Nanostructured Cu Electrodes for Energy-Efficient Conversion of CO_2 to Fuel

Investigator

Matthew W. Kanan, Assistant Professor, Department of Chemistry, Stanford University

Abstract

   Using renewable energy to drive the synthesis of organic compounds from CO_2 and H_2O could produce fuels and chemicals with little or no net CO_2 emissions. A particularly attractive strategy for "CO_2 recycling" is to power a CO_2-fixing electrochemical device with renewable electricity provided by wind or solar energy. One of the greatest technical challenges for this strategy is to develop efficient, selective, and robust electroreduction catalysts that reduce CO_2 and its derivatives to desirable multi-carbon compounds. The genesis of this GCEP project was the discovery of "oxide-derived Cu"—a thin-film metallic Cu material synthesized by reducing a Cu_2O precursor. Compared to conventional Cu electrodes such as polycrystalline Cu foil, single crystal Cu electrodes, or commercial Cu nanoparticles, oxide-derived Cu has higher selectivity for CO_2 reduction to CO and formate (HCO_2^-) at low overpotential, and much higher selectivity and activity for CO reduction to ethanol and acetate at moderate overpotential. The goals of this project are to elucidate the structural origin of the catalytic properties of oxide-derived Cu and use these insights to prepare improved catalysts. In the past year, we have made major progress on both of these objectives. Toward the first goal, we have used temperature programmed desorption to discover that the surfaces of oxide-derived Cu have a significant portion sites that bind CO with higher affinity than either Cu terraces or stepped surfaces. Because adsorption energy directly impacts the potential energy surface for electroreduction reactions, our results suggest that these high-affinity sites are critical for the reduction of CO on oxide-derived Cu. Toward the goal of making improved catalysts, we have used the insights from our studies of oxide-derived Cu to develop the first experimentally validated design principles for nanoparticle CO_2 and CO reduction catalysts. In particular, we have shown that the specific activity for CO_2 reduction to CO is directly correlated with the density of grain boundaries in Au nanoparticles, and the specific activity for CO reduction to ethanol and acetate is directly correlated to the density of grain boundaries in Cu nanoparticles. The most grain boundary–rich Cu catalysts are the most active and selective CO electroreduction catalysts reported to date. Our results provide validation for the use of grain boundary engineering to create highly active fuel-synthesizing catalysts.

Introduction

Fossil fuels have provided abundant energy and the feedstocks for chemical synthesis over the past century. The grand challenge for the next century is to achieve sustainability by drastically reducing greenhouse gas emissions without compromising quality of life for a growing population. Using renewable energy to drive the synthesis of organic compounds from CO_2 and H_2O could produce fuels and chemicals with little or no net CO_2 emissions. In order to be implemented on a significant scale, these "CO_2 recycling" processes must be cost-competitive with fossil fuels. A key technical challenge is to efficiently transform CO_2 into multi-carbon compounds because these targets generally have higher value, greater energy density, and more applications than C_1 compounds. A particularly attractive CO_2 recycling strategy is to power a CO_2-fixing electrochemical system with a source of renewable electricity. This strategy enables the use of both wind and solar energy, in contrast to photoelectrochemical approaches. One of the greatest technical challenges for this strategy is to develop efficient, selective, and robust electroreduction catalysts that reduce CO_2 and its derivatives to desirable multi-carbon compounds.

We envision a two-step process to produce liquid fuels and commodities (**Figure 1**): i) CO_2 conversion to CO; ii) CO conversion to multi-carbon oxygenates. The cathodic reactions of these processes are the $2e^-$, $2H^+$ reduction of CO_2 to CO, and the multi-electron, multi-proton reduction of CO with concomitant C–C bond formation to form an oxygenate (e.g. $8e^-$, $8H^+$ reduction to ethanol). The anodic reaction in both cases is the $4e^-$, $4H^+$ oxidation of H_2O to O_2. In order to be useful, electrocatalysts must operate with high rates at potentials as close as possible to the thermodynamic minima (i.e. low overpotential). In addition, electroreduction catalysts must selectively reduce CO_2 or CO instead of reducing H_2O (H^+) to H_2, which is typically the favored reaction. While there are numerous materials capable of reducing CO_2 to CO, they all require substantial overpotentials to achieve high rates and selectivities. The situation is even more challenging for CO reduction. Cu is the only metal with appreciable activity for this reaction, but it requires very large overpotentials in order for CO reduction to out-compete H_2O reduction and produces mostly hydrocarbons instead of oxygenate products.

