

Structure- and Electrolyte-Sensitivity in CO₂ Electroreduction

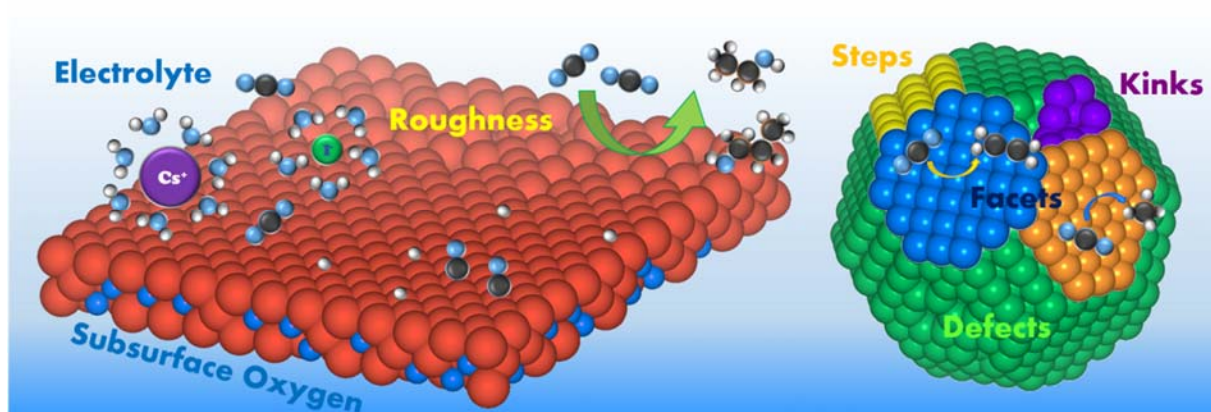
Rosa M. Arán-Ais^{†1,2}, Dunfeng Gao^{†1,2}, Beatriz Roldan Cuenya^{*2}

¹ Department of Physics, Ruhr-University Bochum, 44780 Bochum, Germany

² Department of Interface Science, Fritz-Haber-Institute of the Max Planck Society, 14195 Berlin, Germany

This document is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in Accounts of Chemical Research, copyright © American Chemical Society after peer review. To access the final edited and published work see <https://pubs.acs.org/doi/10.1021/acs.accounts.8b00360>.

CONSPECTUS



The utilization of fossil fuels (i.e., coal, petroleum, and natural gas) as the main energy source gives rise to serious environmental issues, including global warming caused by the continuously increasing level of atmospheric CO₂. To deal with this challenge, fossil fuels are being partially replaced by renewable energy such as solar and wind. However, such energy sources are usually intermittent and currently constitute a very low portion of the overall energy consumption. Recently, the electrochemical conversion of CO₂ to chemicals and fuels with improved energy density driven by electricity derived from renewable energy has been recognized as a promising strategy towards sustainable energy.

The activation and reduction of CO₂, which is a thermodynamically stable and kinetically inert molecule, is extremely challenging. Although the participation of protons in the CO₂ electroreduction reaction (CO₂RR) helps lower the energy barrier, high overpotentials are still needed to efficiently drive the process. On the other hand, the concurrent hydrogen evolution reaction (HER) under CO₂RR conditions leads to lower selectivity toward CO₂RR products. Electrocatalysts that are highly active and selective for multicarbon products are urgently needed to improve the energy efficiency of CO₂RR. The reduction of CO₂ involves multiple proton-electron transfers and has many complex intermediates. Recent reports have shown that the relative stability of the intermediates on the surface of catalysts determines final reaction pathways as well as the product selectivity. Furthermore, this reaction displays a strong structure-sensitivity. The atomic arrangement, electronic structure, chemical composition, and oxidation state of the catalysts significantly influence catalyst performance. Fundamental understanding of the dependence of the reaction mechanisms on the catalyst structure would guide the rational design of new nanostructured CO₂RR catalysts. As a reaction proceeding in a complex environment containing gas/liquid/solid interfaces, CO₂RR is also intensively affected by the *electrolyte*. The electrolyte composition in the near surface region of the electrode where the reaction takes place plays a vital role in the reactivity. However, the former might also be indirectly determined by the bulk electrolyte composition via diffusion. Adding to the complexity, the structure, chemical state and surface composition of the catalysts under reaction conditions usually undergo dynamic changes, especially when adsorbed ions are considered. Therefore, in addition to tuning the structure of the electrocatalysts, being able to also modify the electrolyte provides an alternative method to tune the activity and selectivity of CO₂RR. *In situ* and *operando* characterization methods must be employed in order to gain in depth understanding on the structure- and electrolyte-sensitivity of real CO₂RR catalysts under working conditions.

This Account provides examples of recent advances in the development of nanostructured catalysts and mechanistic understanding of CO₂RR. It discusses how the structure of a catalyst (crystal orientation, oxidation state, atomic arrangement, defects, size, surface composition, segregation, etc.) influences the activity and selectivity, and how the electrolyte also plays a determining role in the reaction activity and selectivity. Finally, the importance of *in situ* and *operando* characterization methods to understand the structure- and electrolyte-sensitivity of the CO₂RR is discussed.

1. Introduction

The electrochemical conversion of CO₂ provides a potential solution to address some of the future energy needs by converting greenhouse gases into valuable fuels or feedstocks. The use of renewable energy sources to supply the electrons needed to electroreduce CO₂ makes this process attractive, so that the intermittent electricity coming from solar, wind, or hydro-power technologies could be complemented by the energy stored in the chemical bonds of high-energy-density products coming from captured CO₂. However, this molecule is extremely stable, being the CO₂ electroreduction reaction (CO₂RR) an uphill process that requires high overpotentials and presents numerous other challenges. The multiple electron transfer steps required to reduce CO₂ into fuels, accompanied by the competing hydrogen evolution reaction (HER), leads to poor selectivity towards multicarbon compounds (e.g. ethylene and ethanol). The later species and other so-called C₂₊ products are highly sought due to their higher value, greater energy density, and broader applicability than C₁ products. Therefore, the development of highly active and selective catalysts, as well as an optimum technology that improves the effective CO₂ conversion, are key challenges for practical application of the CO₂RR.

Among all metals, Cu is the only metal capable of efficiently reducing CO₂ to hydrocarbons and alcohols, while hydrogen, CO, and formate are the major products produced by other metals.¹ The CO₂RR is a *structure-sensitive process*, meaning that the atomic arrangement at the catalyst surface affects the adsorption and/or bond cleavage of the reactants, thus determining the catalytic performance. Recent reports have opened new perspectives in exploring both compositional and morphological effects towards the rational design of more selective catalysts. Moreover, optimizing the reaction environment has also been demonstrated to be critical to address some of the challenges of this reaction, such as the low solubility of CO₂, changes in pH, and stabilization of certain active species.

In this Account, we provide an overview of the current understanding of the CO₂RR, focusing on the strategies followed so far for the development of more efficient and selective electrocatalysts. Recurrent topics throughout our report are the need of having access to morphologically and chemically well-defined material systems in order to establish structure/chemical state/composition-reactivity correlations, and to be able to study them *in situ* and under *operando* reaction conditions in order to gain mechanistic insight into CO₂RR.

2. From Molecular Catalysts to Single-Site Heterogeneous Catalysts

Due to the intrinsically high metal atom efficiency, molecular catalysts usually show high turnover frequency (TOF) for many chemical reactions, including CO₂RR.^{2,3} Cobalt porphyrins incorporated in covalent organic frameworks exhibited 90 % Faradaic efficiency (FE) and TOF of 9400 h⁻¹ with an overpotential of -0.55 V for CO₂RR to CO.² Single site heterogeneous catalysts, with isolated metal atoms embedded in a nitrogen-doped carbon matrix, have been explored for CO₂RR.⁴⁻⁶ Ju et al.⁴ studied the CO₂RR performance of a family of single site, metal- and nitrogen-doped nanoporous carbons (Figure 1) containing active M-N_x sites (M = Mn, Fe, Co, Ni, Cu). Fe-N_x and Ni-N_x single-site catalysts showed a unique reactivity and FE for reducing CO₂ to CO, comparable to the mass-based activity of state-of-the-art Au catalysts. Wang et al.⁵ further reported that single-site Co catalysts exhibit a remarkable activity and selectivity towards CO₂RR if the Co-N coordination number decreases from 4 to 2, due to the facilitated activation of CO₂ to the CO₂⁻ intermediate over low-coordinated sites.

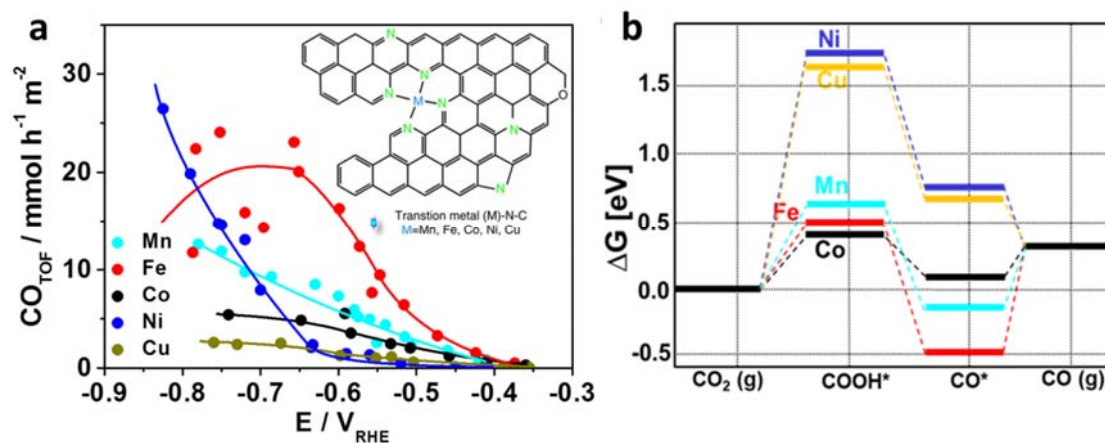


Figure 1. (a) CO production rate of M-N-C catalysts vs. potential. Inset: schematic structure of the M-N-C catalysts. (b) Free energy diagrams of HER and CO₂RR at -0.8 V_{RHE} for M-N-C catalyst. Reproduced with permission from ref. 4. Copyright 2017 Nature Publishing Group.

