annealed Cu foam electrode increases with the applied potential from -0.2 to -0.6 V vs.

RHE and is much higher than those of the pristine Cu foam, demonstrating the high efficiency of annealed Cu foam towards CO₂ reduction, which is the direct result of its large surface areas as indicated in Figure 3c. Comparisons in Figures 4b and 4c show that the annealed Cu foam electrode has a much lower onset potential for CO₂ reduction, where appreciable CO (~9%) and HCOOH (~5%) production starts at ~-0.2 V vs. RHE, corresponding to a 0.09 and 0 V of overpotential for those products, respectively. Moreover, an overpotential of only ~0.14 V (corresponding to -0.25 V vs. RHE) is required to reach a current density of 67.2 and 49.6 $\mu\text{A}/\text{cm}^2$ for CO₂ reduction to CO and HCOOH, respectively. These values are among the lowest overpotential on Cu-related materials reported thus far (Table S1). When the annealed Cu foam electrode is polarized to more negative potentials, an obvious enhancement in both HCOOH and CO FEs is observed with a peak FE of ~39% for CO and ~23% for HCOOH production at potential of ~-0.45 V vs. RHE, whereas the FE of H₂ is 22%. The observed product distribution with varying overpotentials for the annealed Cu foam is consistent with the previously reported results on polycrystalline [13-16] and several oxide derived Cu catalysts [36,43]. However, the annealed Cu foam exhibits a much higher current density at lower overpotential.

In order to get kinetic insights into enhanced CO₂ reduction efficiency and pathway on the annealed Cu foam, the partial current density for each major product (obtained through multiplying j_{gcd} at given potential by the FE for each product) was plotted against applied potentials (Figure S8). As the partial current density is proportional to its turnover frequency (TOF), reaction kinetics can be studied through analyzing reaction rates by means of partial current density [15]. As shown in Figure 4(b), although the H₂ FE on annealed Cu electrode decreases significantly in the potential range of -0.2 to -0.4 V vs. RHE, the partial current densities for H₂ formation is actually constant and increases gradually (Figure S8a), indicating

that the increase in CO₂ reduction selectivity is not due to the decrease in H₂ evolution rate, but the more rapidly increasing production rates for CO and HCOOH. In fact, in the same potential region, there is a substantial increase in the partial current densities for HCOOH and CO. In comparison, for the pristine Cu foam, the H₂ formation rate dominates over CO and HCOOH production rates at the potentials ranging from -0.2 to -0.75 V vs. RHE (Figure S8b), indicating that the CO₂ reduction on the pristine Cu foam requires a much more negative potential to reach an appreciable reaction rate. These results again confirm the high efficiency of the annealed Cu foam for CO₂ reduction. Furthermore, the Tafel plots (overpotential vs. the log of the partial current density) for each product were extracted from the data described above (Figure 4d). The corresponding results under identical conditions for pristine Cu foam are included for comparison. 500 °C-annealed Cu foam electrode shows a slope of 110 mV/dec for CO production, which is comparable to 115 mV/dec for pristine Cu foam, suggesting that the initial electron transfer to CO₂ to form a surface-adsorbed CO₂^{•-} intermediate is the rate-determining step on both electrodes, consistent with the observations on polycrystalline and oxide-derived Cu electrodes [14,15,36]. Most interestingly, a higher slope of 194 mV/dec for H₂ evolution is observed on annealed Cu foam electrode as compared to pristine Cu foam (183 mV/dec). These results suggest that the suppression of H₂ generation on annealed Cu foam electrode is associated with the formation of distinct Cu surface structures [14,15,22,26,43,50].

It has been previously reported that the grain boundary-supported and stabilized metastable active sites are believed to be responsible for the observed high activity and selectivity for CO₂ reduction on oxide-derived Cu and Au electrodes [38,42]; however, the nature of the active sites and their influence on activity and selectivity of CO₂ reduction have not been clearly addressed yet. Moreover, it was well-documented that the CO₂ reduction efficiency and the product

distribution on metal electrodes show an exposed-facet-dependent behaviors, especially when Cu was used as electrocatalyst [13,23,25]. In this context, density functional theory (DFT) calculations have predicted that the adsorbed carboxyl (COOH^*), a key intermediates, on Cu electrodes are more strongly stabilized by the open (211) facet, followed by the close-packed facets ((100) and (111)) with the (111) surface binding the COOH^* most weakly [25]. On the contrary, HCOOH production appears to be more efficient on the more close-packed facets ((111) and (100)) as compared to the (211) facet, presumably due to a change in the reduction mechanism [25]. On the other hand, the DFT calculations also suggested that H_2 production can be largely suppressed on (211) as compared to either of the close-packed surfaces at lower overpotential of <-0.2 V [25].