$$CO_2 \text{ to CO}$$
$$CO_2 + 2e^- + 2HCO_3^- \longrightarrow CO + 2CO_3^{2-} \qquad \text{cathode}$$
$$H_2O + 2CO_3^{2-} \longrightarrow 0.5O_2 + 2e^- + 2H^+ \qquad \text{anode}$$

$$CO \text{ to fuels and chemicals}$$
$$2CO + 8e^- + 7H_2O \longrightarrow CH_3CH_2OH + 8HO^-$$
$$or \qquad \qquad \text{cathode}$$
$$2CO + 4e^- + 3H_2O \longrightarrow CH_3CO_2^- + 3HO^-$$
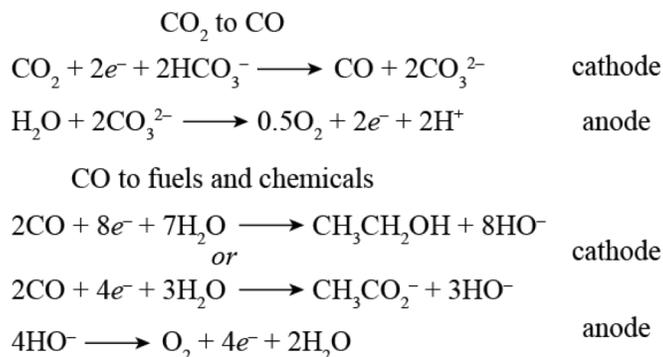$$4HO^- \longrightarrow O_2 + 4e^- + 2H_2O \qquad \text{anode}$$

Figure 1: Two-step electrochemical production of ethanol and acetate.

The genesis of our GCEP project was the discovery of "oxide-derived Cu"—a thin-film metallic Cu material produced by reducing a Cu_2O precursor. Compared to conventional Cu electrodes such as polycrystalline Cu foil, single crystal Cu electrodes, or commercial Cu nanoparticles, oxide-derived Cu (OD-Cu) has higher selectivity for CO_2 reduction to CO and formate (HCO_2^-) at low overpotential, and much higher selectivity and activity for CO reduction to ethanol and acetate at moderate overpotential (see below). Our project has focused on elucidating the structural features of OD-Cu that are responsible for its unusual catalytic properties and using these insights to prepare more effective catalysts. In the past year, we have made two major advancements: i) using temperature-programmed desorption studies, we have gained fundamental insight into OD-Cu by showing it has surface sites with unusually high binding affinity for CO. ii) Our structural studies of oxide-derived metals have led to the first experimentally validated design principle for *nanoparticle catalysts* for CO_2 and CO electroreduction: we have shown that the specific activity for CO_2 reduction to CO and CO reduction to multi-carbon oxygenates is directly proportional to the density of grain boundaries in Au and Cu nanoparticles. This report describes these advances in detail.

Background

Copper is the most heavily studied material for CO_2 and CO reduction catalysis. Polycrystalline and numerous single-crystal Cu electrodes have been evaluated in CO_2-saturated aqueous bicarbonate (HCO_3^-) solutions and CO-saturated neutral or alkaline solutions at ambient temperature.[1-7] These studies have revealed a complex, potential-dependent product distribution. The equilibrium potentials for CO_2 reduction are all close to 0 vs the reversible hydrogen electrode (RHE), while the equilibrium potentials for CO reduction are ca 0.2 V vs RHE. At low overpotential, H_2O reduction to H_2 is the major reaction on conventional Cu electrodes. At moderate to high overpotentials, CO_2 reduction to CO and HCO_2^- become significant products. At very high overpotentials, methane and ethylene are the major products, followed by smaller amounts of oxygenates including ethanol and acetate. In CO-saturated solutions without CO_2, methane, ethylene and oxygenates are also formed but only at similarly negative potentials.[6-8] Sweep voltammetry experiments have observed transient activity for CO reduction to ethylene with an onset potential of –0.3 V on surfaces with Cu(100) facets, but sustained activity in bulk electrolyses has not been demonstrated for these surfaces in this potential range.[8, 9] The requirement for large overpotentials compromises the energetic efficiency of electrosynthesis and promotes electrode deactivation. Computational studies have provided insight into possible reduction pathways on Cu and identified possible potential-determining steps.[10-12] In addition to bulk Cu surfaces, a recent study observed that Cu nanoparticles ranging in size from 2 nm to 15 nm have comparable or worse selectivity for CO_2 vs H_2O reduction than polycrystalline Cu.[13] Very small (<2 nm) Cu nanoparticles showed a greater propensity for H_2O reduction, suggesting that surface atoms with low coordination numbers promote H_2 formation.