3. Metal Cluster and Nanoparticle (NP) Size Effects

Metal clusters and NPs have been explored for CO₂RR due to their high surface-to-volume-ratio and large content of low-coordinated surface sites. For example, Au₂₅ clusters experience a charge redistribution induced by a reversible Au₂₅-CO₂ interaction⁷ that results in a 200-300 mV lower overpotential and a CO production rate 200-700 times higher as compared to 5 nm Au NPs and bulk Au. On the other hand, metal NPs usually show a size effect for CO₂RR.⁸⁻¹³ Enhanced catalytic activity, unfortunately accompanied by a drastic increase in the selectivity for H₂ and CO in detriment of hydrocarbon production, was observed with decreasing Cu NP size (2-15 nm), Figure 2a.⁸ Although size-dependent changes in the electronic structure of clusters are important (a few tens of atoms to about 100 atoms), for larger NPs as those in the previous example, size-dependent changes in surface atomic coordination are held responsible for the distinct catalytic reactivity. Thus, the increased population of low-coordinated surface sites on the smaller Cu NPs (Figure 2b) was linked to the increased activity and surging H₂ and CO production rates. Au NPs showed a similar size effect, but with a more drastic increase in activity with decreasing size,⁹ along with a decrease in CO selectivity which was explained by the weaker binding of the COOH reaction intermediate in the presence of large H coverages on the small Au NPs (Figure 2c).¹⁰ Interestingly, a simultaneous increase in current density and CO FE was observed for Pd NPs with decreasing size (Figure 2d).¹¹ The different behavior between Au and Pd NPs was attributed to the similar activity of the competitive HER on the terrace, edge and corner sites of the Pd NPs, instead of the more favored HER on the undercoordinated sites of the Au NPs.¹⁰

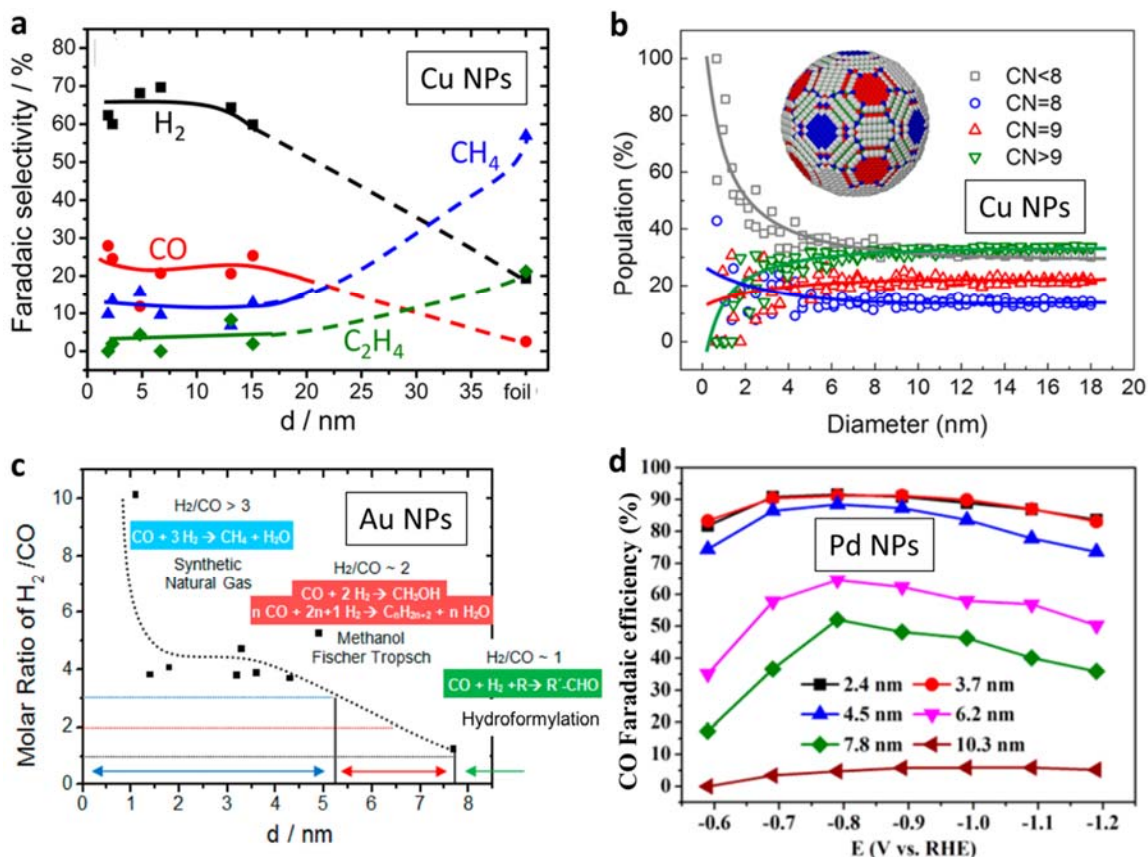


Figure 2. (a) Faradic selectivity and (b) population of specifically coordinated surface atoms as a function of Cu NP size. (c) Molar ratio of H₂ and CO produced at -1.2 V_{RHE} as a function of NP size. (d) CO FE of Pd NPs with different sizes. Reproduced with permission from refs. 8, 10. Copyright 2014 American Chemical Society. Reproduced with permission from ref. 11. Copyright 2015 American Chemical Society.

4. Interparticle Distance/Loading Effect

Apart from the nanoscale structure and composition, mesoscale phenomena such as interparticle reactant diffusion and re-adsorption of intermediates also play a key role in reactivity.¹⁴ Cu NPs with narrow NP size distributions and uniform arrangements were used as model material system. For the same average NP size, a trend of increasing current density with decreasing interparticle (IP) distance was found. Furthermore, on samples with small IP spacing the diffusive transfer between neighboring NPs as well as the re-adsorption and subsequent reduction of the CO

intermediate to hydrocarbons was favored, Figure 3. However, the important role of changes in the local pH resulting from the distinct depletion of reactants and intermediates on samples with different spacings cannot be overlooked. Subsequently, Wang et al.¹⁵ explored indirectly the IP distance effect on the selectivity of CO₂RR on CuO_x NPs by changing the areal particle density. They found that high areal particle density (small IP distance) improved ethylene production and attributed this to dynamically favored CO re-adsorption and reactive *CO dimerization at elevated local interfacial pH. The IP distance effect was also observed for the oxygen reduction reaction over Pt nanoclusters.¹⁶ A distinct potential distribution in the electric double layer (EDL) between the nanoclusters was suggested to lower the adsorption strength of oxygenated species and hence improve the activity at small IP distances.¹⁶ However, this effect cannot explain IP-distance dependent CO₂RR data since the smallest distances studied (≈ 20 nm) are significantly larger than the ones deemed relevant for the EDL overlap in Ref¹⁶ (≤ 3 nm). The role of the Cu loading in the dynamic evolution from densely packed Cu NPs to cube-like particles was also observed by Kim et al.¹⁷ and Manthiram et al.¹⁸ during CO₂RR.

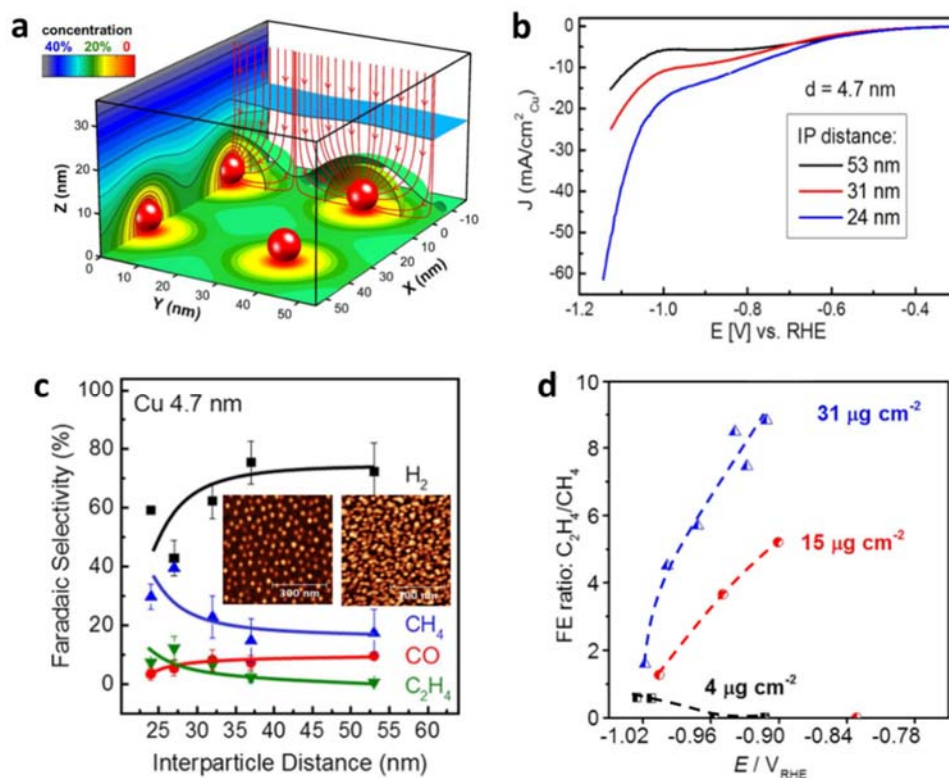


Figure 3. (a) Simulation results of the CO₂ concentration distribution based on diffusion equations. (b) Potential-dependent current density on 4.7 nm Cu NPs with different spacings. (c) Faradaic selectivity of 4.7 nm Cu NPs as a function of the interparticle distance. Reproduced with permission from ref. 14. Copyright 2016 American Chemical Society. (d) Potential-dependent ethylene/methane FE ratio over CuO_x NPs. Reproduced with permission from ref. 15. Copyright 2017 Wiley.

