Nanostructured Electrocatalysts for CO$_2$ Conversion

by

Phil De Luna

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Department of Materials Science & Engineering

University of Toronto

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Abstract

Renewables-powered electrochemical activation and conversion of water + CO$_2$ into hydrocarbons and oxygenates could potentially offer a sustainable, low-net-emissions, route to produce many of the world’s most needed commodity chemicals and fuels. In this thesis I report progress in the synthesis, characterization, and computational modelling of electrocatalyst materials for the CO$_2$ reduction reaction. I show how experiment, theory, and spectroscopy can be used together to uncover physicochemical phenomena; I build nanostructured materials to exploit these phenomena; and I integrate these materials into electrocatalytic systems.

I first begin by examining the pathways toward industrial implementation of CO$_2$ reduction technology. I give a brief technoeconomic analysis and carbon emissions assessment of certain valuable products.

I then describe the concept of Field-Induced Reagent Concentration (FIRC) on gold nanoneedle catalysts. This entails the use of nanostructured morphologies to produce a high local electric field that attracts positively charged cations to stabilize CO$_2$ reaction intermediates to
produce CO with Faradaic efficiencies above 90% and overpotentials of 240 mV. I continue with a description of the potential for tandem catalysis between metal-organic frameworks (MOFs) and gold nanoneedles towards tuning CO\(_2\) reduction. Next, I describe how thin layers of amorphous sulfide-doped tin catalysts on top of gold nanoneedles can modulate CO\(_2\) reduction towards formic acid synthesis with Faradaic efficiencies of 93% and current densities of 55 mA cm\(^{-2}\) over 40 hours. I then demonstrate a new bottom-up synthesis, catalyst electro-redeposition, that allows simultaneous control over morphology and oxidation state of copper to produce ethylene selectively. I use a combination of spectroscopy and computational simulation to explain the electronic structure-property relationships of this new catalyst and report a partial ethylene current density of 160 mA cm\(^{-2}\) and an ethylene/methane ratio of 200.

I conclude by describing emerging directions in the field including greater understanding of electrocatalyst evolution, inspiration from biology, and integration into electrolyzer systems. I discuss the wider relevance of nanostructuring as a means to control and enhance catalytic activity.
Acknowledgments

I begin with an apology for the length of this section – please feel free to skip it completely, I promise to not be offended. The accomplishments described within this thesis are only possible because of the tremendous belief, trust, and support that the following people have graciously given me. Without them, none of this would be possible.

I was a combination of nervous, scared, curious, and excited going into my first one-on-one meeting with Ted. His considerable reputation preceded him. I still remember the intensity of his gaze as we spoke for the first time. Surely a man who has accomplished so much, in such a short time, and with such intensity must be part cyborg, or rather multiple clones, or maybe a brilliant insomniac. Early in my PhD I had written Ted about a falling out with my MSc supervisor, about how grateful I had been for the opportunities and the trust he had shown me, opportunity and trust that I had longed for but never received from my previous mentor. He told me that to get trust you need to give it. The value of trust is sharply obvious in the Sargent group, a bustling hive of exceptional scientists who all work collaboratively and openly. Over the years I have had the joy and privilege to learn more about the man behind the gaze. I have seized every opportunity to probe Ted on his motivations, his plans and strategies, his advice on problems and challenges, all to learn about his success in hopes of recreating a little bit of it for myself. I have learned so much from Ted throughout my PhD, not only about science and academia, but about leadership and communication, about trust and respect, about the courage to fail and the strength to continue when you do. But most of all I learned the power of writing in bullet points.

Ted, thank you for letting me be a part of your lab, for sending me around the world to preach the gospel of the Sargent lab, for trusting me to help build scientific collaborations and organize rich research symposia, for CIFAR, for XPRIZE, for supporting every scholarship, every publication, every conference, every media interview, and every opportunity. I owe my scientific career to you and for that I am eternally grateful. I hope I can live up to the support and trust that you have invested in me.

A PhD is an exercise in determination. Nights can be long waiting for an experiment to finish, working on getting that one figure just right, or finishing slides for a conference. However,
there is some comfort in knowing that sitting next to you are people going through the same thing. I now turn my attention to thanking my fellow students, for bringing fun into the lab and becoming my friends rather than just being my colleagues. To Andrew, for reminding me to be about the music – you’re the sweetest metalhead I’ve ever known. To Rafa, for his company during those cold nights in Saskatoon, the next SkipTheDishes is on you. To Olivier, for the deep conversations about life, career, and happiness on our drives up to Ottawa. To James, for being James – the trap-loving, meme-making, breakfast-building tour de force that you are. To Grant, for being a wise source of advice during the thesis writing sprint. To Petar, for always being the best dressed and giving me an image to aspire to when I grow up. To Andy and Jeff, for always being there to play a little Smash. Thank you to all the former students who have moved on to great things – Brandon, Xiwen, Mengxia, Amireza, Chris – for giving me an example to follow. Thank you to Jeannie, Stacy, and Jennifer for making sure the group continues to exist – without you, we would be in utter chaos. To all the current students and those yet to come whom I didn’t have the privilege to know more deeply, I offer this bit of advice: While the pressures will seem great and the expectations high, while you may feel like time is moving at lightning pace and you haven’t accomplished what you set out to, take a moment to step back, to appreciate where you are and how far you’ve come. A PhD is one of the most rewarding things you will experience, because it is entirely and completely a product of you – you can do this.

When I began in the Sargent group three short years ago the catalysis research effort was essentially four people, Cao, Min, Bo, and Sherry. Today it is a juggernaut of science, 25+ talented researchers publishing discoveries month after month with no end in sight. I feel so privileged and proud to be part of the growth of this group. I want to acknowledge the contributions of every single person who has brought the Sargent group to the forefront of electrocatalysis research. But for brevity’s sake I will acknowledge more deeply two people who I believe are the cornerstones of the catalysis group – Cao and Alex Ip. To Cao, your genius is matched only by your warm spirit. You are an inspirational scientist and engineer, you attack every problem with creativity and vigor, and I have learned so much about electrons and protons and doing good science from you. You have been so humble, knowing full well that you contribute to the success of every person in the catalysis lab more than anyone, and yet you have only been kind and genuine to those who seek your wisdom and help. In the history books of the future I have no doubt in my mind your name
will be mentioned for all the discoveries you have made and the ones you have yet to uncover. To Alex, thank you for all your support and advice throughout the years, I have learned so much about loyalty and hard work from watching you and working beside you. Your leadership and tenacity brought us through the XPRIZE, bringing us closer to a goal we originally thought impossible. Thank you for being an academic big brother and mentor, for always being there to listen to my monthly identity crisis, for bringing me back from the brink when my imposter syndrome would run wild from the pressures of the day.

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To my little sister, whose life is bright and just beginning. My only advice to you is to do what you love, to do it with intensity, and if you don’t know what that is then do anything and everything until you find it. Don’t let the world tell you what you can do, do what you want and let the world figure you out instead. While I wasn’t around much as you were growing up – I was too busy trying to figure out what I loved – I hope I can be around more now that you’re beginning
your journey to adulthood. Thanks for being my sister and I will always be there to help you when you need it.

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# Table of Contents

## Contents

Acknowledgments ................................................................................................................................. iv

Table of Contents ................................................................................................................................. viii

List of Tables ......................................................................................................................................... xi

List of Figures ......................................................................................................................................... xii

List of Appendices ............................................................................................................................... xix

Chapter 1 | Introduction ............................................................................................................................ 1

1.1 Electrocatalytic CO₂ Conversion ..................................................................................................... 2

1.2 Fundamental Catalytic Challenges ................................................................................................. 3

1.3 Scaling Relations and CO₂ Mechanisms ......................................................................................... 5

1.4 Strategies to Increase Activity ........................................................................................................ 7

Chapter 2 | A Current Survey of the CO₂RR Field ...................................................................................... 9

2.1 CO₂RR Figures of Merit ................................................................................................................. 9

2.2 Tools to Explore CO₂RR ................................................................................................................ 12

2.2.1 Density Functional Theory ........................................................................................................ 13

2.2.2 In-situ X-ray Spectroscopy ......................................................................................................... 14

2.3 Pathways toward Industrial Implementation .................................................................................. 16

2.3.1 Technoeconomic and carbon emissions analysis ...................................................................... 17

Chapter 3 | High Local Electric Fields Effects in Catalysis ..................................................................... 21

3.1 Field Induced Reagent Concentration ............................................................................................ 22

3.2 Computational Simulations ........................................................................................................... 23

3.3 Synthesis and Characterization of Gold Nanoneedles .................................................................. 27

3.4 CO₂RR Experiments on Gold Nanoneedles .................................................................................. 28

3.5 Impact of Work ............................................................................................................................... 30
<table>
<thead>
<tr>
<th>Chapter 4</th>
<th>Heterostructures Towards Tandem Catalysis</th>
<th>32</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Metal Organic Frameworks for CO$_2$RR</td>
<td>33</td>
</tr>
<tr>
<td>4.2</td>
<td>Synthesis of thin film MOFs on AuNMEs</td>
<td>34</td>
</tr>
<tr>
<td>4.3</td>
<td>Characterization and Electrochemical Stability</td>
<td>36</td>
</tr>
<tr>
<td>4.4</td>
<td>CO$_2$RR Experiments on MOF@AuNMEs</td>
<td>39</td>
</tr>
<tr>
<td>4.5</td>
<td>Impact of Work</td>
<td>42</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 5</th>
<th>Thin Catalyst Overlayers Modulate Electrocatalysis</th>
<th>44</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Sulfide-Derived Catalysts for Formate Production</td>
<td>45</td>
</tr>
<tr>
<td>5.2</td>
<td>Computational Studies</td>
<td>45</td>
</tr>
<tr>
<td>5.3</td>
<td>Synthesis and Characterization of Sulfur-Modulated Tin Catalysts</td>
<td>48</td>
</tr>
<tr>
<td>5.4</td>
<td>CO$_2$RR Experiments on Sn(S) Catalysts</td>
<td>52</td>
</tr>
<tr>
<td>5.5</td>
<td>Impact of Work</td>
<td>54</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 6</th>
<th>Structural Evolution Controls Activity</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Electro-Redeposition of Copper</td>
<td>56</td>
</tr>
<tr>
<td>6.2</td>
<td>Synthesis and activity of ERD-Cu</td>
<td>57</td>
</tr>
<tr>
<td>6.3</td>
<td>Structural Characterization of ERD-Cu</td>
<td>59</td>
</tr>
<tr>
<td>6.4</td>
<td>In-situ X-ray spectroscopy</td>
<td>62</td>
</tr>
<tr>
<td>6.5</td>
<td>Investigating Structure-Property Relationships</td>
<td>65</td>
</tr>
<tr>
<td>6.6</td>
<td>Impact of Work</td>
<td>69</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 7</th>
<th>Conclusions and Outlook</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Future Research Directions</td>
<td>70</td>
</tr>
<tr>
<td>7.2</td>
<td>Emerging Concepts in CO$_2$RR</td>
<td>71</td>
</tr>
<tr>
<td>7.2.1</td>
<td>Deepening Understanding of Electrocatalyst Functioning</td>
<td>71</td>
</tr>
<tr>
<td>7.2.2</td>
<td>Inspiration from Biology</td>
<td>73</td>
</tr>
<tr>
<td>7.2.3</td>
<td>Integration Toward Working Systems</td>
<td>74</td>
</tr>
</tbody>
</table>
7.3 Summary...................................................................................................................................................... 75

Chapter 8 | Original Contributions ................................................................................................................................. 76

References 80

Appendix A Methods .................................................................................................................................................. 95

Chapter 2 Methods .................................................................................................................................................... 95

Chapter 3 Methods .................................................................................................................................................. 101

Chapter 4 Methods .................................................................................................................................................. 105

Chapter 5 Methods .................................................................................................................................................. 108

Chapter 6 Methods .................................................................................................................................................. 110

Appendix B DFT Tables .............................................................................................................................................. 116

Chapter 3 DFT Tables .............................................................................................................................................. 116

Chapter 5 DFT Tables .............................................................................................................................................. 117

Chapter 6 DFT Tables .............................................................................................................................................. 119

Appendix C Abbreviations & Acronyms ....................................................................................................................... 121

Copyright Acknowledgements .................................................................................................................................. 123
List of Tables

Table 2.1 | Common definitions of CO₂RR figures of merit ................................................................. 9
Table 2.2 | Maximum reported Faradaic efficiency for various CO₂RR products over time. ............ 11
Table 2.3 | Current state of CO₂ electrolyzers in comparison with hydrogen electrolyzers. ............ 12
Table 2.4 | Comparison of production cost and carbon emissions ......................................................... 20
Table 8.1 | Product specific constants .................................................................................................. 98
Table 8.2 | Product constants for the carbon emissions life-cycle assessment .................................... 99
Table 8.3 | Maximum reported FE over time ......................................................................................... 99
Table 8.4 | Summary of simulation parameters as calculated from DFT ............................................. 116
Table 8.5 | Optimized structural parameters ...................................................................................... 117
Table 8.6 | Gas phase molecules and their thermodynamic quantities (eV) ...................................... 117
Table 8.7 | Adsorbate molecules and their thermodynamic quantities (eV) .................................... 117
Table 8.8 | Theoretical limiting potential (V vs. RHE, pH=0, 273 K, 1 atm). ..................................... 118
Table 8.9 | Calculated bader partial atomic charges in units of e .................................................... 118
Table 8.10 | Surface energies for various facets of SnS slab models .................................................... 118
Table 8.11 | Thermodynamic quantites used in DFT calculations ......................................................... 119
Table 8.12 | Gibbs free energy of formation for reaction intermediates and CO binding energies .......... 119
List of Figures

**Figure 1.1 |** Closing the carbon loop. The use of electrocatalytic CO2 reduction to convert captured CO2 (either from flue stacks or directly from the atmosphere) using renewable energy into chemical feedstocks or fuels for long-term energy storage. This figure was created entirely by me..................................................2

**Figure 1.2 |** CO2RR Mechanisms. (a) Reaction mechanism of CO2 reduction to CO on a gold catalyst surface. COOH* and CO* are the main bound intermediates formed after a proton-coupled electron transfer. (b) Reaction energy diagram of CO2 to CO showing the importance of catalysts lowering the kinetic and thermodynamic energy barriers. (c) Linear scaling relations of COOH* and CO* show how the binding energies of different transition metals (yellow circles) are highly correlated and difficult to decouple. This figure was created entirely by me.......................5

**Figure 1.3 |** Strategies to increase CO2RR activity. (a) Scheme of carbon dioxide reduction to carbon monoxide. Catalytic design principles for CO2RR related to (b) composition, (c) coordination environment, and (d) nanostructuring. This figure was created by me in collaboration with Dr. Michael Ross.................................................................7

**Figure 2.1 |** X-ray absorption spectroscopy. (Left) The mechanism of photoelectron emission via high-energy x-rays. (Right) schematic of photoelectron scattering in a periodic material. This figure was created by me.................................................................15

**Figure 2.2 |** Production costs of electrosynthesized chemicals. Technoeconomic analysis of hydrogen, carbon monoxide, ammonia, and ethylene costs as a function of electrolyzer energy conversion efficiency and electricity costs. Assumes a CO2 price of $30/ton, Faradaic efficiency of 90%, current density of 500 mA/cm2, electrolyzer cost of $300/kW, and plant lifetime of 30 years. This figure and the data described therein were created by me. Details on the technoeconomic model can be found in Appendix A Methods.................................................................18

**Figure 2.3 |** The emissions impact of electrosynthesized chemicals. (a) Market size and product intensity, the amount of emissions per kWh, of ethylene, ethanol, carbon monoxide, and formic acid. Carbon emissions assessment of (b) formic acid, (c) carbon monoxide, (d) ethylene, and (e)
ethanol. Assuming a plant capacity of 500 MW and global warming potential of formic acid and carbon monoxide to be 1 kg CO₂/kg product and a GWP of ethylene and ethanol to be 5.75 kg CO₂/kg product. This figure and the data described therein were created by me. Details on the technoeconomic model can be found in Appendix A Methods.

**Figure 3.1** | Thermodynamic barriers for CO₂RR on Au surfaces with and without K⁺. Gibbs free energy ΔG diagrams of the electrochemical reduction of CO₂ to CO on Au(111) (a), Au(100) (b), Au(110) (c) and Au(211) (d) facets in the presence of adsorbed K⁺ and in the absence of adsorbed K⁺.

**Figure 3.2** | Bader charge analysis. Volume slice of the DFT calculated charge density for K⁺ on Au(111). Volume slice of calculated charge densities. Bader partial atomic charges are indicated in black with and without K⁺. The volume slice is visualized from the electron density with an isovalue of 0.5.

**Figure 3.3** | Mean square deviation with K⁺. (a) Average mean square displacement (MSD) of CO₂ on Au(111) surface with and without K⁺ in the system. (b) MSD of CO₂ on Au(111), Au(110), Au(100) and Au(211) surface in the presence of K⁺.

**Figure 3.4** | Radial distribution function and interaction energies. (Left) RDF of CO₂ to Au(111) as a function of potassium from an ensemble average of 25 ab-initio molecular dynamics simulations (5 ps) shows CO₂ is closer to the surface of gold on average in the presence of K⁺ than without K⁺. Snapshot configurations of CO₂ on gold are shown on the left. (Right) Calculated interaction energy of CO₂ vary with C-Au distance under the conditions with or without K⁺. The change in interaction energy increases as the CO₂ approaches the Au(111) surface past its equilibrium distance. The interaction energy is consistently less in the presence of an adsorbed K⁺ (red) than without K⁺ (black).

**Figure 3.5** | Electric Field Simulations. (a) Free electron density distribution on the surface of electrodes is shown as a colour map. Electrostatic field distribution around the electrode is shown as a group of arrows, where the size and direction of each arrow represent the magnitude and direction of the field at the arrow’s spatial position. The tip radius of the structure in each panel is
5 nm (left), 60 nm (middle) and 140 nm (right). Scale bars represent 5 nm. (b) Electrostatic field intensity at the electrode tip increases as the tip radius decreases. Figure prepared by Yuanjie Pang.

**Figure 3.6** | Physical characterization of Au nanoneedles, rods, and particles. (a, e, i), Scanning electron microscopy (SEM) images; (b, f, j,) TEM images; (c, g, k,) Electric field distribution of Au needles, rods and particles deduced using Kelvin probe atomic force microscopy. (d,) SEM image of Au needle with secondarily deposited Au particles. (h,) ECSA-normalized field-induced concentration of adsorbed K$^+$ on Au needles, rods and particles. The concentration of K$^+$ was measured via inductively coupled plasma (ICP) optical emission spectrometry. The inset shows the process of measuring the field-induced adsorbed K$^+$. (i), Current on a single Au needle, rod and particle with a thin TiO$_2$ insulator layer at a bias of −1 V. The inset shows the current measurement conditions. Figure prepared by me and Min Liu.

**Figure 3.7** | CO$_2$RR performance. (a) Current–voltage curves on Au needles, rods and particles obtained from the linear sweep voltammetry scans. Scan rate, 10 mV s$^{-1}$. (b) CO$_2$ reduction activity of Au needles, rods and particles at −0.35 V versus RHE. Total current density (left axis) versus time and CO Faradaic efficiency (right axis) versus time. (c) CO Faradaic efficiencies on Au needles, rods and particles at different applied potentials. (d) ECSA-normalized CO production partial current density versus potential on Au needles, rods and particles. Figure prepared by Min Liu with data input by me.

**Figure 3.8** | CO$_2$RR performance in various electrolyte conditions. (a) Current densities and Faradaic efficiencies versus K$^+$ concentrations on Au needles at −0.35 V versus RHE. (b) Current densities and Faradaic efficiencies versus K$^+$ concentrations on planar Au at −0.4 V versus RHE. (c) CO$_2$ reduction performance of Au needles in saturated KHCO$_3$ solution. Figure prepared by Min Liu with data input by me.

