Highly Selective Electrocatalytic Reduction of CO₂ into Methane on Cu–Bi Nanoalloys

Zhijiang Wang, Qi Yuan, Jingjing Shan, Zhaoxia Jiang, Ping Xu, Yongfeng Hu, Jigang Zhou, Lina Wu, Zhuangzhuang Niu, Jianmin Sun, Tao Cheng, and William A. Goddard

J. Phys. Chem. Lett., **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcllett.0c01261 • Publication Date (Web): 23 Jul 2020

Downloaded from pubs.acs.org on July 23, 2020

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

Highly Selective Electrocatalytic Reduction of CO₂ into Methane on Cu–Bi Nanoalloys

Zhijiang Wang,^{*,†,#} Qi Yuan,[⊥] Jingjing Shan,[†] Zhaohua Jiang,^{†,#} Ping Xu,[†] Yongfeng Hu,[§]
Jigang Zhou,[§] Lina Wu,^{||} Zhuangzhuang Niu,[†] Jianmin Sun,^{*,†} Tao Cheng,^{*,⊥,‡} William A.
Goddard III,^{*,‡}

[†] MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage and [#]State Key Laboratory of Urban Water Resource and Environment, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China;

[⊥] Institute of Functional Nano & Soft Materials (FUNSOM) Jiangsu Key Laboratory for Carbon Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu 215123, China;

^{||} Department of Radiology, Molecular Imaging Research Center of Harbin Medical University, the Fourth Hospital of Harbin Medical University, Harbin 150001, China;

[§] Canadian Light Source Inc., Saskatoon, Saskatchewan S7N 0X4, Canada;

[‡] Materials and Process Simulation Center (MSC) and Joint Center for Artificial Photosynthesis (JCAP), California Institute of Technology, Pasadena, California 91125, United States;

AUTHOR INFORMATION

Corresponding Author

*E-mail: wangzhijiang@hit.edu.cn;

sunjm@hit.edu.cn;

tcheng@caltech.edu;

wag@wag.caltech.edu.

ABSTRACT: Methane (CH_4), the main component of natural gas, is one of the most valuable products facilitating energy storage via electricity conversion. However, the poor selectivity and high overpotential for CH_4 formation with metallic Cu catalysts prevent realistic applications. Introducing a second element to tune the electronic state of Cu has been widely used as an effective method to improve catalytic performance, but achieving high selectivity and activity toward CH_4 remains challenging. Here, we successfully synthesized Cu–Bi NPs, which exhibit a CH_4 Faradaic efficiency (FE) of as high as 70.6% at -1.2 V vs reversible hydrogen electrode (RHE). The FE of Cu–Bi NPs has increased by approximately 25-fold compared with that of Cu NPs. DFT calculations showed that alloying Cu with Bi significantly decreases the formation energy of $^*\text{COH}$ formation, the rate-determining step, which explains the improved performance. Further analysis showed that Cu that has been partially oxidized due to electron withdrawal by Bi is the most possible active site.

KEYWORDS CO₂ reduction reaction; Cu alloy; methane; DFT; faraday efficiency;

The electrochemical reduction of CO₂ into value-added products provides an attractive strategy for reducing atmospheric CO₂ concentrations.¹⁻⁷ Intensive studies focusing on metal-based electrocatalysts for the CO₂ reduction reaction (CO₂RR) have been conducted to distinguish candidates that are capable of reducing CO₂ into value-added chemicals, such as CO,^{8,9} HCOOH,^{10,11} CH₄,^{12,13} C₂H₄,^{14,15} and C₂H₅OH¹⁶. Cu is the only pure metal catalyst that is known to electrochemically convert CO₂ into appreciable amounts of hydrocarbons, such as CH₄ and C₂H₄. Modifying Cu to achieve high activity and stability with exclusive selectivity for a single class of target hydrocarbons is of great interest.