5. Bimetallic Catalysts

Bimetallic catalysts, with various compositions and atomic arrangements, might be used to tune the binding strength of intermediates, to enhance the reaction kinetics and change the reaction pathways for CO₂RR. The relatively low selectivity towards hydrocarbons and oxygenates on Cu NPs may be improved by designing bimetallic CuPd catalysts (Figure 4a).¹⁹ Phase-separated CuPd catalyst were found to achieve high selectivity (>60 %) for C₂, while ordered CuPd catalyst with an alternating Cu-Pd arrangement exhibited the highest selectivity for C₁ (>80 %). Geometric/structural effects, as well as electronic effects induced after mixing Cu with Pd, appear to play an important role in determining the subsequent reaction pathway of the *CO intermediate. Similar geometric effects were also observed for AuCu NPs. In contrast to AuCu alloy NPs which were more active for HER, ordered AuCu NPs selectively converted CO₂ to CO with a FE of 80 % (Figure 4b).²⁰ However, the negative potentials being used for the CO₂RR process are expected to induce significant segregation in bimetallic NPs, such as the formation of an Au-rich surface.²¹ Along these lines, core-shell AuFe@Au NPs with surface defects stabilized by subsurface Fe were found to exclusively produce CO with a 100-fold increase in mass activity compared to Au NPs, Figure 4c.²² AgSn@SnO_x core-shell NPs showed a volcano-like relationship between formate production and Sn concentration, attributed to the compromise of favorable stabilization of OCHO* by lattice expansion and the electron conductivity loss due to the increased thickness of the SnO_x shell (Figure 4d).²³ A greater alcohol to ethylene ratio was achieved by including sulfur atoms in Cu NPs. According to DFT calculations, the resulting Cu vacancies in the NP shell were responsible for the higher alcohol production.²⁴

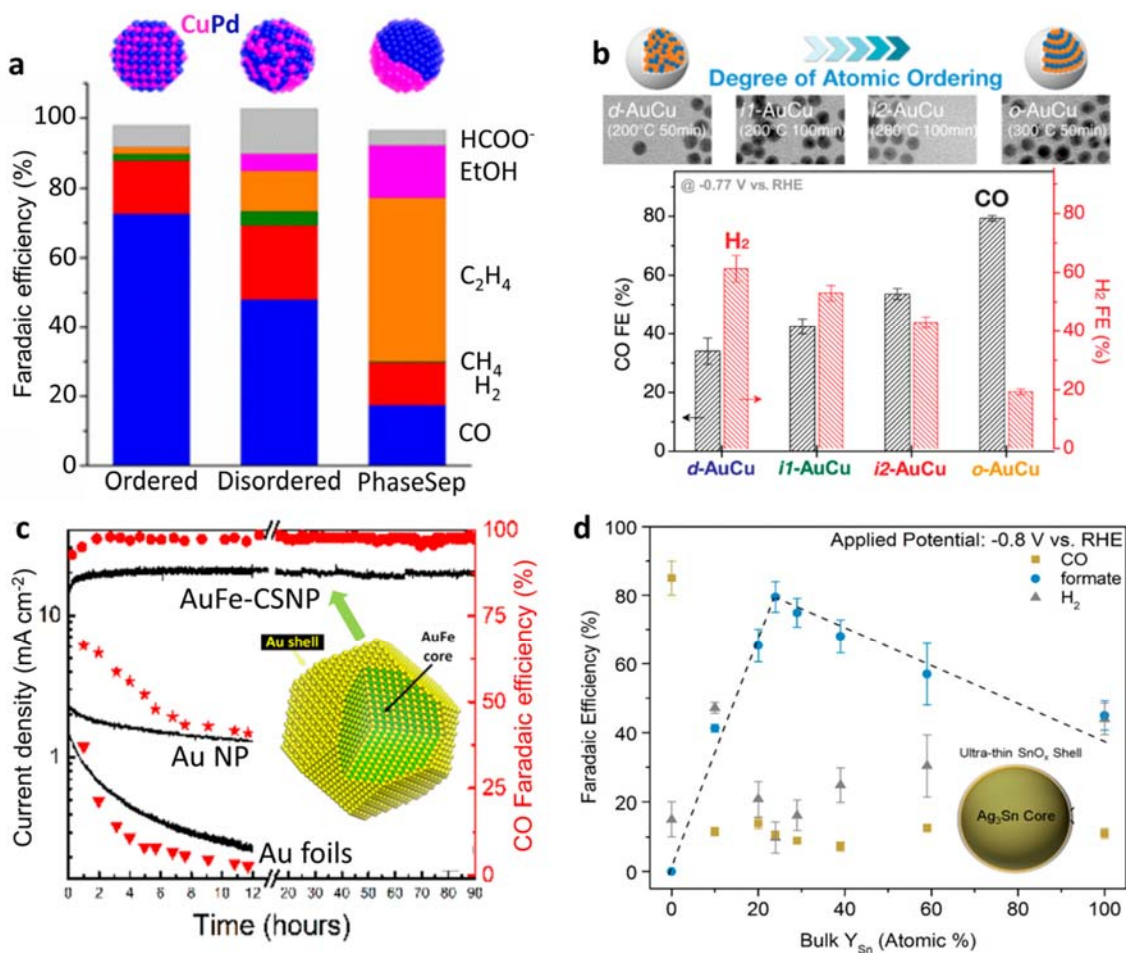


Figure 4. (a) Product distribution of CuPd NPs with different atomic arrangements. (b) CO and H₂ selectivities of AuCu NPs with different atomic ordering. (c) Stability of AuFe@Au core-shell NPs. (d) Correlations between FE of products and composition of AgSn core-shell NPs. Reproduced with permission from refs. 19, 20, 22, 23. Copyright 2017 American Chemical Society.

In addition to NPs, bimetallic films were also used for CO₂RR. By varying the amount of Zn in Cu_xZn film catalysts, the selectivity for ethanol versus ethylene production could be tuned, Figure 5a. It was discussed that CO spillover from Zn to adjacent Cu sites increased the population of free CO, which participates in the formation of ethanol by inserting itself into the bond between the Cu surface and *CH₂.²⁵ Ni_xGa_y (Figure 5b) constitutes an example of hydrocarbon production on non-Cu materials.²⁶ The introduction of Ga into the Ni films weakened the Ni-CO interaction,

resulting in a comparable CO binding strength as CO-Cu. The formation of more reduced products beyond CO was recently described to depend on an optimum binding of both, CO and H.²⁷ This strategy was applied to Pd-modified-Au foils,²⁸ which also produce hydrocarbons (< 5 % FE).

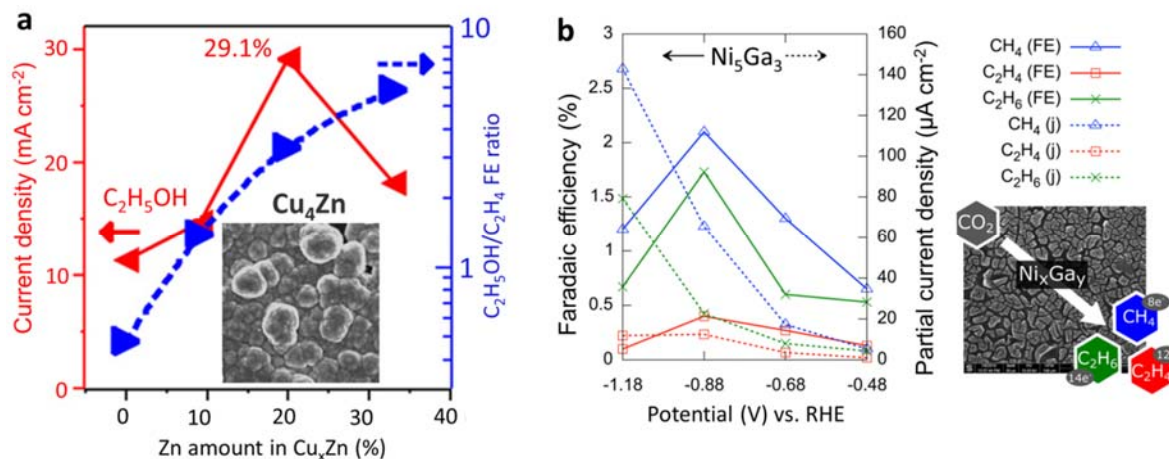


Figure 5. (a) Ethanol FE and ethanol/ethylene ratio as a function of the Zn content in Cu_xZn films. The insert is a SEM image of a Cu₄Zn film. (b) Potential dependent hydrocarbon FEs for Ni₅Ga₃ films. Reproduced with permission from refs. 25, 26. Copyright 2016 American Chemical Society.

6. Facet Effect: from Single Crystal Electrodes to Shaped NPs.

Over the past decades, single crystal studies have provided in depth insight on the influence of the surface structure and order in electrocatalytic processes of technical interest.¹ As aforementioned, Cu is unique at converting CO₂ into hydrocarbons and alcohols, mainly due to its moderate CO binding and the stabilization of certain intermediates.²⁹ Moreover, the product selectivity is highly dependent on the crystalline orientation: Cu(111) yields mainly methane, while Cu(100) favors ethylene, and Cu(110) promotes the production of ethanol, acetate and acetaldehyde.^{1,30} Theoretical studies have shed light into the reaction mechanisms and intermediates responsible for the different selectivity on (111) and (100) surfaces³¹, showing that the atomic configuration of the Cu(100) surface is the most favorable towards the pathway that yields ethylene. This mechanism was argued to take place via CO dimerization, Figure 6a. In this sense, high surface coverage of adsorbed CO* was found essential for the selective formation of

ethylene (Figure 6b).³² Moreover, Cu(751) surfaces show higher selectivity for C₂₊ products at lower overpotentials than lower indexed surfaces, Figure 6c.³³ However, the role played by the distinct facets in CO₂RR is not fully understood, and further studies using model surfaces are still needed to understand the combined effect of surface structure and other parameters such as oxygen content.

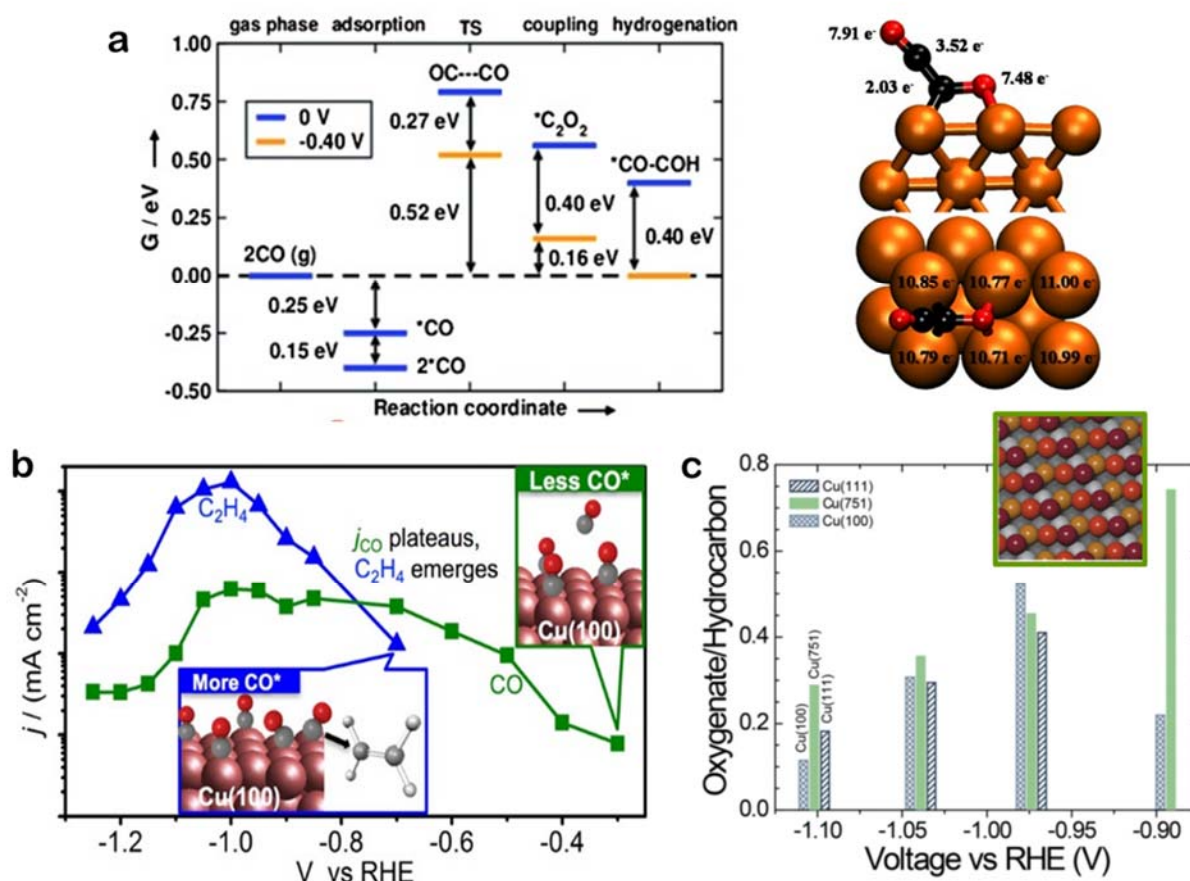


Figure 6. (a) Deconvolution of the first electron–proton transfer on Cu(100). Reproduced with permission from ref. 31. Copyright 2013 Wiley. (b) Relationship between ethylene formation and CO evolution on Cu(100). Reproduced with permission from ref. 32. Copyright 2017 American Chemical Society. (c) Oxygenate/hydrocarbon ratios as a function of potential for Cu(111), Cu(751), and Cu(100). Reproduced with permission from ref. 33. Copyright 2017 Proceedings of the National Academy of Science.

