Computational and experimental demonstrations of one-pot tandem catalysis for electrochemical carbon dioxide reduction to methane

Haochen Zhang1,6, Xiaoxia Chang2,6, Jingguang G. Chen3, William A. Goddard III4, Bingjun Xu2, Mu-Jeng Cheng5 & Qi Lu1

Electroreduction of carbon dioxide to hydrocarbons and oxygenates on copper involves reduction to a carbon monoxide adsorbate followed by further transformation to hydrocarbons and oxygenates. Simultaneous improvement of these processes over a single reactive site is challenging due to the linear scaling relationship of the binding strength of key intermediates. Herein, we report improved electroreduction of carbon dioxide by exploiting a one-pot tandem catalysis mechanism based on computational and electrochemical investigations. By constructing a well-defined copper-modified silver surface, adsorbed carbon monoxide generated on the silver sites is proposed to migrate to surface copper sites for the subsequent reduction to methane, which is consistent with insights gained from operando attenuated total reflectance surface enhanced infrared absorption spectroscopic investigations. Our results provide a promising approach for designing carbon dioxide electroreduction catalysts to enable one-pot reduction of products beyond carbon monoxide and formate.

1State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, 100084 Beijing, China. 2Center for Catalytic Science and Technology, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA. 3Department of Chemical Engineering, Columbia University, New York, NY 10027, USA. 4Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA 91125, USA. 5Department of Chemistry, National Cheng Kung University, Tainan 701, Taiwan. 6These authors contributed equally: Haochen Zhang, Xiaoxia Chang. Correspondence and requests for materials should be addressed to B.X. (email: bxu@udel.edu) or to M.-J.C. (email: mjcheng@mail.ncku.edu.tw) or to Q.L. (email: luqicheme@mail.tsinghua.edu.cn)
The electrochemical reduction of CO₂ to energy-dense chemicals is an attractive strategy for storing the intermittent renewable electricity produced by solar and wind sources. To ensure sustainability of the entire process, the electrochemical CO₂ reduction reaction (CO₂RR) is typically conducted in an aqueous electrolyte, in which the protons required are obtained. In this system, tremendous progress has been made in catalyst design and reactor design to drive the two-electron reduction of CO₂ to produce CO or formate. However, strategies for direct reduction of CO₂ to more valuable fuels and chemicals have been less successful because the catalysts capable of catalyzing this conversion are very limited. Only Cu exhibits appreciable activity and Faradaic efficiency (FE) for reducing CO₂ to hydrocarbons and oxygenates. The lack of predictive catalyst design principles for CO₂RR limits the development of catalysts capable of directly converting CO₂ to products beyond CO and formate.

To achieve higher efficiencies in the CO₂RR toward hydrocarbons and oxygenates, the most common approach involves modifying the Cu surface to produce and/or enrich active sites with a specific structure. These efforts include oxidation and reduction treatment to expose grain boundary-terminated Cu surfaces, plasma treatment, and electro-redeposition to introduce stable Cu⁺ species, morphology control to expose high density low-coordinated surface sites, and alloying with an additional metal to tune the binding strength to the reaction intermediates. Despite the recent progress, the improvement in the performance as compared to the pure Cu remains unsatisfactory. In particular, the selectivity of alloy catalysts toward products beyond CO and formate do not surpass that of pure Cu. Therefore, novel approaches to design more efficient CO₂RR catalysts capable of selectively producing valuable products are highly desirable.

On polycrystalline Cu surfaces, CO₂ is first converted to adsorbed CO (â€“CO) followed by its further reduction to hydrocarbons and oxygenates. However, the optimal sites for these two processes could have quite different properties because the formation of â€“CO requires the optimal binding strength for â€“COOH while the formation of hydrocarbons and oxygenates requires the optimal binding strength for â€“COOH. The simultaneous optimization of the binding strength of â€“COOH and â€“CO on one type of reactive site can be challenging due to the linear scaling relationship. For example, the Au₃Cu nanoparticle catalyst exhibited a very high activity for reducing CO₂ to CO. However, this catalyst was nearly incapable of producing further reduced products. An oxide-derived Cu catalyst exhibited a much improved FE for reducing CO to alcohols. However, this catalyst cannot effectively and directly reduce CO₂ to products beyond CO and formate. Therefore, the conversion of CO₂ using tandem catalysis can be a promising strategy to improve the overall efficiencies for further reduced products. By co-locating Cu with a CO-producing surface (e.g., Au and Ag), the Cu may be supplied with abundant CO via spillover. A higher coverage of CO on the Cu surface can not only increase the rates of hydrocarbon and oxygenate production but also suppress the competing hydrogen evolution reaction (HER) by weakening the binding strength of H₂. Recently, several bimetallic surfaces including Cu-Zn and Cu-Au were investigated in the CO₂RR. The Cu-Zn surface exhibited improved selectivity for ethanol over ethylene, and the Cu-Au surface exhibited an improved partial current density toward production beyond CO from approximately 0.005 to 0.16 mA cm⁻² compared to a bare Cu foil at a low overpotential. A tandem catalysis mechanism was proposed to explain these improvements. However, CO spillover was not demonstrated in these systems. Therefore, the origin of the observed synergistic improvements remains unclear. Another recent study demonstrated that a Cu-Ag bimetallic surface can be more selective for C₂⁺ product formation. However, this improvement was not due to CO spillover but suppression of the HER from the formation of the compressively strained alloy surface. Herein we report a combined computational and experimental study of one-pot tandem catalytic CO₂RR. By constructing well-defined model surfaces with isolated thin Cu layers on a CO-producing substrate (i.e., Au and Ag), the CO produced on the CO-producing Au or Ag would migrate to Cu with a low activation energy and be further reduced by Cu. In comparison to pure Cu, our model surface exhibited better CH₄ selectivity and activity as well as suppressed HER. Operando attenuated total reflectance surface enhanced infrared absorption spectroscopic (ATR-SEIRAS) investigations yielded the first spectroscopic evidence of CO spillover on a Cu-based bimetallic catalyst. More importantly, our results clearly demonstrate a new paradigm for the design of CO₂RR catalysts to achieve further reduced products beyond CO and formate.

