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Coupling of Cu(100) and (110) Facets Promotes Carbon Dioxide Conversion to Hydrocarbons and Alcohols

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Abstract: Copper can efficiently electro-catalyze carbon dioxide reduction to C₂₊ products (e.g., C₂H₄, C₂H₅OH, and n-propanol). However, the correlation between the activity and active sites remains ambiguous, impeding further improvements in their performance. This paper describes the facet effect of copper crystal to promote CO adsorption and C-C coupling and consequently yield a superior selectivity for C₂₊ products. We achieve a high Faradacic efficiency (FE) of 87% and a large partial current density of 217 mA cm⁻² toward C₂₊ products on Cu(OH)₂-D at only -0.54 V versus the reversible hydrogen electrode in a flow-cell electrolyzer. With further coupled to a Si solar cell, record-high solar conversion efficiencies of 4.47% and 6.4% are achieved for C₂H₄ and C₂₊ products, respectively. This study provides an in-depth understanding of the selective formation of C₂₊ products on Cu and paves the way for the practical application of electrocatalytic or solar-driven CO₂ reduction.

Introduction

Solar-driven electrocatalytic carbon dioxide reduction reaction (CO₂RR) to value-added chemicals and fuels is attractive to simultaneously utilize renewable energy source and reduce atmospheric CO₂ concentration to solve the environmental problem ^[1]. In contrast to mono-carbon products such as CO and CH₄, higher value-added C₂₊ (including C₂) hydrocarbons and alcohols have attracted more attention ^[2]. Currently, owing to the specific binding energy of *CO intermediate, copper is the only metal that can effectively catalyze CO₂RR to C₂₊ products ^[3]. Nonetheless, due to the sluggish kinetics and the competition of kinetically favorable hydrogen evolution reaction (HER), poor selectivity and activity still hinder the large-scale implementation of CO₂RR electrolyzers.

Electroreduction of high-valence-state copper has been reported to improve CO₂RR performance ^[4]. HER is largely suppressed over Cu sites derived from high-valence-state copper species (*e.g.*, precursor). However, the FE for C₂₊ products is generally unsatisfied, and the reaction mechanisms are still under debate. Grain boundaries formed by the reduction are firstly proposed to be responsible for the enhanced catalytic activity ^[1c, 5]. Similarly, the Cu(100) facet preferentially formed on the surface also contributes to the enhanced performance ^[6].

The high local pH induced by the increased surface roughness also plays a role [4e, 7]. Additionally, positively charged Cu [4a, 8] and residual subsurface oxygen [9] are proposed to stabilize CO adsorption and promote dimerization and thus significantly enhance the selectivity for C2+ products. However, Cu+ and subsurface oxygen have been revealed experimentally and theoretically to be unstable under reduction conditions during CO₂RR ^[4e, 6, 10]. The geometric structure of surface atoms in catalysts is significant for the catalytic performance [11]. As of yet, it is a great challenge to control the surface atom arrangement due to the random reconstruction of Cu during the reduction process of Cu oxides. Since the Cu-O bond is broken and O (or OH) is released under reduction potential, the pre-catalyst plays a crucial role in the structure reconstruction for Cu preparation. By modifying the structures of precursors (Cu(OH)₂, CuO and Cu₂O), we predict that the exposed surface on the catalysts can be regulated.

This paper describes a Cu catalyst with abundant stepped Cu(110) and highly active Cu(100) sites for CO₂RR to C₂₊ products. Our results reveal that Cu(OH)₂-derived Cu catalysts expose relatively high density of stepped Cu(110) and Cu(100), which are assembled into Cu(210) and Cu(310). The assembled Cu(210) and (310) promote CO adsorption and CO dimerization, leading to improved CO₂RR catalytic activity to C₂₊ products. When evaluated in flow-cell with an alkaline aqueous solution as the electrolyte, the C₂₊ FE of 87% is achieved with a larger current density at low overpotential. We also coupled a cheap Si solar cell with electrochemical cell to construct a PV-EC system for direct solar-driven CO₂ reduction, the most efficient solar conversion efficiency of 4.47% and 6.4% is achieved for C₂H₄ and C₂₊ products, respectively.