**Figure 4.1** | Schematic illustration of MOF thin film growth on AuNMEs. (a) layer-by-layer method or the (b) solvothermal method.
Figure 4.2 | Electrochemical and physical characterization. (a) Cyclic voltammetry (0 to -1 V vs. RHE, 0.1 M KHCO₃) plots of the different thin film MOFs deposited on Au NME. XPS measurements of Zn (b), Cu (c), Y (d), and Al (e) of AuNME/MOF thin films before and after reaction. XRD measurements of ZIF-8, Cu(bdc)·xH₂O (f), RE-ndc-fcu-MOF and Al₂(OH)₂TCPP (g) thin films before and after reaction. ................................................................. 37

Figure 4.3 | SEM images of MOFs. ZIF-8, Cu(bdc)·xH₂O, RE-ndc-fcu-MOF, and Al₂(OH)₂TCPP thin films on AuNME before (top two rows) and after electrochemical reaction (bottom row). ........... 39

Figure 4.4 | Electrocatalytic activity of MOF@AuNMEs. (a) Linear sweep voltammetry (LSV) scans (0 to -1 V vs. RHE, 0.1 M KHCO₃) of different MOF@AuNMEs and AuNME control. (b) Chronoamperometry (CA) plot (-0.5 V vs. RHE, 0.1 M KHCO₃) of MOF@AuNMEs and AuNME control for an hour at -0.5 V vs. RHE. (c) Faradaic efficiencies of MOF@AuNMEs and AuNME control. (d) SEM image of the AuNME tip showing the underlying metal exposed after running at -1.0 V vs. RHE. ........................................................................................................ 41

Figure 5.1 | DFT calculations on Sn(S). (a) Optimized surface slab structures of pure Sn, S-modulated Sn, and SnS. (b) Gibbs free energies of formation (ΔGformation) for HCOO* (yellow), COOH* (gray), and H* (blue) intermediates, which are the rate-limiting intermediates along the reaction pathway to produce formate, carbon monoxide, and hydrogen gas, respectively. (c) Volume slice of the charge densities through the middle of the oxygen atom of a bound HCOO* intermediate. (d) Atomic accessible surface area of the metal slab normalized to the number of tin atoms as a function of sulfur content................................................................. 47

Figure 5.2 | Fabrication of nanostructured Sn(S) catalysts. (a-c) Schematic and SEM images of the process leading to the fabrication of Sn(S) nanostructured electrodes. (a) Au needles. (b) Au needles after SnS deposition by ALD process. (c) Au needles coated with sulfur-modulated-tin films. (d) A SnSₓ slab is conformally deposited by ALD on top of the nanostructured metal backbone. (e) The selective reduction of SnSₓ leads to Sn(S) films, which promotes CO₂RR toward formate. The dashed circle means active sites for formate generation. This figure was prepared by co-first author Xueli Zheng................................................................. 48
Figure 5.3 | Characterization of sulfur-modulated tin catalysts. (a) High-resolution transmission electron microscope (HRTEM) image of the ALD SnSx before reaction showing a highly polycrystalline surface. Scale bar represents 5 nm. (b,c) Fast Fourier transform (FFT) of the polycrystalline region (b) and one specific crystalline grain (c). (d,e) HRTEM image of the reduced Sn(S) active catalyst after reaction showing a uniform amorphous layer on the surface. Scale bar represents 20 nm for (d); scale bar represents 5 nm for (e). Inset is the FFT of the amorphous region. (f-i) STEM image (f) of Sn(S)/Au and the corresponding EDS mapping to show homogeneously dispersed Au (g), Sn (h), and S (i). Scale bar represents 100 nm. This figure was prepared by myself, Yifan Li, and Xueli Zheng.

Figure 5.4 | Electronic structure of Sn(S) and Sn. (a) In situ Sn L\textsubscript{3}-edge XANES spectra of Sn NPs, SnS, Sn NPs at −0.7 V versus RHE, and Sn(S) at −0.7 V versus RHE. Inset shows zoom in of the pre-edge energy range. (b) Sn L\textsubscript{3}-edge spectra of Sn(S) and Sn NPs on carbon paper after reaction (edge shift indicated by a red arrow). (c) Sn K-edge of Sn(S) and relevant controls. Inset shows zoom in of the pre-edge energy range. (d) XPS spectra of Sn(S), Sn NPs, and ALD SnSx. This figure was prepared by Xueli Zheng.

Figure 5.5 | Performance of Sn(S) catalysts. Experiments performed in a three-electrode configuration in CO\textsubscript{2} saturated 0.1 M KHCO\textsubscript{3}. (a) The CO\textsubscript{2}RR polarization curve of catalysts loaded on Au needles and Sn foil, respectively. (b) Potential dependence (with iR corrected) of Faradaic efficiencies and current densities for CO\textsubscript{2}RR on Sn(S)/Au (squares) and Sn NPs/Au (circles). (c) Stability test of Sn(S) at −0.75 V versus RHE (iR corrected). This figure was prepared by Xueli Zheng.

Figure 6.1 | CO\textsubscript{2}RR activity of ERD-Cu. (a) FEs of ERD Cu at a range of applied potentials showing all products. (b) Current densities of the catalyst over 1 h of operation at different applied potentials. c, CO\textsubscript{2}RR gas product FEs. (d) Plot of ethylene/methane ratio versus ethylene partial current density for a range of catalysts.

Figure 6.2 | Growth of ERD-Cu nanostructures. (a) Schematic cartoon of the electro-growth process whereby simultaneous dissolution and re-deposition of copper results in structured deposits. Scale bar is set to 5 μm. (b) SEM images of the key structure features at their specific
applied potentials after at least 1 hour of reaction. (c) Evolution of nanoclusters (-0.7 V vs. RHE), nanoneedles (-1.0 vs. RHE), nanowhiskers (-1.2 V), and dendrites (-1.4 V) at increasing negative potential. All potentials are iR corrected and vs. RHE.

**Figure 6.3** | Surface characterization of ERD-Cu. Dark field microscope images of ERD-Cu after 1 hour of reaction at (a) -0.8 V vs. RHE and (b) -1.6 V vs. RHE, scale bar is 100 μm. TEM images of ERD-Cu before reaction (c) and after reaction (d), scale bar is 100 nm. (e) XRD plot of the ERD-Cu before reaction (red) and after reaction at varying applied potentials. (f) SEM images of ERD-Cu under -1.0 V vs. RHE taken at 2, 5, 20, and 40 minutes from left to right. (g) Scanning Auger microscopy images of ERD-Cu showing the Cu nanostructures (red) on carbon (green).

**Figure 6.4** | X-ray spectroscopy measurements. (a) In-situ Cu L$_3$-edge soft x-ray absorption spectroscopy spectra of ERD-Cu at different applied potentials (solid lines) and ex-situ sXAS spectra of reference standard Cu metal (red dotted), Cu$_2$O (green dotted), and CuO (purple dotted). (b) Cu L$_3$-edge spectra with respect to time of ERD-Cu under a constant applied potential of 0.28 V vs. RHE. (c) ERD-Cu under an applied potential of -1.2 V vs. RHE over the course of 1 hour. (d) Calculated ratio of Cu oxidation states from linear combination fitting as a function of applied potential. (e) Calculated ratio of Cu oxidation with respect to time during 1 hour of reaction at -1.2 V vs. RHE. sXAS 2D mapping of the Cu intensity with the region of interest set to 940 eV with a width of 100 eV (f) before and (g) after running CO$_2$RR.

**Figure 6.5** | Porous copper nanoneedle (NN-Cu) controls. Before (a,b) and after (c,d) reaction at -1.2 V vs. RHE over at least 1 hour of operation.

**Figure 6.6** | Catalytic activity of NN-Cu control. (a) Faradaic efficiencies as a function of applied potential for NN-Cu control. (b) The Faradaic efficiencies of C1 vs C2+ products as a function of applied potential. (c) Chronoamperometry plots showing the steady current density of NN-Cu. (d) the Faradaic efficiency of CO$_2$RR gaseous products.

**Figure 6.7** | DFT studies of ERD-Cu. C1 and C2 electroproduction as a function of metal oxidation state. (a) The reaction mechanisms for the hydrogenation of bound CO to CH$_4$ (red) and the CO-CO dimerization pathway to C$_2$H$_4$ (blue). (b) The Gibbs free energy of formation of COH* and
OCCOH* on Cu(111), Cu(211), ERD-Cu(111), and ERD-Cu(211) representative of flat copper, high-curvature copper, flat ERD-Cu, and high-curvature ERD-Cu respectively. (c) Optimized structure of bound OCCOH* on ERD-Cu at the interface of Cu+ and Cu0 species.

**Figure 7.1** | Emerging concepts in CO₂RR technology. (a) *In situ* spectroscopy and density functional theory approaches for improved understanding catalysis at the interface (b) New material interfaces, bio-inspired motifs, and tandem catalyst designs for improved catalytic activity. (c) Integration of catalysts and new motifs into systems that locally concentrate carbon dioxide gas at the surface, which can greatly improve catalytic turnover. This figure was created by me with collaboration from Dr. Michael Ross.
List of Appendices

Appendix A | Methods ........................................................................................................ 93

Appendix B | DFT Tables .................................................................................................... 114

Appendix C | Acronyms & Abbreviations ............................................................................. 119
Chapter 1 | Introduction

Society’s reliance on inexpensive sources of energy has grown rapidly and consistently since the Industrial Revolution. With increasing global energy usage, combined with intensifying anthropogenic climate change and rising CO$_2$ emissions, there exists an urgent need to lessen dependence on fossil fuels. Fossil fuel dependence presents climatological, economic, and national security challenges. Today we rely on fossil fuels not only as portable and dispatchable energy carriers; we also remain reliant on them to make chemical feedstocks, materials, and fertilizers. For these reasons, secure and dependable access to these chemicals is essential to society.

Technologies that consume CO$_2$, utilizing it as a feedstock and transforming it into value-added chemicals, are therefore of intense interest. The growing abundance of renewable sources of electricity enable these transformations to become increasingly renewables-powered. At the heart of such technologies is a catalyst that drives the CO$_2$ reduction reaction (CO$_2$RR): the pathway from energy, H$_2$O, and CO$_2$ toward useful chemical products. CO$_2$RR technologies offer avenues to seasonal-scale electrical grid-level storage, chemical feedstocks and fertilizers, transportation fuels, and even specialty chemicals and pharmaceuticals. Renewables-powered strategies achieve these goals while closing the carbon cycle.

This thesis examines strategies in nanostructure engineering to control and amplify catalytic activity for a broad range of materials for CO$_2$RR. It begins in Chapter 1 with an overview and discussion of challenges for electrochemically converting CO$_2$. Chapter 2 describes the important figures of merit for CO$_2$RR, the tools we use to understand catalysis, and the targets needed to reach economic viability. Chapter 3 describes the use of nanostructured metals that exhibit high local electric fields to increase catalytic activity. Chapter 4 describes a first attempt at tandem catalysis by interfacing a porous material with a high-curvature metal substrate support. Chapter 5 shows how these nanostructures can be used to enhance and modulate the activity of overlaying catalyst materials. Chapter 6 presents a study on how the electronic and morphological evolution of catalysts during reaction can be used to dictate their product selectivity. Chapter 7
provides an outlook on the pathway to industrial implementation and the unsolved challenges in catalyst understanding and design.

Much of the work presented here was in close collaboration with colleagues. I have made this explicit at the start of each chapter. I describe which data I acquired personally in the lab, versus which figures and tables include data acquired in collaboration with others.

1.1 Electrocatalytic CO₂ Conversion

The electrochemical conversion of CO₂ to fuels and feedstocks, CO₂RR, closes the carbon cycle when it is coupled with the use of renewable energy sources. In this process, CO₂ is converted to hydrocarbons using water and renewable electricity (Figure 1.1). From a capital equipment perspective, the systems hold analogy with commercialized hydrogen polymer electrolyte membrane electrolyzers. In the case of the net-carbon-neutral H₂/H₂O couple, the hydrocarbon/CO₂ couple is also net-carbon-neutral when renewables-powered.

Figure 1.1 | Closing the carbon loop. The use of electrocatalytic CO₂ reduction to convert captured CO₂ (either from flue stacks or directly from the atmosphere) using renewable energy into chemical feedstocks or fuels for long-term energy storage. This figure was created entirely by me.
Electrochemical transformation of renewable energy into high energy density liquid fuels using captured CO$_2$ offers the prospect of long term, large-scale, seasonal energy storage and allows for integration of renewable electricity into the transportation system and in chemical production. A carbon-based strategy has advantages in implementation and logistics, since, compared to H$_2$ and battery storage, it takes advantage of an expansive already-built infrastructure created for gaseous and liquid carbon-based fuels.

Inroads into curbing CO$_2$ emissions from point sources can potentially be made in the coming decades using carbon capture technologies. The capture and conversion of CO$_2$ offers a path to limit the warming of the planet to below 2 degrees Celsius. The long-term seasonal storage of renewable energy in chemical form holds potential to increase the adoption and penetration of renewable energy sources.

Renewables-powered electrochemical CO$_2$ reduction to chemicals could be implemented to utilize point sources of pure CO$_2$ emissions, such as those released from cement manufacturing, breweries and distilleries, or from fuel processing facilities. Electrosynthesis of commodity chemicals can be carried out at the point of use, requiring less storage, handling and distribution infrastructure than is necessary for fuels production. However, a key challenge will be matching the manufacturing scales of downstream chemicals and the emissions of point sources. This optimization problem will rely heavily on the type and scale of CO$_2$ source.

1.2 Fundamental Catalytic Challenges

CO$_2$ is a highly stable molecule, requiring input energy to reduce it to more desirable products. The thermodynamic cost of reducing CO$_2$ is comparable to that for hydrogen evolution: for example, products such as carbon monoxide and ethylene are thermodynamically formed at -0.11 and +0.07 V (vs. RHE, reversible hydrogen electrode), respectively. However, in practice the energy input required for electrochemical CO$_2$ reduction is far from the thermodynamic ideal. Higher energy input, i.e. greater electrochemical overpotential beyond the thermodynamic requirement, is required to drive the CO$_2$RR at appreciable rates.

In addition to the CO$_2$ activation barrier, CO$_2$ reduction pathways involve multiple single-
step reactions that further add to the chemical sluggishness of \( \text{CO}_2 \)RR—the latter can be thought of as kinetic contributions to the overpotential. Because the adsorption strengths of similar molecules are related, there are limited degrees of freedom by which complex, multi-step reaction pathways can be optimized.\(^9\) The need for proton donors to participate in \( \text{CO}_2 \)RR, either directly or through proton coupled electron transfer (PCET) steps,\(^10\) further complicates catalysis because protons can also be readily reduced to \( \text{H}_2 \). Additionally, the large number of available catalytic pathways also leads to multiple products at higher overpotentials, limiting selectivity.

The main competing reaction with \( \text{CO}_2 \)RR is the hydrogen evolution reaction (HER), whereby bound proton intermediates (\( \text{H}^+ \)) are reduced to \( \text{H}_2 \). Because protons are necessary to reduce carbon dioxide, but are also readily reduced themselves, several strategies to manipulate HER relative to \( \text{CO}_2 \)RR have been developed. The inclusion of electrolyte additives such as ionic liquids lowers the onset potential for \( \text{CO}_2 \)RR by stabilizing the \( \text{CO}_2^- \) intermediate, thereby helping to overcome HER.\(^11,12\) In addition, catalyst morphology can help control the diffusion of various reagents for both \( \text{CO}_2 \)RR and the competing HER. Such a strategy was employed to limit the diffusion of HER species kinetically, thereby increasing \( \text{CO}_2 \)RR selectivity.\(^13\) Lastly, it has been shown that hydrogen binding may be weakened in the presence of \( \text{CO}_2 \)RR intermediates, suggesting that HER may also be suppressed simply by a judicious choice of transition metals.\(^14\)

The low \( \text{CO}_2 \) solubility in water is another important limiting factor in aqueous electrocatalysis that restricts the reaction rate for even the most active \( \text{CO}_2 \)RR catalysts to current densities within the range of few tens of mA/cm\(^2\).\(^8,15\) In traditional \( \text{H} \)-cell architectures, \( \text{CO}_2 \) from the gas phase first dissolves in solution, resulting in aqueous \( \text{CO}_2 \). This aqueous \( \text{CO}_2 \) reacts with water to form carbonic acid (\( \text{H}_2\text{CO}_3 \)); however, the dominant species in a \( \text{CO}_2^- \)-saturated aqueous solution (pH 6.8) is bicarbonate (\( \text{HCO}_3^- \)).\(^16\) Aqueous electrolytes saturate at 33 mM \( \text{CO}_2 \) at ambient conditions, limiting the rate at which \( \text{CO}_2 \) can be transported to the electrocatalyst assuming typical Nernstian diffusion layers: this mass transport challenge ultimately must be overcome to reach industrially viable \( \text{CO}_2 \) reduction rates.\(^17\) Additionally, the local concentrations of \( \text{CO}_2 \) and protons – and thus the pH – vary during catalysis, further complicating our understanding and ability to design electrocatalytic interfaces.\(^18,19\) To increase the current density for \( \text{CO}_2 \)RR to the
order of hundreds of mA/cm² required for practical application, electrocatalytic architectures that overcome mass transport limitations are needed.

1.3 Scaling Relations and CO₂ Mechanisms

The thermodynamic energies of adsorbed intermediates along the multielectron pathway scale linearly with each other across different surfaces. Because the kinetic reaction energy barriers to CO₂ electroreduction depend on intermediate adsorption energies, the linear scaling relations between different bound intermediates makes selective catalysis a challenge. In many reports, multicarbon products are frequently coupled (e.g. ethylene and ethanol) and tuning selectivity is difficult. In combination with the Sabatier principle – the concept that an intermediate must be bound neither too strongly nor too weakly – linear scaling relations provide a useful lens through which CO₂RR selectivity can be considered.

After solvation and equilibration, the first step involving the electrocatalytic surface involves the activation of CO₂ (Figure 1.2a). This requires the adsorption of CO₂ in a conformation that prepares it for further reactivity. The two dominant activation geometries are *OCHO and *COOH. After adsorption, a series of proton and electron transfers occur, where *OCHO is reduced to formate while *COOH is reduced to CO. While these are thought to be the primary modes of CO₂ activation toward CO and formate, numerous other activation geometries can be envisioned, and cross-reactivity between these pathways can also occur, e.g. *COOH being reduced to formate.

![Figure 1.2 CO₂RR Mechanisms](image)

Figure 1.2 CO₂RR Mechanisms. (a) Reaction mechanism of CO₂ reduction to CO on a gold catalyst surface. COOH⁺ and CO⁺ are the main bound intermediates formed after a proton-coupled electron transfer. (b) Reaction energy diagram of CO₂ to CO showing the importance of catalysts lowering the kinetic and thermodynamic energy barriers. (c) Linear scaling relations of COOH⁺ and CO⁺ show how the binding
energies of different transition metals (yellow circles) are highly correlated and difficult to decouple. This figure was created entirely by me.

The challenge of scaling relations can be seen clearly even in the synthesis of a single carbon product such as CO. The reaction first proceeds by a proton-coupled electron transfer to CO\(_2\) to form bound *COOH. Next another proton-coupled electron transfer occurs which liberates H\(_2\)O, leaving a bound *CO intermediate. Finally, this bound *CO desorbs in a chemical step to form the gaseous CO product (Figure 1.2b). Here, the binding energies of *COOH (~ 0 eV) and *CO (~ -0.6 eV) scale linearly with each other, a consequence of the fact that both intermediates interact with the catalyst through similar C-metal bonds. Due to linear scaling relations, engineering a heterogeneous catalyst to have the optimal *CO binding would result in weaker *COOH binding and vice versa (Figure 1.2c). The challenges of linear scaling relations are compounded when targeting multi-carbon products, where competing reaction pathways provide many possible bound intermediates. The unification of comprehensive materials design with understanding of each rate determining step along the path from gaseous CO\(_2\) to a final product remains an elusive goal toward selective CO\(_2\)RR.