**Results**

**Theoretical investigations of carbon monoxide spillover.** Ag and Au are known to be the most efficient monometallic surfaces for CO production from the CO₂RR. Our computational investigation begins with examination of the possibility for CO spillover from a CO-producing Ag or Au site to a surface Cu site prior to further reduction. The surface is divided into eight regions along the direction from bare Ag (or Au) sites toward surface Cu sites for the discussion of CO spillover, and only the ΔGCO of sites with the strongest binding energy in each region on the Cu-added Ag or Au surface are considered in the CO spillover discussion (Fig. 1a and Supplementary Table 1). As shown in Fig. 1b, *CO adsorption is typically more stable on surface Cu sites than Ag or Au sites. The ΔGCO at bare substrate sites nonadjacent to Cu (i.e., site nos. 1–3) exhibit similar values (i.e., ~0.73 eV for Ag and ~0.34 eV for Au, respectively). As the CO molecule approaches the surface Cu, ΔGCO decreases substantially (stronger adsorption) and reaches a minimum value at site no. 5 on Ag (~0.34 eV) and Au (~0.75 eV) where CO forms a bond with the surface Cu atoms. Significantly better CO adsorption is observed on surface Cu than its substrate for both Ag (1.07 eV) and Au (1.09 eV). Moreover, the free energy barrier for CO spillover on both surfaces is calculated to be very small (no more than 0.16 eV), which can be easily surmounted at room temperature (Supplementary Table 2) and is consistent with previous works. Thus our computational results indicate that CO spillover from the Ag or Au substrate to the surface Cu is thermodynamically and kinetically feasible. The one-pot tandem reduction of CO₂ may be viable by converting CO₂ to CO on a CO-producing substrate followed by CO spillover and further reduction on a surface Cu site.

**Theoretical investigations of carbon monoxide reduction after spillover.** The further reduction of CO on surface Cu after spillover is investigated. The conversion of CO to C₁ products is chosen as the model reaction process for this investigation because (a) this process is less controversial and the results can be supported by previous work, and (b) other processes require C-C coupling via mechanisms that are unclear and currently under debate. The kinetics and thermodynamics for all possible pathways toward C₁ products are calculated (Fig. 2, Supplementary Fig. 1 and Supplementary Table 3). Different from traditional calculations with a fixed electron number, the number of electrons in each calculation is adjusted to maintain a potential of ~1.0 V SHE, which is more representative of experimental conditions.
reaction conditions. The most energetically favored pathway toward CH₄ at −1.0 V_{SHE} is determined to be *CO → *CHO → *CHOH → *CH → *CH₃ → *CH₄ + CH₄ on both the Ag-Cu and Au-Cu surfaces (Fig. 2 and Supplementary Fig. 1). The surface Cu exhibits the ability to reduce CO to CH₄ at −1.0 V_{SHE}. As suggested by the results in Fig. 2 and Supplementary Fig. 1, the hydrogenation of *CO to *CHO, which is the most difficult reaction among all the reaction steps, exhibits the highest free energy barrier (ΔG*) with a value of 0.57 and 0.50 eV for the Ag-Cu and Au-Cu surfaces, respectively. All reactions along the pathway at a potential bias of −1.0 V_{SHE} are thermodynamically downhill and kinetically feasible with ΔG* values being <0.75 eV; a number leading to a turnover frequency of approximately 1 s⁻¹ at room temperature based on the transition state theory.³⁴,³⁵ The hydrogenation of *CH, *CH₂, and *CH₃ exhibits no free energy barrier. Similar results were also reported by Chan et al. in the study of CO₂ reduction on stepped copper.⁴¹,⁴² This result indicates that CO reduction by the surface Cu on Ag or Au will be kinetically feasible. In contrast, pathways toward other possible C₁ product methanol are kinetically unfavorable, although they are thermodynamically favorable. Accordingly, both the thermodynamics and kinetics indicate that the surface Cu on Ag or Au can reduce CO₂ to CH₄ in a one-pot tandem fashion.

**Ag-Cu model surface for electrochemical study.** The Ag-Cu surface rather than the Au-Cu surface is chosen as the model catalyst for electrochemical investigations due to the cost-effectiveness of Ag over Au. The Cu-modified Ag surface is prepared at the beginning of CO₂ electrolysis by conducting the reaction in a bicarbonate electrolyte containing a predetermined (ppm) level of Cu⁺. Owing to the reduction potential of Cu⁺ (Cu⁺(aq) + 2e⁻ → Cu(s) (+0.16 V_{SHE} for ppm level Cu⁺)) being significantly more positive than the electrode-reduction potential of CO₂ (typically −1.3 V_{SHE}), the ppm-level Cu⁺ is instantly electrochemically deposited onto the Ag foil when the electrolysis is initiated, making the deposition process indistinguishable during chronoamperometry. This is supported by the observation that the reduction current of Cu⁺ is indistinguishable in current profiles at all potentials (Supplementary Fig. 2). Further, the surface morphologies at the early stage and at the conclusion of the electrolysis are similar (Supplementary Fig. 3). The deposited Cu form islands that are a few tens of nanometers in size on the Ag surface (Fig. 3a–c), which is consistent with previous results using a similar technique.⁴³ The coverage of surface Cu can be tuned by controlling the initial Cu⁺ concentration in the electrolyte and is characterized using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) (Fig. 3a–c, Table 1, Supplementary Fig. 4). The highly crystalline nature of surface Cu is confirmed by high-resolution transmission electron microscope (HR-TEM) with samples prepared using focused ion beam technique (Supplementary Fig. 5).

The CO₂ electrolysis study of these Ag-Cu surfaces is conducted at −1.1 V_{RHE} because Ag foil exhibits the highest FE for CO production at this potential (Fig. 4c). The distribution of the major products is shown in Fig. 3d. As the Cu₂⁺ concentration increases from 0 to 1.5 ppm, which corresponds to a Cu coverage increases from 0% to 50.2% (Table 1), the CH₄ FE increases substantially from 0% to approximately 60%, and the CO FE decreases concomitantly from >80% to approximately 10% (Fig. 3d). The CH₄ FE achieved on this partially Cu-covered Ag-Cu surface (i.e., Cu coverage of 50.2%) is much higher that on a bare polycrystalline Cu foil at the same potential (Supplementary Fig. 6). This result indicates that CH₄ production on Cu can be efficiently improved via the prior reduction of CO₂ to CO on a nearby Ag surface. Because a further increase in the Cu coverage decreases the CH₄ FE, the essential role of Ag surface exposure is to provide sufficient CO supply to achieve a high CH₄ FE. At a Cu₂⁺ concentration of 2.5 ppm, the Cu coverage reaches 85.3%, and the CH₄ FE value decreases to approximately 35%, which is consistent with results obtained on a polycrystalline Cu foil at the same potential (Supplementary Fig. 6). The Ag-Cu surfaces are not very selective to C₂H₄, which is most likely due to the preferential adsorption of those *CO that migrates from the Ag surface on the edge of Cu islands where the reduced dimension may promote the exposure of low-coordinated surface sites. These low-coordinated sites may bind *CO too strongly that prevent the further movement of *CO for dimerization.