Results and Discussion

Synthesis and characterization of catalysts. We prepared three types of precursors. $Cu(OH)_2$ supported on copper foil $(Cu(OH)_2/Cu$ foil) was prepared by converting commercial Cu foil in an alkaline solution ^[12]. CuO supported on Cu foil (CuO/Cu foil) and Cu₂O supported on Cu foil (Cu₂O/Cu foil) were obtained from annealing Cu(OH)₂/Cu foil in air and N₂ atmosphere, respectively (for details, please see the Methods Section). The

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structures of Cu(OH)₂/Cu foil, CuO/Cu foil, and Cu₂O/Cu foil are confirmed with X-ray diffraction spectroscopy (XRD) patterns, Raman spectra, X-ray photoelectron spectroscopy (XPS) (Figures S1a-c), and scanning electron microscopy (SEM) images (Figure S1d-f).



Figure 1. Structure characterization of the catalysts. (a) Schematic illustration of the preparation of $Cu(OH)_2$ -D/Cu foil, CuO-D/Cu foil, and Cu_2O -D/Cu foil. *In situ* Raman spectra of (b) $Cu(OH)_2$ /Cu foil, (c) CuO/Cu foil, and (d) Cu_2O/Cu foil in CO₂-saturated 0.1 M KHCO₃ at -0.5 V vs. RHE. (e) and (f) Aberration-corrected HAADF-TEM images of $Cu(OH)_2$ -D. (g) Models showing coordination numbers of (310) and (210) facets; the yellow square marked area is the square Cu(100).

To prepare the designed catalysts, the Cu(OH)₂/Cu, CuO/Cu and Cu₂O/Cu foils were placed in a CO₂-saturated 0.1 M KHCO₃ aqueous solution and reduced under the bias potential of -0.5 V versus the reversible hydrogen electrode (vs. RHE) for ~800 s (Figure 1a). The obtained samples were denoted as Cu(OH)2-D/Cu foil, CuO-D/Cu foil, and Cu2O-D/Cu foil, respectively. Figure. S2 shows time-dependent current density curves for the reduction of Cu(OH)₂/Cu foil, CuO/Cu foil, and Cu₂O/Cu foil, in agreement with the reduction of Cu hydroxide/oxide to metallic Cu [4e]. In situ Raman was employed to investigate the reduction process (Figure 1b-d). The Raman spectra of these samples collected in the open circuit are similar to the spectra of precursors measured ex-situ (Figure S1b). After several minutes reduction in the CO₂-saturated 0.1 M KHCO₃ aqueous solution at -0.5 V vs. RHE, all of the characteristic Raman bands associated with Cu(OH)₂, CuO and Cu₂O disappear. These results demonstrate that all three samples are reduced to metallic copper, agreeing well with the thermodynamics equilibria displayed in the Cu-pourbaix diagram ^[13]. Moreover, other than Cu peaks, no other peaks attributed to Cu hydroxide/oxide are observed in XRD patterns, further confirming that all the Cu hydroxide/oxide have been reduced to metallic Cu (Figure S3). XPS analysis (Figure S4) reveals that Cu mainly presents a metallic state. Only a small amount of Cu2+ is detected, probably due to the surface oxidation during sample transfer. It should be noted that we could not exclude the possible presence of Cu⁺ (with the binding energy very closed to Cu⁰) due to the oxidation in air. High resolution TEM images also

demonstrate the precursors were converted to metallic Cu, where exhibit lattice fringes of Cu(200) and (111) (Figure S5).

Transmission electron microscopy (TEM) images show that Cu(OH)₂-D, CuO-D, and Cu₂O-D have essentially inherited the rod structure of the precursors (Figure S6). Interesting, Cu(OH)2-D gives more roughness structure than CuO-D and follows by Cu₂O-D, it is large likely due to the more substantial lattice change during the reduction of Cu(OH)₂ to metallic Cu (the lattice distance of Cu(OH)2, CuO, Cu2O, and Cu gives a decreasing trend observed from the XRD results). Nevertheless, due to the rough surface structure of Cu(OH)₂ (Figure S6), highindex stepped surfaces, such as $Cu(310)=3(100) \times (110)$ and $Cu(210)=2(110) \times (100)$, composed by Cu(100) and Cu(110), can be observed in Cu(OH)₂-D (Figure. 1, e-g). The Cu(100) domains in Cu(310) and Cu(210) also inherit the nature of the stepped Cu(110) with low-coordinations (Figure 1g). Additionally, to further validate the surface roughness of Cu(OH)₂-D/Cu foil, we compare the double-laver capacitance (C_{dl}) between the electrodes and polished Cu foil to calculate their electrochemical surface area (ECSA) (Figure S7). The Cu(OH)₂-D/Cu foil has the largest ECSA of 84.3, followed by 72.4 and 64.9 for CuO-D/Cu foil and Cu₂O-D/Cu foil, respectively (table S1).