Considerable progress has been made toward improving catalytic performance in the reduction of CO₂ on Cu-based electrodes.¹⁷ The selectivity for the production of C₂+ species in CO₂RR has been greatly enhanced by tuning the effects of particle size,¹⁸ surface structure,¹⁹ oxidation state,²⁰ grain boundaries,²¹ crystal facets,²² and components²³ on the performance of Cu electrocatalysts, especially the introduction of Cu₂O compositions.^{14,15,18,24,25}

Alloying has been proven to be a powerful method for tailoring the electronic properties of metal catalysts; it is based on synergistic effects that can break the scaling relationship to enhance reaction directionality toward a specific hydrocarbon.²⁶ Various Cu-based binary electrocatalysts, such as Au–Cu,²⁷ Cu–Pd,²⁸ and Cu–In alloy,²⁹ for the CO₂RR have been synthesized. These electrodes exhibit improved catalytic performances compared with pure metals. CO is the major product of most Cu-based alloys in most cases.³⁰ Achieving high selectivity for CH₄ over Cu is desired but remains a massive challenge.

CH₄ is the main component of natural gas and an important energy storage medium with high energy density owing to its high H content (25 wt%). However, the poor selectivity of CH₄ production through CO₂ reduction prevents its further industrial utilization. The reaction pathway toward CH₄ production requires the addition of a proton to the *CO intermediate to generate *CHO or *COH.³¹ However, activated protons also tend to combine with each other to produce H₂, competing with the formation of CH₄. *CO is a quite stable intermediate that requires extensive energy to be protonated. As a result, few catalysts have good selectivity for CH₄ production.

Herein, we develop a novel Cu–Bi bimetallic nanocatalyst that presents high efficiency and selective activity for the electrochemical reduction of CO₂ into CH₄. Charge transfer occurs within Cu and Bi elements such that the Cu in Cu–Bi is promoted to the Cu¹⁺ valence state. The electronic property and CO₂RR performance of the Cu¹⁺ in Cu–Bi are significantly different from those of the Cu¹⁺ in Cu₂O. This feature accounts for the 25-fold enhancement in the ratio of CH₄ to the competing C₂H₄ products shown by the Cu–Bi nanoalloy compared with that exhibited by pure Cu. This ratio is the highest among currently reported Cu-based CO₂RR catalysts.

Cu–Bi bimetallic nanoparticles (NPs) were prepared through a facile one-step method by using copper nitrate and bismuth nitrate as precursors and sodium borohydride as the reductant (see SI for experimental details). Transmission electron microscopy (TEM) images show that the as-synthesized Cu–Bi NPs have a core diameter of approximately 5 nm and interconnected dendritic morphologies (Figures 1 and S1–S5). Cu–Bi NPs with similar morphologies and particles sizes can be prepared with various stoichiometric ratios (Cu, Cu₉Bi₁, Cu₇Bi₁, Cu₃Bi₁, and Bi). Thus, the enhancement in CO₂RR performance cannot be a size effect. The results of energy-dispersive X-ray spectroscopy elemental analysis for Cu₇Bi₁ NPs (Figure 1D) show that the distribution ranges for Cu (red) and Bi (green) almost completely overlap. This close correlation indicates that Cu and Bi atoms mix randomly within the alloy NPs, forming a solid solution structure. This feature is consistent with the Cu–Bi phase diagram obtained at room temperature. The absence of characteristic Bi peaks in the X-ray diffraction (XRD) patterns of the Cu–Bi NPs (Figure S6) further confirms the formation of a solid solution wherein Bi atoms are distributed within the Cu matrix. HRTEM images (Figure S1–S5) and XRD patterns (Figure S6) show that the lattice distance shifts to a high value as the amount of Bi is increased. This shift can be attributed to the enhanced amount of Bi within the Cu matrix. Meanwhile, the XRD peaks of the synthesized samples exhibit broad band width and low intensity, indicating that the samples have very small particle sizes in agreement with TEM observations.

The electronic structure of heterogeneous catalysts plays a key role in their catalytic activity. To understand the electronic structure of Cu-based electrocatalysts, we performed X-ray absorption spectroscopy (XAS). Figure 2A shows the Cu K-edge X-ray absorption near-edge structural (XANES) spectra of Cu, Cu₉Bi₁, Cu₇Bi₁, Cu₃Bi₁, and Bi NPs. Comparison with the Cu reference spectra clearly indicates that the Cu in these samples is different from CuO and is similar to

reduced Cu, such as metallic Cu and Cu₂O, and likely has partial +1 oxidation character.