**Potential dependence study at the silver–copper surface.** The Ag-Cu surface with the optimal Cu coverage achieved at a Cu₂⁺ concentration of 1.5 ppm is employed to further investigate the one-pot tandem catalysis in the CO₂RR. The potential range for the electrolysis experiment is −0.6 V_{RHE} to −1.3 V_{RHE} (equivalent to −1.0 V_{SHE} to −1.7 V_{SHE}) to drive sufficient but not excessive activities. The Ag-Cu surface at these potentials exhibits nearly identical morphologies (Supplementary Fig. 7). This is most likely due to the large deposition overpotentials (>1.16 V) for only ppm-level Cu⁺ in the electrolyte and the deposition processes are limited by the diffusion of Cu⁺ rather than the electrode potential. This is supported by the observation in a
previous study that the electrodeposition of Cu begins to be diffusion-limited with an overpotential of >300 mV at a Cu\(^{2+}\) concentration of 0.15 M\(^4\). When the overpotential is >800 mV, such deposition process is completely diffusion-limited and the deposited Cu exhibits near identical morphologies\(44,45\).

Fig. 2 Kinetics and free energy diagram for all possible pathways toward C\(_1\) products. CO is reduced to C\(_1\) products on the Ag-Cu surface. The values shown blue (upper) and dark blue (bottom) are the free energy barrier and free energy change at \(-1.0\) V\(_{\text{RHE}}\) for all steps, respectively. Adsorbates with an asterisk correspond to species that are adsorbed on the surface. Null stands for no free energy barrier.

Fig. 3 Silver–copper model catalyst surface with different copper coverages. Scanning electron microscopic images of Ag-Cu surfaces achieved at Cu\(^{2+}\) concentrations of 0.5 ppm (a), 1.5 ppm (b) and 2.5 ppm (c). d Faradaic efficiencies of Ag-Cu surfaces with different Cu coverages for CO\(_2\) electrolysis at \(-1.10\) V\(_{\text{RHE}}\). The error bars represent the standard deviation from at least three independent measurements.

![Diagram](image)

**Table 1 Surface Cu coverage with different Cu\(^{2+}\) concentrations in the electrolyte**

| Cu\(^{2+}\) concentration/ppm | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
|-------------------------------|-----|-----|-----|-----|-----|
| Surface Cu coverage           | 2.7%| 32.3%| 50.2%| 70.0%| 85.3%|
| Surface Ag coverage           | 97.3%| 67.7%| 49.8%| 30.0%| 14.7%|

becomes more negative due to the increased overpotential (Fig. 4b, d). The increase in CO production is more significant than that of H\(_2\) production, resulting in an increase in CO FE and a decrease in H\(_2\) FE (Fig. 4a–c). As the potential becomes more negative than \(-1.0\) V\(_{\text{RHE}}\), the Ag-Cu surface exhibits a substantial increase in the CH\(_4\) partial current density with a concomitant decrease in the CO partial current density (Fig. 4b). However, for the bare Ag surface, the CO partial current density continuously increases and begins to plateau at \(-1.1\) V\(_{\text{RHE}}\), which is most likely due to mass transport limitations (Fig. 4d). This result clearly demonstrates that the exposed Ag surface on Ag-Cu behaves very differently from the bare Ag. If the exposed Ag surface merely converts CO\(_2\) to molecular CO that leaves the Ag-Cu surface, as is the case for the bare Ag surface, the CO partial current density should increase as the potential becomes more negative until mass-transport limitation. In contrast, the exposure of Ag sites to CO on the Ag-Cu surface changes the overpotential for both CO and H\(_2\) production, indicating that the extra CO produced on exposed Ag sites becomes more negative due to the increased overpotential (Fig. 4b, d). The increase in CO production is more significant than that of H\(_2\) production, resulting in an increase in CO FE and a decrease in H\(_2\) FE (Fig. 4a–c). As the potential becomes more negative than \(-1.0\) V\(_{\text{RHE}}\), the Ag-Cu surface exhibits a substantial increase in the CH\(_4\) partial current density with a concomitant decrease in the CO partial current density (Fig. 4b). However, for the bare Ag surface, the CO partial current density continuously increases and begins to plateau at \(-1.1\) V\(_{\text{RHE}}\), which is most likely due to mass transport limitations (Fig. 4d). This result clearly demonstrates that the exposed Ag surface on Ag-Cu behaves very differently from the bare Ag. If the exposed Ag surface merely converts CO\(_2\) to molecular CO that leaves the Ag-Cu surface, as is the case for the bare Ag surface, the CO partial current density should increase as the potential becomes more negative until mass-transport limitation. In contrast, the CO partial current density of Ag-Cu surface actually decreases at more negative potentials where CH\(_4\) formation starts to increase (Fig. 4b), indicating that the extra CO produced on exposed Ag sites...
beyond a potential of $-1.0 \text{ V}_{\text{RHE}}$ is consumed in other processes (i.e., CO spillover). In addition, at $-1.0 \text{ V}_{\text{RHE}}$, the CO partial current density of Ag-Cu (1.0 mA cm$^{-2}$) is approximately 46% of that of the bare Ag surface (2.2 mA cm$^{-2}$). This value is consistent with the 49.8% exposed Ag on the Ag-Cu surface because its CO partial current density is primarily attributed to the exposed Ag due to the very low CO activity of Cu (less than 0.1 mA cm$^{-2}$ at potentials more negative than $-1.0 \text{ V}_{\text{RHE}}$). As the potential decreases from $-1.0 \text{ V}_{\text{RHE}}$ to $-1.1 \text{ V}_{\text{RHE}}$, the CO partial current density on the bare Ag increases from 2.23 to 4.82 mA cm$^{-2}$ representing a factor of 2.16 increase (Fig. 4d). However, the CO partial current density on the Ag-Cu surface decreases slightly from 1.0 to 0.9 mA cm$^{-2}$ under the same condition (Fig. 4b), assuming that the Ag sites on the Ag-Cu surface would produce more CO with the same factor of 2.16 and the missing portion (i.e., 1.26 mA cm$^{-2}$) is further converted to CH$_4$ by the surface Cu. The CH$_4$ partial current density can be estimated to be 5.04 mA cm$^{-2}$ (1.26 mA cm$^{-2}$ x 4) since CH$_4$ production requires four times as many electrons as CO production. Indeed, this value is consistent with the experimentally measured value (i.e., 4.9 mA cm$^{-2}$). This result indicates that, at the optimal Cu coverage, nearly 60% of the CO produced on Ag is further reduced to CH$_4$ on the Cu surface via the tandem process. At more negative potentials, significant HER activity is observed on both surfaces, which results in the decreased FE of CO$_2$RR. The drastically increased HER activity on the Ag-Cu surface is most likely due to the rapid HER on surface Cu sites at high potential bias (Supplementary Fig. 6). CO$_2$ electrolysis at extended time (2 h) is also conducted on Ag-Cu and bare Ag surfaces (Supplementary Fig. 8). The CH$_4$ formation is stable in the first hour with an FE of approximately 60%. After that, the CH$_4$ FE gradually increases to 67% at the end of the 2-h electrolysis, which is accompanied by the concomitant decrease of CO and C$_2$H$_4$ FE. The further increase in CH$_4$ FE is likely due to the surface reconstruction of Cu under CO$_2$ electroreduction conditions that favors CH$_4$ formation. Further development of more advanced Ag-Cu catalysts combining Cu and Ag with optimized material structure is a promising approach to achieve better performance in CO$_2$RR.