Nanoparticles synthesized with a particular morphology generally have a well-defined surface structure. Therefore, tailoring the shape of the NPs can lead to materials with superior activity and selectivity. Facet effects on metals like Pd³⁴, Ag³⁵ and Au³⁶ have been explored for CO₂RR, showing the importance of the structure for CO and formate production. For instance, Ag(100) facets lead to an ultralow overpotential for CO₂ reduction to CO on triangular Ag nanoplates (Figure 7a), while enhanced activity and selectivity for either formate or CO was found for Pd and Au NPs, respectively (Figures 7b-c). Regarding Cu, cubic-shaped NPs composed of (100) facets were found to display increased ethylene selectivity while suppressing methane production.^{37,38} The presence of small well-ordered (100) domains, combined with numerous steps and edges could be responsible for this selectivity trend as proposed for stepped surfaces.¹ However, other facts might also determine the selectivity towards the formation of C₂₊ products. Gao et al.³⁸ recently demonstrated the combined effect of morphology, defect density and oxygen content on the activity and selectivity of Cu nanocubes modified by plasma treatments. The presence and stabilization of subsurface oxygen and Cu⁺ species under reaction conditions were key parameters to favor C₂₊ product selectivity (Figure 7d).

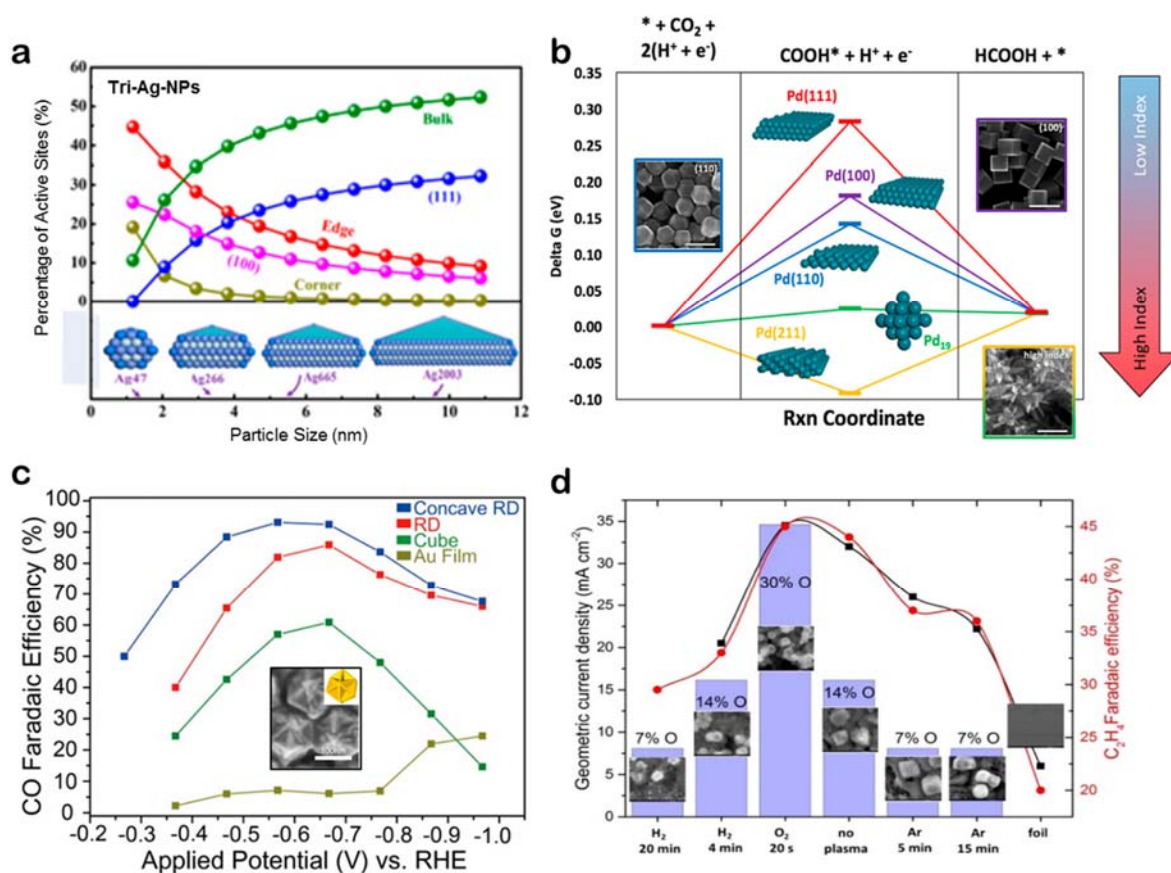


Figure 7. (a) Active adsorption site density on Tri-Ag-NPs. Reproduced with permission from ref. 35. Copyright 2017 American Chemical Society. (b) Free energy diagrams for CO₂RR to formic acid on Pd. Reproduced with permission from ref. 34. Copyright 2016 American Chemical Society. (c) CO FE of an Au film and shaped Au NPs at $-1.0 V_{RHE}$. Reproduced with permission from ref. 36. Copyright 2015 American Chemical Society. (d) Current density and ethylene FE at $-1.0 V_{RHE}$ for different plasma-treated Cu nanocubes and an electropolished Cu foil. Reproduced with permission from ref. 38. Copyright 2017 American Chemical Society.

7. Stability and Support Effect.

Dynamic changes in the morphology of shaped electrocatalysts in the course of the CO₂RR cannot be neglected, since they might have ascribed concomitant changes in the resulting activity and selectivity. For example, surface roughening, defect and pore formation, and the disappearance of well-defined (100) facets on Cu nanocubes deposited on carbon, together with a reduction of

CuO_x species were found to be responsible of a significantly lower selectivity towards ethylene and ethanol in favor of methane.³⁹ The effect of the support was also explored, showing an enhanced morphological durability and greater stability of Cu⁺ species under CO₂RR when a Cu foil was used as support instead of carbon. Furthermore, the Cu cubes on Cu-foil³⁸ displayed a lower overpotential and higher FE for C₂+ products than those on C (Figure 8a).³⁹ Carbon supports with different morphologies have also been explored for Cu NPs in order to increase the CO surface concentration and thus facilitate its dimerization and ethylene production (Figure 8b).⁴⁰ Strong interactions at metal/metal-oxide interfaces were found to be responsible for higher reactivity and stability. For instance, Au NPs supported on CeO_x showed higher CO FE than those supported on C, which was ascribed to an enhanced CO₂ activation at the Au-CeO_x interface (Figure 8c).⁴¹

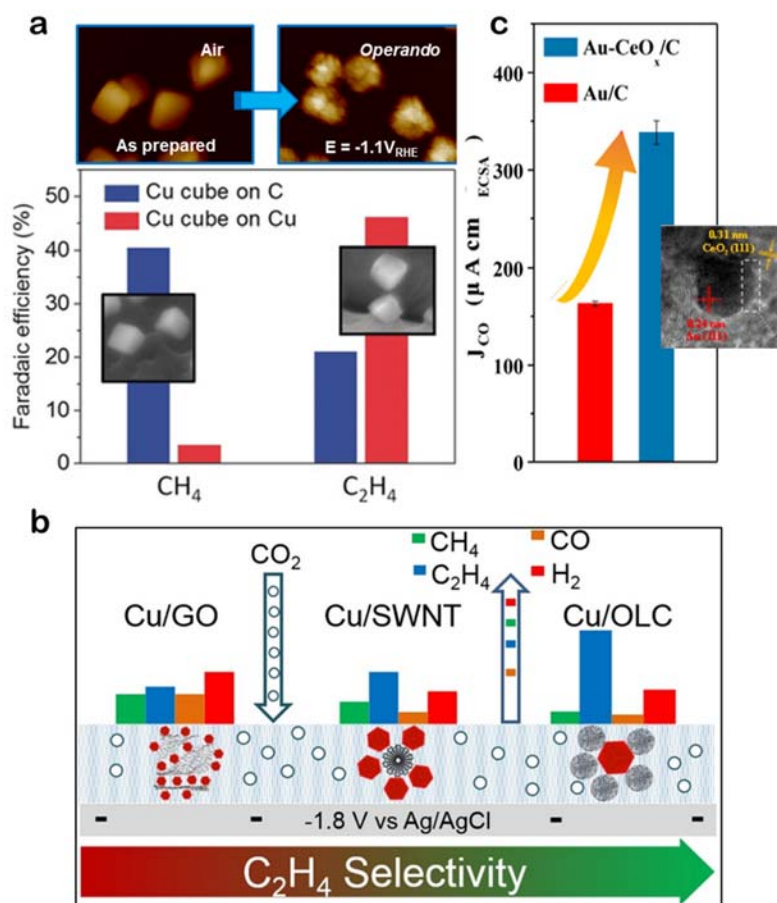


Figure 8. (a) EC-AFM images of Cu-cubes on HOPG before and during CO₂RR at -1.1V_{RHE}, and effect of the support (C vs. Cu) in methane and ethylene FEs. Reproduced with permission from

ref. 39. Copyright 2018 Wiley. **(b)** Structure effect of the C support on CO₂RR over Cu NPs: single wall carbon nanotubes (SWNT), reduced graphene oxide (RGO) and onion-like carbon (OLC). Reproduced with permission from ref. 40. Copyright 2017 Elsevier. **(c)** Enhanced CO production on Au-CeO_x catalysts. Reproduced with permission from ref. 41. Copyright 2017 American Chemical Society.