For CO\(_2\)RR, the Sabatier heuristic can guide toward the optimal material to generate a given product by relating the binding strengths of reaction intermediates with material properties.\(^5\,8\,9\) Integration between mechanistic understanding and materials design has driven improved electrocatalytic generation of both CO and formate. For formate, a variety of field-leading catalysts contain Sn, and indeed where its electronic properties sit near the Sabatier optimum for *OCHO.\(^{24}\) However, many of the best-performing catalysts for formate are not composed solely of Sn\(^0\); oxide-based materials often are superior, enhancing Faradaic efficiencies toward CO\(_2\)RR products 2 – 6-fold.\(^{26}\) These materials have brought about interesting mechanistic questions and discrepancies, where theoretical calculations, electrochemical analysis, and \textit{in situ} spectroscopy are not presently in agreement about the essential intermediate steps.\(^{23}\) Most electrochemical analyses and theoretical models assume bidentate coordination of some COO\(^-\) species, whereas recent \textit{in situ} vibrational spectroscopy on SnO\(_2\) suggest that a O-coordinated COOH-species is present.\(^{23-25}\)
1.4 Strategies to Increase Activity

The activity (current density or reaction rate) of CO$_2$RR catalysts can be improved using three broad and orthogonal strategies: (i) increase the intrinsic activity of each active site, (ii) increase the number of active sites, and (iii) increase their activity in a given environment. This can be achieved by tuning the electronic and geometric structure of the active sites, which in turn fine-tunes intermediate binding strengths.

![Diagram of CO$_2$RR activity](image)

**Figure 1.3 | Strategies to increase CO$_2$RR activity.** (a) Scheme of carbon dioxide reduction to carbon monoxide. Catalytic design principles for CO$_2$RR related to (b) composition, (c) coordination environment, and (d) nanostructuring. This figure was created by me in collaboration with Dr. Michael Ross.

Manipulating material composition enables design of an active site with a specific intermediate binding strength using d-band theory and thermodynamic scaling relations. Because the binding properties of intermediates are determined by the electronic properties of a metal, i.e. the nature of the d-band electrons, alloying has proven to be a powerful tool for designing and tuning CO$_2$RR materials. This tunability has been demonstrated by alloying Au and Cu to produce Au$_x$Cu$_{1-x}$ materials that exhibit a linear combination of the bulk electronic properties, thus enabling tuning the intermediate binding strength to a near-optimal value. Both electronic and geometric effects were found to function as important catalytic descriptors for CO$_2$RR. More recently ordered AuCu mixtures were shown to reduce overpotentials by 200 mV and increasing turnover 3-fold toward CO, and Cu-overlayered on Au was demonstrated as a strategy for manipulating the composition of syngas through the 0.6–4.0 range of industrial interest. Overall, the systematic tuning of alloyed materials has provided a rich territory to
explore catalytic activity while remaining linked with the gating mechanistic step toward CO. Additionally, a recent study on Cu-Pd bimetallic NPs suggests that geometric effects may play a bigger role for CO$_2$RR, though the balance of these two effects is not yet clear.$^{33}$

While alloying provides a straightforward means to tuning molecular binding strength by modulating electronics, local structure also plays an important role for manipulating activity. The specific coordination environments provided by different facets or faces of a crystalline nanomaterial can more finely control the nature of d-band electrons in a site-specific manner.$^{34}$ For CO$_2$RR, it has been seen that Au nanowires with ‘predominant edge sites’ (>16%) promote 94% Faradaic efficiency of CO generation at a potential of -0.35 V vs RHE.$^{35}$ Facet effects have also been shown to be a key determinant in C$_2$ product selectivity. C$_2$+ selectivity was observed to be heavily dependent on faceting in early experiments.$^{36}$ The (100) facet was found to promote C$_2$ formation, with C$_2$H$_4$:CH$_4$ ratios 2 orders of magnitude greater than the (111) facet. Given that CO$_2$ and CO reduction have similar facet dependent product distributions, the observed structural sensitivity further supports the importance of CO dimerization on Cu. Further evidence supports that (100) terraces have the lowest barrier to CO dimerization,$^{37,38}$ and recent theoretical work has shown that dimerization can be further modulated by a charged water layer,$^{39}$ local field perturbations,$^{40}$ and high CO coverages.$^{41}$

On an electrode, the number of active sites can be increased by controlling the morphology of the catalyst and the dispersion of the catalyst on a high surface area support. For example, nanoporous silver electrocatalysts with high surface area are able to reduce CO$_2$ to CO with approximately 92% selectivity at a rate over 3,000 times higher than polycrystalline counterparts under moderate overpotentials of <0.50 V.$^{42}$ Together, these structural modifications beyond the active site can significantly increase current densities.

Nanostructuring is another strategy to increase catalytic activity and different nanostructures lead to different effects. The topics within this thesis primarily center around nanostructuring effects on CO$_2$RR for different catalyst systems.
Chapter 2 | A Current Survey of the CO\(_2\)RR Field

The previous chapter made the case that CO\(_2\)RR offers the potential to produce renewable fuels and feedstocks, but also poses certain challenges that need to be overcome before CO\(_2\)RR has its full impact. This chapter will discuss the current state of the CO\(_2\)RR field, the tools and methods used to study how CO\(_2\)RR electrocatalysts operate, and a roadmap for industrial implementation. First, I establish the most important and relevant metrics to assess CO\(_2\)RR activity. Next, I provide a survey of the current best electrocatalysts based on those metrics. I then provide a tutorial on the tools and methods used to assess electrocatalyst activity. Finally, I close by providing a techno-economic analysis to motivate targets for CO\(_2\)RR to be realized industrially.

2.1 CO\(_2\)RR Figures of Merit

In its most basic implementation, CO\(_2\)RR cells are comprised of a cathode, an anode, a CO\(_2\)-containing electrolyte, and a membrane. The cathode is the electrocatalyst that facilitates the conversion of CO\(_2\). The anode provides a site for oxidation, such as the oxygen evolution reaction (OER) which supplies a source for protons and electrons to react. The electrolyte is required to enable transport of charged species, to facilitate transport of CO\(_2\) to the electrocatalyst surface, and plays a critical role (via its pH, both global (by choice of salt or salt mixtures) and local (by OH\(^-\) generation under CO\(_2\)RR)) in influencing the energetics of CO\(_2\) reduction. The membrane separates the products of oxidation and reduction while maintaining charge balance. This thesis focuses primarily on the CO\(_2\) reduction electrocatalyst (cathode), looking particularly at the latest physical principles that promote design and improve selectivity, overpotentials, and productivity. The terms and figures of merit for CO\(_2\)RR are listed below in Table 2.1 below.

Table 2.1 | Common definitions of CO\(_2\)RR figures of merit

<table>
<thead>
<tr>
<th>Faradaic Efficiency (F.E.)</th>
<th>A measure of selectivity; the percentage of electrons that are used for the desired electrochemical reaction, e.g. the reduction of CO(_2) to ethylene.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overpotential</td>
<td>A measure of energy cost; the amount of additional potential (expressed in V or mV) beyond that which is thermodynamically required for an electrochemical reaction.</td>
</tr>
<tr>
<td><strong>Current Density</strong></td>
<td>A measure of catalytic activity; the overall number of electrons passed through the electrode at a given potential per second, normalized by the electrode area.</td>
</tr>
<tr>
<td>--------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>Current Density (Geometric)</strong></td>
<td>Where the area in the above definition refers to the footprint of the electrode. This is a practical term that can be easily translated to working systems which operate under the constraints of electrode size.</td>
</tr>
<tr>
<td><strong>Current Density (Specific)</strong></td>
<td>Where the area refers to the real electrochemically active surface area of the catalyst, including roughness factor. This term is more directly applicable to the concept of turnover, or the intrinsic activity of an active site.</td>
</tr>
<tr>
<td><strong>Current Density (Partial)</strong></td>
<td>The multiplicative product of Faradaic efficiency for a specific chemical product with overall current density; the resulting value describes the rate of production of a single desired chemical product. This value is frequently used to describe the activity of a catalyst towards an intended chemical output.</td>
</tr>
<tr>
<td><strong>Energy Conversion Efficiency</strong></td>
<td>A measure of the total conversion efficiency from energy to chemical output. Typically, this is reported as a cathode energy conversion efficiency, or partial energy conversion efficiency, system assuming no losses due to factors aside from the cathode overpotential, such as anode overpotential, solution resistance, membrane resistance, and other system-level transfer loss.</td>
</tr>
</tbody>
</table>

The Faradaic efficiency relates most directly to the product ratio and thus is calculated from the measured product either typically via gas chromatography (for gaseous products) or NMR (for liquid products). The Faradaic efficiency is calculated as:

\[
F.E = \frac{eFn}{Qt} = \frac{eFn}{jt} \tag{1}
\]

where \(e\) is the number of electrons transferred in the reaction, \(F\) is Faraday’s constant, \(n\) is the number of moles of the product, \(Q\) is the charge passed and is equal to the current \((j)\) multiplied by the time \((t)\) of the reaction.

Potentials in CO\(_2\)RR are typically expressed in using the Reversible Hydrogen Electrode scale (vs. RHE), which provides a way to compare the potentials between different systems. Within the context of this thesis all experiments are conducted using a Ag/AgCl reference electrode and the potential vs. RHE is defined as:

\[
E_{RHE} = E_{Ag/AgCl} + 0.197V + 0.0591pH \tag{2}
\]
where $E_{Ag/AgCl}$ is the measured potential vs. the Ag/AgCl reference electrode and $pH$ is the pH of the electrolyte system.

The current of the system is measured directly using a potentiostat in either a chronoamperometric (constant potential) or chronopotentiometric (constant current) mode. Operation at a fixed potential is most similar to how a cell would operate in an industrial setting and provides important information on the activity and also the point of activity failure as a function of time. Operation at a fixed current allows one to measure the overpotentials at a given activity and is useful for probing intrinsic thermodynamic catalysis.

The most industrially relevant metric is the as defined as the energy conversion efficiency and combines information on Faradaic efficiency and overpotential into one number. It is defined as:

$$ECE = \frac{F.E.}{100} \times \frac{E}{E + \eta}$$

(3)

where $\eta$ and $E$ represent the overpotential and thermodynamic cell potential of the full cell.

The Faradaic efficiencies (Table 2.2) and energy conversion efficiencies (Table 2.3) towards many CO$_2$RR products have been increased steadily over the last 3 decades. Simpler C1 products such as CO and formic acid showed high initial selectivities even on simple metal foils as far back as the 1980s with the first reports of CO$_2$RR. However, more sophisticated catalyst, electrolyte, and cell engineering was required to make significant improvements on selectivity for C2 products, due to the difficulty of C-C coupling. The large step changes for the Faradaic efficiency increases can be attributed largely to catalyst engineering while the increases in energy conversion efficiencies requires system and cell engineering in conjunction with catalyst engineering to realize improvements.

**Table 2.2 | Maximum reported Faradaic efficiency for various CO$_2$RR products over time.**

<table>
<thead>
<tr>
<th>Year</th>
<th>Product</th>
<th>Faradaic efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1987</td>
<td>CO</td>
<td>35</td>
<td>43</td>
</tr>
<tr>
<td>1990</td>
<td>CO</td>
<td>80</td>
<td>44</td>
</tr>
<tr>
<td>2008</td>
<td>CO</td>
<td>85</td>
<td>45</td>
</tr>
<tr>
<td>2012</td>
<td>CO</td>
<td>98</td>
<td>46</td>
</tr>
</tbody>
</table>
Table 2.3 | Current state of CO\textsubscript{2} electrolyzers in comparison with hydrogen electrolyzers.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Product</th>
<th>Cell Voltage (V)</th>
<th>Current Density (mA/cm\textsuperscript{2})</th>
<th>Faradaic Efficiency (%)</th>
<th>Energy Conversion Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu\textsuperscript{54}</td>
<td>7 M KOH</td>
<td>Ethylene</td>
<td>2.4</td>
<td>110</td>
<td>70</td>
<td>34</td>
</tr>
<tr>
<td>Au\textsuperscript{55}</td>
<td>2 M KOH</td>
<td>Carbon Monoxide</td>
<td>2.0</td>
<td>99</td>
<td>98</td>
<td>64</td>
</tr>
<tr>
<td>Ag\textsuperscript{56}</td>
<td>1 M KOH</td>
<td>Carbon Monoxide</td>
<td>3.0</td>
<td>350</td>
<td>101</td>
<td>45</td>
</tr>
<tr>
<td>Ag\textsuperscript{57}</td>
<td>0.5 M K\textsubscript{2}SO\textsubscript{4} : 1 M KHCO\textsubscript{3}</td>
<td>Carbon Monoxide</td>
<td>2.9</td>
<td>197</td>
<td>87</td>
<td>50</td>
</tr>
<tr>
<td>Ag\textsuperscript{58}</td>
<td>0.5 M K\textsubscript{2}SO\textsubscript{4} : 1 M KHCO\textsubscript{3}</td>
<td>Carbon Monoxide</td>
<td>4.7</td>
<td>233</td>
<td>78</td>
<td>25</td>
</tr>
<tr>
<td>Sn\textsuperscript{59}</td>
<td>0.5 M KCl</td>
<td>Formate</td>
<td>4.0</td>
<td>163</td>
<td>84</td>
<td>32</td>
</tr>
<tr>
<td>Pb\textsuperscript{60}</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>Formate</td>
<td>2.8</td>
<td>50</td>
<td>95</td>
<td>49</td>
</tr>
<tr>
<td>Sn\textsuperscript{61}</td>
<td>0.5 M KHCO\textsubscript{3} + 2 M KCl</td>
<td>Formate</td>
<td>3.1</td>
<td>133</td>
<td>83</td>
<td>33</td>
</tr>
<tr>
<td>Pt\textsuperscript{a}</td>
<td>Polymer Electrolyte\textsuperscript{a}</td>
<td>Hydrogen</td>
<td>1.2-2.2</td>
<td>2000</td>
<td>100</td>
<td>74</td>
</tr>
<tr>
<td>Pt\textsuperscript{b}</td>
<td>Alkaline\textsuperscript{b}</td>
<td>Hydrogen</td>
<td>1.5-2.0</td>
<td>1000</td>
<td>100</td>
<td>66</td>
</tr>
</tbody>
</table>

\textsuperscript{a,b} Industrial hydrogen electrolyzer metrics based on 2018 DOE Hydrogen Fuel R&D Annual Merit Review.

2.2 Tools to Explore CO\textsubscript{2}RR

More sophisticated tools are required to uncover the inner works of CO\textsubscript{2}RR catalysis that go beyond the traditional electrochemist or materials scientist toolkit. While electrochemistry is used to probe and measure the activity of catalysts and microscopy techniques can provide structural characterization information post-reaction, these are not sufficient to provide a robust understanding of how an electrocatalyst works under operating conditions. Two important tools that are used throughout this thesis are quantum mechanical simulations using DFT and in-situ x-
ray absorption spectroscopy. DFT provides an in-silico understanding of the catalytic mechanisms based on ground state energies and thermodynamics. In-situ XAS provides information on the local coordination environment and oxidation state of the metal catalysts.

2.2.1 Density Functional Theory

Density functional theory states that the ground state energy of a system can be approximated from its electron density. Once the energetics of a system can be calculated, one can also calculate the energies of a metal slab, or of a molecule interacting with that slab, or of possible intermediates along a reaction on top of that metal slab. This gives an atomic level view of the reaction based on principles of quantum mechanics and is a powerful tool to interrogate the mechanisms of catalysis – to envision how molecules can be transformed and the energies required to spur that transformation.

For example, the interaction or binding energies of CO$_2$ to catalyst can be described as such:

$$E_{\text{Binding}} = E_{\text{CO}_2^*} - (E_{\text{Catalyst}} + E_{\text{CO}_2})$$

where $E_{\text{CO}_2^*}$ is the energy of the system where CO$_2$ is on top of the catalyst surface (or within a distance of interaction, typically less than 12 Å away). $E_{\text{Catalyst}}$ is the energy of the catalyst surface and $E_{\text{CO}_2}$ is the energy of a CO$_2$ molecule in the gas phase.

The binding energy is an excellent proxy for activity, but it does not provide the entire picture of catalysis. A full reaction pathway examines the changes in free energy from the beginning to the end of a reaction, based on the intermediates of reaction. The full reaction pathway is based on the Gibbs free energies which involve entropic terms in addition to enthalpic terms. The Gibbs free energies at 298K and 1 atm is outlined below:

$$G = H - TS = E_{\text{DFT}} + E_{\text{ZPE}} + \int_{0}^{298} C_v dT - TS$$

where $E_{\text{DFT}}$ is the DFT calculated electronic energy, $E_{\text{ZPE}}$ is the zero-point vibrational energy, $\int_{0}^{298} C_v dT$ is the heat capacity, T is the temperature, and S is the entropy. Gas phase molecules
such as CO$_2$ and H$_2$ are treated using the ideal gas approximation while adsorbates were treated using a harmonic approximation to generate entropic contributions.

The computational hydrogen electrode model (CHE) states that the Gibbs free energy of a proton-coupled electron transfer can be approximated to half the energy of a gas phase hydrogen gas molecule (H$_2$). This reference against gas phase H$_2$ is a way to computational account for proton transfer without explicitly calculating a charged H$^+$ ion in the system (which can be computationally demanding and lead to errors).

While DFT provides a powerful tool to study reactions on an atomistic scale, there still exist many limitations to the computational theory. First, there is a limit to the number of atoms that can be simulated in a quantum mechanical fashion. This results in idealistic close-packed perfect crystalline models that may not accurately represent a catalyst material, especially as catalyst active sites are typically defects and the surface is dynamically changing with time. Secondly, the treatment of solvent interactions, ions, and properly modelling an applied electrical potential is a non-trivial problem that requires a large amount of computational resources. Lastly, the conformational and chemical search space for multi-carbon product synthesis is vast and impossible for DFT to model completely. New machine learning approaches are being developed to speed up calculations and search through complicated reaction pathways in an automated and iterative way.

2.2.2 In-situ X-ray Spectroscopy

X-ray absorption spectroscopy (XAS) is an experimental characterization technique that can provide information on a material’s oxidation state and coordination environment. It requires the use of very high-powered x-rays that can only be generated at synchrotron light source – large specialized particle accelerator facilities spread around the world.

In XAS, an X-ray hits an atom with enough energy to excite a core electron from the 1s or 2p level (Figure 2.1a). This electron can be promoted to an unoccupied level or, with high enough energy, become ejected from the atom completely – leaving behind a hole. Since these are core electron excitations, the energies need are on the order of thousands of electron volts and high-energy X-ray excitation. X-ray energy starts at about 104 eV where soft x-rays are
described between 100 eV – 3k eV and hard x-rays are above 3k eV corresponding to the wavelengths around 1 Angstrom. Importantly, this wavelength is similar to the magnitude of atom-atom separation in molecular and material structures, meaning that signals arising from this excitation provide local structure information of atoms (Figure 2.1b). For a 3D periodic structure, XAS can characterize local atomic environments based on characteristic X-ray absorption fingerprints which arise from the scattering interactions of neighbouring atoms. XAS is non-destructive (to a degree) and allows for characterization with specially designed cells to probe catalysis \textit{in-situ} under operation with aqueous electrolytes.

\textbf{Figure 2.1 | X-ray absorption spectroscopy.} \textbf{(Left)} The mechanism of photoelectron emission via high-energy x-rays. \textbf{(Right)} schematic of photoelectron scattering in a periodic material. This figure was created by me.

Depending on the X-ray energy, different events can occur. At lower X-ray energies the photoelectron actually has just enough kinetic energy to be able to escape into the continuum. Multiple scattering processes occur here, between multiple surrounding atoms that neighbor the absorbing atom. At very high kinetic energy the photoelectron can escape and weak backscattering occurs in a single scattering process between only one neighbor atom.