**Operando spectroscopic investigations.** To gain further insights into the CO spillover on the Ag-Cu surface, operando ATR-SEIRAS is employed to monitor the adsorbed CO at conditions closely mimicking those in the reactivity studies. Experiments on bare Ag, bare Cu, and Ag-Cu surface (1.5 ppm Cu$^{2+}$) at $-0.4 \text{ V}_{\text{RHE}}$ are conducted in a custom-designed stirred spectroelectrochemical cell (Supplementary Fig. 9). The bare Ag
surface in the ATR-SEIRAS study is prepared by electrochemical deposition of Ag film in a silver cyanide plating bath on an Au film that is chemically deposited onto the reflecting plane of a Si prism. The Ag-Cu surface is then prepared in the same fashion as in the reactivity study, i.e., by conducting the experiments in a Cu\(^{2+}\)-containing bicarbonate on the Ag film. The bare Cu surface is prepared via the chemical deposition method. The bare Ag surface exhibits a C≡O stretching band at 2094 cm\(^{-1}\) (Fig. 3), which is typically attributed to CO molecule bound in an atop geometry. The bare Cu surface shows two stretching bands of atop-bound CO in the 2000–2120 cm\(^{-1}\) range, with the 2088 and 2055 cm\(^{-1}\) bands being attributed to CO adsorption on defect sites and terraces sites, respectively. This is also consistent with previous studies by Waegle et al. under similar electrolysis conditions. The 2094 cm\(^{-1}\) band on the Ag-Cu surface is identical to that of bare Ag surface, as the peak position and width are both identical. The deconvoluted C≡O stretching band on surface Cu has a broad feature centered at 2048 cm\(^{-1}\), which is consistent with a previous report. The difference between the CO adsorption feature on the bare Cu and the Ag-Cu surface shows that the underlying Ag exerts an impact on the properties of Cu. Remarkably, the Ag-Cu surface exhibits a band in the 1800–1900 cm\(^{-1}\) range, typically assigned to bridge CO with stronger binding strength, which is absent on both bare Ag and Cu surfaces. This band is much more intense than the atop CO band, thus the major CO species on the Ag-Cu surface according to Beer–Lambert law. The spectroscopic observations clearly indicate that the Ag-Cu surface is different from a simple superposition of bare Cu and Ag surfaces. This is consistent with our one-pot tandem catalysis theory that the *CO produced on the exposed Ag sites can migrate to stronger binding sites on the Ag-Cu surface for further reduction. In addition, the exclusive band on the Ag-Cu surface is not due to some new reactive site existing on the Ag-Cu bimetalic interface. If this is the case, the CO produced on the exposed Ag sites on Ag-Cu will not be consumed by further reduction, and the CO production should be promoted at more negatively biased potential until mass-transport limitation, similar as the case of bare Ag foil. This contradicts the experimental results shown in Fig. 4b, d.

**Constant and square-wave potential electrolysis of CO on the Ag-Cu surface.** To further probe CH\(_4\) formation over Ag-Cu surface with respect to local *CO concentration, the electrochemical CO reduction reaction is conducted at −1.1 VRHE using the same bicarbonate electrolyte, and the results are compared to those obtained using a bare Cu foil. At constant potential, the Ag-Cu surface produces fewer hydrocarbons than the bare Cu foil in CO electrolysis (Fig. 6). This result can be rationalized that Ag is not active in CO electoreduction, thus fewer active Cu sites are present on the Ag-Cu surface than on the Cu foil surface. Therefore, the observed enhancement of CH\(_4\) formation on the Ag-Cu surface in CO\(_2\)RR is apparently due to the tandem chemistry between Ag and Cu.

In CO\(_2\)RR, CO adsorption can be difficult because CO adsorbate is suggested to come from the transformation of radical anion CO\(_2^{-}\) instead of direct CO adsorption. In addition, the surface CO adsorption can also be negatively impacted by the near electrode cations that are attracted by electrostatic forces as the electrode potential is negatively biased during the electrolysis. However, the near electrode cations can be effectively removed at a more positive potential (e.g., 0.4 VRHE), and CO adsorption can be promoted. Based on these insights, square-wave potential electrolysis (inset of Fig. 6) of CO is employed to probe the catalytic behavior of our Ag-Cu surface with an increased local *CO concentration. The potential is alternated between 0.4 VRHE \((U_0)\) for a fixed time interval of 0.01 s, at which the CO adsorption is maximized, and an electrolysis potential (i.e., −1.1 VRHE, \(U_b\)) at which the CO reduction is expected to occur. By flipping the electrode potential at a frequency of approximately 1 Hz, the FE toward hydrocarbon formation on the Ag-Cu surface is significantly improved from 5% to 18%, which surpassed that on a bare Cu surface. By increasing the frequency to approximately 2 Hz, the FE toward hydrocarbon formation is further increased to 30%, which is twice as high as that of bare Cu. These results suggest that the increase of electrode *CO concentration can efficiently improve

---

**Fig. 5** Studies of surface-adsorbed CO on Cu, bare Ag and Ag-Cu films. Operando attenuated total reflectance surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) of surface adsorption. **a** The atop-bonded CO band on different surfaces under −0.4 VRHE. **b** The bridge-bonded CO band on Ag-Cu film under −0.4 VRHE. The background is collected at 0.1 VRHE under Ar purge.

