Tunable Cu Enrichment Enables Designer Syngas Electrosynthesis from CO₂

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Supporting Information

ABSTRACT: Using renewable energy to recycle CO₂ provides an opportunity to both reduce net CO₂ emissions and synthesize fuels and chemical feedstocks. It is of central importance to design electrocatalysts that both are efficient and can access a tunable spectrum of products. Syngas, a mixture of carbon monoxide (CO) and hydrogen (H₂), is an important chemical precursor that can be converted downstream into small molecules or larger hydrocarbons by fermentation or thermochemistry. Many processes that utilize syngas require different syngas compositions: we therefore pursued the rational design of a family of electrocatalysts that can be programmed to synthesize different designer syngas ratios. We utilize in situ surface-enhanced Raman spectroscopy and first-principles density functional theory calculations to develop a systematic picture of CO₄ binding on Cu-enriched Au surface model systems. Insights from these model systems are then translated to nanostructured electrocatalysts, whereby controlled Cu enrichment enables tunable syngas production while maintaining current densities greater than 20 mA/cm².

INTRODUCTION

Relentless improvements in renewable energy generation provide new opportunities for storing and harnessing electrical energy. In particular, increasingly abundant and inexpensive sources of electrons provide synthetic opportunities to replace conventional chemical processes with renewable powered ones. In addition to mild reaction conditions, these renewable powered electrochemical reactions could enable decreased production costs relative to conventional approaches, particularly for the production of feedstock chemicals from CO₂. However, CO₂ reduction reaction (CO₂RR) electrocatalysts have several remaining fundamental and performance-related challenges, particularly related to low production rates, limited product versatility, and poor energy efficiencies.

Although direct electrosynthesis of multcarbon products remains elusive, catalytic efficiencies and production rates for single-carbon products, such as CO and formic acid, provide more immediate opportunities for electrochemical CO₂ valorization. Synthesis gas (syngas) made using renewable powered CO₂RR is particularly attractive because it can subsequently be upgraded to longer hydrocarbons by Fischer–Tropsch chemistry, syngas fermentation, and individual small-molecule syntheses. Desirably, the syngas electrosynthesis catalyst will operate at room temperature, in a single reactor, and with high efficiency and production rates. These attributes, combined with the ability to tailor the composition of syngas for each downstream process (such as 0.6 H₂:CO for Fischer–Tropsch reactors, 2 H₂:CO for methanol synthesis, and 0.3–1 H₂:CO for syngas fermentation), would provide a flexible platform for integration with existing chemical infrastructure. Several electrocatalytic systems provide either rapid reaction turnovers or a variety of syngas compositions; however, there exist no prior reports of a single electrocatalyst that exhibits high production rates (at low overpotential) combined with systematic and wide-ranging syngas composition control.

Herein, we report a strategy where the composition of syngas produced by a nanostructured Au electrocatalyst can be finely controlled using Cu underpotential deposition while maintaining high geometric current densities (production rates) at low overpotentials for CO₂RR. Within this scope, underpotential deposition provides a quantitative and systems-
atic means by which the ratio of Au and Cu atoms at the surface can be tuned. Such control changes the electronic structure at the catalyst surface,7,16,17 which we hypothesized would influence CO binding and thereby provide a method for tuning the relative selectivity of CO electrosynthesis and the hydrogen evolution reaction (HER).18,19 In situ surface-enhanced Raman spectroscopy (SERS) is used to interrogate changes in the coordination and binding characteristics of adsorbed CO (CO\(^*\)) on model Au SERS substrates. In turn, fundamental insights from both in situ SERS and density functional theory (DFT) calculations are translated from model systems to nanostructured electrocatalysts that provide high electrochemical activity (>20 mA/cm\(^2\)) for the most industrially relevant syngas compositions.