Through the close comparison of the “white-line” feature of Cu XANES spectra (Figure S7A), the white-line area can be integrated and used to estimate the charge of Cu, as shown in Figure S7B. The peak area of all Cu–Bi NPs is relatively higher than that of the nano-Cu, indicating the presence of a slightly oxidized Cu state in the Cu–Bi NPs. With the increase in the Bi fraction, the peak area increases in the alloys, indicating the transfer of charge from Cu to Bi at the atomic scale.^{8, 32-34}

Figure 1. Morphology characterization of Cu and Cu₇Bi₁ NPs. TEM image of (A) Cu and (B) Cu₇Bi₁ NPs, (C) HRTEM image and (D) EDX mapping of Cu₇Bi₁ NPs.

The k^3 -weighted and Fourier transformed extended X-ray absorption fine structure (EXAFS) spectra of the Cu₇Bi₁ NPs and Cu₂O reference are presented in Figure 2B. The peak of 1.42 Å is assigned to Cu–O interaction. The peak of 2.72 Å is attributed to Cu–Cu interaction.³⁵ The Cu FT-EXAFS feature of Cu₇Bi₁ NPs is different from that of the Cu₂O reference, suggesting that

the alloying of Bi with Cu has affected Cu–O and Cu–Cu interactions. The Cu 2*p* X-ray photoemission spectroscopy (XPS) peaks in Figure 2C show the peaks locating at 931.5 eV and 951.0 eV for Cu NPs are shifted to the higher energy of 932.2 eV and 952.1 eV for Cu₇Bi₁ nanoalloys, respectively. This feature confirms the oxidized state of Cu upon the alloying of Bi with Cu and is in agreement with the Cu XAS results. In Figure 2D, the Bi 4*f* peaks for Cu–Bi alloys shift to a lower energy compared with those for nano-Bi, with the Bi 4*f* of Cu₇Bi₁ NPs at the lowest binding energy. Taking the XAS and XPS results together, we conclude that a strong interaction exists between Cu and Bi within Cu–Bi NPs. In this interaction, electrons are donated from Cu to Bi within the Cu–Bi nanoalloy, leading to a Cu¹⁺ valence feature.

Figure 2. Characterization of the chemical state for the catalysts. (A) Cu K-edge XANES spectra and (B) Cu FT-EXAFS spectra of samples; (C) Cu 2*p* and (D) Bi 4*f* XPS spectra of samples.

The CO₂ reduction activities of Cu–Bi NPs with various Cu/Bi atomic ratios were determined by performing constant potential electrolysis in 0.5 M KHCO₃ electrolyte saturated with CO₂. The

Cu and Cu–Bi NPs reduce CO₂ into multiple products, including CH₄, C₂H₄, CO, and HCOOH (Figure S8). Bi NPs convert CO₂ into HCOOH and CO. All these processes are accompanied by the competing hydrogen evolution reaction (HER).

The Cu alloyed with Bi sharply increases CH₄ selectivity and activity with the following notable observations:

- As-synthesized Cu NPs produce CH₄ with an onset potential of -0.7 V versus the reversible hydrogen electrode (RHE, hereafter all the potentials mentioned are referenced to RHE) and reach a peak Faradaic efficiency (FE) of 20.7% at -1.2 V (Figure 3A).
- Cu₉Bi₁ NPs yield a peak CH₄ FE of 45.1% at -1.2 V.
- For Cu₇Bi₁ NPs, the maximum CH₄ FE reaches 70.6% at -1.2 V.
- The selectivity for CH₄ formation decreases with further increases in the amounts of Bi in the Cu–Bi alloy, such as Cu₃Bi₁, leading to the FE of 14.7% at the potential of -1.2 V.

Among the Cu–Bi NPs, Cu₇Bi₁ NPs have the lowest onset potential at -0.6 V. C₂H₄ yield is also sensitive to the amount of Bi in the alloy (Figure 3B). The increased amount of Bi in the alloy decreases the production of C₂H₄. The alloying of Bi with Cu is also beneficial for reducing H₂ formation. The Cu₇Bi₁ NPs have the best performance for suppressing the HER (Figure 3C).

Figure 3D shows the FE ratios of CH₄/C₂H₄ at various applied potentials for four kinds of Cu–Bi NPs. Compared with pure Cu NPs, all Cu–Bi NPs show very high selectivity for CH₄ formation. Compared with that of pure Cu NPs, the selectivity of Cu₇Bi₁ NPs is enhanced 25-fold in terms of the ratio of CH₄ to competing C₂H₄ at the applied potential of -1.2 V and is far higher than

that of previously reported Cu-based catalysts, such as Cu nanowires,³⁶ Cu cubes,³⁷ Cu NPs,³⁸ Cu-CeO₂³⁹ and Cu(111)⁴⁰ (Figure 3E).