We reported OD-Cu and its CO_2 reduction activity in 2012 and its activity for CO reduction to liquid fuels in 2014.[14, 15] OD-Cu is prepared by reducing a ≥1 μm–thick Cu_2O precursor, either via electroreduction or treatment with H_2 at 130 °C. Compared to Cu foil and Cu nanoparticles, OD-Cu has lower specific activity (current per Cu area) for H_2O reduction to H_2 and specific activity for CO reduction to multi-carbon oxygenates.

As a result, OD-Cu attains higher selectivity for CO_2 reduction to CO and HCO_2^- at low overpotentials and higher selectivity for CO reduction to ethanol and acetate at moderate overpotential. A number of independent studies since our initial report of OD-Cu have described variants with similar CO_2 vs H_2O reduction properties.[16-19]

Transmission electron microscopy (TEM) and grazing incidence X-ray diffraction studies have revealed that OD-Cu materials are nanocrystalline, meaning that they are comprised of continuous networks of nanocrystals linked by grain boundaries (**Figure 2**).[15] Based on this characterization, we hypothesized that the grain boundaries are responsible for the unusual catalytic properties of OD-Cu. Grain boundary surface terminations may contain active sites that are not otherwise stable[20] and the grain boundaries impose irregular shapes on the nanocrystals that may affect the step density on the particle surfaces that are distal from the grain boundaries. Testing this model explicitly with OD-Cu is challenging because it is difficult to modulate and quantify the grain boundary density in this material. It is also unclear if the factors that determine the catalytic properties of a nanocrystalline film will be applicable to discrete nanoparticles that are not part of a continuous material. Developing design principles for nanoparticles is essential for electrochemical devices because nanoparticles have much higher (orders of magnitude) surface area-to-mass ratios than thin-film catalysts. These considerations inspired us to broaden our investigation of grain boundaries beyond oxide-derived materials to study of their effects on nanoparticles.
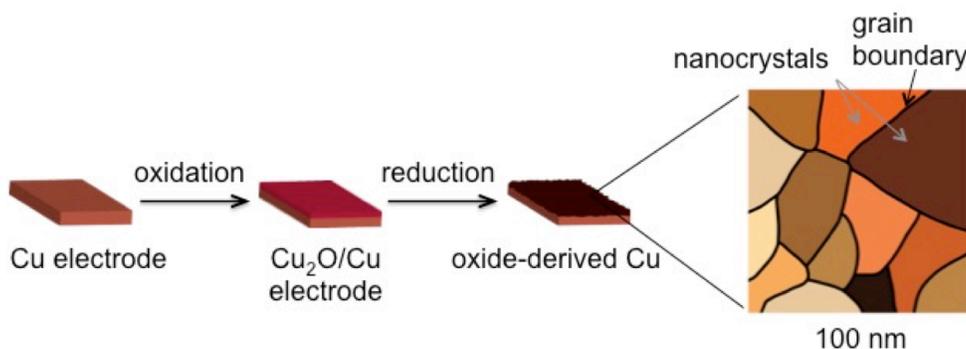

Figure 2: Schematic depiction of the synthesis of oxide-derived Cu and its nanocrystallinity.

Results

Our efforts over the past year have focused on two major objectives: i) probing the surface properties of oxide-derived Cu using temperature-programmed desorption spectroscopy; ii) determining the relationship between grain boundary density and electrocatalytic activity in metal nanoparticles. These efforts have demonstrated that oxide-derived Cu has enhanced binding affinity for CO and have provided the first quantitative correlations between grain boundaries and activity for both CO_2 and CO electroreduction. The most significant results are summarized below and further information is available in the publications.

Probing the surfaces of oxide-derived Cu by temperature programmed desorption

Compared to conventional Cu electrodes such as polycrystalline Cu, single crystals or commercial nanoparticles, OD-Cu has higher specific activity for CO reduction. Our previous studies have focused on characterizing the bulk properties of OD-Cu.