■ RESULTS AND DISCUSSION

Design of Cu-Enriched Model Electrocatalysts. We focus on structures in which Au surface atoms are replaced with Cu atoms in ordered monolayers; this serves as an approximation of surfaces that are increasingly Cu-enriched (Figure 1b). Indeed, the calculated projected density of states, which describes the electronic states at the surface, shows each Cu-enriched slab has distinct electronic properties. Importantly, these differences are most pronounced in the d-band electrons that dominate molecular adsorption, suggesting that Cu-enriched slabs should exhibit catalytic activity distinct from pure Au and Cu or their alloys.18–20 To realize such architectures, electrochemical underpotential deposition (UPD) was used to control the extent of Cu enrichment (Figure 2a). UPD occurs when the electrochemical deposition of a less noble species onto a more noble metal is thermodynamically favorable, but the deposition of the less noble species onto itself in unfavorable. This enables precise control over metal deposition because UPD is self-terminating at a single monolayer.21 Additionally, the use of Au as a substrate provides a platform where the binding of CO\(^*\) can be monitored in situ with SERS, a nondestructive technique where the Raman scattering of surface-adsorbed molecules can be enhanced by 10\(^{5}\)–10\(^{10}\).22 By combining the precision of UPD with the sensitivity of SERS, one can manipulate the electronic and geometric properties of the catalyst surface (Figure 1b), by virtue of changing the extent of Cu enrichment, while monitoring changes in CO\(^*\).

Figure 2. Sub-monolayer Cu underpotential deposition on Au SERS-active model electrodes. (a) Scheme of Cu underpotential deposition. (b) Cyclic voltammograms for increasingly wide Cu underpotential deposition windows (no Cu, yellow; 1/3 of the window, orange; 2/3 blue; and 3/3 purple). (c) Scanning electron micrographs of a roughened Au SERS-active electrode before (top, yellow box) and after (bottom, purple box) deposition of Cu using the full (3/3) underpotential deposition window; scale bars are 100 nm. (d) Representative Au (top) and Cu (bottom) X-ray photoelectron spectra (here from the 3/3 window Cu underpotential deposition).

Synthesis and Characterization of Cu Enriched Electrocatalysts. Cu-enriched Au electrodes were synthesized by electrochemical roughening, which renders them SERS-active, followed by Cu UPD (Figure 2b, SI, Methods), where stable cyclic voltammetry (CV) traces are indicative of Cu (sub-)monolayer deposition. Throughout this work three potential windows were used that correspond to approximately 1/3 monolayer Cu\(_{\text{UPD}}\) (\(\Theta = 1/3\)), 2/3
monolayer Cu$_{\text{UPD}}$ ($\Theta = 2/3$), and one full monolayer Cu$_{\text{UPD}}$ ($\Theta = 1$). Although previous literature has shown that ordered Cu monolayers can form on single-crystalline Au surfaces, the broad features in the voltammograms indicate that Cu is deposited onto a variety of coordination environments on the polycrystalline Au surface.\textsuperscript{21,23}

Further characterization indicates that the extent of Cu enrichment is controlled while the electrode morphology is maintained after UPD. Scanning electron microscopy (SEM) does not indicate restructing of the SERS-active nanoscale features (Figure 2c), while X-ray photoelectron spectroscopy (XPS) confirms that wider UPD windows increase the ratio of Cu to Au atoms at the surface (Figure 2d, Table S1). Additionally, SERS spectra of the Au substrate before and after UPD indicate the displacement of adsorbed chloride remaining after the roughening procedure without showing any new features related to Cu–O bonding that would form after bulk Cu deposition (Figure S2). Finally, analysis of the 2p\textsubscript{3/2} XPS and Cu L$_3$M$_4$M$_4\text{M}5\text{M}5$ Auger spectra suggest that the UPD Cu may be primarily in a metallic state (Figure S3), consistent with recent studies of full Cu monolayers on Au.\textsuperscript{24} Together, these data show that UPD can be used to controllably enrich Au surfaces with Cu while preserving the nanoscale morphology that will provide Raman enhancement.