Figure 3. CO₂ electroreduction performance of the synthesized NPs. (A) FE of CH₄, (B) FE of C₂H₄, (C) FE of H₂, (D) FE ratio of CH₄/C₂H₄, (E) Comparison on the CH₄ selectivity of current work with prior reports, (F) CH₄ partial current densities.

The CH₄ partial current densities (j_{CH_4}) of different NPs are shown in Figure 3F. The Cu₇Bi₁ NPs possess the highest j_{CH_4} over the applied cathode potential range of −0.6 V to −1.3 V. Its j_{CH_4} reaches 37.8 mA/cm² at −1.2 V. By contrast, the j_{CH_4} of pure Cu NPs is 9.5 mA/cm² at −1.2 V. Thus, the CH₄ partial current densities of Cu₇Bi₁ NPs has increased by 4-fold relative to that of sole Cu. As shown in Figure S9, the Cu₇Bi₁ NPs also present significantly improved stability compared with Cu NPs. The alloying of Bi with Cu dramatically prolongs the lifetime of Cu-based catalysts.

We carried out density functional theory (DFT) calculations to investigate the reaction mechanism of CO₂ reduction on Cu and Cu₇Bi₁ NPs by calculating the formation energy of key intermediates. Cu(111) was utilized to simulate Cu NPs. Cu₇Bi₁ (111) was constructed by replacing one Cu with Bi in the Cu primitive cell and used to simulate Cu₇Bi₁ NPs (additional details regarding the simulation models are presented in the SI). Our previous work⁴¹ indicates that either *COH formation or *CHO formation is the potential rate-determining step that is dependent on the Cu facet. The formation energy of *COH ($\Delta E_{\text{*COH}}$) is:

$$\Delta E_{\text{*COH}} = E_{\text{*COH}} - (E_{\text{*CO}} + 0.5 \cdot E_{\text{H}_2}) \quad (1)$$

The formation energy of *CHO ($\Delta E_{\text{*CHO}}$) is:

$$\Delta E_{\text{*CHO}} = E_{\text{*CHO}} - (E_{\text{*CO}} + 0.5 \cdot E_{\text{H}_2}) \quad (2)$$

Here, $E_{\text{*COH}}$, $E_{\text{*CHO}}$, and $E_{\text{*CO}}$ are the potential energies of *COH, *CHO, and CO predicted from DFT calculations. In our calculations, we found that the formation energy of *CHO on Cu₇Bi₁ is 0.81 eV, and the formation energy of *COH is 0.77 eV. Therefore, the formation energy of *COH is 0.04 eV lower than that of *CHO, indicating that *COH is highly likely to be

the first reduction product on Cu_7Bi_1 NPs. Meanwhile, we carried out free energy calculations to predict the reaction barriers and found that the free energy barrier of $^*\text{COH}$ formation is 0.89 eV while the free energy barrier of $^*\text{CHO}$ formation is 1.02 eV. Therefore, we concluded that the formation of $^*\text{CHO}$ is kinetically blocked. The optimized atomic structures of $^*\text{COH}$ on Cu_7Bi_1 NPs and Cu NPs are shown in Figures 4A to D.

Figure 4. The optimized atomic structures of $^*\text{COH}$ on Cu from side view (A) and top view (C), on Cu_7Bi_1 from side view (B) and top view (D), (E) formation energy of $^*\text{COH}$ (in eV) of Cu and Cu_7Bi_1 , and $^*\text{CHO}$ on Cu_7Bi_1 . The colors are Cu in orange, C in gray, O in red, and H in white.