Understanding the origin of its unusual catalytic properties requires structural information about its surfaces. Temperature programmed desorption of CO (CO-TPD) provides information on the strength of CO binding to surface sites, which directly affects the potential energy surface for CO electroreduction.[21] Using CO-TPD, we have found that OD-Cu has CO binding sites with significantly higher affinity (by 7 kJ/mol) than the Cu terraces or highly stepped Cu surfaces. The presence of these high-affinity sites is qualitatively correlated with specific activity for CO electroreduction, suggesting that at least a portion of these surfaces contain highly active sites for these reactions. The details of this initial CO-TPD study are described below.

Direct grain-boundary–activity correlations for CO_2 and CO electroreduction

We have previously proposed that the unusual catalytic properties of oxide-derived metals are a consequence of the grain boundaries in these nanocrystalline materials. Testing this model explicitly with oxide-derived metals is very challenging because it is difficult to quantify and control their grain boundary densities. In addition, even if a grain boundary–activity relationship could be quantitatively established for oxide-derived metals, it is unclear if the relationship would also pertain to nanoparticles. Establishing a design principle for nanoparticles is very important for applications because nanoparticles have much higher surface area-to-mass ratios than nanocrystalline films, which enables much lower catalyst loadings. In light of these issues, we sought to investigate the relationship between grain boundaries and catalytic activity with metal nanoparticles whose grain boundary densities could be varied and quantified directly by TEM without laborious sample preparation. Using metal vapor deposition and thermal annealing, we have prepared electrodes composed of Au or Cu nanoparticles on carbon nanotubes (Au/CNT or Cu/CNT) with different grain boundary densities that can be quantified by TEM. Using these electrodes, we have shown that there is a direct correlation (linear relationship) between the fraction of the nanoparticle surfaces comprised of grain boundary surface terminations (hereafter referred to as the "grain boundary surface density) and the specific activity for CO_2 reduction to CO (with Au/CNT) and CO reduction to ethanol and acetate (with Cu/CNT). Our work with Au was recently published.[22] The results for Cu are described in greater detail below. To our knowledge, these results are the first quantitative grain boundary–activity correlations for any electrochemical reaction.

Oxide-derived Pb

We completed the work on oxide-derived Pb (OD-Pb) described in last year's technical report and published the results in *ACS Catalysis*.[23] The remarkable feature of OD-Pb electrodes is that they suppress the H_2O reduction reaction by up to 700-fold relative to Pb foil electrodes (i.e. 700-fold less specific current density for H_2 evolution) while retaining the same specific activity for CO_2 reduction. Based on electrokinetic experiments, we proposed that OD-Pb electrodes have a very high coverage of a thin Pb oxide layer that blocks H_2 evolution but is catalytically active for CO_2 reduction. In this respect, Pb is similar to Sn. We previously showed that Sn electrodes require the presence of a surface Sn oxide in order to reduce CO_2.[24] This conclusion was supported by recent in situ IR studies from another group.[25]

Progress

In the past year, our finding of a quantitative correlation between grain boundary density and catalytic activity has provided the first experimentally validated design principle for metal nanoparticle catalysts of CO_2 and CO reduction. This development marks a major step towards "CO_2 recycling" applications. Nanoparticles are desirable for electrolytic devices because they have high surface area-to-volume ratios, which enables low catalyst loading, and they can be integrated with diverse electrode morphologies. Indeed, most industrial heterogeneous catalysts are nanoparticles. Nearly all efforts to develop new nanoparticle electrocatalysts have focused on improving activity by tailoring nanoparticle size, shape, and (alloy) composition. Our results show quantitatively the advantage of using bulk defects—grain boundaries—to create catalytically active surfaces. Our most grain boundary-rich Cu nanoparticle catalysts are the most active and selective CO electroreduction catalysts that have been reported to date, with 3–6-fold higher specific activity than oxide-derived Cu, the genesis of this project, and up to 73% selectivity for CO vs H_2O reduction at low overpotential. Their mass activity is 1.5 A of CO reduction current per g of Cu at –0.3 V, setting the benchmark for this reaction. The linearity of the structure–activity relationship both for CO reduction with Cu and CO_2 reduction with Au indicates that there is substantial room for improvement by further increasing grain boundary density in nanoparticle catalysts. We anticipate that our work will spur the development of new synthetic methods to prepare nanoparticles with maximal grain boundary density, as well as the use of "grain boundary engineering" to target specific types of grain boundaries.