Figure 2. Surface structure. (a) CV curves collected in Ar-saturated 1 M KOH for Cu(OH)₂-D/Cu foil, CuO-D/Cu foil and Cu₂O-D/Cu foil, scan rates = 5 mV s⁻¹. (b) Grazing incident XRD (α = 0.1°) patterns of Cu(OH)₂-D/Cu foil, CuO-D/Cu foil, and Cu₂O-D/Cu foil.

Cyclic voltammetry (CV) curves were collected in Ar-saturated 1 M KOH to further probe the surface structure of Cu(OH)₂-D/Cu foil, CuO-D/Cu foil and Cu2O-D/Cu foil. Different Cu facets exhibit unique OH-adsorption/desorption peaks in the CV curves ^[14]. As displayed in Figure. 2a, the peaks centered at ca. 0.34, 0.37, and 0.43 V can be assigned to the OH-electrosorption on Cu(100), Cu(110) and Cu(111), respectively [14]. The peaks of OH-electrosorption on Cu(100) and Cu(110) are more prominent for Cu(OH)₂-D/Cu foil, demonstrating Cu(OH)₂-D/Cu foil expose more stepped Cu(110) and Cu(100) surface, followed by CuO-D/Cu foil and Cu₂O-D/Cu foil (Figure 2a). As revealed by aberration-corrected HAADF-TEM image mentioned above, the facets are homogeneously distributed, rather than exist separately, which can form high-index stepped facets, such as Cu(210) and Cu(310). Grazing incident XRD (α = 0.1 $^{\circ}$, probe depth of ca. 2 nm) also revealed the decreasing trend of exposed Cu(100) and Cu(110) facets ratio in the surface from Cu(OH)₂-D/Cu foil to CuO-D/Cu foil and Cu₂O-D/Cu foil (Figure. 2b).

CO2RR performance. CO2RR performance was carried out in CO₂-saturated 0.1M KHCO₃ (pH=6.9) in an anion-conducting membrane separated two-compartment cell (H-cell) with Cu(OH)₂-D/Cu foil (CuO-D/Cu foil or Cu₂O-D/Cu foil) as the working electrode, saturated Ag/AgCl as the reference electrode and Pt plate as counter electrodes, respectively. The Faradaic efficiency (FE) for each product associated with the change of potential is presented in Figure 3. Similar to previous studies, the hydrocarbons and alcohols are dominant products at the high overpotentials, while H₂ and CO are instead dominant at low overpotentials ^[15]. Due to the formation path of HCOOH is different from other products [1a], and usually appeared at low applied potential with low current density, we don't evaluate HCOOH product in H-cell. Specifically, the selectivity for H₂ on Cu(OH)₂-D/Cu foil, CuO-D/Cu foil, and Cu₂O-D/Cu foil gradually increasing follows an order of (Cu(OH)2-D/Cu foil < CuO-D/Cu foil < Cu₂O-D/Cu foil). In addition, Cu(OH)₂-D/Cu foil and CuO-D/Cu foil showed relatively higher FE for CO than Cu₂O-D/Cu foil at low overpotentials.



Figure 3. CO_2 reduction reaction performance in H-Cell. Faradaic efficiency of (a) $Cu(OH)_2$ -D/Cu foil, (b) CuO-D/Cu foil, and (c) Cu_2O -D/Cu foil in CO_2 -saturated 0.1 M KHCO₃ aqueous solution. (d) The C_{2+} FEs for $Cu(OH)_2$ -D/Cu foil, CuO-D/Cu foil, and Cu_2O -D/Cu foil.

The Cu(OH)₂-D/Cu electrode exhibits higher selectivity for C₂₊ products than CuO-D/Cu and Cu₂O-D/Cu (Figure 3). Specifically, Cu(OH)₂-D/Cu displays the maximum FE of ~41%, 21%, and 11% for C₂H₄, C₂H₅OH, and n-propanol at ca. -1.08, -0.87, and -0.98 V, respectively. As displayed in Figure. 3D, Cu(OH)₂-D/Cu foil exhibits the highest FE of ~59% for C₂₊ products at ca. -0.98 V, as compared to ~45% for CuO-D/Cu foil and ~21% for Cu₂O-D/Cu foil at ca. -1.03 V and -1.23 V, respectively. The trend for C₂₊ hydrocarbons and alcohols consists well with that of exposed stepped Cu(110) and Cu(100) surface of Cu(OH)₂-D/Cu foil, CuO-D/Cu foil and Cu₂O-D/Cu foil as mentioned above (Figure. 2 and Figure. 3d), suggesting that the Cu(100) and stepped Cu(110) surface may be responsible for the enhanced formation of C₂₊ products in OD-Cu catalysts.