We also investigated the formation energies of $^*\text{CHOH}$, $^*\text{CH}$, $^*\text{CH}_2$, and $^*\text{CH}_3$, which are essential reactive intermediates of CH_4 formation. All the formation energies of these products are less than 0.77 eV, indicating that $^*\text{COH}$ formation is the potential determining step (PDS) in CH_4 formation on Cu_7Bi_1 NPs. The complete reaction pathway of CH_4 formation is in SI. We also calculated that the formation energy of $^*\text{COH}$ on Cu is 1.03 eV. This value is consistent

with our previously reported value. Thus, introducing Bi into Cu does not change the reaction mechanism but significantly decreases the formation energy of $^*\text{COH}$, which determines PDS. This effect explains the experimental observations indicating that Cu_7Bi_1 NPs exhibit improved performance in CO_2RR into CH_4 . Lowdin population analysis shows a 0.13 e^- transfer from Cu to Bi that dramatically influences the chemical binding of this intermediate to the catalyst surface. This result is consistent with the results of the above XAS analysis.

C_2 formation potentially competes with C_1 formation. Thus, we also consider the formation energy of $^*\text{OC-COH}$, the widely accepted potential determining step of C_2 formation, in our simulation. Our prediction showed that the formation energy of $^*\text{OC-COH}$ is 0.91 eV , very close to the previous predictions of 0.95 eV . Considering that the formation energy of $^*\text{COH}$ is 0.77 eV , it is likely that CO can be directly reduced to CH_4 instead of waiting for another CO to couple to form a C_2 product. Our prediction is consistent with experimental observations. Meanwhile, the surface net charge and hydrogen bond (HB) network have been demonstrated to have influence on the DFT predications^{42,43}. we have included the solvation effect and HB by including both implicit solvation model and one explicit water, which represents the minimal simulation model with both effects the hydrogen bond network. Our simulation results show that the formation energy for $^*\text{CO}$ to $^*\text{COH}$, which all with on explicit water and implicit solvation model, is 0.605 eV . Thus, with consideration of solvation and HB interaction, the formation of $^*\text{COH}$ is further stabilized by 0.165 eV , making the CH_4 formation through $^*\text{COH}$ is more favorable, which is consistent with the gas phase prediction.

In summary, we successfully synthesized a Cu–Bi bimetallic nanocatalyst with improved activity and selectivity for the electrochemical transformation of CO_2 into CH_4 . Compared with pure Cu NPs, the Cu_7Bi_1 NPs show selectivity at -1.2 V for CH_4 over C_2H_4 that has been enhanced by

25-fold and CH₄ partial current densities that have been enhanced by 4-fold. DFT calculations suggested that introducing Bi significantly decreases the formation energy of the PDS of CO₂ into CH₄. This effect explains the improvement in CH₄ activity and selectivity. Further analysis demonstrated that the highly electropositive Bi withdraws electron from Cu, resulting in partially oxidized Cu, which is the most likely active site for CO₂RR into CH₄. These results provide insight into the rational design of efficient Cu-based alloy catalysts for the conversion of CO₂ into specific products.

ASSOCIATED CONTENT

Supporting Information Supporting Information includes Experimental Procedures and Supporting Figures (PDF)

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (51572062, 81771903, 21972034). This work was 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 No. DE-SC0004993. The computations used the Extreme Science and Engineering Discovery Environment (XSEDE) which is supported by National Science Foundation grant number ACI-1053575. This work is also a project supported

by the Fund for Collaborative Innovation Center of Suzhou Nano Science & Technology, the Priority Academic Program Development of Jiangsu Higher Education Institutions. XAS analysis was performed at the Canadian Light Source, a national research facility of the University of Saskatchewan, which is supported by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council (NSERC), the National Research Council (NRC), the Canadian Institutes of Health Research (CIHR), the Government of Saskatchewan, and the University of Saskatchewan.

