Engineering Cu surfaces for the electrocatalytic conversion of CO₂: Controlling selectivity toward oxygenates and hydrocarbons

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In this study we control the surface structure of Cu thin-film catalysts to probe the relationship between active sites and catalytic activity for the electroreduction of CO₂ to fuels and chemicals. Here, we report physical vapor deposition of Cu thin films on large-format (~6 cm²) single-crystal substrates, and confirm epitaxial growth in the <100>, <111>, and <751> orientations using X-ray pole figures. To understand the relationship between the bulk and surface structures, in situ electrochemical scanning tunneling microscopy was conducted on Cu(100), (111), and (751) thin films. The studies revealed that Cu(100) and (111) have surface adlattices that are identical to the bulk structure, and that Cu(751) has a heterogeneous kinked surface with (110) terraces that is closely related to the bulk structure. Electrochemical CO₂ reduction testing showed that whereas both Cu(100) and (751) thin films are more active and selective for C–C coupling than Cu(111), Cu(751) is the most selective for >2e[−] oxygenate formation at low overpotentials. Our results demonstrate that epitaxy can be used to grow single-crystal analogous materials as large-format electrodes that provide insights on controlling electrocatalytic activity and selectivity for this reaction.

carbon dioxide reduction | epitaxy | electrocatalysis | copper

The electrochemical reduction of CO₂ (CO₂R) is a process that could couple to renewable energy from wind and solar to directly produce fuels and chemicals in a sustainable manner. However, developing catalysts is a major challenge for this reaction, and significant advances are needed to overcome the issues of poor energy efficiency and product selectivity. One reason for these issues is that there are a limited number of catalysts that can effectively convert CO₂ to products that require more than two electrons (>2e[−] products), e.g., methane, methanol, ethylene, etc. (1, 2). Therefore, developing catalysts that are effective for CO₂R to >2e[−] products would greatly improve prospects for utilization, and such an endeavor requires a deeper understanding of the relevant surface chemistry.

Out of the polycrystalline metals, Cu is the only one that has shown a propensity for CO₂R to >2e[−] products at considerable rates and selectivity (2, 3). To date, its uniqueness is reflected by how nearly all work on catalysts with improved activity and selectivity for >2e[−] products is based on Cu (4–6). However, polycrystalline Cu is not particularly selective toward any one >2e[−] reduction product (7). Thus, it is critical to understand what active site motifs lead to this unique selectivity for further reduced products and to apply this knowledge to develop new materials with this electrocatalytic behavior.

Single-crystal studies on Cu have shown that CO₂R activity and selectivity are extremely sensitive to surface structure. In particular, facet sensitivities for C–C coupling are the most widely studied, with experimental reports concluding that Cu(100) terraces and any orientation of step sites are more active and selective for C–C coupling than Cu(111) (8). Similarly, single-crystal

investigations of CO reduction have demonstrated low overpotential production of ethylene, the simplest C–C coupled hydrocarbon, on Cu(100), while observing no early onset of ethylene on Cu(111) (9). Theoretical studies have shown that this difference in activity could be due to lower kinetic barriers for C–C coupling on Cu(100) vs. Cu(111) (10, 11). Whereas the aforementioned single-crystal studies have elucidated design motifs for the synthesis of surface-structure-engineered electrocatalysts with higher C–C coupling selectivity and activity, much remains to be learned regarding structure sensitivity for this reaction. Electrodes consisting of single crystals are notably small (<0.1 cm²) to achieve a high degree of uniformity across the surface. Such small electrodes, however, pose challenges to identifying and quantifying all products of the reaction. Also, single crystals that exhibit interesting catalytic behavior are difficult to integrate into devices. These challenges motivate implementing synthetic routes to larger-format electrodes for CO₂R with surfaces analogous to that of single crystals and the compatibility to be incorporated into a device architecture.

One method for growing single-crystal analogous materials is epitaxy, where an underlying single-crystal substrate is used to control the growth orientation of an overlayer via interfacial energetics. For transition metals such as Cu, vacuum growth studies

Significance

Anthropogenic global warming necessitates the development of renewable carbon-free and carbon-neutral technologies for the future. Electrochemical CO₂ reduction is one such technology that has the potential to impact climate change by enabling sustainable routes for the production of fuels and chemicals. Whereas the field of CO₂ reduction has attracted great interest, current state-of-the-art electrocatalysts must be improved in product selectivity and energy efficiency to make this pathway viable for the future. Here, we investigate how controlling the surface structure of copper electrocatalysts can guide CO₂ reduction activity and selectivity. We show how the coordination environment of Cu surfaces influences oxygenate vs. hydrocarbon formation, providing insights on how to improve selectivity and energy efficiency toward more valuable CO₂ reduction products.