Simultaneously, the FEs towards CH_4 on $Cu(OH)_2$ -D/Cu foil and CuO-D/Cu foil are below 2%, while that for Cu_2O -D/Cu foil increased from ~2% to ~24% at the potential lower than ca. - 1.29 V (Figure 3, a-c). Furthermore, $Cu(OH)_2$ -D/Cu foil gives a higher maximum C_{2+}/C_1 ratio (ca. 24 at -0.98 V) than that of CuO-D/Cu foil (ca. 23 at -1.14 V) and Cu₂O-D/Cu foil (ca. 0.8 at -1.23 V) (Figure S8).

Current density is another key factor in evaluating CO2RR performance. Cu(OH)₂-D/Cu foil exhibits a higher current density than CuO-D/Cu foil, followed by Cu₂O-D/Cu foil (Figure S9a). Cu(OH)₂-D/Cu foil also shows a larger partial current density for C2+ products than CuO-D/Cu foil and Cu2O-D/Cu foil (Figures S9b-d and S10). For CuO-D/Cu foil and Cu2O-D/Cu foil, the peak partial current density for C₂H₄ is -10.6 and -5.6 mA cm⁻² at ca. -1.14 and -1.23 V, respectively (Figure S9c and d). Nevertheless, the highest C2H4 partial current density on Cu(OH)₂-D/Cu foil is -18.4 mA cm⁻², which is 1.74-fold and 3.29fold of aforementioned, respectively, at ca. -1.18 V (Figure S9b). Additionally, the highest total current density for C₂₊ products is ca. -22.7, -15.8, and -5.6 mA cm-2 on Cu(OH)2-D/Cu foil, CuO-D/Cu foil and Cu₂O-D/Cu foil, respectively (Figure S10). Such a high C₂₊ product current density of ca. -22.7 mA cm⁻² for Cu(OH)₂-D/Cu foil is close to the limiting current density (ca. -20 mA cm⁻²) for CO₂ reduction due to the low solubility of CO₂ in aqueous solution (ca. 34 mM at 25 °C) [4c].

The low current densities for CuO-D/Cu foil and Cu₂O-D/Cu foil can be attributed in part to their reduced surface area. To further understand the intrinsic activities of these catalysts, ECSA was employed to normalize the current density. As illustrated in Figure S11a, Cu(OH)2-D/Cu foil still shows the largest normalized current density, followed by CuO-D/Cu foil and Cu₂O-D/Cu foil. In particular, Cu(OH)₂-D/Cu foil also exhibit a larger normalized partial current density of C2+ products than CuO-D/Cu foil and Cu2O-D/Cu foil, indicating the excellent intrinsic C₂₊ activity of Cu(OH)₂-D/Cu foil (Figure S11b). Figure S12 shows suppressed C1 partial current density for Cu(OH)2-D/Cu foil and CuO-D/Cu foil. The higher C1 activity of Cu2O-D/Cu foil might be ascribed to the larger proportion of Cu(111) facet exposed in Cu₂O-D/Cu foil (Figure 2), which has been revealed to favor CH₄ by CO₂RR experiments on a single crystal ^[16]. Moreover, local pH has been proposed as another important factor influencing the selectivity of CO_2RR products ^[4d, 7, 17]. Due to a higher OH-production rate per geometric electrode area during H₂O/CO₂ reduction for high roughness Cu(OH)₂-D/Cu foil, its local pH is higher than that of CuO-D/Cu foil and Cu₂O-D/Cu foil. The increased pH suppresses methane production without affecting intrinsic C_{2+} activity (Figure S13) ^[4d, 18].

We also evaluate the stability of Cu(OH)₂-D/Cu foil at ca. -1.08 V. As displayed in Figure S14a, the FE of C₂H₄ only decreased less than 4% after 11 h, implying the excellent stability of Cu(OH)₂-D/Cu foil. Additionally, there was only a slight reduction in current density, and the morphologic still maintained after 11 h (Figures S14b, S15 and S16). The excellent stability of our Cu(OH)₂-D/Cu foil may be due to the electroreduction of precatalyst to a relatively stable state during the preparation process and its large particle size which is unsatisfied for reconstruction [¹⁹].