8. Roughness and Defects

Nanostructured materials show better catalytic activity and selectivity than flat surfaces. The presence of low coordinated sites such as steps, edges and defects⁴², grain boundaries⁴³ or certain periodic spacing between the facets at the electrode surface¹, are thought to be responsible for the enhanced reactivity. The *in situ* electrochemical reduction of metal oxides offers a way to prepare roughened and highly defective structures that exhibit higher current densities compared to flat surfaces due to their larger electrochemically active surface areas.⁴⁴ However, the selectivity for CO₂RR of these systems is also drastically modified. Roughened and highly defective Cu surfaces display preferential selectivity towards multicarbon products and oxygenates.^{38,42,45–47}

On the other hand, high CO yield at lower overpotentials has been found for highly porous Au, Ag and Zn catalysts. For example, the improved catalysis in oxide-derived (OD) Au electrodes, which showed >96 % FE for CO at -0.35 V vs RHE over the course of 8 h electrolysis, has been ascribed to a better stabilization of the CO₂^{•-} intermediate (Figure 9a).⁴⁸ In the same way, O₂-plasma pre-treated highly defective nanostructured Ag catalysts showed CO FE above 90 % at -0.6 V vs RHE, a notable enhancement over flat Ag foils, which reduces CO₂ at overpotentials below -0.9 V vs RHE⁴⁹. The *operando* X-ray absorption fine-structure spectroscopy (XAFS) and *quasi in situ* X-ray Photoelectron Spectroscopy (XPS) characterization of these samples revealed that the surface AgO_x species are reduced within the first 3 min of the reaction, and that subsurface oxygen or AgO_x is not detected either in the bulk of the foil after 35 min, ruling out the role of AgO_x or O in their improved reactivity, Figure 9b. Instead, DFT calculations indicated that defects created by the plasma treatment lead to locally enhanced negative electric fields which resulted in a decrease in the overpotential needed to produce CO.

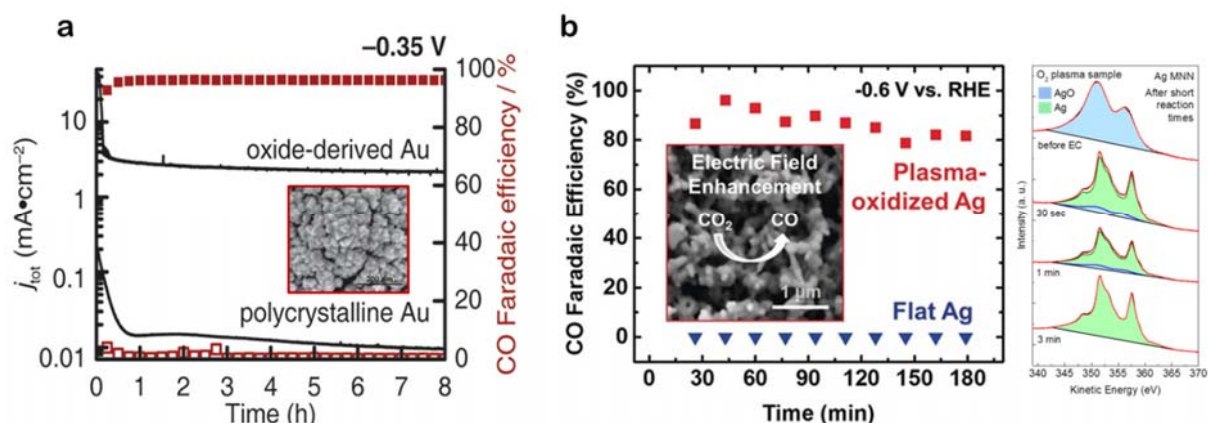


Figure 9. Comparison of CO_2R selectivity of planar polycrystalline M (M=Cu, Au, Ag) with that of (a) OD- Au NPs and (b) O_2 plasma-treated Ag foil. The Ag MNN Auger region of the former sample before and after short CO_2RR reaction times is shown. Reproduced with permission from ref. 48 (copyright 2012 American Chemical Society) and ref. 49 (copyright 2017 Wiley).

9. Oxidation State Effect.

Oxide-derived Cu catalysts have been proven to be very selective for the formation of C_2+ products.⁵⁰ Structural factors such as roughness effects, defects and grain boundaries left behind by the oxygen pre-treatment have been initially deemed responsible for the former unusual reactivity, although more recently the presence of Cu^+ and residual subsurface oxygen have been suggested to influence the formation of ethylene and alcohols.^{51,52} Still, significant reduction of the OD Cu catalyst to metallic state is bound to occur when electroreducing CO_2 .⁵³ In fact, a number of studies have reported metallic Cu as the only stable and active species during CO_2RR .^{29,58} However, special sites can be created in the Cu structures to stabilize the Cu^+ species or sub-surface oxygen. For instance, the inclusion of boron as a modifier element can change the electronic structure of Cu and stabilize $\text{Cu}^{\delta+}$. The latter was theoretically and experimentally linked to a higher selectivity towards C_2 products from CO_2RR .⁵⁴

The presence of Cu^+ species and sub-surface oxygen during CO_2RR was experimentally demonstrated via *operando* XAFS (Figure 10a).⁴⁵ Although the roughness of these plasma-treated

OD-catalysts played a role in contributing to their increased activity, their outstanding ethylene selectivity (up to 60 %) was found to correlate with the presence of Cu^+ and subsurface oxygen. The role of CuO_x species and oxygen in Cu had been also previously discussed by others⁵⁵, but only based on *ex situ* measurements,⁵⁶ which had been questioned due to the facile oxidation of Cu upon air exposure for the characterization. A subsequent theoretical study described a synergistic effect between neighboring Cu^+ and Cu^0 in Cu surfaces leading to improved kinetics and thermodynamics of both CO_2 activation and CO dimerization, while hindering the C_1 pathways (Figure 10b).⁵⁷ Despite these promising results, the catalytic role of Cu^+ and subsurface oxygen is a current topic of strong controversy.⁵⁸

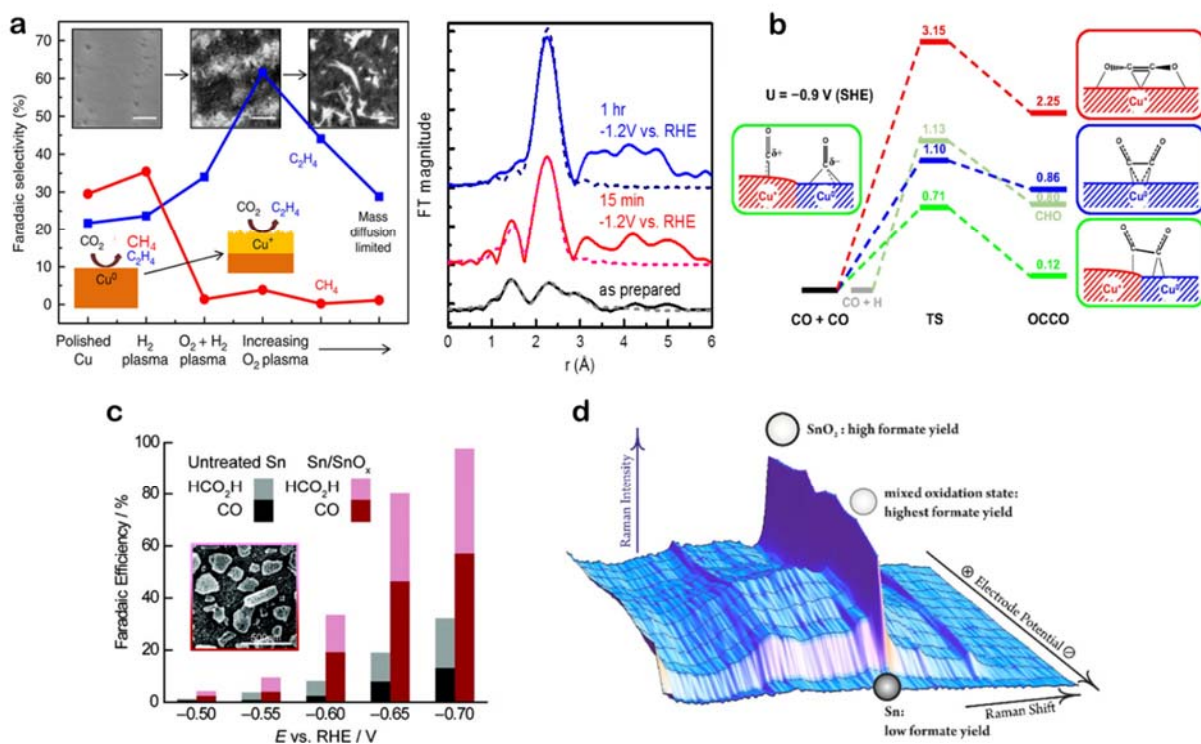


Figure 10. (a) Hydrocarbon selectivity of plasma-treated Cu foils and EXAFS spectra with fits acquired under *operando* CO₂RR conditions. Reproduced with permission from ref. 45. Copyright 2016 Nature Publishing Group. (b) Free energy profiles of CO dimerization on a fully oxidized (red), metallic (blue) and Cu metal in oxidized (green) matrixes. Reproduced with permission from refs. 57. Copyright 2017 Proceedings of the National Academy of Science. (c) HCO₂H and CO FE for Sn foil and *in situ*-deposited Sn/SnO_x thin film electrodes. Reproduced with permission from ref. 60. Copyright 2012 American Chemical Society. (d) Potential-

dependent *operando* Raman spectra of a SnO₂ surface. Reproduced with permission from ref. 61. Copyright 2015 American Chemical Society.

The effect of the metal oxidation state and the presence of sub-surface oxygen is not only important for Cu. SnO_x is essential for CO₂R catalysis on Sn electrodes. DFT calculations point out that oxygen vacancies on the SnO surface are decisive for the selective reduction of CO₂ to formate.⁵⁹ Moreover, SnO_x appears to provide chemical functionality that stabilizes the CO₂^{•-} intermediate, mediating the direct electron transfer that yields CO and HCO₂H (Figure 10c).⁶⁰ Furthermore, based on *operando* Raman spectroscopy, a decrease in the formate FE was assigned to the reduction of SnO_x to metallic Sn (Figure 10d).⁶¹ These results may open new perspectives in the preparation of metal/metal oxide composites with superior activity and selectivity.