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Fig. 2. X-ray pole figures for (A) Cu on Ti/Al₂O₃(0001); Cu(200) intensities are shown, (B) Cu on Si(100); Cu(111) intensities are shown, and (C) Cu on Si(111); Cu(111) intensities are shown. (D) An inverse pole figure shows highest intensities for the (751) plane, indicating that Cu on Si(111) is predominantly oriented in the $\langle 751 \rangle$ direction out-of-plane.

These results demonstrate that PVD can be used to epitaxially grow large-format electrodes in both low and high Miller index orientations.

Comparison of Ideal Surface Structures. To investigate structure–activity relationships for CO₂R, it is important to correlate the growth orientation of Cu thin films with the expected surface structure. According to XRD results, Cu thin films are epitaxially grown in the $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 751 \rangle$ orientations on Al₂O₃(0001), Si(100), and Si(111), respectively. These samples will henceforth be discussed as Cu(111), (100), and (751) for simplicity. As shown in Fig. 3, the epitaxial Cu films are expected to have either a flat (Fig. 3 A and B) or kinked (Fig. 3C) surface structure depending on the growth direction of the film. The flat Cu(111) and Cu(100) surfaces (Fig. 3 A and B) are expected to have ninefold and eightfold coordination for all atoms on their surfaces, respectively. Unlike Cu(111) and Cu(100), Cu(751) is kinked, so microfacet notation is used to determine the ratios of the low Miller index facets (111), (110), and (100) present in a (751) unit cell (Fig. S3). With this notation, Cu(751) can be described as Cu S-[1₁(111) + 4₂(110) + 2₁(100)], indicating that there are one (111), two (110), and one (100) unit cells in a (751) unit cell (22). Using these ratios, Cu(751) can be visualized as a kinked surface with narrow (110) terraces and a high density of (100) and (111) step sites. The presence of all fcc low Miller index facets suggests a high degree of site heterogeneity on the Cu(751) surface. This heterogeneity is clearly observed in Fig. 3C, where the kinks in Cu(751) are shown to have sites with six-, seven-, and eightfold coordination. Although there are additional sites with 10- and 11-fold coordination, these atoms are expected to be subsurface and have a minimal impact on electrocatalysis. In summary, the different copper surfaces can be placed in the order Cu(751) $\leq$ Cu(100) $<$ Cu(111) in terms of coordination number.

Electrochemical Scanning Tunneling Microscopy. To understand the correlation between bulk orientation and surface structure in

electrolyte solution, electrochemical scanning tunneling microscopy (ECSTM) was used to examine the in situ surface structure of Cu(111), (100), and (751) thin films. For the ECSTM study, the Cu(111) thin film was grown on Si(110) instead of $\text{Al}_2\text{O}_3(0001)$ to allow for electrical back-contact to the sample. The different single-crystal substrates yielded Cu films that are identical in texture (Fig. S4). Each sample was immersed in 0.1 M HClO_4 and scanned from the open-circuit potential to -0.76 V vs. reversible hydrogen electrode (RHE) at 50 mV s^{-1} to reduce the surface oxide into Cu metal. Afterward, ECSTM images were collected at -0.24 V vs. RHE. Additional details about these experiments can be found in *Supporting Information*. Low-magnification ECSTM images show the morphological similarities of the three Cu thin-film orientations (Fig. S5). A large-scale view of the Cu(111) surface (Fig. S5A) depicts multiple stacks of Cu layers that are randomly interspersed from each other. The hexagonal topographic unit in each stack shares similar corner internal angles, although a few edges appear irregular and almost rounded. A similar magnification view of the Cu(100) surface (Fig. S5B) shows stacks that are more interconnected than those of Cu(111). A large number of Cu layers still appear stacked on top of each other but, unlike their Cu(111) counterpart, the constituent units form a spiral ramp that implies the formation of screw dislocations during growth. For Cu(751), only a nondescript film terrain is observed with grains of various sizes that range from 20 to 60 nm (Fig. S5C). Similarly, all samples show evidence that epitaxy likely proceeds through either a Volmer–Weber or Stranski–Kraustanov growth mechanism. This is consistent with previous studies that show epitaxy of Cu on Si proceeds through 3D growth (13, 16).