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Figure 4. DFT calculations and *in situ* ATR-SEIRAS and *in situ* Raman spectroscopy characterization. (a) CO_2 reduction procedure. *In situ* ATR-SEIRAS spectra of (b) $Cu(OH)_2$ -D (c) CuO-D and (d) Cu_2O-D from 0.2 to -1 V vs. RHE in CO-saturated 0.1 M KOH aqueous solution. The background is collected in the Arsaturated electrolyte at 0.2 V vs. RHE. (e) The activation energy barrier of CO dimerization. (f) Configurations of *CO dimerization. The solvent water molecules are hidden for viewing convenience. The colors are Cu in yellow, C in gray, and O in red. The region of Cu(100) on Cu(210) and Cu(310) are marked as orange. (g) *In situ* Raman spectra of Cu(OH)₂-D/Cu foil from -0.1 to -1 V vs. RHE in CO-saturated 0.1 M KOH aqueous solution.

DFT calculations and in situ spectroscopy study. We use DFT calculations and in situ spectroscopy to gain further insight into the reaction mechanism. The dimerization of two adjacent *CO to form *COCOH is known as the rate-dependent step (RDS) for C₂₊ products (Figure 4a) ^[20]. In situ attenuated total reflectance-surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) was employed to confirm CO adsorption (the key intermediate to C2+ products) (Figures 4b-d). The spectra were collected from 0.2 to -1.0 V vs. RHE in CO-saturated 0.1 M KOH. As displayed in Figure. 4, B-D, the vibrational bands centered at ca. 2050 cm⁻¹, corresponding to linearly-bonded CO (CO_L), is observed between 0.2 and -1.0 V [21]. The shift of bands associated with the applied potential is caused by the Stack turning effect ^[21]. The peaks of adsorbed CO_L over Cu(OH)₂-D is in higher wavenumbers than CuO-D and Cu₂O-D, corresponding to the strong binding of CO_L on $Cu(OH)_2$ -D with more lowcoordinated stepped (110) surface, followed by CuO-D and Cu₂O-D, which is crucial for building up sufficient CO coverage to promoting CO-CO coupling (Figure 4b-d) [22]. As shown in Figure 4e-f, the activation energy of CO dimerization on Cu(100) facets and the Cu(100) regions in (210) and (310) facets are similar, and lower than that on Cu(110) and Cu(111) facts (Figure S17). These results suggest that Cu(100) regions in (210) and (310) with low-coordination, help to build sufficient CO coverage and to facilitate the CO-CO coupling, which is responsible for the enhanced activity to form C2+ products. It should be noted that the rougher surface of Cu(OH)2-D may contain more low-coordinated sites. We also calculated the

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formation energy of *COCOH ^[20a, 23] on Cu(111), (100), and lowcoordinated (211) and (321) to understand whether the lowcoordinated sites are beneficial for C-C coupling or not (Figure S18). Our results revealed that the formation energy of *COCOH on low-coordinated (211) and (321) are higher than that on (100), implying that low-coordinated sites alone may not help to promote CO-CO coupling, consisting with previously reported ^[19, 24]. Low-coordinated square Cu(100) is essential to improve the formation of C₂₊ products in Cu(OH)₂-D.

Additionally, in situ Raman spectroscopy was also employed to catch the adsorbed intermediate further (Figure S19). As displayed in Figure 4g, three bands centered at ca. 276, 354 and 392 $\text{cm}^{\text{-1}}$ are observed on $\text{Cu}(\text{OH})_2\text{-}\text{D}/\text{Cu}$ foil in low-frequency area. The band at ca. 276 cm⁻¹ is attributed to the rotation of adsorbed CO on the Cu surface, and the other two bands at ca. 354 and 392 cm⁻¹ is derived from the Cu-CO stretch ^[25]. We note that C=O stretching modes displayed at ca. 1862, 2073, and 2164 cm⁻¹ and the bands of $*CH_2$ at ca. 2855 and 2925 cm⁻¹ can be observed at less negative applied potentials, demonstrating CO can be easily reduced to hydrocarbons or alcohols on $Cu(OH)_2\mbox{-}D/Cu$ foil (Figures 4g and h) $^{\rm [25a]}\mbox{-}.$ Whereas, Cu-CO stretch in the low-frequency area (ca. 354 and 276 cm⁻¹) and C \equiv O stretching modes in the high-frequency area (ca. 2073 and 2164 cm⁻¹), which are attributed to CO bound on more open Cu sites, are not obvious on CuO-D/Cu foil and Cu2O-D/Cu foil (Figure S20) [26]. Due to the weak adsorption of CO, the bands of CH₂ on CuO-D/Cu foil and Cu₂O/Cu foil are not obvious either (Figure S20). Besides, we also noted the presence of $C \equiv O$

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stretching modes displayed slightly lower than 2073 cm⁻¹ (at ca. 2046 cm⁻¹) on Cu(OH)₂-D/Cu foil, which can be attributed to the relatively weaker CO bound on fully coordinated Cu(100) or/and Cu(111) ^[26]. The *in situ* Raman also indicates that Cu(OH)₂-D/Cu foil promotes the adsorption of CO intermediate and C₂₊ product formation, agreeing well with the *in situ* ATR-SEIRAS results and DFT calculations.