**Fig. 6** Faradaic efficiencies of major carbon monoxide electroreduction products. Constant potential electrolysis at −1.1 VRHE is conducted on the bare Cu and Ag-Cu surfaces. Square-wave potential electrolysis alternating between 0.4 VRHE \((U_0)\) and −1.1 VRHE \((U_b)\) is conducted on the Ag-Cu surface. Inset: schematic representation of the square-wave potential profile employed in the electrolysis.
the formation of further reduced products. The one-pot tandem catalysis mechanism that utilizes the complementary surface chemistry between a CO-producing material and Cu can be a very effective strategy for achieving this goal. However, to achieve more valuable products (e.g., C2+ products) requires further development employing more active CO-producing catalysts (e.g., nanoporous Ag or oxide-derived Au) and CO reduction catalysts (e.g., oxide-derived Cu) as well as their combination pattern and structure design for binding *CO to more desired sites after spillover.

Discussion

Density functional theory (DFT) calculations were carried out to investigate the one-pot tandem catalysis of the CO2RR on Cu-modified Ag and Au surface models. We found that the surface Cu stabilized *CO by 1.07 and 1.09 eV compared to Ag and Au, respectively, indicating that the abundant *CO produced on the Ag or Au surface can migrate to surface Cu for further reduction. We found that all reactions along the possible pathways are downhill under a potential bias of −1.0 V_{SHE}, indicating that the migrated *CO from the Ag surface can be further reduced on the surface Cu with barriers that are not larger than those on a bare Cu surface. Electrochemical studies were conducted using well-defined Ag-Cu surfaces with tunable Cu coverages to confirm our computational predictions. The CO spillover phenomenon was experimentally demonstrated for the first time. At optimum Cu coverage, nearly 70% of the CO produced on Ag can be further reduced on surface Cu, resulting in a high CH4 FE of approximately 60%. This FE is much higher than that on a bare Cu surface, which has intrinsically limited surface *CO. In addition, operating ATR-SEIRAS was employed to investigate the spillover of CO on the Ag-Cu surface. A dominating C≡O stretching band on the Ag-Cu surface with stronger binding strength was found at −0.4 V_{RHE}, which was absent on the bare Ag and Cu surface, suggesting that the major *CO was not from CO2RR on Cu. The stronger adsorption of *CO on Cu as compared to Ag strongly suggest the CO spillover as a viable pathway. Moreover, we conducted square-wave potential electrolysis of CO to assess the role of a higher *CO concentration on hydrocarbon formation over the Ag-Cu surface. By alternating the electrolysing potential between a reductive point and a point that removes the near-surface cations, the FE for hydrocarbon formation was significantly enhanced owing to increased *CO adsorption. These results suggest that the increase of surface *CO could efficiently improve the formation of further reduced products. We conclude that the one-pot tandem catalysis mechanism utilizing the complementary surface chemistry between a CO-producing material and Cu can be a very effective strategy for achieving this goal. Further development employing more active CO-producing catalysts (e.g., nanoporous Ag or oxide-derived Au) and CO reduction catalysts (e.g., oxide-derived Cu) as well as their combination pattern and structure design provides a very promising route to achieve efficient CO2RRs toward more valuable products (e.g., C2+ products).

Methods

Computational details. The total energy of the Cu-modified Ag(111) and Au(111) surfaces with different adsorbates were calculated using DFT with the Perdew-Burke-Ernzerhof exchange-correlation functional in plane-wave pseudopotentials, as implemented in the Vienna ab initio Simulation Package (VASP)  

\[
\text{V}_{\text{SHE}} = \text{Fermi energy} + \text{Fermi level} \times \text{Fermi density}
\]

The empirical D3 approach as implemented in VASP was employed to describe the van der Waals interactions  

The calculated energy values were extrapolated to \( k_B T = 0 \). A Monkhorst-Pack K-point net of \( 5 \times 6 \times 1 \) was chosen to sample the reciprocal space for the slab calculations, and only the gamma point was sampled for the molecule calculations. A metal slab (4 x 2) consisting of 3 layers with the bottom layer fixed in its bulk position was employed to simulate the surface of Ag and Au, and a single layer of Cu with a coverage of 1/2 ML (monolayer) was placed on the substrate, as shown in Fig. 1a. A vacuum of 25 Å was introduced to each side to avoid interactions between successive metal slabs. Cubic cells of all calculation models are provided (Supplementary Information).

The transition state for each reaction was first approached using the nudged elastic band (NEB) method in the neutral state  

\[
\Delta G_{\text{transition state}} = \Delta G_{\text{reactant}} - \Delta G_{\text{product}}
\]

The force of the dimer calculation was converged to \( <0.1 \text{eV Å}^{-1} \) to accurately locate the saddle point, i.e., the transition state. After that, the free energy of transition state was calculated using a zero-constant potential. An explicit water molecule was used as the proton source as previous work suggested.

To establish the electrochemical interface, the approach proposed by Head-Gordon et al., Goddard et al., and Sautet et al. was applied  

\[
\text{Fermi energy} = \text{Fermi level} \times \text{Fermi density}
\]

1. The plane-wave cutoff, smearing parameter and structure design for binding *CO to more desired sites after spillover.

Electrolysis and product quantification. Ag foil (thickness 0.1 mm, 99.998% metal basis), Cu foil (thickness 0.1 mm, 99.9999% metal basis), Ti foil (thickness 0.127 mm, 99.99% + 5% metal basis), and Ni wire (99.9%) were purchased from Alfa Aesar. A used as the working electrode in the CO2RR and CO electrolysis experiments. The Ag foil was mechanically polished using sand paper (1200 G, 3 M) and thoroughly cleaned in an ultrasonic bath with deionized water prior to electrolysis. The Cu foil was mechanically polished using sand paper (1200 G, 3 M) followed by electrochemical polishing in phosphoric acid (85 wt.% in H2O, Sigma-Aldrich, 99.99% metal basis) at 2.0 V vs a Ti foil counter electrode and thorough rinsing in fresh 0.1 M NaHCO3 solution to remove phosphoric acid residue prior to each experiment. Ni wires were welded to the edge of these Ag and Cu foil pieces as current collectors. The 0.1 M NaHCO3 solution was prepared by dissolving Na2CO3 (99.999%, Fluka) in deionized water that was obtained from a Millipore system (18.2 MΩ•cm) and converted to NaHCO3, using CO2 (99.99%, Air Liquid). The electrolyte was treated using Chelex® 100 resin (Sigma-Aldrich) prior to electrolysis. The 1 mM Cu2+ solution was prepared by dissolving CuSO4·5H2O (99.999%, Sigma-Aldrich) in 0.05 M sulfuric acid (99.999%, Sigma-Aldrich) in 0.05 M sulfuric acid (99.999%, Sigma-Aldrich) according to a previously reported protocol.