REFERENCES

- (1) Goeppert, A.; Czaun, M.; Jones, J. P.; Prakash, G. S.; Olah, G. A. Recycling of carbon dioxide to methanol and derived products—closing the loop. *Chem. Soc. Rev.* **2014**, *43*, 7995-8048.
- (2) Olah, G. A.; Prakash, G. K. S.; Goeppert, A. Anthropogenic Chemical Carbon Cycle for a Sustainable Future. *J. Am. Chem. Soc.* **2011**, *133*, 12881-12898.
- (3) Montoya, J. H.; Seitz, L. C.; Chakthranont, P.; Vojvodic, A.; Jaramillo, T. F.; Nørskov, J. K. Materials for solar fuels and chemicals. *Nat. Mater.* **2017**, *16*, 70-81.
- (4) Rosen, B. A.; Salehi-Khojin, A.; Thorson, M. R.; Zhu, W.; Whipple, D. T.; Kenis, P. J. A.; Masel, R. I. Ionic Liquid-Mediated Selective Conversion of CO₂ to CO at Low Overpotentials. *Science* **2011**, *334*, 643-644.
- (5) Wang, Z.; Wu, L.; Sun, K.; Chen, T.; Jiang, Z.; Cheng, T.; Goddard, W. A. Surface Ligand Promotion of Carbon Dioxide Reduction through Stabilizing Chemisorbed Reactive Intermediates. *J. Phy. Chem. Lett.* **2018**, *9*, 3057-3061.
- (6) Mistry, H.; Varela, A. S.; Kuehl, S.; Strasser, P.; Cuenya, B. R. Nanostructured electrocatalysts with tunable activity and selectivity. *Nat. Rev. Mater.* **2016**, *1*, 1-14.

- (7) Liu, M.; Pang, Y.; Zhang, B.; De Luna, P.; Voznyy, O.; Xu, J.; Zheng, X.; Dinh, C. T.; Fan, F.; Cao, C.; de Arquer, F. P. G.; Safaei, T. S.; Mepham, A.; Klinkova, A.; Kumacheva, E.; Filleter, T.; Sinton, D.; Kelley, S. O.; Sargent, E. H. Enhanced electrocatalytic CO₂ reduction via field-induced reagent concentration. *Nature* **2016**, *537*, 382-386.
- (8) Sun, K.; Wu, L.; Qin, W.; Zhou, J.; Hu, Y.; Jiang, Z.; Shen, B.; Wang, Z. Enhanced electrochemical reduction of CO₂ to CO on Ag electrocatalysts with increased unoccupied density of states. *J. Mater. Chem. A* **2016**, *4*, 12616-12623.
- (9) Wang, Z.; Sun, K.; Liang, C.; Wu, L.; Niu, Z.; Gao, J. Synergistic Chemisorbing and Electronic Effects for Efficient CO₂ Reduction Using Cysteamine-Functionalized Gold Nanoparticles. *ACS Appl. Energy Mater.* **2019**, *2*, 192–195.
- (10) Gao, S.; Lin, Y.; Jiao, X.; Sun, Y.; Luo, Q.; Zhang, W.; Li, D.; Yang, J.; Xie, Y. Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. *Nature* **2016**, *529*, 68-71.
- (11) 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.* **2012**, *134*, 1986-1989.
- (12) Manthiram, K.; Beberwyck, B. J.; Aivisatos, A. P. Enhanced Electrochemical Methanation of Carbon Dioxide with a Dispersible Nanoscale Copper Catalyst. *J. Am. Chem. Soc.* **2014**, *136*, 13319-13325.
- (13) Kuhl, K. P.; Hatsukade, T.; Cave, E. R.; Abram, D. N.; Kibsgaard, J.; Jaramillo, T. F. Electrocatalytic Conversion of Carbon Dioxide to Methane and Methanol on Transition Metal Surfaces. *J. Am. Chem. Soc.* **2014**, *136*, 14107-14113.
- (14) Mistry, H.; Varela, A. S.; Bonifacio, C. S.; Zegkinoglou, I.; Sinev, I.; Choi, Y. W.; Kisslinger, K.; Stach, E. A.; Yang, J. C.; Strasser, P.; Roldan Cuenya, B. Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene. *Nat. Commun.* **2016**, *7*, 12123.