10. Electrolyte Effect

CO₂RR performance is generally measured in aqueous electrolytes, typically potassium bicarbonate solutions. Alkali metal cations have been reported to facilitate CO₂ adsorption and stabilize reaction intermediates.⁶² On Cu electrodes, increasing the cation size leads to a decrease in FEs of H₂ and C₁, as well as an increase in C₂₊ (Figure 11a).⁶²⁻⁶⁴ This selectivity change could be explained by the preferential hydrolysis of the cations, lowering the local pH near the electrode, leading to higher local CO₂ concentration.⁶² Bicarbonate is considered to contribute to the enhanced CO₂RR activity by increasing the effective CO₂ concentration near the electrode surface.⁶⁵⁻⁶⁷ In addition, the bicarbonate solution can also suppress the increase of the local pH near the electrode surface, which significantly affects the reaction pathways for the production of methane and ethylene on Cu.⁶⁸ CO₂RR conducted in highly concentrated (10 M) KOH (high pH) over a Cu gas diffusion electrode revealed that the onset of ethylene evolution (-0.165 V vs RHE) occurs almost simultaneously with the CO production.⁶⁹ Similarly, the major product on Ag switched from CO at pH 7 to formate at pH > 15 (Figure 11b).⁷⁰

Since the CO₂RR performance is very sensitive to the composition and nature of the electrolyte, a number of studies exist trying to improve C₂₊ production via electrolyte design.^{62,63,71,72} For example, by adding halide ions into the bicarbonate electrolyte, the CO₂RR

activity could be significantly increased without sacrificing the intrinsically high C₂₊ selectivity of plasma-oxidized Cu catalysts (Figure 11c). Halide ions such as I⁻ can also induce significant nanostructuring of the oxidized Cu surface, even at open circuit potential. The stabilization of Cu⁺ species made the halide effect on oxidized Cu different from that on metallic Cu, where an increased methane production is observed in contrast to C₂H₄ production over CuO_x.⁷²

In aqueous electrolytes, the reaction rate of CO₂RR is usually mass transport-limited due to the low CO₂ solubility in water (33 mM at 25 °C, 1 atm). To overcome this disadvantage, high CO₂ pressure⁷³ and supercritical CO₂⁷⁴ have been explored to increase the CO₂ concentration in aqueous electrolytes. Additionally, organic solvents such as acetonitrile, methanol and N,N-dimethylformamide are also used due to their improved CO₂ solubility compared to water. Ionic liquids can also be employed as co-catalysts, either as electrolytes dissolved in a solvent, or as combined solvent/electrolyte. Rosen et al.⁷⁵ reported an electrocatalytic system with 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) as an electrolyte in water which was able to reduce CO₂ to CO at overpotentials below 0.2 V with >96 % FE. The ionic liquid lowered the energy of the (CO₂)⁻ intermediate and the initial reduction barrier (Figure 11d).

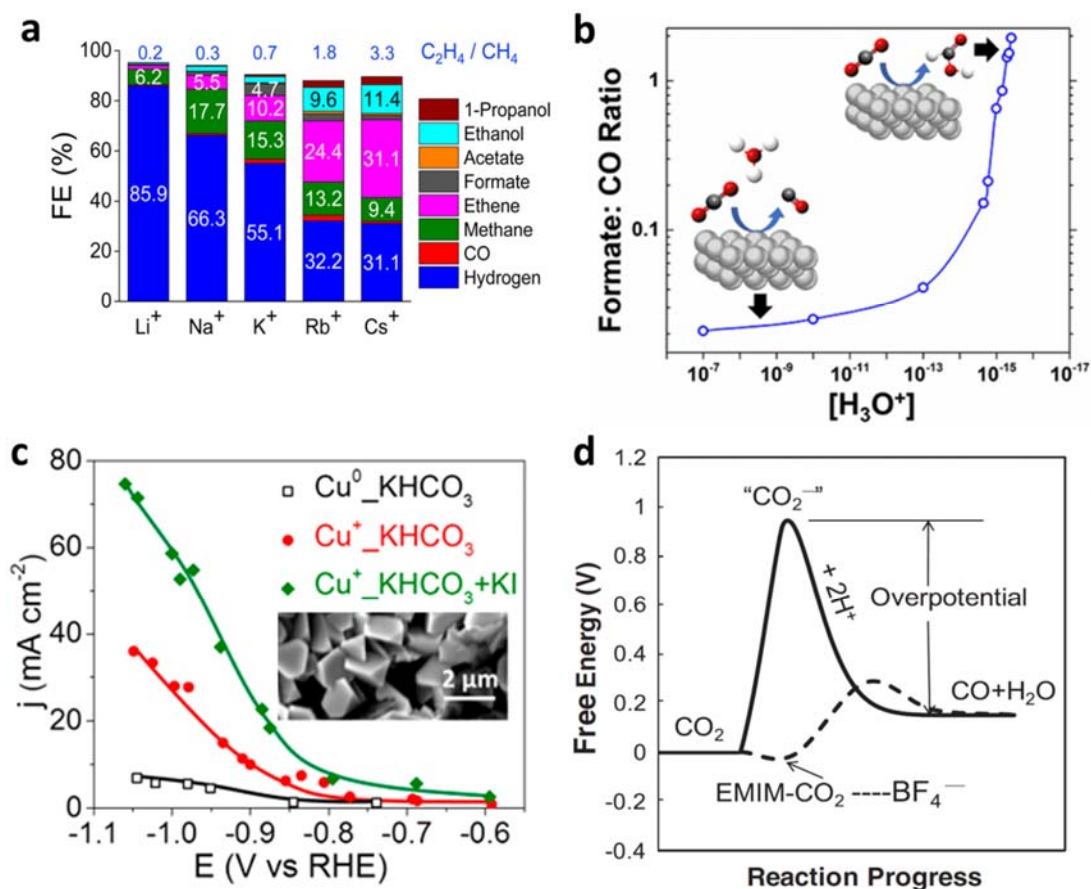


Figure 11. (a) FEs for CO₂RR products over Cu at -1 V vs RHE in CO₂-saturated 0.1 M M HCO₃ (M = Li, Na, K, Rb, Cs) electrolyte. Reproduced with permission from ref. 62. Copyright 2016 American Chemical Society. (b) Formate:CO FE ratio as a function of hydronium concentration on Ag. Reproduced with permission from ref. 70. Copyright 2018 American Chemical Society. (c) Halide effect on the reactivity and surface reconstruction (inset) of O₂-plasma pre-treated Cu foils. Reproduced with permission from ref. 71. Copyright 2017 American Chemical Society. (d) Free energy of CO₂ electroreduction to CO on Ag with and without EMIM-BF₄. Reproduced with permission from ref. 75. Copyright 2011 Science Publishing Group.

11. Conclusion

In summary, structure- and electrolyte-reactivity relationships in CO₂RR have been exemplified over a number of molecular, nanostructured, and single crystal catalysts. Although the dynamic

changes of the morphology, atomic arrangement, coordination number, and oxidation state of the catalysts under reaction conditions can already be monitored by advanced *operando* microscopy and spectroscopic techniques, improved surface sensitivity of some of these methods (e.g. XAFS) is still needed when surface-modified bulk systems are studied. Furthermore, challenges still exist when trying to conduct truly surface-sensitivity measurements (e.g. XPS) not only *quasi in situ*, but also in a flow-cell configuration under potential control.

Moreover, the greater complexity of real catalysts compared to model single crystals further motivates researchers to try to synthesize well-defined nanoscale systems where one could obtain in depth understanding of the different parameters affecting CO₂RR by isolating, when possible, different contributions, as for example the role of the NP size, shape, structure, oxidation state, composition, interparticle distance, etc. Adding to this challenging task is the need of understanding the complexity of electrified solid/liquid and solid/liquid/gas interfaces. For instance, the adsorption of anions and cations on the electrode surface is usually different in the presence of applied potentials, and the adsorbed species also interact with CO₂ and reaction intermediates differently when electric fields are considered.

In the coming years, being able to gain in depth atomistic/molecular insight into the complexity of electrode/electrolyte interfaces, including their interaction under different environmental conditions will be key for understanding CO₂RR mechanisms and further designing more active and selective catalysts.

Author information

Corresponding Author

*E-mail for B.R.C: roldan@fhi-berlin.mpg.de

Author Contribution

‡Contributed equally to this work.

Notes

The authors declare no competing financial interest.

Acknowledgments

This work was supported by the European Research Council under grant ERC-OPERANDOCAT (ERC-725915) and the German Federal Ministry of Education and Research (BMBF) under grants #03SF0523C-‘CO2EKAT’ and #033RCOO4D-‘e-Ethylene’.

Biographical Information

Rosa M. Arán Ais obtained her B.Sc. in Chemistry from the University of Alicante (Spain) in 2010, and her Ph.D. at the same University in 2016. She is now a postdoctoral researcher in the Department of Physics at the Ruhr-University Bochum, Germany. Her research interests include gaining fundamental insight on electrocatalytic processes based on single crystal work, as well as the synthesis, characterization, and electrocatalysis of size- and shape-controlled metal NPs.

Dunfeng Gao received his B.Sc. in Materials Chemistry from the China University of Petroleum in 2009 and Ph.D. in Physical Chemistry from the Dalian Institute of Chemical Physics, Chinese Academy of Sciences in 2015. Currently, he is a postdoctoral researcher in the Department of Interface Science at the Fritz Haber Institute of the Max Planck Society, Germany. His research focuses on developing highly efficient nanostructured catalysts for CO₂RR.

Beatriz Roldán Cuenya completed her B.S. in Physics from the University of Oviedo, Spain in 1998. She obtained her Ph.D. from the Department of Physics of the University of Duisburg-Essen (Germany) in 2001. She then became a postdoctoral scholar in the Department of Chemical Engineering at the University of California Santa Barbara (2001–2003). In 2004 she joined the Department of Physics at the University of Central Florida (UCF) as Assistant Professor where she moved through the ranks to become a full professor in 2012. In 2013 she became a chair professor of Solid State Physics in the Department of Physics, Ruhr-University Bochum (2013-2017). Currently, she is the director of the Department of Interface Science at the Fritz-Haber Institute of the Max Planck Society (Berlin, Germany). Her research program explores physical and chemical properties of nanostructures, with emphasis on advancements in nanocatalysis based on *operando* microscopic and spectroscopic characterization.