The oxidation states of metals can be inferred based on the energy at which these transitions occur. The coordination number and even the atom-atom distances can be calculated through a fitting of spectra and more complex modelling. When applied to electrocatalysis, XAS becomes very important in measuring the oxidation state and local binding environments of
catalysis \textit{while} they are undergoing reaction. Catalyst structure often changes during reaction and after reaction. This dynamism makes it very difficult to design better catalysts since most of the characterization techniques happen post-mortem, after the reaction and usually after the catalyst has failed. XAS is one of the only techniques that can give us a glimpse into the electronic structure of the catalyst as it is working.

However, there exist limitations to XAS in terms of depth profiling of the catalyst material. XAS, especially with higher X-ray energies, are a bulk sensitive technique when operating in fluorescence mode. This means the surface interfacial region of the catalyst where the reaction is occurring can be washed out by the bulk material signal. Soft XAS is slightly more surface sensitive as the penetration depth of X-rays are shorter at lower energies. The only truly surface sensitive XAS method is by measuring the total electron yield (TEY) of the catalyst during operation. However, it is difficult to separate the electron yield signal from x-ray absorption and the current due to Faradaic processes.

2.3 Pathways toward Industrial Implementation

Decades of research have proven effective in developing efficient catalysts for the electrochemical generation of hydrogen and oxygen from water to the point of commercialization. Since these electrochemical transformations require, in principle, similar components to CO$_2$RR, lessons learned from the engineering scale up and device design of hydrogen electrolyzers can be highly transferable.

Several factors position the electrochemical conversion of CO$_2$ for accelerated technological development. First, the products of CO$_2$RR already exist within many petrochemical supply chains, and therefore the chemical industry infrastructure is more readily prepared to adapt to CO$_2$RR. Second, the need to reduce emissions along with the gradual adoption of carbon capture technologies is resulting in large energy consumers and carbon emitters facing the challenge of what to do with the CO$_2$ once it is captured.$^4$ CO$_2$RR provides a way to recover value from what would otherwise be a tremendous sunken cost.
Despite a favourable ecosystem for renewable chemical feedstocks, there still exist challenges and risk towards industrial scale up. The electrolyte needs to be optimized with careful consideration of cost, environmental impact, and availability to reach the scales necessary for meaningful emissions reductions. Public policy of CO₂ utilization technologies needs to be carefully crafted and social acceptance of the field needs to be managed. Most importantly, catalysts and system efficiencies for this technology need to be vastly improved to be economically viable.

2.3.1 Technoeconomic and carbon emissions analysis

There exist many technoeconomic analyses of solar fuels that have analyzed the needed Faradaic efficiencies and over-potentials required to match fossil-fuel derived sources.⁴,⁶⁴–⁶⁸ Among them, the largest influence on the levelized cost of production has consistently been the price of electricity. Building upon previous studies, I have calculated the cost of electrosynthesized hydrogen, carbon monoxide, ammonia, and ethylene as a function of the energy conversion efficiency and electricity cost (Figure 2.2) to provide a comparison to current market prices (Refer to SI for calculation details). Using optimistic assumptions based on industrially mature polymer electrolyte membrane (PEM) water electrolyzer specifications, I show that when electricity costs fall below 4 cents/kWh and energy efficiency is at least 60%, all products become competitive with current market prices for these products derived from fossil-fuel sources. To put this into perspective, the best systems today have demonstrated full cell energy efficiencies of approximately 40-50% for CO, approaching cost competitive targets. Considering that CO₂RR to CO technologies are in the early stages of development, it is expected that with further catalyst and electrochemical cell designs, improved performance can be obtained. While renewable electricity prices continue to plummet, the scientific challenge is elevating the energy efficiencies of these electrochemical processes.
Figure 2.2 | Production costs of electrosynthesized chemicals. Technoeconomic analysis of hydrogen, carbon monoxide, ammonia, and ethylene costs as a function of electrolyzer energy conversion efficiency and electricity costs. Assumes a CO$_2$ price of $30$/ton, Faradaic efficiency of 90%, current density of 500 mA/cm$^2$, electrolyzer cost of $300$/kW, and plant lifetime of 30 years. This figure and the data described therein were created by me. Details on the technoeconomic model can be found in Appendix A Methods.

While the challenge of electrosynthesis of commodity chemicals is daunting, the reward is great. To quantify the potential impact that electrochemical synthesis of common carbon-based commodity chemicals has on carbon emissions, we performed a simple life cycle assessment for formic acid, carbon monoxide, ethylene, and ethanol. Of these products, ethylene has the largest global market size at $230B and the lowest product intensity (Figure 2.3a), suggesting it is an attractive target for meaningful CO$_2$ emissions reductions. The grid carbon intensity, a measure of how clean the electricity generation is, and the conversion, the percentage of CO$_2$ that gets converted instead of emitted, were found to be the most sensitive factors affecting overall CO$_2$ emissions (Figure 2.3b-e). Assuming a plant capacity of 500 MW, an average grid carbon intensity
for the USA (0.45 kg CO$_2$e/kWh in 2016), and an energy conversion efficiency of 70%, all products result in either neutral (ethylene) or net negative (ethanol, carbon monoxide, and formic acid) carbon emissions. This simple analysis shows the potential for electrosynthesized commodity chemicals to have a real impact on global CO$_2$ emissions.

![Figure 2.3](image)

**Figure 2.3 | The emissions impact of electrosynthesized chemicals.** (a) Market size and product intensity, the amount of emissions per kWh, of ethylene, ethanol, carbon monoxide, and formic acid. Carbon emissions assessment of (b) formic acid, (c) carbon monoxide, (d) ethylene, and (e) ethanol. Assuming a plant capacity of 500 MW and global warming potential of formic acid and carbon monoxide to be 1 kg CO$_2$/kg product and a GWP of ethylene and ethanol to be 5.75 kg CO$_2$/kg product. This figure and the data described therein were created by me. Details on the technoeconomic model can be found in Appendix A Methods.

To benchmark these results, I provide a comparison of electrocatalytic, biocatalytic, and traditional fossil fuel derived processes for ethylene, carbon monoxide, ethanol, and formic acid production (Table 2.4). Bio-ethylene production using bio-ethanol precursors is economically competitive in Brazil due to the ample availability of cheap sugarcane feedstock. Petrochemical ethylene is produced mainly from steam cracking of fossil fuels. The majority of carbon monoxide is produced as a component of syngas through coal gasification. Ethanol is primarily produced through fermentation of sugars or corn. Formic acid is primarily produced through chemical processes using tertiary amines. I find that when using optimistic targets (Faradaic
efficiency = 90%, energy conversion efficiency = 70%), electrocatalysis is cost competitive with fossil fuel derived sources and more economical than biocatalytic processes. Additionally, I find that electrocatalysis, when powered by renewable electricity, has the lowest carbon emissions of all processes and are even negative for carbon monoxide, ethanol, and formic acid. With these targets in mind, electrocatalysis as a means to the sustainable production of alcohols, olefins, fertilizer, and syngas begins to become economically viable.

Table 2.4 | Comparison of production cost and carbon emissions

<table>
<thead>
<tr>
<th>Product</th>
<th>Technology</th>
<th>Production Cost ($/tonne)</th>
<th>Carbon Emissions (t CO2e/t prod)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>Electrocatalytic</td>
<td>1100</td>
<td>-0.01</td>
</tr>
<tr>
<td></td>
<td>Biocatalytic</td>
<td>1200 - 2600</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Fossil Fuel Derived</td>
<td>600 - 1300</td>
<td>6</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>Electrocatalytic</td>
<td>200</td>
<td>-0.85</td>
</tr>
<tr>
<td></td>
<td>Biocatalytic</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fossil Fuel Derived</td>
<td>150</td>
<td>0.05</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Electrocatalytic</td>
<td>515</td>
<td>-1.00</td>
</tr>
<tr>
<td></td>
<td>Biocatalytic</td>
<td>670</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>Fossil Fuel Derived</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>Electrocatalytic</td>
<td>108</td>
<td>-1.63</td>
</tr>
<tr>
<td></td>
<td>Biocatalytic</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fossil Fuel Derived</td>
<td>570</td>
<td>0.01</td>
</tr>
</tbody>
</table>

*Electrocatalysis assumes Faradaic efficiencies of 90%, energy conversion efficiency of 70%, capacity factor of 0.9, and grid intensities of 0.35 kg CO2e/kWh.

The goal of this chapter was to establish an understanding of the metrics by which CO2RR electrocatalysts are compared, to provide a description on how DFT and XAS are used to study these electrocatalysts, and to frame the economics to provide a clear goal to reach. To summarize below:

- The most important metrics in CO2RR are the Faradaic efficiency, the overpotential, the current density and the stability.
• DFT provides atomic level insight on the energetics of a reaction pathway and can be used to help understand existing catalysts or provide predictions and targets for experiments to pursue.

• XAS is a powerful tool that provides local atomic and electronic structure of a catalyst, even during reaction. This technique is one of the only ways to measure a catalyst in-situ.

• Technoeconomics show that electricity costs need to decrease to less than 3 cents/kWh and the energy conversion efficiency needs to reach 60%.

I end this chapter with a brief discussion on the specific gaps in literature that the thesis presented here hopes to fill. Specifically, I list the tangible insights, concepts, or ideas that did not exist prior to my thesis below:

1. The use of nanostructuring to enhance the local electric field and thus adsorbed cation concentrations.

2. A systematic analysis of the failure modes thin film metal-organic frameworks on metal nanostructures for electrochemical CO₂RR.

3. The promotion of undercoordinated sulfide-derived tin and its implications for electrochemical formate production.

4. Direct experimental spectroscopic observation of a Cu⁺ species during CO₂RR under negative applied potentials.

Chapter 3| High Local Electric Fields Effects in Catalysis

In the previous chapters I described the challenges in CO₂RR, strategies to increase activity, and I outlined the metrics by which CO₂RR electrocatalysts are judged. In this chapter I describe how high-curvature nanostructures can be used to promote electric field effects that enhance CO₂RR.

High-curvature nanostructures have interesting properties in electrochemistry. For example, they have been shown to increase the sensitivity of DNA-probe biosensors. In this
chapter I introduce the concept of field-induced reagent concentration (FIRC), wherein a nanostructured electrode produces a local high electric field at low applied overpotential. The high field concentrates electrolyte cations, and the cations stabilize CO$_2$ intermediates at the active CO$_2$RR surface. Simulations reveal that nanometrically sharp tips on metallic electrodes achieve 10-fold higher electric fields compared to quasi-planar regions. I then show how bottom-up nanomaterials chemistry is used to synthesize gold nanoneedle electrodes that provide CO$_2$RR with record-low onset potential ($\eta_{CO} = 0.07$ V) and record-high geometric current density ($j_{CO}$) of 22 mA cm$^{-2}$ at the low potential of $-0.35$ V ($\eta_{CO} = 0.24$ V) with nearly quantitative (>95%) Faradaic efficiency for CO$_2$ to CO production. The geometric density surpasses by an order of magnitude the performance of the best gold nanorods, nanoparticles, and oxide-derived noble metal catalysts.

The work in this chapter has been published as a letter titled “Enhanced electrocatalytic CO$_2$ reduction via field-induced reagent concentration” in Nature, 537 (7620), 382–386 (2016). Text and figures have been reproduced here with permission from Springer Nature. As a co-first author, I performed the DFT calculations and analysis, performed electrocatalysis experiments with varying cation identity, and contributed to manuscript preparation. Post-Doctoral Fellow Min Liu performed many of the electrocatalytic experiments and controls and Post-Doctoral Fellow Yuanjie Pang performed the finite element multi-physics simulations. In this chapter I include data and figures that were prepared by them in order to present a complete picture of the scientific discovery and I am explicit about their contributions where necessary.

3.1 Field Induced Reagent Concentration

Alkali metal cations are well-known to facilitate electrocatalytic reactions via non-covalent interactions with adsorbed reagent species.$^{81}$ For example, high K$^+$ and Na$^+$ concentrations have been shown to enhance water splitting, CO$_2$ reduction, and fuel cell performance.$^{18,82}$ While these concentration effects have been demonstrated in bulk solutions, there exist practical limits to the concentrating of cations in light of the limited solubility of relevant salts [e.g. 3.3 mol L$^{-1}$ for potassium bicarbonate (KHCO$_3$) in water]. Electrical strategies show promise, and high electric fields from solvated cations in the electric double layer stabilize key intermediates *CO$_2$ and *COOH.$^{83}$
I begin by exploring how locally concentrating the electric field even at low electrode potentials, and thereby concentrating cations, could overcome the limitations of bulk- and applied-potential-concentration. The main hypothesis was that a high surface area density of adsorbed cations could stabilize intermediates and speed up the otherwise sluggish kinetics of the CO$_2$RR.

### 3.2 Computational Simulations

To provide an atomic level description of cation influence on CO$_2$RR, density functional theory (DFT) calculations were performed on gold surface models of various facets [(111), (100), (110) and (211)] at 298 K, 1 atm and 0 V versus reversible hydrogen electrode (RHE, hereafter, all potentials are reported with respect to RHE.) (Figure 3.1). The free energy ($\Delta G$) diagrams show that the presence of an adsorbed K$^+$ atom directly lowers the thermodynamic energy barrier for reaction consistently, a trend that holds regardless of gold facet. In the case of Au(111) the presence of K$^+$ stabilizes the COOH* and CO* intermediates by 0.89 eV and 0.24 eV respectively (Figure 3.1a). The adsorbed K$^+$ also stabilizes the rate-determining COOH* intermediate for Au(100) and Au(110) by 0.66 eV and 0.69 eV respectively (Figure 3.1b and 3.1c). In order to approximate under-coordinated surfaces, a stepped Au(211) facet was also modelled and similarly showed a stabilization of COOH* and CO* in the presence of K$^+$ (Figure 3.1d).
Figure 3.1 | Thermodynamic barriers for CO$_2$RR on Au surfaces with and without K$^+$. Gibbs free energy $\Delta G$ diagrams of the electrochemical reduction of CO$_2$ to CO on Au(111) (a), Au(100) (b), Au(110) (c) and Au(211) (d) facets in the presence of adsorbed K$^+$ and in the absence of adsorbed K$^+$.

To provide more electronic insight, Bader charge analysis was performed. The results show that a surface with an adsorbed K$^+$ shows greater electron density on the carbon of the COOH$^*$ intermediate suggesting a stronger C-Au bond (Figure 3.2). It can be shown that in the presence of K$^+$ the Bader charge on the carbon of COOH$^*$ has decreased from +0.7 to +0.41 suggesting higher electron density and thus a stronger C-Au bond.

Figure 3.2 | Bader charge analysis. Volume slice of the DFT calculated charge density for K$^+$ on Au(111). Volume slice of calculated charge densities. Bader partial atomic charges are indicated in black with and without K$^+$. The volume slice is visualized from the electron density with an isovalue of 0.5.
To provide additional information on kinetics at the surface, ab-initio molecular dynamics simulations were carried out. It was found that the CO$_2$ molecule prefers to stay adsorbed on the surface when K$^+$ is present rather than when it is not (Figure 2.3a). The mean square deviation of CO$_2$ was found to be approximately 3 Å when K$^+$ is in on the surface but 10 Å without. This ensemble average is taken over 25 ab initio molecular dynamics simulations all with identical starting positions and shows CO$_2$ is more diffuse without a K$^+$ cation to facilitate CO$_2$ surface binding. It was also found that regardless of facet the CO$_2$ remained close to the surface of Au when K$^+$ was present (Figure 3.3b).

![Figure 3.3](image)

**Figure 3.3 | Mean square deviation with K$^+$.** (a) Average mean square displacement (MSD) of CO$_2$ on Au(111) surface with and without K$^+$ in the system. (b) MSD of CO$_2$ on Au(111), Au(110), Au(100) and Au(211) surface in the presence of K$^+$. Radial distribution function analyses between C (of the CO$_2$) and Au further show the increased affinity of CO$_2$ to Au in the presence of K$^+$ (Figure 3.4 left). Additionally, the interaction energy of CO$_2$ as it approaches the Au surface is consistently less in the presence of an adsorbed K$^+$ (Figure 3.4 right). These findings suggest that an adsorbed cation can fundamentally modulate the reaction thermodynamics of CO$_2$RR to get favorable energetics.
Figure 3.4 | Radial distribution function and interaction energies. (Left) RDF of CO$_2$ to Au(111) as a function of potassium from an ensemble average of 25 ab-initio molecular dynamics simulations (5 ps) shows CO$_2$ is closer to the surface of gold on average in the presence of K$^+$ than without K$^+$. Snapshot configurations of CO$_2$ on gold are shown on the left. (Right) Calculated interaction energy of CO$_2$ vary with C-Au distance under the conditions with or without K$^+$. The change in interaction energy increases as the CO$_2$ approaches the Au(111) surface past its equilibrium distance. The interaction energy is consistently less in the presence of an adsorbed K$^+$ (red) than without K$^+$ (black).

With the importance of adsorbed cation influencing thermodynamic barriers established from DFT, we sought to find a way to locally concentrate these cations at reactive sites by use of an increased local electric field.

The data below was calculated by PDF Dr. Yuanjie Pang and is included in this thesis to present a full account of the work. Yuanjie used a finite element numerical method to investigate the prospects of tip-enhanced nanoscale field intensification. Cones with rounded tips of varying radii were used to represent the key physics of sharp electrode tips immersed in an electrolyte. The tip-concentrated electron density (Figure 3.5a) increases as the electrodes sharpen. The locally-enhanced electrostatic field is generated by, and points to, the locally-concentrated free electron density on the surface of the electrodes (arrows in Figure 3.5a). The electrostatic field intensity (Figure 3.5b) at the tip of the electrode, at the potential corresponding to reversible CO$_2$ to CO conversion ($-0.11$ V), is enhanced by one order of magnitude when the tip is sharpened from radius of 140 nm to radius 5 nm. The intense field originates from the migration of free electrons to regions of sharpest curvature on a charged metallic electrode, an effect that arises due to electrostatic repulsion.
Figure 3.5 | Electric Field Simulations. (a) Free electron density distribution on the surface of electrodes is shown as a colour map. Electrostatic field distribution around the electrode is shown as a group of arrows, where the size and direction of each arrow represent the magnitude and direction of the field at the arrow’s spatial position. The tip radius of the structure in each panel is 5 nm (left), 60 nm (middle) and 140 nm (right). Scale bars represent 5 nm. (b) Electrostatic field intensity at the electrode tip increases as the tip radius decreases. Figure prepared by Yuanjie Pang.

3.3 Synthesis and Characterization of Gold Nanoneedles

In light of this dramatic field concentration, and its capacity to concentrate cations and hence stabilize CO$_2$ intermediates, we sought a convenient and scalable means to prepare the desired sharp-tipped electrodes. The majority of the experimental work described below was carried out by PDF Dr. Min Liu.

Since suitably-controlled (via potential, reagent and electrolyte concentration) electrodeposition has previously been shown to program the morphology of noble-metal nanostructured electrodes, we obtained a diverse set of programmable nanostructures that featured a judiciously-selected suite of available tip radii ranging (Figure 2.6a-k) from large-diameter particles (~140 nm radius of curvature) to intermediate-diameter rods (~60 nm radius of curvature) to high curvature nanoneedles (~5 nm radius of curvature). Electrochemical surface area measurements yielded electrochemical roughness factors of 52, 33 and 12 for Au needle, rod and particle electrodes, respectively.

To thoroughly investigate the presence of FIRC effect, we developed a carefully crafted set of experiments. Kelvin probe atomic force microscopy confirms that, as expected, electric fields are highest for the needles and lowest for large particles (Figure 2.6c, g and k). Secondary Au nanoparticle electrodeposition preferentially occurs at the tip of Au needles (Figure 2.6d), decreases on Au rods and almost disappears on Au particles. Au needles have the largest electric-field-induced locally absorbed K+ concentration under performance-testing conditions (Figure
with conductive atomic force microscopy proving that the nanoscale local current at Au needle tips is higher than the current on Au rods and particles (Figure 2.6l). These results all support the local presence of large electric fields and the FIRC effect at the Au needle tips.