- (15) Liang, Z. Q.; Zhuang, T. T.; Seifitokaldani, A.; Li, J.; Huang, C. W.; Tan, C. S.; Li, Y.; De Luna, P.; Dinh, C. T.; Hu, Y.; Xiao, Q.; Hsieh, P. L.; Wang, Y.; Li, F.; Quintero-Bermudez, R.; Zhou, Y.; Chen, P.; Pang, Y.; Lo, S. C.; Chen, L. J.; Tan, H.; Xu, Z.; Zhao, S.; Sinton, D.; Sargent, E. H. Copper-on-nitride enhances the stable electrosynthesis of multi-carbon products from CO₂. *Nat. Commun.* **2018**, *9*, 3828.
- (16) Morales-Guio, C. G.; Cave, E. R.; Nitopi, S. A.; Feaster, J. T.; Wang, L.; Kuhl, K. P.; Jackson, A.; Johnson, N. C.; Abram, D. N.; Hatsukade, T. Improved CO₂ reduction activity towards C₂⁺ alcohols on a tandem gold on copper electrocatalyst. *Nat. Catal.* **2018**, *1*, 764.
- (17) Aran-Ais, R. M.; Gao, D.; Cuenya, B. R. Structure- and Electrolyte-Sensitivity in CO₂ Electroreduction. *Accounts Chem. Res.* **2018**, *51*, 2906-2917.
- (18) De Luna, P.; Quintero-Bermudez, R.; Dinh, C. T.; Ross, M. B.; Bushuyev, O. S.; Todorović, P.; Regier, T.; Kelley, S. O.; Yang, P.; Sargent, E. H. Catalyst electro-redeposition controls morphology and oxidation state for selective carbon dioxide reduction. *Nat. Catal.* **2018**, *1*, 103.
- (19) Li, C. W.; Kanan, M. W. CO₂ reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu₂O films. *J. Am. Chem. Soc.* **2012**, *134*, 7231-7234.
- (20) Ren, D.; Deng, Y.; Handoko, A. D.; Chen, C. S.; Malkhandi, S.; Yeo, B. S. Selective electrochemical reduction of carbon dioxide to ethylene and ethanol on copper (I) oxide catalysts. *ACS Catal.* **2015**, *5*, 2814-2821.
- (21) Li, C. W.; Ciston, J.; Kanan, M. W. Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper. *Nature* **2014**, *508*, 504.
- (22) Cheng, T.; Xiao, H.; Goddard, W. A. Reaction mechanisms for the electrochemical reduction of CO₂ to CO and formate on the Cu (100) surface at 298 K from quantum mechanics free energy calculations with explicit water. *J. Am. Chem. Soc.* **2016**, *138*, 13802-13805.

- (23) Verdaguer-Casadevall, A.; Li, C. W.; Johansson, T. P.; Scott, S. B.; McKeown, J. T.; Kumar, M.; Stephens, I. E.; Kanan, M. W.; Chorkendorff, I. Probing the active surface sites for CO reduction on oxide-derived copper electrocatalysts. *J. Am. Chem. Soc.* **2015**, *137*, 9808-9811.
- (24) Favaro, M.; Xiao, H.; Cheng, T.; Goddard, W. A.; Yano, J.; Crumlin, E. J. Subsurface oxide plays a critical role in CO₂ activation by Cu(111) surfaces to form chemisorbed CO₂, the first step in reduction of CO₂. *P. Natl. Acad. Sci.* **2017**, *114*, 6706-6711.
- (25) Jung, H.; Lee, S. Y.; Lee, C. W.; Cho, M. K.; Won, D. H.; Kim, C.; Oh, H.-S.; Min, B. K.; Hwang, Y. J. Electrochemical Fragmentation of Cu₂O Nanoparticles Enhancing Selective C–C Coupling from CO₂ Reduction Reaction. *J. Am. Chem. Soc.* **2019**, *141*, 4624-4633.
- (26) Peterson, A. A.; Norskov, J. K. Activity Descriptors for CO₂ Electroreduction to Methane on Transition-Metal Catalysts. *J. Phys. Chem. Lett.* **2012**, *3*, 251-258.
- (27) Kim, D.; Resasco, J.; Yu, Y.; Asiri, A. M.; Yang, P. Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold–copper bimetallic nanoparticles. *Nat. Commun.* **2014**, *5*, 4948.
- (28) Ma, S.; Sadakiyo, M.; Heima, M.; Luo, R.; Haasch, R. T.; Gold, J. I.; Yamauchi, M.; Kenis, P. J. Electroreduction of carbon dioxide to hydrocarbons using bimetallic Cu–Pd catalysts with different mixing patterns. *J. Am. Chem. Soc.* **2016**, *139*, 47-50.
- (29) Rasul, S.; Anjum, D. H.; Jedidi, A.; Minenkov, Y.; Cavallo, L.; Takanabe, K. A highly selective copper–indium bimetallic electrocatalyst for the electrochemical reduction of aqueous CO₂ to CO. *Angew. Chem. Int. Ed.* **2015**, *54*, 2146-2150.
- (30) Lee, C. W.; Yang, K. D.; Nam, D. H.; Jang, J. H.; Cho, N. H.; Im, S. W.; Nam, K. T. Defining a Materials Database for the Design of Copper Binary Alloy Catalysts for Electrochemical CO₂ Conversion. *Adv. Mater.* **2018**, *30*, 1704717.