Future Plans

Having established a quantitative grain-boundary–activity correlation, our future work will aim to elucidate the structural basis for this relationship and further develop catalysts that are suitable for electrosynthetic devices. Specific tasks include: i) probing grain boundary geometry (i.e. mis-orientation angle) in Cu/CNT and Au/CNT electrodes to determine its effect on activity; ii) obtaining high-resolution images of grain boundary surface terminations in Au/CNT and Cu/CNT electrodes; iii) performing CO-TPD on Cu/CNT electrodes to determine the relationship between grain boundary surface density and CO binding sites; iv) imaging grain boundary migration at elevated temperature using high-resolution TEM with a temperature-controlled sample holder; v) developing alternatives to vapor deposition for the synthesis of grain boundary–rich Cu nanoparticles; vi) measuring the electrokinetics of CO reduction of grain boundary–rich Cu nanoparticles at high CO flux; vii) testing grain boundary-rich catalysts in flow cells to determine their performance under conditions relevant to practical electrosynthesis.

Publications and Patents

1. Lee, C. H.; Kanan, M. W. Controlling H^+ vs CO_2 Reduction Selectivity on Pb Electrodes. *ACS Catal.* **5**:1, 465–469 (2015).
2. Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. Grain-Boundary-Dependent CO_2 Electroreduction Activity. *J. Am. Chem. Soc.* **137**:14, 4606–4609 (2015).
3. Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. A direct grain-boundary–activity correlation for CO electroreduction on Cu. *submitted* (2015).
4. Verdaguer-Casadevall, A.; Li, C. W.; Johansson, T. P.; Scott, S. B.; McKeown, J. T.; Stephens, I. E. L.; Kanan, M. W.; Chorkendorff, I. Probing the active surface sites for CO reduction on oxide-derived copper electrocatalysts. *in preparation* (2015).