Figure 3.6 | Physical characterization of Au nanoneedles, rods, and particles. (a, e, i), Scanning electron microscopy (SEM) images; (b, f, j), TEM images; (c, g, k), Electric field distribution of Au needles, rods and particles deduced using Kelvin probe atomic force microscopy. (d), SEM image of Au needle with secondarily deposited Au particles. (h), ECSA-normalized field-induced concentration of adsorbed K⁺ on Au needles, rods and particles. The concentration of K⁺ was measured via inductively coupled plasma (ICP) optical emission spectrometry. The inset shows the process of measuring the field-induced adsorbed K⁺. (i), Current on a single Au needle, rod and particle with a thin TiO₂ insulator layer at a bias of −1 V. The inset shows the current measurement conditions. Figure prepared by me and Min Liu.

3.4 CO₂RR Experiments on Gold Nanoneedles

To validate to prediction of FIRC on CO₂RR, we then explored the CO₂ reduction activity of Au needles, rods and particles in CO₂-saturated 0.5 M KHCO₃ (pH 7.2). Products were quantified using gas chromatography. From the linear sweep voltammetry curves, a clear reduction peak was observed for the Au needles in the range −0.30 – −0.50 V (Figure 2.7a). In contrast, only smooth current-voltage curves were observed in Au rods and particles. Notably, Au needles exhibited a
stable total geometric current density \( (j_{\text{tot}}) \) of \(~15\ mA\ cm^{-2}\) at the low potential of \(-0.35\ V\) during 8 hours of continuous reaction (Figure 2.7b). Since the \( \text{CO}_2 \) reduction equilibrium potential is \(-0.11\ V\) versus RHE in protic media, \(-0.35\ V\) potential correspond to \(0.24\ V\) of overpotential for \( \text{CO} \) production \( (\eta_{\text{CO}}) \). Faradaic efficiency (FE) for \( \text{CO} \) production was nearly quantitative (>95%) throughout the electrocatalytic process. No obvious changes in the morphology, crystal structure and surface state were observed after long term \( \text{CO}_2 \)RR indicating the Au needles are stable under electrocatalytic conditions. Au rods and particles exhibited \( j_{\text{tot}} \) of \(~0.7\ mA\ cm^{-2}\) and \(~0.1\ mA\ cm^{-2}\) after \(8\ h\) reaction. Their FEs for \( \text{CO} \) were \(~25\%\) and \(~3\%\), respectively. To explore the kinetics of \( \text{CO}_2 \) reduction on the Au needles, we carried out Tafel analysis (Figure 2.7d).

**Figure 3.7 | \( \text{CO}_2 \)RR performance.** (a) Current–voltage curves on Au needles, rods and particles obtained from the linear sweep voltammetry scans. Scan rate, \(10\ mV\ s^{-1}\). (b) \( \text{CO}_2 \) reduction activity of Au needles, rods and particles at \(-0.35\ V\) versus RHE. Total current density (left axis) versus time and \( \text{CO} \) Faradaic efficiency (right axis) versus time. (c) \( \text{CO} \) Faradaic efficiencies on Au needles, rods and particles at different applied potentials. (d) ECSA–normalized \( \text{CO} \) production partial current density versus potential on Au needles, rods and particles. Figure prepared by Min Liu with data input by me.
Au needles exhibit a Tafel slope of 42 mV dec$^{-1}$ compared with 80 mV dec$^{-1}$ and 96 mV dec$^{-1}$ for the rod and particle counterparts. Previous studies suggest that during two-electron CO$_2$RR, the first one-electron step of CO$_2$ to COOH$^*$ or CO$_2$$^•$ intermediates is rate-determining for the combined process.$^{46}$ The Tafel slope for the reference particles of 96 mV dec$^{-1}$ agrees well with prior reports$^{46}$ (114 and 129 mV dec$^{-1}$); in comparison, the much lower Tafel slope of 42 mV dec$^{-1}$ for the needles indicates a faster first-electron transfer step, confirming the superiority of Au needles in CO$_2$ reduction. This low Tafel slope is associated with the fast electrosorption of CO$_2$ to the surface of gold.

![Figure 3.8](image_url) **Figure 3.8** | **CO$_2$RR performance in various electrolyte conditions.** (a) Current densities and Faradaic efficiencies versus K$^+$ concentrations on Au needles at −0.35 V versus RHE. (b) Current densities and Faradaic efficiencies versus K$^+$ concentrations on planar Au at −0.4 V versus RHE. (c) CO$_2$ reduction performance of Au needles in saturated KHCO$_3$ solution. Figure prepared by Min Liu with data input by me.

To explore the impact of the cation on CO$_2$RR, I performed additional experiments at varying K$^+$ concentrations. It was found that CO$_2$RR performance increases with K$^+$ concentration (Figure 2.8a,b). Notably, Au needles exhibited a $j_{co}$ of approximately 22 mA cm$^{-2}$ at −0.35 V after 8 h by using a saturated KHCO$_3$ solution (Figure 2.8c). The long-term steady-state CO$_2$ reduction current density for the highest-performing Au needle morphology is over one order of magnitude higher at −0.35 V than for any previously reported CO$_2$ reduction catalysts in aqueous solution with inorganic electrolyte.

### 3.5 Impact of Work

The sharp-tip enhancement effect may have contributed to previous studies identifying particularly active CO$_2$RR sites at corners and ridges,$^{28,32}$ since such sites are locally high-curvature regions. It remains to be explored whether it will be effective in industrial electrolyzers operating at current densities of 300 mA cm$^{-2}$ (that is, with reaction rates ten times faster than studied here),
but enhanced control over the density of sharp tips and use of high bulk CO₂ concentrations could enhance CO₂RR rates further towards the goal of industrial electrosynthesis of carbon-based fuels. In a wider electrochemistry context, the tip-enhanced field phenomenon can be extended to concentrate the reagents locally in other reactions and as such suggests a general principle for the design of efficient electrodes for catalysis.

This chapter discussed the role of field-induced reagent concentration (FIRC) on gold nanoneedle catalysts. I showed how nanostructured morphology can be used to tune physical characteristics such as electric field effects towards increased catalytic activity and the importance of local cation effects. It provided a combined and cohesive computational and experimental picture of the underlying chemical and physical phenomena of cation and electric field effects.
Chapter 4 | Heterostructures Towards Tandem Catalysis

In the previous chapter I established the concept of using sharp nanostructures to produce high local electric fields that could concentrate cations close to the catalyst surface. This system produced CO at high rate. However, C2+ products are more valuable and also more energy rich, making them attractive targets. Since gold can intrinsically only produce CO, I sought to explore a way to upgrade CO further by interfacing the gold nanoneedles with a porous secondary catalyst material in hopes of promoting tandem catalysis. This chapter will discuss an initial attempt at interfacing a porous metal-organic framework material with gold nanoneedles for CO₂RR.

In tandem catalysis, two distinct catalytic materials are interfaced to feed the product of one reaction into the next one. This approach, analogous to enzyme cascades, can potentially be used to upgrade small molecules such as CO₂ to more valuable hydrocarbons. Here, I investigate the materials chemistry of metal–organic framework (MOF) thin films grown on gold nanostructured microelectrodes (AuNMEs), focusing on the key materials chemistry challenges necessary to enable the applications of these MOF/AuNME composites in tandem catalysis. I applied two growth methods—layer-by-layer and solvothermal—to grow a variety of MOF thin films on AuNMEs and then characterized them using scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The MOF@AuNME materials were then evaluated for electrocatalytic CO₂ reduction. The morphology and crystallinity of the MOF thin films were examined, and it was found that MOF thin films were capable of dramatically suppressing CO production on AuNMEs and producing further-reduced carbon products such as CH₄ and C₂H₄. This work illustrates the use of MOF thin films to tune the activity of an underlying CO₂RR catalyst to produce further-reduced products.

The work in this chapter has been published as a research article titled “Metal–Organic Framework Thin Films on High-Curvature Nanostructures Toward Tandem Electrocatalysis” in ACS Applied Materials & Interfaces, 10 (37), 31225–31232 (2018). Text and figures have been reproduced here with permission from The American Chemical Society. I am first author and performed all electrocatalysis experiments, synthesized the gold nanoneedles, performed SEM characterization, and wrote the manuscript. My collaborators from the King Abdullah University...
of Science and Technology (KAUST) grew the MOF thin layers, Andrew Proppe performed XPS measurements, and Petar Todorovic performed XRD measurements. All figures in this chapter were prepared by me.

4.1 Metal Organic Frameworks for CO$_2$RR

The past two decades have seen impressive advances in metal-organic frameworks (MOFs) - crystalline porous materials that are constructed via the assembly of metal ions or metal clusters and polytopic organic ligands. MOFs have attracted attention as a result of their modular nature, designed topology, high surface area and chemical tunability.$^{85,86}$

The hybrid organic–inorganic nature of MOFs permits reticular chemistry: predesigned molecular building blocks (MBBs) that possess designed-in chemical function, connectivity and geometry, enable a wide range of MOFs with prescribed topologies, pore systems, and chemical binding affinities.$^{87}$ Additionally, many types of MOFs can also be further functionalized using post-synthetic methods and by incorporation of other functions using a host-guest approach.$^{88}$ Conductive MOFs have also been recently developed whereby charge is propagated through the metal secondary building unit (SBU).$^{89}$ The versatile properties of MOFs enable their application in gas storage, separation, catalysis, sensing, and light harvesting.$^{90-92}$

Sensor devices and membranes employing MOFs depend on the fabrication and deployment of these porous materials as thin films.$^{93-95}$ There exist several techniques for the deposition of MOF thin films including the direct growth from precursor solutions, the self-assembly of precursors, and layer-by-layer growth (also known as liquid-phase epitaxy) onto desired substrates.$^{93,96}$

As described in Chapter 3, high-curvature gold nanostructured microelectrodes (AuNMEs) are a new class of materials for electrochemical biosensing and electrocatalysis. These have been shown to increase probe display for DNA biosensing applications, leading to highly sensitive detection of biomolecules using electrochemical readout.$^{80}$ AuNMEs have been deployed in the detection of cancer biomarkers,$^{97}$ infectious pathogens,$^{98}$ and in organ transplant assessment.$^{99}$
MOFs have seen intensified interest recently for CO$_2$RR, both electrochemically and photochemically.$^{100-105}$ Recent advances have focused on the use of MOFs deposited on inert substrates such as carbon paper.$^{106}$ Pioneering recent reports have begun to explore the combination of MOFs with highly active catalytic materials: a Re$_3$-MOF coated on silver nanocubes achieved plasmon-enhanced photocatalytic CO$_2$RR to CO.$^{100,107}$ In this work, the Ag nanocubes provided plasmon enhancement under visible light that led to an enhancement in photocatalytic activity on Re active centers covalently attached in the MOF pore.

MOFs combined with electrocatalysts offer promise in tandem catalysis, where the product at one catalytic center becomes the reactant at another catalytic center, analogous to biological enzyme cascades. One target for tandem catalysis is the reduction of CO$_2$ at the surface of a first catalyst CO; followed by ensuing reaction within the pores of a MOFs (proximate to the MOF:Catalyst interface) to generate further-reduced higher-value products. To advance this goal, a first step is the development of the materials chemistry to form of MOF thin films on nanostructured electrodes. In this development, the investigation of the electrochemical stability of the resultant materials is of particular importance, and merits a focused study. A challenge of particular interest will be to develop MOF:electrocatalyst hybrids that reduce CO$_2$ to products of greater value than CO.

### 4.2 Synthesis of thin film MOFs on AuNMEs

For the synthesis of MOF thin films on AuNMEs, I primarily focused on four well-studied stable MOFs: ZIF-8, Cu(bdc)$_x$H$_2$O, RE-ndc-fcu-MOF (ndc = 1,4-naphthalenedicarboxylic acid (ndc), and Al-TCPP (TCPP = Tetrakis(4-carboxyphenyl)porphyrin). ZIF-8 (Zn(MeIM)$_2$, MeIM = 2-methylimidazole) were selected for its high chemical and thermal stability (> 500 °C) and large pore size (11.6 Å).$^{108,109}$ ZIF-8 has been explored for a range of catalytic applications,$^{110,111}$ including CO oxidation with embedded gold nanoparticles.$^{112}$ Cu(bdc)$_x$H$_2$O contains open metal sites that are coordinated to water molecules, which may act as a catalytic active sites.$^{32}$ This MOF has been investigated for CO$_2$ capture and was found to be particularly active when present as 2D nanosheets.$^{33}$ Tunable rare earth fcu MOFs (Re-fcu-MOF) are a class of MOFs composed of [RE$_6$(μ$_3$-OH)$_8$(O$_2$C−)$_{12}$] hexanuclear MBBs (MBB=molecular building block) bridged by a ditopic ligand, where the carbon atoms of the coordinated carboxylates act as points of extension. This
RE-fcu-MOF is highly thermally stable up to 500°C and chemically stable in water, acidic, and basic conditions. The fcu-MOF platform has been explored mostly for its molecular sieving capabilities and hydrocarbon separations and have not previously been investigated for electrocatalysis. Al$_2$(OH)$_2$TCPP has porphyrin molecular units and was shown to be hydrolytically stable and thermally stable up to 400°C. Furthermore, it was found to be electrocatalytically active in CO$_2$RR for the production of CO.

To fabricate MOF thin films on AuNMEs, our collaborators at KAUST utilized two distinct thin film growth approaches: layer-by-layer (or liquid phase epitaxy) and solvothermal methods (Figure 4.1). ZIF-8 and Cu(bdc)-xH$_2$O were fabricated using the layer-by-layer method while the RE-ndc-fcu-MOF and Al$_2$(OH)$_2$TCPP MOF were fabricated via the solvothermal method. In the layer-by-layer method, AuNME substrate was first functionalized by an OH-terminated self-assembled monolayer. Next the surface-functionalized AuNME was immersed in the metal-containing precursor, rinsed with solvent, and then dipped in the organic ligand precursor and repeated to the desired film thickness. In the solvothermal method, AuNME substrates were first functionalized using an OH-terminated self-assembled monolayer; then the functionalized surface was immersed in a solution containing the metal precursor, the ligand precursor, and solvent; and the mixture was then heated at a fixed temperature for a specified time. Full synthesis details are available in the Appendix A Methods section.

![Figure 4.1](image)

**Figure 4.1 | Schematic illustration of MOF thin film growth on AuNMEs.** (a) layer-by-layer method or the (b) solvothermal method.
4.3 Characterization and Electrochemical Stability

To study the electrochemical stability of the resultant thin film MOFs on AuNMEs, I performed cyclic voltammetry experiments in the range of 0 V vs. RHE to -1 V vs. RHE in CO\textsubscript{2} saturated 0.1 M KHCO\textsubscript{3} electrolyte (Figure 4.2a). The CV range with an upper limit of -1 V vs. RHE was chosen to minimize irreversible reduction of the MOF.

For each MOF, the CV plots were found to be stable after 3 scans. ZIF-8, Cu(bdc)\textcdot xH\textsubscript{2}O, and Al\textsubscript{2}(OH)\textsubscript{4}TCPP exhibited reduction peaks that differed notably from that of the AuNME control. All MOFs showed similar reduction onset potentials of ~-0.35 V vs. RHE for either HER or CO\textsubscript{2}RR.

Interestingly, the RE-ndc-fcu-MOF showed a similar CV curve to the AuNME control with no characteristic oxidation or reduction peak features as observed for the other evaluated MOFs. This suggests that RE-ndc-fcu-MOF is not electrochemically active; or that the RE-ndc-fcu-MOF degraded immediately. To determine the chemical composition and the associated crystal structure after CO\textsubscript{2}RR, X-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD) experiments on the AuNME/MOF composites was performed. CO\textsubscript{2}RR was performed in a three-electrode H-cell set up with CO\textsubscript{2} saturated 0.1M KHCO\textsubscript{3} as the electrolyte, platinum as the counter-electrode, and Ag/AgCl as the reference electrode. An applied potential of -0.5 V vs. RHE was applied unless otherwise stated and sustained for over an hour of reaction. XPS results (Figure 4.2b-e) confirm the presence of Zn, Cu, and Al on the surface of the AuNME after reaction, indicating that the metal component of the MOF remains.
**Figure 4.2 | Electrochemical and physical characterization.** (a) Cyclic voltammetry (0 to -1 V vs. RHE, 0.1 M KHCO$_3$) plots of the different thin film MOFs deposited on Au NME. XPS measurements of Zn (b), Cu (c), Y (d), and Al (e) of AuNME/MOF thin films before and after reaction. XRD measurements of ZIF-8, Cu(bdc)$\cdot$xH$_2$O (f), RE-ndc-fcu-MOF and Al$_2$(OH)$_2$TCPP (g) thin films before and after reaction.

To assess the alteration/decrease of the MOF metal content after vs. before reaction, XPS studies were performed to calculate the metal atomic percent. It was found that ZIF-8 was the most stable, with only a 2.3% decrease of Zn; Al$_2$(OH)$_2$TCPP exhibited a 12% decrease of Al, Cu(bdc)$\cdot$xH$_2$O showed a 32% decrease of Cu, and RE-ndc-fcu-MOF had the greatest amount with a 71% decrease of Y. These results suggest very little Y remaining after the reaction (**Figure 4.2d**), suggesting that the Y metal has leached into the electrolyte solution. This agrees with the CV experiments that show RE-ndc-fcu-MOF exhibits a similar CV curve to AuNME. A peak around 932 eV (indicative of Cu$^0$) appeared in the Cu$^{2p}$ spectrum after reaction (**Figure 4.2c**) suggesting that some of the copper within Cu(bdc)$\cdot$xH$_2$O was reduced during reaction. Both the Zn and Al spectra (**Figure 4.2b,e**) showed no immediate change suggesting that ZIF-8 and Al$_2$(OH)$_2$TCPP are more electrochemically stable than Cu(bdc)$\cdot$xH$_2$O and RE-ndc-fcu-MOF X-ray diffraction measurements show the clear change in crystal structure for the various MOF thin films before and after reaction. All XRD patterns showed characteristic peaks of the (002) planes at 26$^\circ$ from the carbon paper substrate. All MOFs thin film show representative peaks corresponding to the respective MOFs.
materials. For Cu(bdc)-xH$_2$O, there is a prominent peak at 8.4° and 17.8° which is indicative of the (001) and (002) planes respectively,$^{118}$ but after reaction this peak diminishes and a peak at 18.1° appears which is originated from the formation of a different material. ZIF-8 shows a peak around 7.5°, 10.1° and 12.5° before reaction that corresponds to the (110), (200) and (211) planes,$^{109}$ but these peaks disappear after reaction suggesting a loss in crystallinity. The XRD pattern of Al$_2$(OH)$_2$TCPP shows a peak at 7.5° before reaction, but no discernable peaks remaining after CO$_2$RR reaction. Interestingly, RE-ndc-fcu-MOF show a highly crystalline structure with strong peaks at 7.2° and 8.3° corresponding to the (111) and (200) planes respectively. After reaction the crystallinity is severely diminished with only a weak peak at 7.2° remaining. These results suggest that CO$_2$RR conditions change/destroy the crystal structure of the deposited MOFs thin film.

Scanning electron microscopy (SEM) images reveal the morphology of the MOF thin films before and after CO$_2$RR reaction (Figure 4.3). There are distinct differences between all structures and preparation methods, i.e layer-by-layer vs. solvothermal. The layer-by-layer deposited ZIF-8 thin film coated the Au nanoneedles uniformly, with the nanostructured morphology remaining, which shows the power of the layer-by-layer method.$^{108,118}$ The contrast in the SEM images before reaction suggest that the MOF thin film is thicker at the base of the needles rather than the tips (Figure 4.3). After reaction, the morphology of the MOFs thin film was minimally changed, but the contrast between the base and tips of the nanoneedles was decreased, suggesting a degradation of the MOF. The Cu(bdc)-xH$_2$O morphology enveloped the Au nanoneedle structure and encased the needles, rather than uniformly coating them. The tips show a MOF thin film having a porous morphology before reaction; after reaction, the thin film MOF morphology has condensed and formed dendritic crystal structures atop the nanoneedles. After reaction, the crystal structure of the MOF thin film again condensed, but this time rather than forming dendritic shapes such as with Cu(bdc)-xH$_2$O, the Al$_2$(OH)$_2$TCPP showed thin flake like structures. This suggests the structure lost porosity and the final compressed structure shows an interesting correlation to the morphology before reaction, where porous MOF thin film make dendrites whereas sheet thin films make large flake like structures.
The solvothermal-deposited RE-ndc-fcu-MOF thin films formed octahedral crystals of approximately 50 μM in size rather than uniformly coating the AuNMEs. The RE-ndc-fcu-MOF crystals envelop the AuNME nanoneedles and some gold nanoneedles can be seen protruding from the sides and edges of the RE-ndc-fcu-MOF crystal. The maintained high crystallinity is reflected on the associated XRD pattern with many sharp peaks. For Al₂(OH)₂TCPP, the thin films show a similar morphology to Cu(bdc)·xH₂O with the thin film coating the AuNMEs and covering up their underlying nanoneedle morphology. A high magnification SEM image shows that the thin film MOFs are made up of aggregation of sheet-like crystals of Cu(bdc)·xH₂O.