- (31) Qiu, Y.; Zhong, H.; Xu, W.; Zhang, T.; Li, X.; Zhang, H. Tuning the electrocatalytic properties of a Cu electrode with organic additives containing amine group for CO₂ reduction. *J. Mater. Chem. A* **2019**, *7*, 5453-5462.
- (32) Sun, K.; Cheng, T.; Wu, L.; Hu, Y.; Zhou, J.; Maclellan, A.; Jiang, Z.; Gao, Y.; Goddard, W. A.; Wang, Z. Ultrahigh Mass Activity for Carbon Dioxide Reduction Enabled by Gold–Iron Core–Shell Nanoparticles. *J. Am. Chem. Soc.* **2017**, *139*, 15608-15611.
- (33) Bzowski, A.; Sham, T.; Yiu, Y. Ag L-edge x-ray-absorption near-edge-structure study of charge redistribution at the Ag site in Au-Ag alloys. *Phys. Rev. B* **1994**, *49*, 13776-13779.
- (34) Zhang, P.; Zhou, X.; Tang, Y.; Sham, T. K. Organosulfur-Functionalized Au, Pd, and Au–Pd Nanoparticles on 1D Silicon Nanowire Substrates: Preparation and XAFS Studies. *Langmuir* **2005**, *21*, 8502-8508.
- (35) Iwasawa, Y.; Asakura, K.; Tada, M. XAFS Techniques for Catalysts, Nanomaterials, and Surfaces. *Springer*: **2017**, 39-50.
- (36) Li, Y.; Cui, F.; Ross, M. B.; Kim, D.; Sun, Y.; Yang, P. Structure-Sensitive CO₂ Electroreduction to Hydrocarbons on Ultrathin 5-fold Twinned Copper Nanowires. *Nano Lett.* **2017**, *17*, 1312-1317.
- (37) Grosse, P.; Gao, D. F.; Scholten, F.; Sinev, I.; Mistry, H.; Roldan Cuenya, B. Dynamic Changes in the Structure, Chemical State and Catalytic Selectivity of Cu Nanocubes during CO₂ Electroreduction: Size and Support Effects. *Angew. Chem. Int. Ed.* **2018**, *57*, 6192-6197.
- (38) Lum, Y.; Kwon, Y.; Lobaccaro, P.; Chen, L.; Clark, E. L.; Bell, A. T.; Ager, J. W. Trace Levels of Copper in Carbon Materials Show Significant Electrochemical CO₂ Reduction Activity. *ACS Catal.* **2016**, *6*, 202-209.
- (39) Wang, Y.; Chen, Z.; Han, P.; Du, Y.; Gu, Z.; Xu, X.; Zheng, G. Single-Atomic Cu with Multiple Oxygen Vacancies on Ceria for Electrocatalytic CO₂ Reduction to CH₄. *ACS Catal.* **2018**, *8*, 7113-7119.

- (40) Huang, Y.; Handoko, A. D.; Hirunsit, P.; Yeo, B. S. Electrochemical Reduction of CO₂ Using Copper Single-Crystal Surfaces: Effects of CO* Coverage on the Selective Formation of Ethylene. *ACS Catal.* **2017**, *7*, 1749-1756.
- (41) Cheng, T.; Xiao, H.; Goddard, W. A. Free-Energy Barriers and Reaction Mechanisms for the Electrochemical Reduction of CO on the Cu(100) Surface, Including Multiple Layers of Explicit Solvent at pH 0. *J Phys. Chem. Lett.* **2015**, *6*, 4767-4773.
- (42) Kim, D.; Shi, J.; Liu, Y. Substantial Impact of Charge on Electrochemical Reactions of Two-Dimensional Materials. *J. Am. Chem. Soc.* **2018**, *29*, 9127-9131.
- (43) Zhao, X.; Liu, Y. Unveiling the Active Structure of Single Nickel Atom Catalysis: Critical Roles of Charge Capacity and Hydrogen Bonding. *J. Am. Chem. Soc.* **2020**, *12*, 5773-5777.