References

- (1) Hori, Y. Electrochemical CO₂ Reduction on Metal Electrodes. *Mod. Asp. Electrochem.* **2008**, No. 42, 89–189.
- (2) Lin, S.; Diercks, C. S.; Zhang, Y.-B.; Kornienko, N.; Nichols, E. M.; Zhao, Y.; Paris, A. R.; Kim, D.; Yang, P.; Yaghi, O. M.; Chang, C. Covalent Organic Frameworks Comprising Cobalt Porphyrins for Catalytic CO₂ Reduction in Water. *Science.* **2015**, *349*, 1208–1213.
- (3) Göttle, A. J.; Koper, M. T. M. Determinant Role of Electrogenenerated Reactive Nucleophilic Species on Selectivity during Reduction of CO₂ Catalyzed by Metalloporphyrins. *J. Am. Chem. Soc.* **2018**, *140*, 4826–4834.
- (4) Ju, W.; Bagger, A.; Hao, G. P.; Varela, A. S.; Sinev, I.; Bon, V.; Roldan Cuenya, B.; Kaskel, S.; Rossmeisl, J.; Strasser, P. Understanding Activity and Selectivity of Metal-Nitrogen-Doped Carbon Catalysts for Electrochemical Reduction of CO₂. *Nat. Commun.* **2017**, *8*, 944–953.
- (5) Wang, X.; Chen, Z.; Zhao, X.; Yao, T.; Chen, W.; You, R.; Zhao, C.; Wu, G.; Wang, J.; Huang, W.; Yang, J.; Hong, X.; Wei, S.; Wu, Y.; Li, Y. Regulation of Coordination Number over Single Co Sites: Triggering the Efficient Electroreduction of CO₂. *Angew. Chemie. Int. Ed.* **2017**, *57*, 1944–1948.
- (6) Huan, T. N.; Ranjbar, N.; Rouse, G.; Sougrati, M.; Zitolo, A.; Mougel, V.; Jaouen, F.; Fontecave, M. Electrochemical Reduction of CO₂ Catalyzed by Fe-N-C Materials: A Structure-Selectivity Study. *ACS Catal.* **2017**, *7*, 1520–1525.
- (7) Kauffman, D. R.; Alfonso, D.; Matranga, C.; Qian, H.; Jin, R. Experimental and Computational Investigation of Au₂₅ Clusters and CO₂: A Unique Interaction and Enhanced Electrocatalytic Activity. *J. Am. Chem. Soc.* **2012**, *134*, 10237–10243.
- (8) Reske, R.; Mistry, H.; Behafarid, F.; Roldan Cuenya, B.; Strasser, P. Particle Size Effects in the Catalytic Electroreduction of CO₂ on Cu Nanoparticles. *J. Am. Chem. Soc.* **2014**, *136*, 6978–6986.
- (9) Zhu, W.; Michalsky, R.; Metin, Ö.; Lv, H.; Guo, S.; Wright, C.; Sun, X.; Peterson, A.; Sun, S. Monodisperse Au Nanoparticles for Selective Electrocatalytic Reduction of CO₂ to CO. *J. Am. Chem. Soc.* **2013**, *135*, 16833–16836.

- (10) Mistry, H.; Reske, R.; Zeng, Z.; Zhao, Z. J.; Greeley, J.; Strasser, P.; Roldan Cuenya, B. Exceptional Size-Dependent Activity Enhancement in the Electroreduction of CO₂ over Au Nanoparticles. *J. Am. Chem. Soc.* **2014**, *136*, 16473–16476.
- (11) Gao, D.; Zhou, H.; Wang, J.; Miao, S.; Yang, F.; Wang, G.; Wang, J.; Bao, X. Size-Dependent Electrocatalytic Reduction of CO₂ over Pd Nanoparticles. *J. Am. Chem. Soc.* **2015**, *137*, 4288–4291.
- (12) Kim, C.; Jeon, H. S.; Eom, T.; Jee, M. S.; Kim, H.; Friend, C. M.; Min, B. K.; Hwang, Y. J. Achieving Selective and Efficient Electrocatalytic Activity for CO₂ Reduction Using Immobilized Silver Nanoparticles. *J. Am. Chem. Soc.* **2015**, *137*, 13844–13850.
- (13) Zhang, S.; Kang, P.; Meyer, T. J. Nanostructured Tin Catalysts for Selective Electrochemical Reduction of CO₂ to Formate. *J. Am. Chem. Soc.* **2014**, *136*, 1734–1737.
- (14) Mistry, H.; Behafarid, F.; Reske, R.; Varela, A. S.; Strasser, P.; Roldan Cuenya, B. Tuning Catalytic Selectivity at the Mesoscale via Interparticle Interactions. *ACS Catal.* **2016**, *6*, 1075–1080.
- (15) Wang, X.; Varela, A. S.; Bergmann, A.; Köhl, S.; Strasser, P. Catalyst Particle Density Controls Hydrocarbon Product Selectivity in CO₂ Electroreduction on CuO_x. *ChemSusChem* **2017**, *10*, 4642–4649.
- (16) Nesselberger, M.; Roefzaad, M.; Fayçal Hamou, R.; Ulrich Biedermann, P.; Schweinberger, F. F.; Kunz, S.; Schloegl, K.; Wiberg, G.K.H.; Ashton, S.; Heiz, U.; Mayrhofer, K.J.J.; Arenz, M. The Effect of Particle Proximity on the Oxygen Reduction Rate of Size-Selected Platinum Clusters. *Nat. Mater.* **2013**, *12*, 919–924.
- (17) Kim, D.; Kley, C. S.; Li, Y.; Yang, P. Copper Nanoparticle Ensembles for Selective Electroreduction of CO₂ to C₂–C₃ Products. *Proc. Natl. Acad. Sci.* **2017**, *114*, 10560–10565.
- (18) Manthiram, K.; Beberwyck, B. J.; Alivisatos, A. P. Enhanced Electrochemical Methanation of CO₂ with a Dispersible Nanoscale Copper Catalyst. *J. Am. Chem. Soc.* **2014**, *136*, 13319–13325.
- (19) Ma, S.; Sadakiyo, M.; Heim, M.; Luo, R.; Haasch, R. T.; Gold, J. I.; Yamauchi, M.; Kenis, P. J. A. Electroreduction of CO₂ to Hydrocarbons Using Bimetallic Cu-Pd Catalysts with Different Mixing Patterns. *J. Am. Chem. Soc.* **2017**, *139*, 47–50.
- (20) Kim, D.; Xie, C.; Becknell, N.; Yu, Y.; Karamad, M.; Chan, K.; Crumlin, E. J.; Nørskov, J. K.; Yang, P. Electrochemical Activation of CO₂ through Atomic Ordering Transformations

- of AuCu Nanoparticles. *J. Am. Chem. Soc.* **2017**, *139*, 8329–8336.
- (21) Mistry, H.; Reske, R.; Strasser, P.; Roldan Cuenya, B. Size-Dependent Reactivity of Gold-Copper Bimetallic Nanoparticles during CO₂ Electroreduction. *Catal. Today* **2017**, *288*, 30–36.
- (22) 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 CO₂ Reduction Enabled by Gold–Iron Core–Shell Nanoparticles. *J. Am. Chem. Soc.* **2017**, *139*, 15608–15611.
- (23) Luc, W.; Collins, C.; Wang, S.; Xin, H.; He, K.; Kang, Y.; Jiao, F. Ag–Sn Bimetallic Catalyst with a Core–Shell Structure for CO₂ Reduction. *J. Am. Chem. Soc.* **2017**, *139*, 1885–1893.
- (24) Zhuang, T.-T.; Liang, Z.-Q.; Seifitokaldani, A.; Li, Y.; De Luna, P.; Burdyny, T.; Che, F.; Meng, F.; Min, Y.; Quintero-Bermudez, R.; Dinh, C.T.; Pang, Y.; Zhong, M.; Zhang, B.; Li, J.; Chen, P.; Zheng, X.; Liang, H.; Ge, W.; Ye, B.; Sinton, D.; Yu, S.; Sargent, E.H. Steering Post-C–C Coupling Selectivity Enables High Efficiency Electroreduction of CO₂ to Multi-Carbon Alcohols. *Nat. Catal.* **2018**, *1*, 421–428.
- (25) Ren, D.; Ang, B. S. H.; Yeo, B. S. Tuning the Selectivity of CO₂ Electroreduction toward Ethanol on Oxide-Derived Cu_xZn Catalysts. *ACS Catal.* **2016**, *6*, 8239–8247.
- (26) Torelli, D. A.; Francis, S. A.; Crompton, J. C.; Javier, A.; Thompson, J. R.; Brunshwig, B. S.; Soriaga, M. P.; Lewis, N. S. Nickel-Gallium-Catalyzed Electrochemical Reduction of CO₂ to Highly Reduced Products at Low Overpotentials. *ACS Catal.* **2016**, *6*, 2100–2104.
- (27) Bagger, A.; Ju, W.; Varela, A. S.; Strasser, P.; Rossmeisl, J. Electrochemical CO₂ Reduction: A Classification Problem. *ChemPhysChem* **2017**, *18*, 3266–3273.
- (28) Kortlever, R.; Peters, I.; Balemans, C.; Kas, R.; Kwon, Y.; Mul, G.; Koper, M. T. M. Palladium-Gold Catalyst for the Electrochemical Reduction of CO₂ to C₁–C₅ Hydrocarbons. *Chem. Commun.* **2016**, *52*, 10229–10232.
- (29) Peterson, A. A.; Abild-Pedersen, F.; Studt, F.; Rossmeisl, J.; Nørskov, J. K. How Copper Catalyzes the Electroreduction of CO₂ into Hydrocarbon Fuels. *Energy Environ. Sci.* **2010**, *3*, 1311–1315.
- (30) Schouten, K. J. P.; Qin, Z.; Pérez Gallent, E.; Koper, M. T. M. Two Pathways for the Formation of Ethylene in CO Reduction on Single-Crystal Copper Electrodes. *J. Am. Chem. Soc.* **2012**, *134*, 9864–9867.

- (31) Calle-Vallejo, F.; Koper, M. T. M. Theoretical Considerations on the Electroreduction of CO to C₂ Species on Cu(100) Electrodes. *Angew. Chemie. Int. Ed.* **2013**, *52*, 7282–7285.
- (32) 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.
- (33) Hahn, C.; Hatsukade, T.; Kim, Y.-G.; Vailionis, A.; Baricuatro, J. H.; Higgins, D. C.; Nitopi, S. A.; Soriaga, M. P.; Jaramillo, T. F. Engineering Cu Surfaces for the Electrocatalytic Conversion of CO₂: Controlling Selectivity toward Oxygenates and Hydrocarbons. *Proc. Natl. Acad. Sci.* **2017**, *114*, 5918–5923.
- (34) Klinkova, A.; De Luna, P.; Dinh, C.-T.; Voznyy, O.; Larin, E. M.; Kumacheva, E.; Sargent, E. H. Rational Design of Efficient Palladium Catalysts for Electroreduction of CO₂ to Formate. *ACS Catal.* **2016**, *6*, 8115–8120.
- (35) Liu, S.; Tao, H.; Zeng, L.; Liu, Q.; Xu, Z.; Liu, Q.; Luo, J.-L. Shape-Dependent Electrocatalytic Reduction of CO₂ to CO on Triangular Silver Nanoplates. *J. Am. Chem. Soc.* **2017**, *139*, 2160–2163.
- (36) Lee, H.-E.; Yang, K. D.; Yoon, S. M.; Ahn, H.-Y.; Lee, Y. Y.; Chang, H.; Jeong, D. H.; Lee, Y.-S.; Kim, M. Y.; Nam, K. T. Concave Rhombic Dodecahedral Au Nanocatalyst with Multiple High-Index Facets for CO₂ Reduction. *ACS Nano* **2015**, *9*, 8384–8393.
- (37) Roberts, F. S.; Kuhl, K. P.; Nilsson, A. High Selectivity for Ethylene from CO₂ Reduction over Copper Nanocube Electrocatalysts. *Angew. Chemie. Int. Ed.* **2015**, *54*, 5179–5182.
- (38) Gao, D.; Zegkinoglou, I.; Divins, N. J.; Scholten, F.; Sinev, I.; Grosse, P.; Roldan Cuenya, B. Plasma-Activated Copper Nanocube Catalysts for Efficient CO₂ Electroreduction to Hydrocarbons and Alcohols. *ACS Nano* **2017**, *11*, 4825–4831.
- (39) Grosse, P.; Gao, D.; 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. Chemie. Int. Ed.* **2018**, *57*, 6192–6197.
- (40) Baturina, O.; Lu, Q.; Xu, F.; Purdy, A.; Dyatkin, B.; Sang, X.; Unocic, R.; Brintlinger, T.; Gogotsi, Y. Effect of Nanostructured Carbon Support on Copper Electrocatalytic Activity toward CO₂ Electroreduction to Hydrocarbon Fuels. *Catal. Today* **2017**, *288*, 2–10.
- (41) Gao, D.; Zhang, Y.; Zhou, Z.; Cai, F.; Zhao, X.; Huang, W.; Li, Y.; Zhu, J.; Liu, P.; Yang,