4.4 CO₂RR Experiments on MOF@AuNMEs

To investigate the electrocatalytic activity of MOFs thin film on AuNMEs I carried out CO₂RR for one hour and examined CO₂RR activities after at least one hour of reaction. Linear sweep voltammetry (LSV) scans on all MOF thin films on AuNMEs and on an AuNME control were performed to assess their catalytic onset potentials (Figure 4.4a). The potential range was chosen...
to be from 0 V vs. RHE to -1 V vs. RHE to avoid the electrochemical decomposition of the organic linkers within the MOFs.

Overall, the catalytic activity of MOF@AuNMEs lay below that of the native AuNME. Since MOFs typically have a modest electrical conductivity, they produce a lower rate of charge transfer to the catalytic active sites compared to the native AuNME. MOFs block a portion of CO-2RR active sites on the gold AuNME, decreasing CO production. Additionally, the porous confined structure of the MOF may retard the diffusion of both reactants and products.

The current densities at -1.0 V vs. RHE ranged from 20 mA/cm² (for ZIF-8, Cu(bdc)·xH₂O, and RE-ndc-fcu-MOF) to 35 mA/cm² (Al₂(OH)₂TCPP). Interestingly, the only MOF that displayed a similar LSV curve to the AuNME control was Al₂(OH)₂TCPP suggesting good conductivity within the MOF@AuNME sample. The current densities at -0.5 V vs. RHE show an initial decrease in current density followed by a stable and sustained operation for up to 1 hour (Figure 4.4b). ZIF-8 showed almost no activity with a stable current density of -0.1 mA/cm²; while Cu(bdc)·xH₂O was slightly higher with -1.7 mA/cm². RE-ndc-fcu-MOF showed a current density of -2.5 mA/cm², and Al₂(OH)₂TCPP exhibited a current density of -3.1 mA/cm². The noise that appears in the RE-ndc-fcu-MOF around 16 mins of operation is indicative of bubble generation: gas bubble evolution accelerated at this time due to a change in the stir rate. The trends in current density remain consistent with the LSV curves.
Figure 4.4 | Electrocatalytic activity of MOF@AuNMEs. (a) Linear sweep voltammetry (LSV) scans (0 to -1 V vs. RHE, 0.1 M KHCO₃) of different MOF@AuNMEs and AuNME control. (b) Chronoamperometry (CA) plot (-0.5 V vs. RHE, 0.1 M KHCO₃) of MOF@AuNMEs and AuNME control for an hour at -0.5 V vs. RHE. (c) Faradaic efficiencies of MOF@AuNMEs and AuNME control. (d) SEM image of the AuNME tip showing the underlying metal exposed after running at -1.0 V vs. RHE.

The gaseous products were then determined using gas chromatography and the Faradaic efficiencies were calculated (Figure 4.4c). NMR analysis of the electrolyte after reaction showed no trace of liquid products. It was found that all MOF thin films produced mostly hydrogen with Faradaic efficiencies (FE) for HER from 35 ± 3 % (ZIF-8) to 56 ± 8 % (Cu(bdc)-xH₂O). All MOFs showed trace amounts of methane (CH₄) at <1 % FE and Al₂(OH)₃TCP even showed an ethylene (C₂H₄) FE of 1.1 ± 0.4 %. The only MOF that exhibited CO production, the main product for the AuNME substrate, was RE-ndc-fcu-MOF with a FE of 18 ± 2 %. The MOFs that completely covered the AuNME either by conformally coating or by enveloping the morphologies showed no CO production. As RE-ndc-fcu-MOF crystals grew on the AuNME in segregated particles, there were still many exposed AuNME active sites that could contribute to CO production, explaining the 18% FE for thin film RE-ndc-fcu-MOF on AuNME.
To test whether the CO production was attributed only to the underlying AuNMEs, I sought a way to remove partially the MOF thin film from the AuNME. Thus, I ran the CO$_2$RR at a more negative potential of -1.0 V vs. RHE in hopes of electrochemically reducing a portion of the MOF. At -1.0 V vs. RHE, the CO FE of Cu(bdc)$\cdot$xH$_2$O was 15.7 ± 3 %, an increase from no CO production at -0.5 V vs. RHE. SEM images reveal that the Cu(bdc)$\cdot$xH$_2$O were selectively removed only from the tips of the AuNME (Figure 4.4d). This suggests that the activity of the AuNME is located at the tips, which is a direct experimental evidence for the proposed field-induced reagent concentration phenomenon as previously reported in Chapter 3.$^{47,119}$ All MOFs that uniformly coated the AuNMEs were able to fully suppress the CO production from AuNMEs, attesting to the coverage quality of the MOF thin films deposited via layer-by-layer and solvothermal methods. While the majority of the current went towards HER, all MOFs produced detectable amounts of CO$_2$RR products. If these products came from the degradation of the MOF itself, one would expect an additional set of diverse carbon species in the NMR spectra, but no further products were found in NMR. This suggests that the MOFs@AuNME were capable of producing CO$_2$RR products CH$_4$ and C$_2$H$_4$ that are further reduced from CO. Of note was the C$_2$H$_4$ production with Al$_2$(OH)$_2$TCPP. This production is most likely from reaction of CO$_2$ with the porphyrin linker. Previous reports on a copper-porphyrin complex deposited on carbon paper also showed CH$_4$ and C$_2$H$_4$ as minor CO$_2$RR products.$^{120}$ Ethylene production has been shown to rely heavily on CO coverage and occur via CO dimerization.$^{121}$ Ideally, high local CO generation at the surface of AuNME could promote C$_2$H$_4$ formation at a proximate MOF active site. This suggests one explanation for why CH$_4$ and C$_2$H$_4$ were observed in the case of the porphyrin-containing Al$_2$(OH)$_2$TCPP. The MOF conductivity was not directly measured but the conductivity is expected to be low as the self-assembled monolayer (11-mercapto-undecanol) used to anchor the MOF to the gold is non-conductive.

4.5 Impact of Work

This chapter described a first attempt at interfacing AuNMEs with another distinct and separate material system. While the promise of tandem catalysis, where CO$_2$ is converted on the surface of gold to one product and then in turn may be converted in the pores of a MOF, is attractive, there remain areas of improvement that I list below:
1. Electrical conductivity of the MOF.
2. The electrochemical stability of the MOF at reducing potentials.
3. The catalytic activity of the MOF.
4. Uniform coating of MOFs to retain underlying nanostructure.
5. Sufficient pore size capable of adsorbing/concentrating CO₂ and afford product diffusion to and from the metal/MOF interface.

An effective MOF for tandem applications should be sufficiently conductive to carry charge from the underlying metal substrate to the active sites within the MOF pores, be catalytically active for CO₂RR, be highly stable and not susceptible to electrochemical reduction or change under applied bias and have large enough pores to facilitate product and reactant kinetics. Solutions to these challenge areas include using non-aqueous solvent, co-catalysts, and flow-cell configurations that allow stable operation of CO₂RR at a three-phase interface.⁵⁴
Chapter 5 | Thin Catalyst Overlayers Modulate Electrocatalysis

In Chapter 3 I introduced gold nanoneedles and electric field effects and in Chapter 4 I attempted to combine gold nanoneedles with MOFs to explore tandem catalysis. So far, the main product that has been demonstrated with the nanoneedle morphology has been CO due to the ability of gold to produce CO. However, the question remained regarding how applicable nanostructured effects were to other products. The focus of this chapter will be on promotion of undercoordinated amorphous catalytic sites of thin catalyst overlayers on gold nanoneedles for formic acid production. I hope to show to the reader that the gold nanoneedles can be used as a support to increase the current density of other catalyst materials.

In this chapter, I describe how the presence of sulfur atoms in the catalyst surface can promote undercoordinated sites, and thereby improve the electrochemical reduction of $\text{CO}_2$ to formate. I explored, using density functional theory, how the incorporation of sulfur into tin may favor formate generation. I used atomic layer deposition of SnS$_x$ followed by a reduction process to synthesize sulfur-modulated tin (Sn(S)) catalysts. X-ray absorption near-edge structure (XANES) studies reveal higher oxidation states in Sn(S) compared with that of tin in Sn nanoparticles. Sn(S)/Au accelerates CO$_2$RR at geometric current densities of 55 mA cm$^{-2}$ at $-0.75$ V versus reversible hydrogen electrode with a Faradaic efficiency of 93%. Furthermore, Sn(S) catalysts show excellent stability without deactivation (<2% productivity change) following more than 40 hours of operation.

The work in this chapter has been published as a letter titled “Sulfur-Modulated Tin Sites Enable Highly Selective Electrochemical Reduction of CO2 to Formate” in Joule, 1 (4), 794–805 (2017). Text and figures have been reproduced here with permission from Cell Press. As a co-first author, I performed all DFT calculations and analysis, performed electrocatalysis experiments, and x-ray absorption spectroscopy experiments, and contributed to manuscript preparation. My co-first author Xueli Zheng performed ALD synthesis, electrocatalysis experiments, characterization, and control experiments. Where applicable I explicitly state which figures were prepared by myself and which were prepared by Xueli.
5.1 Sulfide-Derived Catalysts for Formate Production

Formate is one interesting product among the variety that can be synthesized via CO$_2$RR. It can be directly used as a fuel, as a means of H$_2$ storage, or as a feedstock in the synthesis of fine chemicals of interest to the pharmaceutical industry. A recent paper utilizing a gross-margin model for defining technoeconomic benchmarks for CO$_2$ reduction showed that formate and carbon monoxide may offer paths to economically viable products. Unfortunately, in the case of formate, high selectivity has been achieved only at the expense of low current density, yielding impractically low partial current densities ($j_{HCOO^-}$). In addition, many catalysts exhibit rapid deactivation within hours.

Metal surfaces have been widely used for the heterogeneous electroreduction of CO$_2$ due to their robustness and superior catalytic activity. Different strategies have been explored to control selectivity, reduce overpotentials, and increase energy efficiency. From a materials perspective, the choice of metals can be used to tailor CO$_2$RR selectivity. For example, metals such as Pd, Pb, Co, Hg, In, Bi, Cd, or Sn have been reported to favor selectivity toward formate over carbon monoxide or hydrogen. On the other hand, it has been shown that the presence of high-index facets, undercoordinated sites, and adatoms can improve CO$_2$RR energetics as the energy required for the intermediate steps in the electroreduction of CO$_2$ is lowered.

The use of metal-oxide-derived catalysts has been found to increase performance in CO$_2$ reduction when compared with their fully reduced counterparts. Metal electrodes obtained from the reduction of metal oxides exhibit a prominent increase in selectivity and provide lower overpotentials in the electrosynthesis of CO and ethylene. This is ascribed to a combination of an increased number of undercoordinated sites, the presence of oxygen promoters in metal oxides, and the synergetic effect between remaining oxide species and native metal atoms.

5.2 Computational Studies

I first sought to model the effect on the catalytic activity of CO$_2$RR to formate provided by doping sulfur atoms into Sn slabs. To this end, I carried out a computational study in which I systematically varied the sulfur content from pure tin to tin (II) sulfide. Density functional theory (DFT) calculations were used to probe the energetics along the different CO$_2$RR pathways towards
formate, carbon monoxide, and hydrogen. Different sulfur content is expected to modify surface morphology and electronic structure thereby affecting the CO$_2$RR activity. The electrochemical reduction of CO$_2$ to formate is known to proceed via an initial proton-coupled electron transfer (PCET) to form a bound formate intermediate (HCOO$^*$). Other competing reaction pathways have different predominant intermediates. Carbon monoxide evolution, for example, typically proceeds via a bound carboxylate intermediate (COOH$^*$). The hydrogen evolution reaction (HER), on the other hand, requires a bound proton (H$^*$) intermediate.

A highly selective catalyst for the production of formic acid will favour the formation of formate over carboxylate and proton intermediates. To assess the selectivity and limiting potentials for each product, we calculated the Gibbs free energy of formation ($\Delta G_f$) for HCOO$^*$, COOH$^*$, and H$^*$ intermediates on the (100) surface of Sn(S) as a function of sulfur content (Figure 5.1b). The bound HCOO$^*$ intermediate visualized with a volume slice of the electronic charge densities through the center of the oxygen atoms is shown in Figure 5.1c. Here the free energy of formation is the reaction free energy necessary to electrochemically reduce CO$_2$ to a surface intermediate species at 0 V vs. RHE at pH=0, 298K, and 1 atm. In the majority of cases, the Gibbs free energy of formation for HCOO$^*$ is lower than that of COOH$^*$. This suggests that the production of formic acid is the energetically preferred pathway. For both formate and carboxylate intermediates, the same trend is observed whereby a slight doping of S into Sn drastically lowers $\Delta G_f$ and, as the content of S increases, so does the free energy of formation. An opposite trend was observed for H$^*$, whereby the free energy of formation increases upon S incorporation. Interestingly, the $\Delta G_f$ for HCOO$^*$ was found to be negative for 3.8% (-0.13 eV), 12.5% (-0.17 eV), and 25% (-0.21 eV) S doped Sn. This suggests that the formation of the rate-limiting formate intermediate is thermodynamically downhill when sulfur is slightly doped into tin.
Figure 5.1 | DFT calculations on Sn(S). (a) Optimized surface slab structures of pure Sn, S-modulated Sn, and SnS. (b) Gibbs free energies of formation ($\Delta G_{\text{formation}}$) for HCOO$^*$ (yellow), COOH$^*$ (gray), and H$^*$ (blue) intermediates, which are the rate-limited intermediates along the reaction pathway to produce formate, carbon monoxide, and hydrogen gas, respectively. (c) Volume slice of the charge densities through the middle of the oxygen atom of a bound HCOO$^*$ intermediate. (d) Atomic accessible surface area of the metal slab normalized to the number of tin atoms as a function of sulfur content.

The theoretical limiting potential for CO$_2$RR — the calculated minimum thermodynamic potential necessary to drive the electrochemical reaction forward — was found to be closest to zero for 3.8% S with a value of -0.07 V vs. RHE at pH=0, 298K, and 1 atm. The limiting potential is taken from the reaction energy diagram as the largest $\Delta G$ along the reaction pathway. For this same composition, the limiting potentials for CO production and HER were much more negative (-1.06 V and -0.75 V respectively). These results suggest that the onset potential for formate production may be lower than that of CO or H$_2$, highlighting the beneficial effects of S incorporation on the energetics of formate generation.

To investigate computationally morphological changes that doping induced on the tin, accessible surface areas were calculated using Connolly surface areas (see SI for more details). It was found that slight doping of sulfur atoms increased the atomic surface area (normalized to the number of tin atoms in the slab) compared to tin sulfide or pure tin by 13% (Figure 5.1d). The 12.5% sulfur doped Sn(S) structure had the largest accessible surface area of 210 Å$^2$ per unit cell whereas the close packed pure tin structure had the lowest accessible surface area of 186 Å$^2$ per
unit cell. This high surface area suggests the surface has a greater degree of accessibility and is more likely to have undercoordinated sites due to the imperfect packing caused by the slight doping of sulfur. This result was validated by comparing the electrochemically active surface area (ECSA) of Sn(S) and NPs as described later in the text.

5.3 Synthesis and Characterization of Sulfur-Modulated Tin Catalysts

A method to achieve a controllably sulfur-doped Sn surface was then required to successfully implement these findings. We took the view that atomic layer deposition (ALD) could provide precise control over both S content and film thickness (Figure 5.2). SnSₓ thin films were deposited from the reaction of tetrakis(dimethylamino)tin(IV) (TDMA-Sn) and H₂S. The resulting films were then electrochemically reduced to partially remove S atoms, thereby increasing the density of active sites. In situ Raman spectra at −1.0 V versus RHE confirmed that the bulk and vast majority of SnSₓ is reduced to Sn metal at high potentials. As discussed later, the catalytic activity of Sn(S)/Au shows significantly superior performance than pure Sn nanoparticles/Au samples, which is in agreement with DFT calculations.

Figure 5.2 | Fabrication of nanostructured Sn(S) catalysts. (a-c) Schematic and SEM images of the process leading to the fabrication of Sn(S) nanostructured electrodes. (a) Au needles. (b) Au needles after
SnS deposition by ALD process. (c) Au needles coated with sulfur-modulated-tin films. (d) A SnSx slab is conformally deposited by ALD on top of the nanostructured metal backbone. (e) The selective reduction of SnSx leads to Sn(S) films, which promotes CO2RR toward formate. The dashed circle means active sites for formate generation. This figure was prepared by co-first author Xueli Zheng.

Morphological strategies have been shown to dramatically increase the rate for CO2RR toward a given product. Field-induced reagent concentration (FIRC) is a catalytic phenomenon that was first reported on nanostructured gold nanoneedles for the reduction of CO2 to CO (Figure 5.2a). Simply, high-curvature nanostructures exhibit a high local negative electric field, which concentrates proximate positively charged cations that help to stabilize CO2 reduction intermediates, promoting CO2RR. Computational studies have since shown that strong local electric fields and the presence of cations proximate to the surface promote CO2RR.119 The concept of sharp nanostructures promoting CO2RR activity and increasing current densities has since been demonstrated for CO2 reduction to formate and formic acid oxidation on branched Pd NPs47 and CO2 reduction to ethylene on copper nanodendrites.126

We sought to explore the synergy between FIRC and sulfur-modulated tin catalysts, building hybrid electrodes that combine the best nanostructured FIRC morphologies of Au nanoneedles with Sn(S), which improves formate evolution energetics (Figure 5.2). This required that the sulfur-modulated tin film be conformally deposited over the Au nanoneedles, maximizing activity toward the desired products and otherwise blocking CO active Au facets. We optimized the ALD process by controlling substrate preparation, pulse duration, and the number of cycles (Figure 5.2b,d). We achieved homogeneously dispersed sulfur elements into the Sn metal by ALD of SnSx followed by an in situ reduction process to give the active Sn(S) catalyst (Figure 5.2c,e). We have found that regardless of starting Sn:S composition (1:1 or 1:2), the majority of the sulfur is removed during the reduction step. These results imply a limitation to the amount of sulfur that can remain after the initial reduction to SnSx.

High-resolution transmission electron microscopy (HRTEM) studies were performed to provide greater insight into the surface structure and morphology of the catalyst before and after reaction (Figure 5.3). HRTEM measurements were performed by our collaborators at UC Berkeley and the Molecular Foundry. It was found that, before reaction, highly polycrystalline tin sulfide is formed with extremely small grain sizes of ~5 nm (Figure 5.3a-c). After reaction, a thin layer of
amorphous tin-based material about 2–3 nm thick forms on the surface (Figure 5.3d,e). Scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) elemental mapping showed a conformal coating of Sn(S) on Au needles, and a uniform, uncorrelated spatial distribution of Au, Sn, and S (Figure 5.3f-i), consistent with the EDS line scan.