Flow-cell and PV-EC configuration performance. To overcome the low solubility limitation of CO₂ in aqueous solution and meet the requirement of industry application (current density > 200 mA cm⁻²), the performance of Cu(OH)-D for CO₂RR was conducted with a flow-cell electrolyzer in 1 M KOH (Figure 5a). CO₂ molecules directly diffuse across the gas diffusion electrode to the electrode/electrolyte interface without dissolved in the electrolyte firstly ^[27]. In addition, it is not realistic to use alkaline electrolytes in batch-cell due to hydroxide ions that can easily combine with dissolved CO₂ to form carbonates. Figure 5b

exhibits the correlation between product FE and applied potential. FEs of H₂ at different potential are suppressed at a level below 20% in 1 M KOH alkaline electrolyte. Cu(OH)2-D shows the maximal FE of 58±1%, 21±0.2%, and 7±0.01% for C₂H₄, C₂H₅OH, and n-propanol, respectively, at -0.54 V with the total current density of 250 mA cm⁻² (Figure 5b and Figure S21). FE and partial current density of C₂₊ products are displayed in Figure 5C and Figure S21. High C2+ FE of ~87% and partial current density of ~217 mA cm⁻² were achieved simultaneously at -0.54 V. The power conversion efficiency (PCE) for C2+ products at different potential or current density are also calculated to evaluate the performance of Cu(OH)2-D (Figure S22). The PCE_{C2+} is increased as the current density or potential rises in our experiments. The maximum PCE_{C2+} of 56.5% was achieved at 250 mA cm⁻² (-0.54 V vs. RHE). The excellent performance is superior to other activities of CO₂ reduction to C₂₊ products reported so far (Figure S23 and table S2).



Figure 5. CO_2 reduction reaction performance in the flow cell and solar-driven CO_2 reduction performance. (a) Flow cell configuration. Cathode: $Cu(OH)_2$ -D/CP (1 cm²); Reference electrode: Hg/HgO (1 M KOH); Membrane: anion-exchange membrane; Anode: Ni foam (1 cm²). (b) Faradaic efficiency, and (c) C_2 + partial current density and faradaic efficiency of $Cu(OH)_2$ -D evaluated by flow cell in 1 M KOH. (d) I–V curve of the solar cell shown in Figure. S24 and I–V curve of the two-electrode electrochemical cell. (e) Solar driven CO_2 reduction current density and faradaic efficiency of products versus time.

The solar cell was employed to drive the CO_2 reduction system and realize artificial photosynthesis directly (Figures S24 and S25). NiFe double-layer hydroxide on Ni foam (NiFe-LDH/NF) with excellent oxygen evolution performance was used as the anode to configure the two-electrode CO_2 reduction cell (Figure S26). The ion-exchange membrane was excluded to minimize the resistance between the two electrodes. The geometric areas of the anode and cathode are 1 cm² and 0.2 cm², respectively. Potential-dependent current density of the electrochemical cell is shown in Figure 5d. The current was determined to be 50.9 mA at a low cell voltage of 2.74 V (Without iR-compensation). The solar cell is composed of fivejunction single-crystal Si photovoltaic, and the I-V curve collected under the illumination of standard AM 1.5G sunlight with 100 mW cm⁻² (1 sun) intensity also displayed in Figure. 5D under the red line. The power of the solar cell system revealed that the optimized working condition is at ca. 2.69 V, which gives the maximum output power (Figure S27). These two I-V curves crossed at the point where the current and cell voltage were respectively 50.9 mA and 2.74 V (operating point), which is close to the maximum power point of the solar cell (Figure 5d). During the long-time unassisted CO₂ reduction powered by simulated solar radiation, a C₂H₄ FE of ~50% was obtained (Figure 5e). The FE of C₂H₅OH and n-propanol were determined to be ~18% and ~4%, respectively. Surprisingly, the solar-to-fuel efficiency of 4.47%, 1.58%, and 0.35% for C₂H₄, C₂H₅OH,

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and n-propanol can be achieved, respectively (details see the Methods Section). The total solar-to-fuel efficiency for C₂₊ products is as high as 6.4%. The extremely high solar-to-C₂H₄ or C₂₊ efficiency is also higher than all of the reported ones as yet (table S3).