- F.; Wang, G.; Bao, X. Enhancing CO₂ Electroreduction with the Metal–Oxide Interface. *J. Am. Chem. Soc.* **2017**, *139*, 5652–5655.
- (42) Jeon, H. S.; Kunze, S.; Scholten, F.; Roldan Cuenya, B. Prism-Shaped Cu Nanocatalysts for Electrochemical CO₂ Reduction to Ethylene. *ACS Catal.* **2018**, *8*, 531–535.
- (43) Mariano, R. G.; McKelvey, K.; White, H. S.; Kanan, M. W. Selective Increase in CO₂ Electroreduction Activity at Grain-Boundary Surface Terminations. *Science*. **2017**, *358*, 1187–1192.
- (44) Dutta, A.; Rahaman, M.; Luedi, N. C.; Mohos, M.; Broekmann, P. Morphology Matters: Tuning the Product Distribution of CO₂ Electroreduction on Oxide-Derived Cu Foam Catalysts. *ACS Catal.* **2016**, *6*, 3804–3814.
- (45) 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 CO₂ Reduction to Ethylene. *Nat. Commun.* **2016**, *7*, 1–8.
- (46) 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.
- (47) Tang, W.; Peterson, A. A.; Varela, A. S.; Jovanov, Z. P.; Bech, L.; Durand, W. J.; Dahl, S.; Nørskov, J. K.; Chorkendorff, I. The Importance of Surface Morphology in Controlling the Selectivity of Polycrystalline Copper for CO₂ Electroreduction. *Phys. Chem. Chem. Phys.* **2012**, *14*, 76–81.
- (48) Chen, Y.; Li, C. W.; Kanan, M. W. Aqueous CO₂ Reduction at Very Low Overpotential on Oxide-Derived Au Nanoparticles. *J. Am. Chem. Soc.* **2012**, *134*, 19969–19972.
- (49) Mistry, H.; Choi, Y.-W.; Bagger, A.; Scholten, F.; S. Bonifacio, C.; Sinev, I.; J. Divins, N.; Zegkinoglou, I.; Jeon, H.; Kisslinger, K.; Stach, E. A.; Yang, J. C.; Rossmeisl, J.; Roldan Cuenya, B. Enhanced CO₂ Electroreduction to CO over Defect-Rich Plasma-Activated Silver Catalysts. *Angew. Chemie. Int. Ed.* **2017**, *56*, 11394–11398.
- (50) Pander, J. E.; Ren, D.; Huang, Y.; Loo, N. W. X.; Hong, S. H. L.; Yeo, B. S. Understanding the Heterogeneous Electrocatalytic Reduction of CO₂ on Oxide-Derived Catalysts. *ChemElectroChem* **2018**, *5*, 219–237.
- (51) 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. *Proc. Natl. Acad. Sci.* **2017**, *114*, 6706–6711.
- (52) Le Duff, C. S.; Lawrence, M. J.; Rodriguez, P. Role of the Adsorbed Oxygen Species in the Selective Electrochemical Reduction of CO₂ to Alcohols and Carbonyls on Copper Electrodes. *Angew. Chemie. Int. Ed.* **2017**, 12919–12924.
- (53) Ren, D.; Deng, Y.; Handoko, A. D.; Chen, C. S.; Malkhandi, S.; Yeo, B. S. Selective Electrochemical Reduction of CO₂ to Ethylene and Ethanol on Copper(I) Oxide Catalysts. *ACS Catal.* **2015**, *5*, 2814–2821.
- (54) Zhou, Y.; Che, F.; Liu, M.; Zou, C.; Liang, Z.; De Luna, P.; Yuan, H.; Li, J.; Wang, Z.; Xie, H.; Li, H.; Chen, P.; Bladt, E.; Quintero-Bermudez, R.; Sham, T-K.; Bals, S.; Hofkens, J.; Sinton, D.; Chen, G.; Sargent, E.H. Dopant-Induced Electron Localization Drives CO₂ Reduction to C₂ Hydrocarbons. *Nat. Chem.* **2018**, *10*, 974–980.
- (55) Zhang, Y.J.; Peterson, A. Oxygen-Induced Changes to Selectivity-Determining Steps in Electrocatalytic CO₂ Reduction. *Phys. Chem. Chem. Phys.* **2015**, *17*, 4505–4515.
- (56) Kim, D.; Lee, S.; Ocon, J. D.; Jeong, B.; Lee, J. K.; Lee, J. Insights into an Autonomously Formed Oxygen-Evacuated Cu₂O Electrode for the Selective Production of C₂H₄ from CO₂. *Phys. Chem. Chem. Phys.* **2015**, *17*, 824–830.
- (57) Xiao, H.; Goddard, W.; Cheng, T.; Liu, Y. Cu Metal Embedded in Oxidized Matrix Catalyst to Promote CO₂ Activation and CO Dimerization for Electrochemical Reduction of CO₂. *Proc. Natl. Acad. Sci.* **2017**, *114*, 6685–6688.
- (58) Garza, A. J.; Bell, A. T.; Head-Gordon, M. Is Subsurface Oxygen Necessary for the Electrochemical Reduction of CO₂ on Copper? *J. Phys. Chem. Lett.* **2018**, *9*, 601–606.
- (59) Wang, S.; Wang, J.; Xin, H. Insights into Electrochemical CO₂ Reduction on Tin Oxides from First-Principles Calculations. *Green Energy Environ.* **2017**, *2*, 168–171.
- (60) 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.
- (61) Dutta, A.; Kuzume, A.; Rahaman, M.; Veszteg, S.; Broekmann, P. Monitoring the Chemical State of Catalysts for CO₂ Electroreduction: An In Operando Study. *ACS Catal.* **2015**, *5*, 7498–7502.
- (62) Singh, M. R.; Kwon, Y.; Lum, Y.; Ager, J. W.; Bell, A. T. Hydrolysis of Electrolyte Cations Enhances the Electrochemical Reduction of CO₂ over Ag and Cu. *J. Am. Chem. Soc.* **2016**,

- 138, 13006–13012.
- (63) Lum, Y.; Yue, B.; Lobaccaro, P.; Bell, A. T.; Ager, J. W. Optimizing C-C Coupling on Oxide-Derived Copper Catalysts for Electrochemical CO₂ Reduction. *J. Phys. Chem. C* **2017**, *121*, 14191–14203.
- (64) Pérez-Gallent, E.; Marcandalli, G.; Figueiredo, M. C.; Calle-Vallejo, F.; Koper, M. T. M. Structure- and Potential-Dependent Cation Effects on CO Reduction at Copper Single-Crystal Electrodes. *J. Am. Chem. Soc.* **2017**, *139*, 16412–16419.
- (65) Dunwell, M.; Lu, Q.; Heyes, J. M.; Rosen, J.; Chen, J. G.; Yan, Y.; Jiao, F.; Xu, B. The Central Role of Bicarbonate in the Electrochemical Reduction of CO₂ on Gold. *J. Am. Chem. Soc.* **2017**, *139*, 3774–3783.
- (66) Zhu, S.; Jiang, B.; Cai, W.-B.; Shao, M. Direct Observation on Reaction Intermediates and the Role of Bicarbonate Anions in CO₂ Electrochemical Reduction Reaction on Cu Surfaces. *J. Am. Chem. Soc.* **2017**, *139*, 15664–15667.
- (67) Wuttig, A.; Yoon, Y.; Ryu, J.; Surendranath, Y. Bicarbonate Is Not a General Acid in Au-Catalyzed CO₂ Electroreduction. *J. Am. Chem. Soc.* **2017**, *139*, 17109–17113.
- (68) Schouten, K. J. P.; Pérez Gallent, E.; Koper, M. T. M. The Influence of pH on the Reduction of CO and CO₂ to Hydrocarbons on Copper Electrodes. *J. Electroanal. Chem.* **2013**, *716*, 53–57.
- (69) Dinh, C.; Burdyny, T.; Kibria, G.; Seifitokaldani, A.; Christine, M. CO₂ Electroreduction to Ethylene via Hydroxide-Mediated Copper Catalysis at an Abrupt Interface. *Science*. **2018**, *360*, 783–787.
- (70) Seifitokaldani, A.; Gabardo, C. M.; Burdyny, T.; Dinh, C.-T.; Edwards, J. P.; Kibria, M. G.; Bushuyev, O. S.; Kelley, S. O.; Sinton, D.; Sargent, E. H. Hydronium-Induced Switching between CO₂ Electroreduction Pathways. *J. Am. Chem. Soc.* **2018**, *140*, 3833–3837.
- (71) Gao, D.; Scholten, F.; Roldan Cuenya, B. Improved CO₂ Electroreduction Performance on Plasma-Activated Cu Catalysts via Electrolyte Design: Halide Effect. *ACS Catal.* **2017**, *7*, 5112–5120.
- (72) Varela, A. S.; Ju, W.; Reier, T.; Strasser, P. Tuning the Catalytic Activity and Selectivity of Cu for CO₂ Electroreduction in the Presence of Halides. *ACS Catal.* **2016**, *6*, 2136–2144.
- (73) Todoroki, M.; Hara, K.; Kudo, A.; Sakata, T. Electrochemical Reduction of High Pressure CO₂ at Pb, Hg and In Electrodes in an Aqueous KHCO₃ Solution. *J. Electroanal. Chem.*

1995, 394, 199–203.

- (74) Melchaeva, O.; Voyame, P.; Bassetto, V. C.; Prokein, M.; Renner, M.; Weidner, E.; Petermann, M.; Battistel, A. Electrochemical Reduction of Protic Supercritical CO₂ on Copper Electrodes. *ChemSusChem* **2017**, 10, 3660–3670.
- (75) 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.