At higher magnification, atomically resolved ECSTM images (Fig. 4) show the in situ surface structures of Cu(111), (100), and (751) thin films. A high-resolution image of the Cu(111) surface (Fig. 4A) shows a threefold rotational symmetry that is indicative of a well-ordered close-packed Cu(111) structure. Imaging of Cu(100) at various points in the spirals unveiled a square Cu(100) net with an interatomic distance of 0.27 ± 0.01 nm (Fig. 4B). These ECSTM results demonstrate that for Cu(111) and (100) thin films, the majority of the in situ surface structure is identical to the bulk orientation (Fig. 2B and Fig. S4) and the ideal atomic models (Fig. 3A and B). Throughout the several-hour duration of the measurements, the surface structure of the epitaxial Cu thin

Fig. 3. Color-coded atomic models showing coordination numbers for the (A) Cu(111), (B) (100), and (C) (751) surfaces.

Fig. 5. Current efficiencies for $>2e^-$ C1, C2, and C3 products as a function of potential for Cu(111), (751), and (100).

undercoordinated surfaces, further work will be necessary to elucidate how the geometry of kinked surfaces affects kinetic barriers. Nevertheless, these results demonstrate that PVD can be used to surface-structure-engineer large-format electrodes that have analogous electrocatalytic properties to Cu single crystals.

Among the $>2e^-$ products, it is useful to compare selectivity toward oxygenates and hydrocarbons to help understand elements of the reaction mechanism, because oxygenates are less reduced than hydrocarbons with the same number of carbons. Examining the product distribution in this manner also assesses possibilities for developing catalysts with desired selectivity for a number of important chemical products. In particular, achieving greater selectivity toward oxygenates is of interest because hydrocarbons with the same number of carbons are typically less valuable (26). By grouping the current efficiencies for $>2e^-$ products into the categories hydrocarbons and/or oxygenates (Fig. S6), it is clearly shown that Cu(111), (100), and (751) are all more selective for hydrocarbons than oxygenates across the measured range of potentials (Figs. S9 and S10). In particular, high selectivity for the hydrocarbons CH_4 and C_2H_4 has been commonly observed for Cu of any surface orientation (8). Whereas all epitaxial Cu thin films show higher selectivity toward hydrocarbons, examining the potential dependence of oxygenate/hydrocarbon ratios can aid in determining which active site motifs lead to greater oxygenate production (Fig. 6). At the highest potential of -0.89 V vs. RHE, both Cu(751) and Cu(100) have higher oxygenate/hydrocarbon ratios than that of Cu(111), which makes only hydrocarbons at this potential. Whereas both Cu(751) and (100) are both selective and active at this potential for C-C coupling, the higher oxygenate/hydrocarbon ratio for Cu(751) than (100) indicates a clear distinction between the surfaces in oxygenate selectivity. A comparison of Cu(751) and (100) indicates that the primary distinctions in surface structure on the former are the step sites and narrow (110) terraces, which lead to differences in geometry and a lower average coordination number (Figs. 3 and 4). Therefore, these trends suggest that the geometry of undercoordinated sites on Cu surfaces can be engineered to guide selectivity toward greater oxygenate production.

To hypothesize why undercoordinated sites are more selective for oxygenates, it is useful to examine how the geometry and coordination of atoms will impact the surface coverage of intermediates during CO_2R . Online electrochemical mass spectrometry experiments demonstrate a strong correlation between the applied