**In Situ Spectroscopic Interrogation and Theoretical Analysis of CO\textsuperscript{*} Binding.** To monitor the electrosynthesis of CO in situ, the electrode was mounted within a CO$_2$RR electrochemical cell integrated with a confocal Raman microscope (Figure 3a, top). This allows one to probe the vibration of the C–O bond ($\nu_{C-O}$) in CO\textsuperscript{*} in situ as a function of applied potential (Figure 3a, bottom). Before the application of bias on the fully Cu-enriched electrode (∼1 monolayer Cu, Figure 3b, gray), the primary peaks observed are (bi)carbonate species (1450/1200 cm$^{-1}$) and water (1600 cm$^{-1}$), both from the electrolyte.\textsuperscript{25,26} At an applied potential of −0.2 V vs RHE, a peak at ∼2100 cm$^{-1}$ is observed that is attributed to CO\textsuperscript{*} on the atop position (Figure 3b).\textsuperscript{26,27} As a function of potential, both the relative intensity and position of $\nu_{C-O}$ change; variations in intensity can be understood by changes in the relative concentrations of CO\textsuperscript{*} at the surface.\textsuperscript{26} The red-shifting of $\nu_{C-O}$ at more negative potentials is due to the electrochemical Stark effect, a phenomenon where the electrostatic field at an electrode can shift the vibrational frequencies of an adsorbate (Figure S4).\textsuperscript{23} Overall, these data indicate that electrochemically synthesized CO can be detected in situ and that the $\nu_{C-O}$ characteristics observed here are consistent with past observations.\textsuperscript{26,27}

To understand how Cu enrichment influences CO\textsuperscript{*}, one can compare $\nu_{C-O}$ for increasing extents of Cu enrichment at a fixed potential (Figure 3c). At −0.3 V (and at −0.5 V vs RHE, Figure S5), it is clear that $\nu_{C-O}$ red-shifts with increasing Cu coverage (a roughened Cu sample is provided for reference).\textsuperscript{28} These data are indicative of CO\textsuperscript{*} adsorption in distinct chemical environments, where the changing coordination environment is reflected in $\nu_{C-O}$.\textsuperscript{25,26} To better understand the relationship between chemical environment and $\nu_{C-O}$, DFT calculations were performed on CO adsorbed on increasingly Cu-enriched Au(111) slabs (Figure 3d and e, Figure S6). For the intermediate Cu enrichments (Figure 3e), CO can be adsorbed at either Cu sites (Figure 3d, solid) or Au sites (Figure 3d, dashed). Overall, the trend is consistent with the experiment where $\nu_{C-O}$ red-shifts for increasingly Cu-rich surfaces (Figure S7), although there is some site-dependent variation observed (note that previous comparisons of calculated and experimentally measured $\nu_{C-O}$ exhibit disagreements between 20 and 50 cm$^{-1}$).\textsuperscript{29}
Qualitatively, the red-shifting of $\nu_{C-O}$ with increasing Cu content can be understood through analysis of the CO–metal interaction, which can be described by charge donation to the metal surface by the highest occupied molecular orbital (HOMO, $5\sigma$) of CO, which leads to charge back-donation into its lowest unoccupied molecular orbital (LUMO, $2\pi^*$). \cite{20,30}

Within this model, the result of charge transfer to the antibonding $2\pi^*$ orbital is a longer C–O bond and a red-shifted $\nu_{C-O}$. Due to their respective d-band positions (Figure 1b), this is consistent with what one would expect trending from pure Au to pure Cu. \cite{17} Additionally, red-shifting of $\nu_{C-O}$ is typically associated with a stronger metal–CO interaction. \cite{29}

Although shifts in $\nu_{C-O}$ often exhibit a linear relationship with the C–metal bond length and with the energetics of adsorption, deeper analysis of these Cu-enriched Au architectures reveals a departure from this behavior, which is discussed further in text S2 and Figures S7–S11. These data, along with Bader charge (the electronic charge density) analysis (Figure S11) at both the adsorption site and at the nearest neighbor atoms, confirm that Cu enrichment directly changes the electronic structure and molecular coordination environment on Au surfaces. \cite{19,20,31}

Importantly, despite the simplistic nature of the DFT model slabs compared to the polycrystalline electrodes measured in solution, the dominant trends observed in the experiments are captured by the DFT calculations.