Conclusion

Comparing the performance of different copper hydroxide/oxides derived copper, we reveal that the stepped Cu(110) and Cu(100) sites in Cu(OH)₂-D/Cu foil are crucial for the enhanced selectivity/activity of C2+ products. In situ ATR-SEIRAS, DFT calculations, and in situ Raman spectra demonstrate that (110) facilitating CO adsorption and (100) promoting the C-C coupling to C_{2+} products. $Cu(OH)_2$ -D show the FEs of ~58% for C_2H_4 and ~87% for C_{2+} hydrocarbons and alcohols with the C_{2+} partial current density of ~217 mA cm⁻² only at -0.54 V in the flow-cell electrolyzer. We achieve a power conversion efficiency of 56.5% for C₂₊ hydrocarbons and alcohols at the same potential. Coupling to a Si solar cell, the solar conversion efficiency for C_2H_4 and C_{2+} products is as high as 4.47% and 6.4%, respectively. This study paves a facile stratagem to develop efficient catalysts for (solar driven) CRR to C2+ products and guides the development of Cu catalysts for efficient CO₂ reduction.

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Keywords: Solar-driven \cdot CO₂ reduction \cdot Cu (100) and (110) \cdot C₂₊ products

- a) D. D. Zhu, J. L. Liu, S. Z. Qiao, *Adv. Mater.* 2016, *28*, 3423-3452; b)
 R. M. Arán-Ais, D. Gao, B. Roldan Cuenya, *Acc. Chem. Res.* 2018; c)
 C. W. Li, J. Ciston, M. W. Kanan, *Nature* 2014, *508*, 504-507.
- [2] M. Jouny, W. Luc, F. Jiao, Ind. Eng. Chem. Res. 2018, 57, 2165-2177.
- a) S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. Stephens, K. Chan, C. Hahn, *Chem. Rev.* 2019, 119, 7610-7672; b) Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, *Electrochim. Acta* 1994, 39, 1833-1839.
- [4] a) H. Mistry, A. S. Varela, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y. W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser, B. R. Cuenya, *Nat. Commun.* 2016, *7*, 12123; b) C. W. Li, M. W. Kanan, *J. Am. Chem. Soc.* 2012, *134*, 7231-7234; c) D. Ren, J. Fong, B. S. Yeo, *Nat. Commun.* 2018, *9*, 925; d) K. Jiang, R. B. Sandberg, A. J. Akey, X. Liu, D. C. Bell, J. K. Nørskov, K. Chan, H. Wang, *Nat. Catal.* 2018, *1*, 111-119; e) D. Ren, Y. Deng, A. D. Handoko, C. S. Chen, S. Malkhandi, B. S. Yeo, *ACS Catal.* 2015, *5*, 2814-2821.
- [5] A. Verdaguer-Casadevall, C. W. Li, T. P. Johansson, S. B. Scott, J. T. McKeown, M. Kumar, I. E. Stephens, M. W. Kanan, I. Chorkendorff, J. Am. Chem. Soc. 2015, 137, 9808-9811.
- [6] M. G. Kibria, C. T. Dinh, A. Seifitokaldani, P. De Luna, T. Burdyny, R. Quintero Bermudez, M. B. Ross, O. S. Bushuyev, F. P. García de Arquer, P. Yang, *Adv. Mater.* **2018**, *30*, 1804867.