In order to clarify the effect of the change in surface structures on catalytic properties, we have investigated the electrosorption of oxygenated species (e.g., O and/or OH) on the resulting Cu foam surfaces to identify the exposed facets, as shown in Figures 5 and S9. According to the previous report [51], the electrosorption of oxygenated O and/or OH takes place at certain oxidative potentials on different Cu facets. Based on these results, we are able to assign the peaks observed in the cyclic voltammogram (CV) to the features of various exposed facets, allowing the qualitative investigation on the change in the surface structures. As shown in Figure 5, CV curves of pristine Cu foam and annealed Cu foam prepared at 120°C are featureless, probably due to the extremely low ECSA. In contrast, all the Cu foam electrodes annealed at higher temperatures ($>300^\circ\text{C}$) shows three typical oxidation peaks during anodic scans that can be assigned to the electrosorption features of oxygenated species on low-index facets of fcc Cu, e.g. (100) at $0.38\sim 0.40$ V, (110) at $0.43\sim 0.46$ V, and (111) at $0.49\sim 0.52$ V vs. RHE. In Figure S9, the observed absolute current densities for those features increase obviously at higher annealing

temperatures, suggesting the generation of relatively more Cu nanocrystals with preferably formed low-index facets from the surface reconstruction, leading to a high catalytic current density for CO₂ reduction on annealed Cu foam electrodes as shown in Figure 3b. In addition, the average sizes of Cu (111), (200), and (220) microcrystals/micrograins for annealed Cu foam were calculated to be 22.7, 21.1, and 25.8 nm, respectively, which are much smaller than those of pristine Cu foam (31.6, 29.6, 35.9 nm) (Figure S10), suggesting that more active facets were formed on annealed Cu foam compared to pristine Cu foam during surface-reconstruction process, presumably increasing the density of the grain-boundaries formed between surface Cu crystals. This enhancement in grain-boundary will enhance the number of metastable active sites and was proposed to improve the activity and selectivity of CO₂ reduction on oxide-derived Cu and Au electrocatalysts [38, 42].

Moreover, it is noted that the enhancements in peak intensity for the (100) and (110) facets are even more pronounced as compared to (111) facet. Consistent with the previously reported results [25,36,43], these observations clearly suggest that the enhanced activity and selectivity of the annealed Cu foam for CO₂ reduction to CO and HCOOH over H₂O reduction is associated with the formation of more active low-index Cu facets, especially the (100) facets [43]. This conclusion is also supported by the enhanced specific activity of annealed Cu foam electrode as compared to pristine Cu foam. The CO partial current density was normalized by the electrochemical surface area to calculate the specific activity. 500 °C-annealed Cu foam electrode demonstrates the highest specific activity of 68.8 $\mu\text{A}/\text{cm}^2$, which is ~7 times higher than that of pristine Cu foam (10.0 $\mu\text{A}/\text{cm}^2$), suggesting that the effect of electrochemical surface area is not the sole contributor to the enhanced CO₂ reduction performance and the formation of the distinct surface structure are responsible for the higher activity and selectivity of annealed Cu

foam toward electrocatalytic reduction of CO₂ to CO. Moreover, as predicted by DFT calculations, when more (111) facets are present on Cu surface, the production of HCOOH from CO₂ reduction could also be promoted at lower overpotential while the H₂ selectivity is suppressed [25], which is consistent with our observations that the HCOOH FE increases with the increase in (111) facet. This conclusion is supported by the XRD analysis (Figure S10), revealing that the ratio of the (111) facets for annealed Cu foam increased slightly compared to pristine Cu foam. It has also been observed that the FE ratio of CO to HCOOH increases with the higher annealing temperatures even though the estimated peak current density ratio of (100) to (111) ($I_{(100)}/I_{(111)}$) and (110) to (111) ($I_{(110)}/I_{(111)}$) only increases slightly, indicative of a possible synergistic effect between multi-exposed facets on Cu surface, which may dramatically influence the product distribution.