Figure 5.3 | Characterization of sulfur-modulated tin catalysts. (a) High-resolution transmission electron microscope (HRTEM) image of the ALD SnSₓ before reaction showing a highly polycrystalline surface. Scale bar represents 5 nm. (b,c) Fast Fourier transform (FFT) of the polycrystalline region (b) and one specific crystalline grain (c). (d,e) HRTEM image of the reduced Sn(S) active catalyst after reaction showing a uniform amorphous layer on the surface. Scale bar represents 20 nm for (d); scale bar represents 5 nm for (e). Inset is the FFT of the amorphous region. (f–i) STEM image (f) of Sn(S)/Au and the corresponding EDS mapping to show homogeneously dispersed Au (g), Sn (h), and S (i). Scale bar represents 100 nm. This figure was prepared by myself, Yifan Li, and Xueli Zheng.

To elucidate the electronic configuration of the resulting Sn(S) layer in the final structure, X-ray absorption spectroscopy (XAS) on Sn(S) and Sn NPs before, in situ, and after reaction (Figure 5.4) was performed. XAS was performed at the Canadian Light Source by myself and Xueli Zheng. Sn NPs were used as a control of Sn(S). We analyzed the edge position of each compound as it shifts to higher energies with increasing oxidation of Sn. In situ Sn L₃-edge spectra at −0.7 V versus RHE indicate that the reduction of SnSₓ to Sn(S) resulted in an oxidation state between Sn⁰ and Sn²⁺, while Sn NPs do not change oxidation state (Figure 5.4a). This suggests Sn(S) at −0.7 V versus RHE was more oxidized than Sn metal, which agreed with the in-situ S K-edge spectra. The trend observed from the Sn L₃-edge (Figure 5.4b) indicates that sulfur-doped Sn possessed a higher oxidation state than Sn NPs after reaction (edge shift indicated by a red arrow), consistent
with Sn K-edge measurements (Figure 5.4c). Sn(S) exhibited a higher oxidation state than Sn NPs after reaction because Sn(S) was more readily oxidized to high valence after exposure to the open circuit potential and air. We propose that Sn(S) may have more undercoordinated Sn sites than the Sn NP control. The surface chemical compositions of SnSₓ, Sn(S) after reaction, and Sn NPs after reaction were further probed by X-ray photoelectron spectroscopy (XPS). The S 2p spectra of Sn(S) after reaction revealed the survival of sulfur throughout the reaction (Figure 5.4d). Based on the results from XPS analysis, the content of S in the Sn(S) catalyst was calculated to be 3.2%.

Figure 5.4 | Electronic structure of Sn(S) and Sn. (a) In situ Sn L₃-edge XANES spectra of Sn NPs, SnS, Sn NPs at −0.7 V versus RHE, and Sn(S) at −0.7 V versus RHE. Inset shows zoom in of the pre-edge energy range. (b) Sn L₃-edge spectra of Sn(S) and Sn NPs on carbon paper after reaction (edge shift indicated by a red arrow). (c) Sn K-edge of Sn(S) and relevant controls. Inset shows zoom in of the pre-edge energy range. (d) XPS spectra of Sn(S), Sn NPs, and ALD SnSₓ. This figure was prepared by Xueli Zheng.
5.4 CO₂RR Experiments on Sn(S) Catalysts

We then proceeded to evaluate the catalytic performance of the Sn(S)-FIRC hybrid electrodes. Linear sweep voltammetry traces reveal the superior current density of S-modulated Sn samples over bare Sn NPs (Figure 3.5a). The Faradaic efficiency of S-modulated Sn samples approaches 100% for potentials more negative than −600 mV versus RHE. The resulting partial current density is significantly higher than that of Sn samples (Figure 3.5b). A record Faradaic efficiency of 93% with a total current density of 55 mA cm⁻² (normalized to geometric surface area) is obtained at −0.75 V versus RHE for Sn(S)/Au. This formate partial current density on Sn(S)/Au represents higher than that of the best non-noble metal. To evaluate the effect of surface area, we measured the ECSA for Sn(S)/Au, Sn NPs/Au, and sputtered Sn/Au from the electrochemical double-layer capacitance of the catalytic surface. From ECSA normalized performance of CO₂ reduction to formate, the high catalytic activity of Sn(S)/Au includes an appreciable intrinsic (not surface-area-related) contribution. The partial current density for formate on Sn(S)/Au, normalized by ECSA, is between 1.2 and 3 times higher than that of Sn NPs/Au and sputtered Sn/Au.
Figure 5.5 | Performance of Sn(S) catalysts. Experiments performed in a three-electrode configuration in CO$_2$ saturated 0.1 M KHCO$_3$. (a) The CO$_2$RR polarization curve of catalysts loaded on Au needles and Sn foil, respectively. (b) Potential dependence (with iR corrected) of Faradaic efficiencies and current densities for CO$_2$RR on Sn(S)/Au (squares) and Sn NPs/Au (circles). (c) Stability test of Sn(S) at −0.75 V versus RHE (iR corrected). This figure was prepared by Xueli Zheng.

One of the most critical aspects of formate production from CO$_2$RR is the deactivation of the catalyst over time. Although Pd catalysts only require low potential for CO$_2$ to formate, CO poisoning has limited its potential practical application.$^{47}$ To characterize the performance stability of the Sn(S) catalysts, we performed CO$_2$ reduction with the Sn(S) catalyst under a constant potential of −0.75 V versus RHE continuously for 40 hours. We observed no appreciable decrease (<2%) in current (Figure 3.5c) during this time interval. Furthermore, we performed potential-cycling experiments that showed no degradation in activity over five 1-hr cycles. We also confirmed the Faradaic efficiency for formate generation was nearly quantitative (>93%) throughout the electrocatalytic process. This formate partial current density on Sn(S)/Au is higher than the previously reported non-noble metal catalysts in aqueous solution confirming that the undercoordinated tin sites greatly increased the catalytic activity of CO$_2$ to formate.
5.5 Impact of Work

Within the field of CO$_2$RR, the concept of oxide-derived catalysts were impactful. The premise was that rapid reduction of a metal oxide would give rise to grain boundaries and under coordinated metal sites due to the kinetic strain of oxygen removal. This chapter discussed using a similar sulfide-derived approach to increase activity for formic acid on sulfide-derived tin catalysts. Here the concept of nanostructuring with gold nanoneedles was maintained and utilized as a current density-increasing substrate. Interestingly, the high-resolution TEM and DFT calculations, taken together, show the emergence of an amorphous layer of sulfur-doped metal after prolonged CO$_2$ reduction. In this chapter I hoped to show the universality of these nanostructured effects in terms of increasing current density and also how undercoordinated sites may increase intrinsic activity.
Chapter 6 | Structural Evolution Controls Activity

So far in this thesis, the catalysts described have produced primarily C1 products (CO and formic acid). However, C2 products such as ethylene carry a much higher market value and represent a larger global market as described in Chapter 2. Engineering catalysts to selectively produce C2 products over C1 products is of importance. This chapter discusses a combined computational, experimental, and spectroscopic study on copper electro-redeposited catalysts towards selective ethylene production. By controlling the bottom-up growth of metal nanostructures from a metal-oxychloride solgel matrix, I was able to produce high-curvature nanostructures with Cu$^+$ species present even at highly reducing conditions.

Here I present electro-redeposition, the dissolution and redeposition of copper from a sol–gel, to enhance copper catalysts in terms of their morphology, oxidation state and consequent performance. I utilized in situ soft X-ray absorption spectroscopy to track the oxidation state of copper under CO$_2$ reduction conditions with time resolution. The sol–gel material slows the electrochemical reduction of copper, enabling control over nanoscale morphology and the stabilization of Cu$^+$ at negative potentials. CO$_2$ reduction experiments, in-situ X-ray spectroscopy and density functional theory simulations revealed the beneficial interplay between sharp morphologies and Cu$^+$ oxidation state. This is the first time that Cu$^+$ species have been observed during reaction, answering a long-standing question within the field of CO$_2$RR. The catalyst exhibits a partial ethylene current density of 160 mA cm$^{-2}$ ($-1.0$ V versus reversible hydrogen electrode) and an ethylene/methane ratio of 200.

The work in this chapter has been published as a research article titled “Electro-redeposited catalysts control morphology and oxidation state for selective carbon dioxide reduction” in *Nature Catalysis*, 1, 103–110 (2018). Text and figures have been reproduced here with permission from Spring Nature. As first author, I performed all electrocatalysis experiments, in-situ x-ray absorption spectroscopy experiments, DFT calculations, SEM characterization, and wrote the manuscript. Rafael Quintero-Bermudez assisted with XAS experiments, performed XPS measurements, and calculated spectra curve fittings. Oleksandr Bushuyev assisted with NMR
measurements. Michael B. Ross assisted with TEM measurements. I prepared all figures in this chapter.

6.1 Electro-Redeposition of Copper

As described earlier, oxide-derived (OD) copper is one class of catalyst that has shown enhanced CO$_2$RR activity and increased selectivity toward multi-carbon products.$^{130-132}$ The selectivity of these catalysts is dependent on structural morphology and copper oxidation state.$^{36,133-140}$ Electrochemical reduction of copper oxide catalyst films can lead to grain boundaries, under-coordinated sites, and roughened surfaces that are hypothesized to be catalytically active sites.$^{132,141}$ Residual oxides, proposed to play a key role in catalysis, may exist after electrochemical reduction.$^{131}$ A recent report of oxygen plasma-activated OD copper catalysts achieved an ethylene FE of 60% at -0.9 V vs. reversible hydrogen electrode (RHE),$^{133}$ with activity attributed to the presence of Cu$^+$ species. In-situ hard x-ray absorption spectroscopy (hXAS) experiments have suggested stable Cu$^+$ species exist at highly negative CO$_2$RR potentials of $\sim$1.0 vs. RHE.$^{133}$ However, the presence of Cu$^+$ species during CO$_2$RR is still the subject of debate; $^{131,142}$ and in-situ tracking of the copper oxidation state with time resolution during CO$_2$RR has remained elusive.

Morphological effects of copper nanostructures have a significant effect on the selectivity of CO$_2$RR to multi-carbon products.$^{28,143-146}$ Copper catalysts with different morphologies have been synthesized through annealing, chemical treatments on thin films, colloidal synthesis, and electrodeposition from solution.$^{130,140,147,148}$ For example, recent work reported selective ethylene production on bromide-promoted copper dendrites with a maximum ethylene FE of 57%.$^{148}$ The selectivity of this catalyst was attributed to the high-index facets and undercoordinated sites on the high-curvature structures.$^{148}$ Furthermore, high-curvature structures such as nanoneedles as described in the previous chapters promote nucleation of smaller gas bubbles,$^{149}$ and benefit from field-induced reagent concentration (FIRC),$^{47,119,150}$ where high local negative electric fields concentrate positively-charged cations to help stabilize CO$_2$ reduction intermediates,$^{151}$ enhancing CO$_2$RR. However, combining high-curvature morphology with Cu$^+$ promotion to enable selective chemical conversion has yet to be explored.
Here I report the electro-redeposition (ERD) of copper from a sol-gel precursor. This process enables simultaneous control over morphology and oxidation state. Time-resolved tracking of the copper oxidation state under *in-situ* CO₂ reduction conditions showed the presence of Cu⁺ at highly negative potentials (less than -1.0 V vs. RHE). ERD exhibits simultaneous *in-situ* dissolution and re-deposition of copper from a sol-gel copper oxychloride, enabling a broad range of nanostructures of varying sharpness to be grown from within the bulk material itself. By using *in-situ* soft X-ray absorption (sXAS) spectroscopy, I tracked in time the reduction of copper, revealing the ratio of copper species under different applied potentials. I found the transition from Cu²⁺ to Cu⁺ occurs rapidly (within 5 minutes) whereas the Cu⁺ to Cu⁰ transition is much slower. Surprisingly, 23% of the catalyst exists as Cu⁺ species under a negative applied bias as low as -1.2 V vs. RHE for over an hour of operation. The copper oxychloride sol-gel slows the reduction kinetics of copper, stabilizing Cu⁺ at more negative applied potentials. At -1.2 V vs. RHE the ERD-Cu catalyst exhibits a FE of 54% for C2+ products (ethylene, acetate, ethanol) compared to a FE of 18% for C1 products (carbon monoxide, methane, formate). ERD-Cu displays a high ethylene partial current density, within H-cell (22 mA/cm² at -1.2 V vs. RHE) and flow-cell (161 mA/cm² at -1.0 V vs. RHE) configurations with significant methane suppression and a high ethylene/methane ratio of 200. DFT calculations reveal that the formation energy of the ethylene intermediate (OCCOH*) is substantially lowered compared to the methane intermediate (COH*) on a high-curvature surface with Cu⁺ species. The *in-situ* XAS and DFT studies, taken together, portray a catalyst in which stabilization of Cu⁺ improves selectivity and high-curvature morphology improves activity of C2 production.

6.2 Synthesis and activity of ERD-Cu

I synthesized the sol-gel copper oxychloride (Cu₂(OH)₃Cl) precatalyst using an epoxide gelation approach to yield a polycrystalline porous material with amorphous regions. Scanning electron microscopy (SEM) micrographs of the surface of Cu₂(OH)₃Cl deposited on carbon paper reveal aggregated clusters with 10 nm pores and micrometer void spaces consistent with previous sol-gel reports. To form the active catalyst, a constant potential was applied in the presence of CO₂ saturated 0.1 M KHCO₃ electrolyte to reduce Cu₂(OH)₃Cl.
During CO₂RR, the FE₇Η₂ was found to range from 20% to 36% depending on applied potential (Figure 6.1a). The total FE₇CO₂RR was steady at 70% ± 5%. However, the product distribution changed: the major CO₂RR products were C1 products (CO and formate) at lower potentials; and C2+ products (ethylene, acetate, and ethanol) at higher negative potentials. The current densities ranged from 10-90 mA/cm² depending on applied potential (Figure 6.1b). The optimal potential for C2+ products (ethylene, acetate, ethanol, and propanol) was -1.2 V vs. RHE with a peak FE of 52% and C2+ partial current density of 31 mA/cm². The FE₇CO starts at 20% at -0.7 V vs. RHE and decreases to < 1% at -1.4 V vs. RHE concomitant with an increase in FE₇C₂H₄ (Figure 6.1c). The maximum FE₇C₂H₄ was 38%. It was found that ERD-Cu consistently suppresses FE₇CH₄ to below 1%.

I then sought to increase the absolute production of ethylene using a gas flowcell electrolyzer. Increased CO₂ gas diffusion in these configurations have resulted in absolute partial ethylene current densities as high as 150 mA/cm². A maximum FE₇C₂H₄ of 36% at an ethylene partial current of 161 mA/cm² at -1.0 V vs. RHE was observed with extremely strong methane suppression (FE₇CH₄ < 0.2%). A plot of ethylene/methane ratio vs. partial current density of ethylene (Figure 6.1d), representative of both selectivity and activity, of various copper catalysts shows ERD-Cu exhibits a partial ethylene current density in H-cell and flowcell systems of 22 mA/cm² and 161 mA/cm² respectively, with a ethylene/methane ratio of 200.
**Figure 6.1 | CO₂RR activity of ERD-Cu.** (a) FE s of ERD Cu at a range of applied potentials showing all products. (b) Current densities of the catalyst over 1 h of operation at different applied potentials. (c) CO₂RR gas product FE s. (d) Plot of ethylene/methane ratio versus ethylene partial current density for a range of catalysts.

### 6.3 Structural Characterization of ERD-Cu

To understand the formation of the catalyst structure, I carried out scanning electron microscopy (SEM), dark-field optical microscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD), and scanning Auger microscopy (SAM) experiments to study ERD-Cu over the course of reaction. Depending on the applied potential, different structural morphologies emerged. This growth is due to the simultaneous dissolution and re-deposition of copper ions from the bulk of the material (**Figure 6.2a**). At -0.7 V vs. RHE rounded nanostructures of approximately 0.5 μm to 5 μm in size formed on the surface (**Figure 6.2b**). At -1.0 V vs. RHE sharper needles approximately 5 μm to 10 μm in length formed. At the more negative potential of -1.2 V vs. RHE, sharper nanowhiskers of ~5 μm to 10 μm with high length to diameter ratios were dominant. Finally, at the highest applied potential of -1.4 V vs. RHE dendrites with rounded
tips appeared. SEM images were taken after the course of at least 1 hour of reduction. The structural features were homogeneously dispersed on the surface of the carbon paper substrate.

Figure 6.2 | Growth of ERD-Cu nanostructures. (a) Schematic cartoon of the electro-growth process whereby simultaneous dissolution and re-deposition of copper results in structured deposits. Scale bar is set to 5 μm. (b) SEM images of the key structure features at their specific applied potentials after at least 1 hour of reaction. (c) Evolution of nanoclusters (-0.7 V vs. RHE), nanoneedles (-1.0 vs. RHE), nanowhiskers (-1.2 V), and dendrites (-1.4 V) at increasing negative potential. All potentials are iR corrected and vs. RHE.

Dark field microscope images of blue Cu₂(OH)₃Cl as deposited on carbon paper showed uniform coverage. Images taken after 1 hour of reaction at -0.7 V vs. RHE and -1.2 V vs. RHE (Figure 6.3a,b) show that regions of metallic copper form on the electrode edges. Microscope images taken of the ERD-Cu at -1.4 V vs. RHE show the surface dominated by metallic copper. TEM images of the catalyst before and after reaction (Figure 6.3c,d) reveal the change in the morphology of the material. Before reaction, regions of both polycrystalline and porous disordered material are present in the sol-gel, but after reaction only reduced polycrystalline
material remains. XRD spectra were taken of the ERD-Cu before and after reaction (Figure 6.3e). The precursor sol-gel was found to have some amorphous regions with broad peaks that correspond primarily to Cu₂(OH)₃Cl.¹⁵³ At an applied potential of -0.7 V vs. RHE all peaks associated with the precursor have disappeared but notably there are peaks corresponding to Cu₂O and metallic copper. At more negative potentials, the peaks corresponding to copper begin to increase while the Cu₂O peak disappears. Using Scherrer’s equation,¹⁵⁵ we calculated the crystallite sizes to be approximately 18 nm, 25 nm, and 57 nm, for the Cu₂(OH)₃Cl {004},¹⁵⁶ Cu₂O {111},¹⁵⁷ Cu {111}¹⁵⁸ and phases respectively, indicating that the crystal grain size increased with applied negative potential. Additional SEM images were taken at 2, 5, 20, and 40 minutes of ERD-Cu to study the onset growth of sharp nanostructures at -1.0 V vs. RHE (Figure 6.3f). At 2 minutes, needle morphologies had begun to form in the sol-gel matrix and continued to increase in size with respect to time. By 20 minutes the needles were fully formed. Scanning Auger microscopy (SAM) was performed to determine that the elemental composition of the nanostructures consist of primarily copper (Figure 6.3g). A line survey scan shows presence of copper and oxygen in the region that the needles grow from. While we cannot exclude the effects of re-oxidation in air, XRD and SAM results, taken together, reveal the morphological evolution of ERD-Cu under applied negative potential.
Figure 6.3 | Surface characterization of ERD-Cu. Dark field microscope images of ERD-Cu after 1 hour of reaction at (a) -0.8 V vs. RHE and (b) -1.6 V vs. RHE, scale bar is 100 μm. TEM images of ERD-Cu before reaction (c) and after reaction (d), scale bar is 100 nm. (e) XRD plot of the ERD-Cu before reaction (red) and after reaction at varying applied potentials. (f) SEM images of ERD-Cu under -1.0 V vs. RHE taken at 2, 5, 20, and 40 minutes from left to right. (g) Scanning Auger microscopy images of ERD-Cu showing the Cu nanostructures (red) on carbon (green).