- [7] A. S. Varela, M. Kroschel, T. Reier, P. Strasser, *Catal. Today* 2016, 260, 8-13.
- [8] P. De Luna, R. Quintero-Bermudez, C.-T. Dinh, M. B. Ross, O. S. Bushuyev, P. Todorović, T. Regier, S. O. Kelley, P. Yang, E. H. Sargent, *Nat. Catal.* 2018, 1, 103-110.
- a) M. Favaro, H. Xiao, T. Cheng, W. A. Goddard, 3rd, J. Yano, E. J. Crumlin, *Proc. Natl. Acad. Sci. USA* 2017, *114*, 6706-6711; b) A. Eilert, F. Cavalca, F. S. Roberts, J. Osterwalder, C. Liu, M. Favaro, E. J. Crumlin, H. Ogasawara, D. Friebel, L. G. Pettersson, A. Nilsson, *J. Phys. Chem. Lett.* 2017, *8*, 285-290.
- [10] a) A. J. Garza, A. T. Bell, M. Head-Gordon, J. Phys. Chem. Lett. 2018, 9, 601-606; b) Y. Lum, J. W. Ager, Angew. Chem. Int. Ed. 2017, 57, 551-554.
- [11] a) D. Kim, J. Resasco, Y. Yu, A. M. Asiri, P. Yang, *Nat. Commun.* 2014, 5, 4948; b) Y. Wang, P. Han, X. Lv, L. Zhang, G. Zheng, *Joule* 2018, 2, 2551-2582.
- [12] Y. Luo, H. Zhou, J. Sun, F. Qin, F. Yu, J. Bao, Y. Yu, S. Chen, Z. Ren, *Energy Environ. Sci.* 2017, 10, 1820-1827.
- [13] E. McCafferty, in *Introduction to Corrosion Science*, Springer, 2010, pp. 95-117.
- [14] J. M. Droog, B. Schlenter, J. Electroanal. Chem. 1980, 112, 387-390.
- [15] A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J. K. Nørskov, Energy Environ. I Sci. 2010, 3, 1311-1315.
- [16] a) J. Phys. Chem. B 2002, 15-17; b) K. J. Schouten, Z. Qin, E. Perez Gallent, M. T. Koper, J. Am. Chem. Soc. 2012, 134, 9864-9867.
- [17] M Jouny, W. Luc, F. Jiao, *Nat. Catal.* **2018**, *1*, 748-755.
- [18] Y. Hori, R. Takahashi, Y. Yoshinami, A. Murata, J. Phys. Chem. B 1997, 101, 7075-7081.
- [19] J. Huang, N. Hormann, E. Oveisi, A. Loiudice, G. L. De Gregorio, O. Andreussi, N. Marzari, R. Buonsanti, *Nat. Commun.* 2018, 9, 3117.
- [20] a) T. Cheng, H. Xiao, W. A. Goddard, *J. Am. Chem. Soc.* 2017, 139, 11642-11645; b) F. Calle-Vallejo, M. T. Koper, *Angew. Chem. Int. Ed.* 2013, *5*2, 7282-7285.
- [21] J. Heyes, M. Dunwell, B. Xu, J. Phys. Chem. C 2016, 120, 17334-17341.
- [22] a) P. Hollins, *Surf. Sci. Rep.* **1992**, *16*, 51-94; b) P. Hollins, K. Davies, J. Pritchard, *Surf. Sci.* **1984**, *138*, 75-83; c) A. Malkani, J. Li, J. Anibal, Q. Lu, B. Xu, *ACS Catal.* **2020**, *10*, 941-946.
- [23] Y. Huang, Y. Chen, T. Cheng, L.-W. Wang, W. A. Goddard, ACS Energy Letters 2018, 3, 2983-2988.
- [24] R. Reske, H. Mistry, F. Behafarid, B. Roldan Cuenya, P. Strasser, J. Am. Chem. Soc. 2014, 136, 6978-6986.
- [25] a) D. Ren, J. Gao, L. Pan, Z. Wang, J. Luo, S. M. Zakeeruddin, A. Hagfeldt, M. Gratzel, *Angew. Chem. Int. Ed.* **2019**, 131, 15178-15182;
 b) T. T. Hoang, S. Verma, S. Ma, T. T. Fister, J. Timoshenko, A. I. Frenkel, P. J. Kenis, A. A. Gewirth, *J. Am. Chem. Soc.* **2018**, *140*, 5791-5797.
- [26] a) C. M. Gunathunge, X. Li, J. Li, R. P. Hicks, V. J. Ovalle, M. M.
 Waegele, *J. Phys. Chem. C* 2017, *121*, 12337-12344; b) S. Jiang, K.
 Klingan, C. Pasquini, H. Dau, *J. Phys. Chem. C* 2019, *150*, 041718.
- [27] C.-T. Dinh, T. Burdyny, M. G. Kibria, A. Seifitokaldani, C. M. Gabardo, F. P. G. de Arquer, A. Kiani, J. P. Edwards, P. De Luna, O. S. Bushuyev, *Science* **2018**, *360*, 783-787.

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This paper describes the facet effect of copper crystal to promote CO adsorption and C-C coupling and consequently yield a superior selectivity (87% Faradaic efficiency) for C_{2+} products. Record-high solar conversion efficiencies of 4.47% and 6.4% are achieved for C_2H_4 and C_{2+} products, respectively.