The CO2RR electrolysis experiments were performed in a gas-tight two-compartment three-electrode electrochemical cell separated by a piece of a proton exchange membrane (Nafion® perfluorinated membrane). A graphite rod (99.999%, Sigma-Aldrich) was used as the counter electrode. The electrolyte compartment contained 18.0 mL of electrolyte and approximately 8.2 mL of headspace. Prior to electrolysis, the electrolyte in the cathodic compartment was purged with CO2 (99.99%, Air Liquid) gas for at least 25 min until a pH of 6.8 was reached. Then the Cu2+ solution was added for the Ag-Cu surface investigations. The electrolyte in the cathodic compartment was stirred at a rate of 800 rpm during the electrolysis.

The CO2RR electrolysis experiments were performed under identical conditions as the CO2RR electrolysis experiments except for the gas feed. Prior to electrolysis, the electrolyte in the cathodic compartment was purged with CO (99.999%, Air Liquid) gas rather than CO2 for at least 25 min, and the pH was measured to be 8.4. The square-wave potential electrolysis was performed by alternating between a potential of 0.4 V_{SHE} (Us) for a fixed time of 0.01 s and −1.1 V_{SHE} (Ut) for 1 and 0.5 s, which is equivalent to a frequency of approximately 1 and 2 Hz, respectively. Only the cathodic charges were counted for the FE calculation. The charges from the capacitive current can be neglected owing to them being ≤1% of the cathodic charges.

A Gamry Reference 600+ potentiostat was used for all electrolysis. All potentials were measured against a Ag/AgCl reference electrode (3.0 M KCl, BASI) and converted to the RHE reference scale using E (vs RHE) = E (vs Ag/AgCl) + 0.210 V + 0.05916 V × pH. The IR compensation function of the potentiostat was used to correct the electrode Ru.

The gas products were quantified using a gas chromatograph (Agilent 7890B). The gas chromatograph was equipped with a ShinCarbon ST Micropacked GC Column. Argon (99.999%, Air Liquid) was used as the carrier gas. First, the column effluent was passed through a thermal conductivity detector where the hydrogen was quantified. Then the effluent was passed through a methanizer where CO was converted to methane and subsequently quantified using a flame ionization detector.

Liquid products were quantified using a Bruker AVIII 400 MHz NMR spectrometer. After electrolysis, 0.5 mL of the electrolyte was mixed with 0.1 mL of D2O. A 20 × 20 × 20 mm3 sample tube (10 mm length) containing D2O (99.9%, Alfa Aesar) was added as an internal standard. The 1H spectrum was measured with water suppression using a presaturation method.
The electrolytic bath was prepared with deionized water and graphite rod as the counter electrode, and saturated Ag/AgCl (BASi) as the reference electrode. The electrolytic bath contained 0.15 M AgNO₃, 0.54 M KCN, and 0.38 M Na₂CO₃. Electrodeposition in a mixture of 0.8 mL HF aqueous solution (2 wt.%) and 4.4 mL Au plating solution (0.25 M NaAuCl₄·2H₂O and NH₄Cl) was purchased from Sigma-Aldrich.

HCHO, 0.02 M CuSO₄, 0.02 M Na₂EDTA (99%), 2,2-bipyridine (99%, Reagent Plus) for 7 min. The pH of the plating solution was adjusted to 12.0 by conducting the experiments in a Cu₂⁺-containing bicarbonate on the electrode surface. The Ag film was rinsed with deionized water and dried with air. The Ag-Cu substrate was then prepared in the same fashion as in reactivity study, i.e., by conducting the experiments in a Cu₂⁺-containing bicarbonate on the Ag film.

The reference electrode directly deposited on the Si prism was prepared using a similar method as described previously. Briefly, the polished Si prism was immersed in NH₄F for 60 s and then immersed into a copper seeding solution (0.5 wt.% CuCl₂ and 750 mM NaCl) for 120 s followed by a plating solution (0.25 M HCHO, 0.02 M CuSO₄, 20 mM Na₂EDTA (99%–101%, ACS Reagent), and 0.3 M 2,2-bipyridine (99%, Reagent Plus)) for 7 min. The pH of the plating solution was adjusted to 12.2 by KOH and the temperature was maintained at 55 °C during the deposition. Afterwards, the obtained Cu film was rinsed with deionized water and dried with air. A two-compartment, three-electrode spectrometer was separated by a Nafion® perfluorinated membrane, was designed to accommodate the Si prism and to avoid any possible cross-contamination from the counter electrode. The spectrometer was coupled with a Solartron SI 1260/1287 system for electrochemical measurements. All spectra were collected at a 4 cm⁻¹ spectral resolution and were presented in absorbance units. In a typical process, the obtained films on Si prisms were used as working electrodes with a graphite rod as the counter electrode and saturated Ag/AgCl as the reference electrode.

Characterization. SEM images were recorded using a Hitachi S-5500 SEM. The accelerating voltage was 5 kV. TEM sample was prepared using Ga⁺ focused ion on a ZEISS AURIGA® Field Emission-SEM incorporated with CrossBeam® Workstations. TEM images were recorded using a JEOL JEM-2100F TEM. The accelerating voltage was 200 kV. XPS measurements were carried out using a PHI Quanta II with Al Kα radiation. The resulting spectra were analyzed using the CasaXPS software package (Casa Software Ltd., U.K.) and peaks were fitted using a Gaussian/Lorentzian product line shape with the Shirley-type background.

Data availability:
The data that support the findings of this study are available from the corresponding author upon request.