Having shown that Cu enrichment of Au can systematically alter the coordination environment of CO*, we now consider how these differences affect CO$_2$RR and its competition with HER. \cite{17,20,31} Thermodynamic adsorption energies ($\Delta G_{ads}$) were calculated for CO* and H* (Figure 3d) for all extents of Cu enrichment (Figure 3d). If we first compare adsorption on Au(111) and Cu(111) surfaces, it is seen that $\Delta G_{ads}$ is more positive (less favorable) for both CO* and H* on Au. Additionally, a difference of $\sim$0.5 eV is observed between CO* and H* on Au(111), whereas on Cu(111) there is a difference of only $\sim$0.25 eV; this difference explains the more favorable release of CO* from Au.\cite{17} Similarly, all of the Cu-enriched Au surfaces exhibit more favorable H adsorption than CO adsorption. On average, increasing extents of Cu enrichment increase the favorability of both CO* and H* adsorption, a trend that is in general agreement with the red-shifting $\nu_{C-O}$ trend observed in situ. At the more energetically favorable Cu sites, the difference between $\Delta G_{ads}$ for CO* and H* narrows to 0.05–0.2 eV, suggesting increased competition between HER and CO$_2$RR.\cite{18} Moreover, calculations comparing the (111), (110), and (100) facets exhibit a similar narrowing of $\Delta G_{ads}$ between CO* and H* (Figures S12, S13, Table S3). Together, these data suggest that Cu enrichment, and the site dependence that results from it, can profoundly influence competition between CO electrosynthesis and H$_2$ production.\cite{18}

In particular, intermediate Cu enrichments will increase HER relative to CO$_2$RR, providing a means by which the composition of synthesis gas can be controlled. As such, we set out to translate these concepts from a model system to a tunable syngas electrocatalyst with high production rates.

**Realization of a Tunable Syngas Electro catalyst.** Au nanoneedle electrodes, which take advantage of field-induced reagent concentration (Figure 4a), were chosen as a platform that provides high CO selectivity at low overpotentials with high current densities (>20 mA/cm$^2$).\cite{32} The Au nanoneedles were enriched with submonolayers of Cu using UPD in an analogous fashion to the model electrodes (Figure 4b), after which their catalytic performance was evaluated in CO$_2$-saturated 0.5 M KHCO$_3$. During electrolysis high current densities are maintained for all catalysts (Figure S14); importantly, the ratio of the production of CO and H$_2$ is sensitive to the extent of Cu enrichment (Figure 4e, Figures S15, S16). To explicitly characterize the composition of the electrolysized syngas, the ratio of H$_2$ and CO faradaic efficiency is compared for all Cu enrichments (Figure 4d). Overall, increasing extents of Cu enrichment result in greater H$_2$ production (increased HER rates), as predicted by the Cu-enriched Au model surfaces. Importantly, this trend is consistent both with the insights gained above from in situ SERS and DFT but also with previous studies of AuCu alloy nanoparticles.\cite{20} For the two highest extents of Cu enrichment, the H$_2$:CO ratio can be tuned to match the syngas compositions used for Fischer–Tropsch synthesis of hydrocarbons (0.6), throughout the range of compositions used for emerging fermentation and short-chain thermochemical synthesis (0.3–1), and to approach the ideal ratio for methanol synthesis (2).\cite{2,5,9} Importantly, after 8 h of electrolysis both the bare Au and 3/3 Cu UPD enriched Au electrocatalysts exhibit stable syngas ratios and >70% retained activity (Figure S17). Moreover, SEM shows that the nanoscale morphology is preserved and XPS suggests that UPD Cu remains at the surface.

**CONCLUSION**

We have shown that controlled Cu enrichment of Au surfaces results in electrocatalysts that can synthesize a range of syngas compositions at high production rates. In *in situ* SERS and DFT
calculations enabled the elucidation of how surface electronic structure can be tuned by Cu enrichment to influence CO binding, which in turn dictates competition between CO and H₂ electrosynthesis. This work is consistent with continued improvements in CO₂RR that are enabled by better understanding of the catalytic interface and the exploration of new electrocatalyst compositions. Furthermore, the fundamental catalytic concepts described herein are applicable outside of CO and H₂ electrosynthesis; they provide insights relevant for the production of other small molecules, hydrocarbons, and fuel mixtures such as lhythane (CH₃ and H₂). Finally, the high performance and stability of these catalysts could facilitate their integration into a broader CO₂-recycling scheme.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jacs.7b04892.

Detailed materials and methods, theoretical details, additional electrochemical characterization, potential-dependent SER spectra, optimized geometries used in theoretical calculations, analysis of spectroscopic trends, full projected densities of states for all materials, facet-dependent binding strength calculations for *CO and *H, and additional electrocatalytic analysis (PDF)

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Notes
The authors declare no competing financial interest.

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