potentials for the hydrogen evolution reaction (HER) and reduction of possible oxygenated CO_2R intermediates on Cu electrodes (27). Recent theoretical studies indicate that C–C coupled product selectivity from Cu is strongly correlated to the coverage of CO^* and H^* simultaneously on the surface (28, 29). These reports suggest that the dominant mechanisms for C–C coupling and hydrogenation at lower overpotentials are chemical (hydride transfer) rather than electrochemical (proton-coupled electron transfer). Therefore, at lower overpotentials the selectivity for oxygenates or hydrocarbons could be determined by the ability of the surface to accommodate simultaneous coverages of CO^* and H^* . By examining structure models and atomically resolved in situ ECSTM images (Figs. 3 and 4), we can postulate how CO^* and H^* coverages depend on the geometry and coordination of atoms on Cu(111), (100), and (751). Whereas the Cu(111) and (100) surfaces have a high density of sites with eight- and ninefold coordination, respectively, the Cu(751) surface has a low density of sites with six-, seven-, and eightfold coordination (Fig. 3). A closer look at the structure models shows that Cu(111), (100), and (751) each have six, four, and two nearest surface neighbors, respectively. It was formerly noted that the in situ surface structure of Cu(751) is better described as $\text{Cu}(\text{S})-[n(110) \times (100)]$, where n varies from 2 to 7, and that the surface heterogeneity changes the distribution of six-, seven-, and eightfold coordination sites. This heterogeneity does not affect the trend in nearest surface neighbors, because the main structural motif of (110) terraces, where each Cu atom will have two nearest surface neighbors, is present in both the composite $\text{Cu}(\text{S})-[n(110) \times (100)]$ (Fig. 4C) and the ideal Cu(751) (Fig. 4D) surface structures. Since it is statistically less likely for a CO^* dimer to be adjacent to H^* atoms on a surface with fewer neighbors, Cu(751) could have greater oxygenate selectivity because it is more difficult to hydrogenate C–C coupled CO_2R intermediates on its surface. This trend in surface neighbors is corroborated by comparing the trend in oxygenate/hydrocarbon ratios at -0.89 V vs. RHE, where $\text{Cu}(751) > \text{Cu}(100) > \text{Cu}(111)$. At more negative potentials, all surfaces have similar oxygenate/hydrocarbon ratios, suggesting that CO^* and H^* coverages may be less important at high overpotentials. The aforementioned theory study predicts that at more negative potentials the barrier height for chemical hydrogenation increases, whereas the barrier height for electrochemical hydrogenation decreases (28). Therefore, these similarities in selectivity at higher

Fig. 6. Oxygenate/hydrocarbon ratios for $>2e^-$ reduction products as a function of potential for Cu(111), (751), and (100).

overpotentials could be due to a shift in the hydrogenation mechanism from chemical to electrochemical. If the predominant mechanism for hydrogenation at these overpotentials is electrochemical, it is expected that the oxygenate/hydrocarbon ratio would be less sensitive to geometry and coverage on the surface because the proton and electron transfers are concerted. For polycrystalline Cu electrodes, the selective production of ethanol from the electrochemical reduction of CO in alkaline solution was achieved by atomic-level surface modification via mild oxidation–reduction cycles (30). Results from the present work provide impetus for the exploration of advanced engineering strategies to design electrocatalytic surfaces with undercoordinated sites that can steer selectivity toward oxygenate formation.

Conclusions

We have investigated PVD as a growth method to surface-structure-engineer large-format Cu thin films for electrochemical CO₂ reduction. X-ray pole figures indicate that the Cu thin films grow epitaxially with $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 751 \rangle$ out-of-plane orientations on Al₂O₃(0001), Si(100), and Si(111), respectively. The XRD results show that Cu can be epitaxially grown in both low and high Miller index directions using different single-crystal substrate orientations. Analysis of the structure in situ using ECSTM confirmed the existence of three unique Cu surface structures from epitaxial growth. Electrochemical testing of these samples for CO₂ reduction led to a number of important observations. Thin-film orientations with more undercoordinated sites are more active and selective for C–C coupling, which is consistent with previous studies on small-format single crystals. This demonstrates that

PVD can be used to grow large-format electrodes that have analogous electrocatalytic properties to single crystals. Furthermore, analysis of oxygenate vs. hydrocarbon selectivity reveals that at -0.89 V vs. RHE, Cu(751) has the highest oxygenate/hydrocarbon ratio of the three Cu orientations. We suggest that this improvement in oxygenate selectivity is related to the fewer number of nearest neighbors on the Cu(S)– $[n(110) \times (100)]$ surface, or the topmost layer of the Cu(751) film, because barriers for hydride transfer are predicted to be lower than those for proton-coupled electron transfer at lower overpotentials. Additional mechanistic details can be unveiled from future investigations that examine fine surface structural nuances under *operando* conditions, akin to the protocols that led to the discovery of Cu(511) as a selective ethanol-generating surface formed from polycrystalline Cu (30). Our results demonstrate that epitaxy can aid in the discovery of structure–activity relationships for CO₂R, providing insights into designing more active and selective electrocatalysts.

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