Received: 16 December 2018 Accepted: 30 June 2019
Published online: 26 July 2019

References
1. Centi, G.; Quadralli, E. A. & Parathoner, S. Catalysis for CO₂ conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries. Energy Environ. Sci. 6, 1711–1731 (2013).
2. Lu, Q., Rosen, J. & Jiao, F. Nanostructured metallic electrode catalysts for carbon dioxide reduction. ChemCatChem 7, 38–47 (2015).
3. Lu, Q. & Jiao, F. Electrochemical CO₂ reduction: electrocatalyst, reaction mechanism, and process engineering. Nano Energy 29, 439–456 (2016).
4. Lu, Q. et al. A selective and efficient electrode catalyst for carbon dioxide reduction. Nat. Commun. 5, 3242 (2014).
5. Chen, Y., Li, C. W. & Kanan, M. W. Aqueous CO₂ reduction at very low overpotential on oxide-derived Au nanoparticles. J. Am. Chem. Soc. 134, 19969–19972 (2012).
6. Chen, Y. & Kanan, M. W. Tin oxide dependence of the CO₂ reduction efficiency on tin electrodes and enhanced activity for tin/tin oxide thin-film catalysts. J. Am. Chem. Soc. 134, 1986–1989 (2012).
7. Verma, S., Lu, X., Ma, S., Masel, R. I. & Kenis, P. J. The effect of electrolyte composition on the electroreduction of CO₂ to CO on Ag based gas diffusion electrodes. Phys. Chem. Chem. Phys. 18, 7075–7084 (2016).
8. Kim, B., Hillman, F., Ariyoshi, M., Fujikawa, S. & Kenis, P. J. A. Effects of composition of the micro porous layer and the substrate on performance in the electroreduction of CO₂ to CO. J. Power Sources 312, 192–198 (2016).
9. Hori, Y., Kukuchi, K. & Suzuki, S. Production of CO and CH₄ in electrochemical reduction of CO₂ at metal electrodes in aqueous hydrogencarbonate solution. Chem. Lett. 14, 1695–1698 (1985).
10. Hori, Y., Kikuchi, K., Mouri, A. & Suzuki, S. Production of methane and ethylene in electrochemical reduction of carbon dioxide at copper electrode in aqueous hydrogencarbonate solution. Chem. Lett. 15, 897–898 (1986).
11. Kuhl, K. P., Cave, E. R., Abram, D. N. & Jaramillo, T. F. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. Energy Environ. Sci. 5, 7050–7059 (2012).
12. Li, C. W. & Kanan, M. W. CO₂ electroreduction at low overpotential on Cu electrodes resulting from the reduction of thick CuO films. J. Am. Chem. Soc. 134, 7231–7234 (2012).
13. Mariano, R. G., McKeilley, K., White, H. S. & Kanan, M. W. Selective increase in CO₂ electroreduction activity at grain-boundary surface terminations. Science 358, 1187–1192 (2017).
14. Mistry, H. et al. Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene. Nat. Commun. 7, 12123 (2016).
15. Gao, D. et al. Plasma-activated copper nanocube catalysts for efficient carbon dioxide electroreduction to hydrocarbons and alcohols. ACS Nano 11, 4828–4831 (2017).
16. De Luna, P. et al. Catalyst electro-redocontrol protects morphology and oxidation state for selective carbon dioxide reduction. Nat. Catal. 1, 103–110 (2018).
17. Tang, W. et al. The importance of surface morphology in controlling the selectivity of polycrystalline copper for CO₂ electroreduction. Phys. Chem. Chem. Phys. 14, 76–81 (2012).
18. Roberts, F. S., Kuhl, K. P. & Nilson, A. Electroreduction of carbon monoxide over a copper nanocube catalyst: surface structure and pH dependence on selectivity. ChemCatChem 8, 1119–1124 (2016).
19. Kim, D., Resasco, J. Y., Yu, A., Arsi, A. M. & Yang, P. Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold-copper bimetallic nanoparticles. Nat. Commun. 5, 4948 (2014).
20. Ren, D., Ang, B. S.-H. & Yeo, B. S. Tuning the selectivity of carbon dioxide electroreduction toward ethanol on oxide-derived Cu₂Zn catalysts. ACS Catal. 6, 8239–8247 (2016).
21. Clark, E. L., Hahn, C., Jaramillo, T. F. & Bell, A. T. Electrochemical CO₂ reduction over compressively strained CuAg surface alloys with enhanced multicovalent oxygenate selectivity. J. Am. Chem. Soc. 139, 15848–15857 (2017).
22. Morales-Guio, C. G. et al. Improved CO₂ reduction activity towards C₂–C₆ alcohols on a tandem gold on copper electrocatalyst. Nat. Catal. 1, 764–771 (2018).
23. Hatsuake, T., Kuhl, K. P., Cave, E. R., Abram, D. N. & Jaramillo, T. F. Insights into the electrocatalytic reduction of CO₂ on metallic silver surfaces. Phys. Chem. Chem. Phys. 16, 13814–13819 (2014).
24. Rosen, J. et al. Mechanistic insights into the electrochemical reduction of CO₂ to CO on nanostructured Ag surfaces. ACS Catal. 5, 4293–4299 (2015).
25. Peterson, A. A., Abd-Pedersen, F., Stauth, F., Rossmeisl, J. & Norskov, J. K. How copper catalyzes the electrochemical reduction of carbon dioxide into hydrocarbon fuels. Energy Environ. Sci. 3, 1311–1315 (2010).
26. Peterson, A. A. & Norskov, J. K. Activity descriptors for CO₂ electroreduction to methane on transition-metal catalysts. J. Phys. Chem. Lett. 3, 251–258 (2012).
27. Li, J. et al. Effectively increased efficiency for electrocatalysis of carbon monoxide using supported polycrystalline copper powder electrocatalysts. ACS Catal. 9, 4709–4718 (2019).
28. Montoya, J. H., Peterson, A. A. & Norskov, J. K. Insights into C-C coupling in CO₂ electroreduction on Copper electrodes. ChemCatChem 5, 737–742 (2013).
29. Montoya, J. H., Shi, C., Chan, K. & Norskov, J. K. Theoretical insights into CO₂ dimerization mechanism in CO₂ electroreduction. J. Phys. Chem. Lett. 6, 2032–2037 (2015).
30. Sandberg, R. B., Montoya, J. H., Chan, K. & Norskov, J. K. CO-CO coupling on Cu facets: coverage, strain and field effects. Surf. Sci. 654, 56–62 (2016).
31. Zhang, Y.-J., Sethuraman, V., Michalsky, R. & Peterson, A. A. Competition between CO₂ reduction and H₂ evolution on transition-metal electrocatalysts. ACS Catal. 4, 3742–3748 (2014).
32. Poelsema, B., Verheij, J. L. & Comsa, G. He-scattering investigation of CO migration on Pt(111). *Phys. Rev. Lett.* 49, 1731–1735 (1982).

33. Klein, K. Adsorption, diffusion, and evaporation of carbon monoxide on tungsten. *J. Phys. Chem.* 31, 1306–1313 (1959).

34. Shi, C., Chan, K., Yoo, J. S. & Norskov, J. K. Barriers of electrochemical CO2 reduction on transition metals. *Org. Process Res. Dev.* 20, 1424–1430 (2016).

35. Cheng, T., Xiao, H. & Goddard, W. A. 3d Full atomistic reaction mechanism with kinetics for CO2 reduction on Cu(100) from ab initio molecular dynamics: free-energy calculations at 298 K. *Proc. Natl Acad. Sci. USA* 114, 1795–1800 (2017).

36. Zhang, H., Goddard, W. A. 3d, Lu, Q. & Cheng, M. J. The importance of grand-canonical quantum mechanical methods to describe the effect of electrode potential on the stability of intermediates involved in both electrochemical CO2 reduction and hydrogen evolution. *Phys. Chem. Chem. Phys.* 20, 2549–2557 (2018).