References

1. Y. Hori, in *Modern Aspects of Electrochemistry,* C. G. Vayenas, White, R. E., Gamboa-Aldeco, M. E., Ed. (Sringer, New York, 2008), vol. 42, pp. 89.
2. K. P. Kuhl, E. R. Cave, D. N. Abram, T. F. Jaramillo, New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energ. Environ. Sci.* **5**, 7050-7059 (2012).
3. Y. Hori, K. Kikuchi, S. Suzuki, Production of CO and CH_4 in Electrochemical Reduction of CO_2 at Metal-Electrodes in Aqueous Hydrogencarbonate Solution. *Chem. Lett.*, 1695-1698 (1985).
4. Y. Hori, A. Murata, R. Takahashi, Formation of Hydrocarbons in the Electrochemical Reduction of Carbon-Dioxide at a Copper Electrode in Aqueous-Solution. *J. Chem. Soc. Farad. Trans. I* **85**, 2309-2326 (1989).
5. Y. Hori, I. Takahashi, O. Koga, N. Hoshi, Selective formation of C_2 compounds from electrochemical reduction of CO_2 at a series of copper single crystal electrodes. *J. Phys. Chem. B* **106**, 15-17 (2002).
6. Y. Hori, A. Murata, R. Takahashi, S. Suzuki, Electroreduction of CO to CH_4 and C_2H_4 at a Copper Electrode in Aqueous-Solutions at Ambient-Temperature and Pressure. *J. Am. Chem. Soc.* **109**, 5022-5023 (1987).
7. Y. Hori, R. Takahashi, Y. Yoshinami, A. Murata, Electrochemical reduction of CO at a copper electrode. *J. Phys. Chem. B* **101**, 7075-7081 (1997).
8. K. J. P. Schouten, Z. S. Qin, E. P. Gallent, M. T. M. Koper, Two Pathways for the Formation of Ethylene in CO Reduction on Single-Crystal Copper Electrodes. *J. Am. Chem. Soc.* **134**, 9864-9867 (2012).
9. K. J. P. Schouten, E. P. Gallent, M. T. M. Koper, Structure Sensitivity of the Electrochemical Reduction of Carbon Monoxide on Copper Single Crystals. *ACS Catal.* **3**, 1292-1295 (2013).
10. A. A. Peterson, J. K. Norskov, Activity Descriptors for CO2 Electroreduction to Methane on Transition-Metal Catalysts. *J. Phys. Chem. Lett.* **3**, 251-258 (2012).
11. J. H. Montoya, A. A. Peterson, J. K. Norskov, Insights into C–C Coupling in CO_2 Electroreduction on Copper Electrodes. *ChemCatChem* **5**, 737-742 (2013).
12. J. H. Montoya, C. Shi, K. Chan, J. K. Norskov, Theoretical Insights into a CO Dimerization Mechanism in CO2 Electroreduction. *J. Phys. Chem. Lett.* just accepted, (2015).
13. R. Reske, H. Mistry, F. Behafarid, B. R. Cuenya, P. Strasser, Particle Size Effects in the Catalytic Electroreduction of CO_2 on Cu Nanoparticles. *J. Am. Chem. Soc.* **136**, 6978–6986 (2014).
14. C. W. Li, M. W. Kanan, CO_2 Reduction at Low Overpotential on Cu Electrodes Resulting from the Reduction of Thick Cu_2O Films. *J. Am. Chem. Soc.* **134**, 7231-7234 (2012).
15. C. W. Li, J. Ciston, M. W. Kanan, Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper. *Nature* **508**, 504-5-7 (2014).
16. R. Kas, R. Kortlever, A. Milbrat, M. T. M. Koper, G. Mul, J. Baltrusaitis, Electrochemical CO_2 reduction on Cu_2O-derived copper nanoparticles: controlling the catalytic selectivity of hydrocarbons. *Phys. Chem. Chem. Phys.* **16**, 12194–12201 (2014).
17. D. Ren, Y. Deng, A. D. Handoko, C. S. Chen, S. Malkhandi, B. S. Yeo, Selective Electrochemical Reduction of Carbon Dioxide to Ethylene and Ethanol on Copper(I) Oxide Catalysts. *ACS Catal.* **5**, 2814-2821 (2015).
18. J. Qiao, M. Fan, Y. Fu, Z. Bai, C. Ma, Y. Liu, X.-D. Zhou, Highly-active copper oxide/copper electrocatalysts induced from hierarchical copper oxide nanospheres for carbon dioxide reduction reaction. *Electrochim. Acta* **153**, 559-565 (2015).
19. D. Kim, S. Lee, J. D. Ocon, B. Jeong, J. K. Lee, J. Lee, Insights into an autonomously formed oxygen-evacuated Cu_2O electrode for the selective production of C_2H_4 from CO_2. *Phys. Chem. Chem. Phys.* **17**, 824-830 (2015).
20. T. Radetic, F. Lancon, U. Dahmen, Chevron defect at the intersection of grain boundaries with free surfaces in Au. *Phys. Rev. Lett.* **89**, 085502 (2002).
21. S. S. Fu, G. A. Somorjai, Interactions of O_2, CO, CO_2, and D_2 with the Stepped Cu(311) Crystal-Face - Comparison to Cu(110). *Surface Science* **262**, 68-76 (1992).
22. X. Feng, K. Jiang, S. Fan, M. W. Kanan, Grain-Boundary-Dependent CO_2 Electroreduction Activity. *J. Am. Chem. Soc.* **137**, 4606-4609 (2015).

23. C. H. Lee, M. W. Kanan, Controlling H^+ vs CO_2 Reduction Selectivity on Pb Electrodes. *ACS Catal.* **5**, 465-469 (2015).
24. Y. H. Chen, M. W. Kanan, Tin Oxide Dependence of the CO_2 Reduction Efficiency on Tin Electrodes and Enhanced Activity for Tin/Tin Oxide Thin-Film Catalysts. *J. Am. Chem. Soc.* **134**, 1986-1989 (2012).
25. M. F. Baruch, J. E. Pander, J. L. White, A. B. Bocarsly, Mechanistic Insights into the Reduction of CO_2 on Tin Electrodes using in Situ ATR-IR Spectroscopy. *ACS Catal.* **5**, 3148-3156 (2015).

Contacts

Matthew Kanan: mkanan@stanford.edu
Xiaofeng Feng: xffeng@stanford.edu
Christina Li: cwli1@stanford.edu
Allison Yau: alliyau@stanford.edu
Changhoon Lee: chl1@stanford.edu