5. Conclusions

In summary, a simple two-step method was used to prepare highly efficient Cu foam electrodes. The large quantity of Cu oxides was firstly generated on Cu foam substrate by annealing in air, followed by electrochemical reduction to produce a Cu foam electrode with high electrochemically active surface areas while retaining 3D open frameworks. A typical catalytic current density as high as $\sim 9.4 \text{ mA/cm}^2$ was achieved for CO₂ electroreduction on optimized Cu foam electrode, resulting in 39% CO FE and 23% HCOOH FE at -0.45 V vs. RHE. The annealed Cu foam exhibited a much lower onset potential (0.09 V (CO) and 0 V (HCOOH) of overpotential) for the CO₂ reduction and an overpotential of only 0.14 V to reach a current density of 1 mA/cm^2 . These results demonstrate that apart from the enhanced surface areas, the preferable formation of low-index Cu facets such as (100) and (111) during the surface reconstruction processes and the synergistic effect between them play key roles for enhancing

the activity and selectivity of annealed Cu foam electrodes towards CO₂ reduction. Our work has advanced the design of Cu-based electrocatalyst that can operate at a high current density by integrating the intrinsic structural properties of Cu foam substrates and surface structure reconstruction. This may provide promising opportunities for the development of advanced electrocatalytic materials for CO₂ reduction for practical applications.

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Appendix A. Supporting information

Table S1-S2 and Figures S1-S10 are included.

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Figure captions:

Figure 1. (a-d) SEM images of pristine Cu foam and those annealed at 200, 300, and 500 °C. (e) 500 °C-annealed Cu foam electrode after electrochemical reduction at -0.45 V vs. RHE in CO₂-saturated 0.1 M KHCO₃.

Figure 2. (a) Raman spectra for annealed Cu foam electrodes obtained with a confocal Raman spectrometer excited by a 532 nm laser. (b) XRD patterns of pristine Cu foam, annealed Cu foam, and the 500 °C-annealed Cu foam electrode after electrochemical reduction. (c) XPS spectra of pristine Cu foam and 500 °C-annealed Cu foam electrode before and after electrochemical reduction.

Figure 3. (a) Average Faradaic efficiencies (FEs) of H₂, CO, and HCOOH for CO₂ reduction electrolysis over pristine Cu foam and annealed Cu foam electrodes at -0.45 V vs. RHE in CO₂-saturated 0.1 M KHCO₃. (b) Steady-state total current density (j_{gcd}) for pristine Cu foam and annealed Cu foams. Inset is the plot of j_{gcd} vs. the amount of charge (Q) required for CuO/Cu₂O reduction. (c) Double-layer capacitance for annealed Cu foam electrodes after subsequent reduction at -0.45 vs. RHE in 0.1 M KHCO₃. (d) Dependence of FEs of CO and HCOOH production on Q.

Figure 4. (a) Total current densities vs. applied potential for pristine Cu foam and 500 °C-annealed Cu foam electrode. (b, c) FEs of the H₂, CO, and HCOOH vs. applied potentials for 500 °C-annealed Cu foam (b) and pristine Cu foam electrode (c). (d) Tafel plots of CO and H₂ production over pristine Cu foam and 500 °C-annealed Cu foam electrode.

Figure 5. Cyclic voltammograms (CVs) of the pristine Cu foam and several Cu foam electrodes prepared by annealing at different temperatures as indicated and subsequently reduction at -0.45 V vs. RHE in CO₂-saturated 0.1 M KHCO₃. The CVs were recorded in 1 M KOH with a scan rate of 2 mV/s. The low-index facets for fcc Cu crystals were labeled by comparing the CVs to those of single crystals shown in ref [51].

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Graphical Abstract

A high surface area and surface-reconstructed Cu foam electrode was prepared for low overpotential and selective CO₂ reduction to CO (39 %) and HCOOH (23%) with an extremely high catalytic current density of ~9.4 mA/cm² at -0.45 V vs. RHE.

Highlights:

- Surface-reconstructed Cu foam electrode is obtained by electroreduction of air-annealed Cu foam.
- The resulting Cu foam shows a current density of $\sim 9.4 \text{ mA/cm}^2$ for CO_2 reduction at -0.45 V vs. RHE , one order higher than pristine Cu foam.
- The resulting Cu foam exhibits 39% CO and 23% HCOOH faradaic efficiencies.
- The high CO_2 reduction performance is attributed to its large surface area and distinct surface crystalline structures.

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