37. Steinmann, S. N., Michel, C., Schwiebertoch, R., Filhol, J. S. & Sautet, P. Modeling the HCOOH/CO2 electrolytic reaction: when details are key. *ChemPhysChem* 16, 2307–2311 (2015).

38. Xiao, H., Cheng, T., Goddard, W. A. 3d & Sundararaman, R. Mechanistic explanation of the pH dependence and adsorption potentials for hydrocarbon products from electrochemical reduction of CO on Cu (111). *J. Am. Chem. Soc.* 138, 483–486 (2016).

39. Goodpaster, J. D., Bell, A. T. & Head-Gordon, M. Identification of possible pathways for C-C bond formation during electrochemical reduction of CO2: new theoretical insights from an improved electrochemical model. *J. Phys. Chem. Lett.* 7, 1471–1477 (2016).

40. Garza, A., Bell, A. T. & Head-Gordon, M. On the mechanism of CO2 reduction at copper surfaces: pathways to C2 products. *ACS Catal.* 8, 1490–1499 (2018).

41. Liu, X. et al. Understanding trends in electrochemical carbon dioxide reduction rates. *Nat. Commun.* 8, 15438 (2017).

42. Liu, X. et al. pH effects on the electrochemical reduction of CO2 to CO2 on copper products on copper cathode. *Nat. Commun.* 10, 32 (2019).

43. Dietterle, M., Will, T. & Kolb, D. The initial stages of copper deposition on Ag (111): an STM study. *Surf. Sci.* 342, 29–37 (1995).

44. Nikolić, N. D., Pavlović, L. J., Kršić, S. R., Pavlović, M. G. & Popov, K. I. Induction of ionic equilibrium in the Cu2O−H2O−H2O system on the formation of irregular electrodeposits of copper. *Chem. Eng. Sci.* 63, 2824–2828 (2008).

45. Orhan, G. & Gegen, G. Effect of electrolysis parameters on the morphologies of copper powder obtained at high current densities. *J. Serb. Chem. Soc.* 77, 651–665 (2012).

46. Kim, Y. G., Barciaturo, J. H., Javier, A., Gregoire, J. M. & Soriaga, M. P. The evolution of the polycrystalline copper surface, first to Cu(111) and then to Cu(100), at a fixed CO2RR potential: a study by operando EC-STM. *Langmuir* 30, 15053–15056 (2014).

47. Kim, Y. G. et al. Surface reconstruction of pure-Cu single-crystal electrodes under CO reduction potentials in alkaline solution: A study by seriation ECSTM-DEMS. *J. Electroanal. Chem.* 780, 290–295 (2016).

48. Dunwell, M. et al. Examination of near-electrode concentration gradients and kinetic impacts on the electrochemical reduction of CO2 using surface-enhanced infrared spectroscopy. *ACS Catal.* 8, 3999–4008 (2018).

49. Wanzenböck, H. D., Mizaikoff, B., Weissenbacher, N. & Kellner, R. Surface enhanced infrared absorption spectroscopy (SEIRA) using external reflection on low-cost substrates. *Fresenius J. Anal. Chem.* 362, 15–20 (1998).

50. Dunwell, M. et al. The central role of bicarbonate in the electrochemical reduction of carbon dioxide on gold. *J. Am. Chem. Soc.* 139, 3774–3783 (2017).

51. Malkani, A. S., Dunwell, M. & Xu, B. Operating spectroscopic investigations of copper and oxide-derived copper catalysts for electrochemical CO2 reduction. *ACS Catal.* 9, 474–478 (2019).

52. Ikezawa, Y., Saito, H., Matsubayashi, H. & Toda, G. Comparative study of CO adsorbed on Pt, Pd, Au and Ag electrodes in neutral solution by IR reflection absorption spectroscopy. *J. Electroanal. Chem.* 252, 395–402 (1988).

53. Gunathunge, C. M. et al. Spectroscopic observation of reversible surface reorganisation of copper electrodes under CO2 reduction. *J. Phys. Chem. C* 121, 12337–12344 (2017).

54. Heyes, J., Dunwell, M. & Xu, B. CO2 reduction on Cu at low overpotentials with surface-enhanced in situ spectroscopy. *J. Phys. Chem. C* 120, 17334–17346 (2016).

55. Gunathunge, C. M., Ovalle, V. J., Li, Y., Janik, M. J. & Waeghele, M. M. Existence of an electrochemically inert CO2 population on Cu electrodes in alkaline phosphate. *ACS Catal.* 8, 7507–7516 (2018).

56. Pérez Gallent, E., Figureido, M. C., Calle-Vallejo, F. & Koper, M. T. M. Spectroscopic observation of a hydrogenated CO dimer intermediate during CO reduction on Cu(100) electrodes. *Angew. Chem. Int. Ed.* 129, 3675–3678 (2019).

57. Kortlever, R., Shen, J., Schouten, K. J. P., Calle-Vallejo, F. & Koper, M. T. M. Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide. *J. Phys. Chem. Lett.* 6, 4073–4082 (2015).

58. Genovese, C., Appel, C., Perathoner, S. & Centi, G. Mechanism of C–C bond formation in the electrocatalytic reduction of CO2 to acetic acid. A challenging reaction to use renewable energy with chemistry. *Green. Chem.* 19, 2406–2415 (2017).

59. Li, C. W., Ciston, J. & Kanan, M. W. Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper. *Nature* 508, 504–507 (2014).

60. Wang, Y., Raciti, D. & Wang, C. High-flux CO reduction enabled by three-dimensional nanocrystalline copper electrodes. *ACS Catal.* 8, 5657–5663 (2018).

61. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 77, 3865 (1996).

62. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* 50, 17953–17979 (1994).

63. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 59, 1758–1775 (1999).

64. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* 47, 558–561 (1993).

65. Henkelman, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 54, 11189–11186 (1996).

66. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* 27, 1787–1799 (2006).

67. Henkelman, G. & Jönsson, H. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.* 113, 9978–9985 (2000).

68. Henkelman, G. & Jönsson, H. A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives. *J. Chem. Phys.* 111, 7010–7022 (1999).

Acknowledgements

This work is supported by the National Key Research and Development Program of China (grant number 2017YFA020800) and the National Natural Science Foundation of China (grant numbers 21872079, 21606142). W.A.G. is supported by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993. X.C. and J.O. acknowledge the support of the National Science Foundation CAREER Program (Award No. CBET-1651625). M.-J.C. acknowledges financial support from the Ministry of Science and Technology of the Republic of China under grant no. MOST 107–2113-M-006–008-MY2.

Author contributions

Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-019-11292-9.

Competing interests: The authors declare no competing interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/.

Peer review information: Nature Communication would like to thank the anonymous reviewers for their contribution to the peer review of this work.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.