6.4 In-situ X-ray spectroscopy

The structural evidence for Cu\(^{+}\) prompted us to investigate further the electronic structure of the catalyst during CO\(_2\)RR. We performed in-situ soft X-ray absorption spectroscopy (sXAS) experiments on ERD-Cu under CO\(_2\) reduction conditions. Previously, in-situ hard XAS (hXAS) experiments measuring the metal K-edge were reported for CO\(_2\)RR catalysis\(^{133,142,159}\). hXAS measurements at the Cu K-edge probe high-energy (9 keV) transitions but do not provide a robust determination of the narrow band transition metal 3d electronic structure because direct excitation of Cu 1s electrons into 3d orbitals are dipole forbidden.
hXAS measurements at the Cu K-edge probe high-energy transitions between 1s and 4p electronic orbitals and are prevalent and can be used as a probe of local coordination environment. However, hXAS weakly captures 3d final states (a descriptor for catalytic activity) as 1s to 3d excitation is dipole-forbidden. As a result, the 3d electron configuration is only faintly present in hXAS as low-intensity pre-edge features that occur due to low probability quadrupole transitions. Thus, hXAS pre-edges do not provide a robust determination of the narrow band transition metal 3d electronic structure. In contrast, sXAS directly measures the dipole allowed, low energy (0.93 keV) excitation of a metal 2p electron to the partially filled 3d shell. Thus, lower energy transitions can be measured with higher spectral resolution, allowing for the acquisition of more feature-rich spectra that show greater contrast to electronic structure changes.

*Ex-situ* sXAS Cu L-edge measurements of reference standards Cu metal, Cu$_2$O, and CuO were taken (Figure 6.4a). These spectra match well in both peak position and line shape to previously published reports. The Cu L-edge spectra of the Cu$_2$(OH)$_3$Cl precursor at OCP shows an L$_3$-edge peak at 930.7 eV and an L$_2$-edge at 950.7 eV which matches well with CuO, clearly indicating that copper begins in the +2 oxidation state. We began by applying a constant potential of 1.13 V vs. RHE and measuring the Cu L-edge over the course of 5 minutes (5 scans x 1 minute each) under CO$_2$RR conditions. I then applied a more negative constant potential and re-measured the Cu L-edge for another 5 minutes continuing in a step-wise fashion up to -1.87 V vs. RHE.

The evolution of the Cu L$_3$-edge as a function of potential was tracked (Figure 6.4a). I found that at applied potentials more positive than 0.28 V vs. RHE, the Cu L-edge exhibits a distinct peak at 931 eV which is consistent with Cu$^{2+}$. At 0.28 V vs. RHE I observed that the sXAS spectra changed rapidly between each 1-minute scan (Figure 6.4b). I tracked, in real-time, the transition of copper from Cu$^{2+}$ to Cu$^+$ as the L$_3$-edge peak associated with Cu$^{2+}$ at 931 eV decreased while another higher energy peak around 934 eV began to emerge, consistent with an L$_3$-edge peak of 933.7 eV of Cu$_2$O. By observing the change in sXAS spectra with respect to time, I found the structural change of copper from Cu$^{2+}$ to Cu$^+$ occurred rapidly within 5 minutes. At applied potentials more negative than 0.28 V vs. RHE, I continued to observe a prominent sharp peak at 933 eV which is consistent with Cu$^+$. As the potentials approach reducing conditions lower than 0
V vs. RHE, the high-energy intensity past the adsorption L₃-edge increases, characteristic of bulk copper and can be explained by transitions into 4s states unhybridized with 3d states. Finally, at the applied potential of -1.87 V vs. RHE I found the spectrum matched bulk copper, indicating a complete transition from Cu⁺ to Cu⁰. There was little variation between scans of the same applied potential indicating the transition from Cu⁺ to Cu⁰ was not as rapid as the Cu²⁺ to Cu⁺ transition.

![Image showing X-ray spectroscopy measurements](image)

**Figure 6.4 | X-ray spectroscopy measurements.** (a) *In-situ* Cu L₃-edge soft x-ray absorption spectroscopy spectra of ERD-Cu at different applied potentials (solid lines) and ex-situ sXAS spectra of reference standard Cu metal (red dotted), Cu₂O (green dotted), and CuO (purple dotted). (b) Cu L₃-edge spectra with respect to time of ERD-Cu under a constant applied potential of 0.28 V vs. RHE. (c) ERD-Cu under an applied potential of -1.2 V vs. RHE over the course of 1 hour. (d) Calculated ratio of Cu oxidation states from linear combination fitting as a function of applied potential. (e) Calculated ratio of Cu oxidation with respect to time during 1 hour of reaction at -1.2 V vs. RHE. sXAS 2D mapping of the Cu intensity with the region of interest set to 940 eV with a width of 100 eV (f) before and (g) after running CO₂RR.

To provide a more quantitative analysis of the oxidation state changes during CO₂RR, I fit the *in-situ* spectra with a linear combination of the Cu metal, Cu₂O, and CuO standards. A linear combination of the sXAS spectra was fit to the Cu L₃-edge spectra taken at 0.43 V vs. RHE, 0.13 V vs. RHE, and -1.87 V vs. RHE. From the linear combination, we calculated the ratio of copper oxidation species present at each applied potential, (Figure 6.4d) assuming the reference measurements provide an accurate representation of the 0, +1, and +2 oxidation state.
Remarkably, I found that Cu(I) existed even at the negative potential of -1.47 V vs. RHE under CO$_2$RR conditions.

I tracked the change, over time and under applied bias (required for ethylene production (-1.2 V vs. RHE)), in order to determine the Cu species present during reaction (Figure 6.4c). Following 2 minutes, the majority of copper (84%) was in the Cu+ oxidation state. After an ensuing ten minutes, this had decreased to 77%. The decrease of 7% of Cu+ over 10 minutes is consistent with the potential dependent in-situ data, which reveal that the transition between Cu$^{2+}$ and Cu$^+$ is a rapid one, while the transition between Cu$^+$ and Cu$^0$ is much slower. After 1 hour under applied potential of -1.2 V vs. RHE, 23% of Cu$^+$ remained. In-situ hXAS experiments also show a more oxidized Cu species on ERD-Cu after 1 hour of operation compared to Cu foil. These results show that Cu$^+$ may be stabilized under an applied potential of -1.2 V vs. RHE for over one hour.

A 2D contour map of the Cu L$\alpha,\beta$ fluorescence intensity (Figure 6.4i,h) reveals that the copper signal is dispersed throughout the sample area before reaction. After reduction, localized regions of higher intensity appear; suggesting copper aggregation. Because halides are known to impact CO$_2$RR, XPS was performed to study the presence of chlorine on the surface of the catalyst. XPS results show that no chlorine remained on the surface of the sample after reaction. Furthermore, the oxygen intensity also decreased substantially after reaction, indicating the reduction of copper oxide. The change in Cu 2p peak is most indicative of reaction: before reaction, a sharp chemical shift is observed typical of a copper hydroxide species like Cu$_2$(OH)$_3$Cl,$^{163}$ while after reaction the Cu 2p$_{3/2}$ exhibits a signature difficult to distinguish between Cu$_2$O and metallic Cu.$^{164,165}$ These results, taken together with the sXAS measurements, evidence the presence of Cu$^+$ in ERD-Cu during CO$_2$RR.

6.5 Investigating Structure-Property Relationships

To explore further structure-property relationships, I sought to study the role of morphology and oxidation state in the catalytic performance of ERD-Cu. First, I synthesized a dendritic copper catalyst via electrodeposition$^{166}$ that exhibits a highly porous structure with nanoneedles (NN-Cu) of high curvature as a control sample representative of a copper catalyst with sharp morphologies but with no Cu$^+$ present. SEM images show that the high-curvature
The morphology of NN-Cu remained consistent before and after reaction at -1.2 V vs. RHE for over an hour (Figure 6.5a-d). This electrode was synthesized using a copper chloride deposition solution onto carbon paper, using the same copper precursor as ERD-Cu.

![Figure 6.5](image)

**Figure 6.5** | **Porous copper nanoneedle (NN-Cu) controls.** Before (a,b) and after (c,d) reaction at -1.2 V vs. RHE over at least 1 hour of operation.

I then performed electrocatalytic experiments to determine the CO$_2$RR activity of the NN-Cu control. Major products for NN-Cu were hydrogen and formate (Figure 5.6a). The majority of products were C1; there existed no applied potential at which $\text{FE}_{\text{C}_2\text{H}_4}$ exceeded $\text{FE}_{\text{C}_1}$ (Figure 5.6b). NN-Cu performed considerably worse in ethylene selectivity with a max $\text{FE}_{\text{C}_2\text{H}_4}$ of only 14%, but retained a relatively low $\text{FE}_{\text{CH}_4}$ of 4% (Figure 5.6d). Despite the decreased selectivity, the current densities of NN-Cu remained similarly high as ERD-Cu (Figure 5.6c). I propose that the high-curvature morphology is responsible for the enhancement in catalytic rate, leading to increased current densities and high local pH.
Figure 6.6 | Catalytic activity of NN-Cu control. (a) Faradaic efficiencies as a function of applied potential for NN-Cu control. (b) The Faradaic efficiencies of C1 vs C2+ products as a function of applied potential. (c) Chronoamperometry plots showing the steady current density of NN-Cu. (d) the Faradaic efficiency of CO$_2$RR gaseous products.

To provide mechanistic insights into the selectivity of ERD-Cu, I used density functional theory (DFT) calculations to explore the production of C$_2$H$_4$ versus CH$_4$. Previous mechanistic studies reveal that the reaction pathways for CH$_4$ and C$_2$H$_4$ differ at the bound CO* intermediate.$^{167-170}$ Hydrogenation of bound CO* to form bound COH* leads towards the formation of methane while the dimerization of two bound CO* intermediates leads to the formation of ethylene (Figure 5.7a). Another recent study showed that the interface between surface Cu$^+$ and Cu$^0$ stabilizes CO-CO dimerization while impeding C1 pathways. This stabilization is due to the electrostatic attraction between oppositely charged carbon atoms induced by the Cu$^+$ and Cu$^0$ interface, promoting C-C coupling.$^{171}$ I therefore concentrate on the Gibbs free energy of formation for COH* and OCCOH* as descriptors for methane formation and CO-CO dimerization to ethylene.$^{172}$
I began by constructing Cu(111) and Cu(211) slabs as model systems of flat and high curvature copper surfaces, respectively. To model ERD-Cu, we constructed a mixed Cu:Cu$_2$O slab with 25% Cu$^+$ species, closely matching the optimal amount of Cu$^+$ determined from sXAS studies. The ERD-Cu(111) and ERD-Cu(211) slabs serve as model systems for flat and high curvature ERD-Cu surfaces respectively.\textsuperscript{119} It was found that the Gibbs free energy of formation ($G_{\text{form}}$) of the OCCOH$^+$ intermediate was lowest (1.13 eV) on the ERD-Cu(211) system, 0.76 eV lower than the Cu(211) system, suggesting the presence of Cu$^+$ is favourable for ethylene production (Figure 5.7b). The only surface where the formation of COH$^+$ was favoured was on Cu(111). ERD-Cu(211) also exhibited the strongest CO binding with a binding energy of -1.45 eV (Figure 5.7c). Interestingly, DFT calculations also suggest that CH$_4$ is more favourable on ERD-Cu than bulk Cu. However, experimentally I observed severe methane suppression which suggests that methane
suppression cannot be explained fully by thermodynamic effects alone. Rather, methane suppression can be rationalized by the morphology induced high current densities which results in high local pH and unfavourable kinetics for CO hydrogenation to COH*. These DFT results suggest that Cu\(^+\) plays a crucial role in stabilizing the OCCOH* intermediate, shifting the reaction towards C2 rather than C1 products, and is consistent with experimental observations of ERD-Cu.

6.6 Impact of Work

In this chapter I described electro-redeposition to stabilize Cu\(^+\) species and promote high-curvature morphologies for highly active and selective ethylene production. I found, using in-situ sXAS, that the ERD-Cu promoted the stability of Cu\(^+\) species at negative potentials far lower than previously reported for up to one hour of reaction. In-situ sXAS is an inherently difficult technique due to the requirement of an ultra-high vacuum environment and the present study, enabled only by advanced reaction cells, represents the first in-situ soft XAS measurement of CO\(_2\) reduction electrocatalysts.

I describe a catalytic trend where sharper structures with higher curvature surfaces favour C2\(^+\) production. Previously it has been shown that sharp tips can improve bubble nucleation, concentrate stabilizing cations, and exhibit high local fields, all of which increase current densities.\(^ {47,119,149,150} \) This high current density also promotes high local pH, limiting the protonation of bound CO that leads to methane formation.\(^ {173} \) This work presents electro-redeposition from a solgel matrix as an unexplored materials strategy used to exploit electronic and morphological effects for increased activity and selectivity of CO\(_2\) reduction catalysts.
Chapter 7 | Conclusions and Outlook

Since the first demonstrations of CO₂-to-chemicals electrosynthesis by Hori et al in the 1980s, the field has come a long way. Much progress has been made synthesizing catalysts that are more active and selective, such that CO₂-to-chemicals systems are approaching commercial viability. Fundamental insights will continue to drive innovation and improvements for CO₂RR, providing much needed clarity with regard to characterizing the nature of the molecular intermediates on the surface, improving long-term electrocatalyst stability, and providing better understanding of the chemical underpinnings that result in the synthesis of C₂ products.

7.1 Future Research Directions

While the work presented in this thesis is robust, it is far from comprehensive. I now discuss future research directions that would build upon this thesis as a guide for those who may follow me.

First is understanding how and why the surface structures of metal catalysts change during electrocatalysis. Chapter 6 established that Cu catalyst surfaces are dynamic under applied bias and when immersed in electrolytes. Understanding how these surfaces change, how these changes effect activity and selectivity, and how to control and stabilize active sites is essential to developing stable and selective catalysts. Building fundamental theoretical models of electrochemical reduction for CO₂RR will be central to this direction.

The second direction focuses on leveraging high-order structure and the interface between organic/inorganic materials. For example, Chapter 4 showed how thin films of metal-organic frameworks or covalent organic frameworks on top of metal electrocatalysts may provide porous confinement effects enhancing catalytic activity on the metal surface. Augmenting heterogeneous catalyst surfaces with organic functional materials is an area that has not yet been explored.

The third direction seeks to incorporate biological motifs and themes from enzymes, such as dynamic active site environments, precise proton control, and high specificity, into heterogeneous electrocatalysis. This will be done through bio-inspired polymer motifs or
tethering molecules to the surface. There is much to be learned from biological enzymes and their primary, secondary, and tertiary structures that may be applied in heterogeneous electrocatalysis. New concepts in enzymology will be applied and tested in inorganic materials.

7.2 Emerging Concepts in CO$_2$RR

This thesis has primarily overviewed recent progress and strategies toward carbon dioxide reduction using nanostructuring of catalysts. There are several outstanding opportunities that remain for electrosynthesizing chemicals; in particular, I highlight both fundamental and applied developments that would be transformative toward more effectively catalyzing the CO$_2$RR.

7.2.1 Deepening Understanding of Electrocatalyst Functioning

Progress toward identifying new catalysts requires an intimate understanding of how they perform under operating conditions. As such, progress in in situ spectroscopy that interrogates the electrochemical interface where reactions occur is essential (Figure 7.1a). In particular, vibrational spectroscopy (infrared, Raman, and SFG) provides specific molecular insights, X-ray absorption spectroscopy (XAS) provides catalyst coordination environment insights, and X-ray photoelectron spectroscopy (XPS) describes the surface and capping species (Figure 7.1a, left). Together, this suite of in situ spectroscopies can provide a comprehensive picture for how the catalyst and reaction progress under bias, elucidating the complexities of catalyst oxidation states,$^{126,133}$ molecular intermediates (particularly toward multi-carbon products),$^{173}$ and nearest neighbor atomic coordination environments.$^{174}$
Figure 7.1 | Emerging concepts in CO$_2$RR technology. (a) In situ spectroscopy and density functional theory approaches for improved understanding catalysis at the interface (b) New material interfaces, bio-inspired motifs, and tandem catalyst designs for improved catalytic activity. (c) Integration of catalysts and new motifs into systems that locally concentrate carbon dioxide gas at the surface, which can greatly improve catalytic turnover. This figure was created by me with collaboration from Dr. Michael Ross.
Complementary to these advanced \textit{in situ} experimental techniques is the use of theoretical simulations, in particular density functional theory (DFT) and molecular dynamics (MD); these methods can often provide insights that are challenging or impossible to interrogate with current experimental capabilities. Together, they allow one to study mechanistic and thermodynamic pathways as well as improving the interpretation of complex \textit{in situ} observations; continued progress here will be essential for identifying specific catalytic intermediates as well as clarifying the complex competition interplay kinetics and solvation effects (\textbf{Figure 7.1a}).\textsuperscript{63,122,136,175,176}

Another major challenge is understanding the selectivity of electrochemical systems within the context of gas phase catalysis; though the metallic properties of elements are immutable, the presence of water, double layers, and charged cations can greatly effect catalytic selectivity at electrochemical interfaces.\textsuperscript{49,119} Describing these phenomena remains a major challenge and will require continued theoretical development. Finally, continued improvements in computer power now enable one to screen new compositions with much greater throughput than experimental approaches often allow.

\section*{7.2.2 Inspiration from Biology}

For the specific design of new catalysts, a number of nature-inspired principles have been proposed (\textbf{Figure 7.1b, left}). Many of these strategies are so-called bio-inspired in that they aim to use insights from biological systems and enzymes to improve typical heterogeneous approaches; these include the design of amorphous structures with confined active sites, the incorporation of molecular co-catalysts, and the synthesis of new kinds of catalytic interfaces. Indeed, amorphous metal catalysts have already been used for developing new kinds of oxygen evolution (OER) catalysts with great success,\textsuperscript{152,177} whereas molecular co-catalysts and electrolytes have been identified to stabilize catalytic intermediates,\textsuperscript{52} resulting in reduced overpotentials and improved catalytic turnovers. There is no doubt there is much progress to be made using these approaches, the translation of these bio-inspired concepts to heterogeneous CO\textsubscript{2}RR is in its infancy.

In addition to mimicking biochemical approaches at the active site, one can also aim to mirror the pathways and steps that biology uses to orchestrate multiple reactions. For example, acetogenic bacteria produce acetate from CO\textsubscript{2} \textit{via} a CO intermediate in the Wood-Ljungdahl
pathway. The ability to drive a similar series of reactions via a tandem interface\textsuperscript{178} or cascade approach would be of great value, reducing energetic costs, synthetic steps, and purification challenges \textit{en route} to a more valuable product (Figure 7.1b, right).

### 7.2.3 Integration Toward Working Systems

I have emphasized throughout this thesis that improvements in activity are essential for the movement in the direction of the commercialization of CO\textsubscript{2}RR for renewable-powered chemical electrosynthesis (Figure 7.1c). For both C1 and multi-carbon products, many of the challenges are similar despite the fact that C1 electrosynthesis is more advanced: the performance of the catalyst remains central to the development of an industrially viable CO\textsubscript{2}RR system. As such, it is essential to test catalyst performance at a systems level, where the highest performing components are integrated into full cell CO\textsubscript{2}-to-chemicals architectures.

Though not the focus of this thesis, integration into a full-cell design will require continued progress for oxygen reduction reaction (OER) catalysis, specifically focusing on lowering overpotentials, moving beyond noble metals, and improving stability. Additionally, electrolyte and cells designs that surpass the limits of aqueous CO\textsubscript{2} solubility and mass diffusion limits will be essential for reaching practical chemical production levels.\textsuperscript{49} Indeed, developments in this area will require improvements in ion-permeable membranes as well as improved understanding of the gas-liquid interface during electrochemical catalysis (Figure 7.1c). Finally, separating products is both complex and costly; higher Faradaic efficiencies can partly mitigate this challenge, though separating unreacted CO\textsubscript{2} remains a challenge. The ideal CO\textsubscript{2}RR system will likely incorporate several of these insights, incorporating the best-of-class catalysts, membranes, cell designs, and electrolytes, ideally in a modular fashion.

The energy and chemical industries face disruption within the coming years as renewable energy sources continue to proliferate and the appetite for reducing carbon emissions grows. The electrosynthesis of feedstock chemicals represent technologies that can provide the material supplies that the world needs without carbon emissions. Chemical feedstocks derived from CO\textsubscript{2} are attractive targets for electrocatalysis development and scale up. But this comes with its challenges and opportunities. Challenges include catalyst stability, electrolyzer efficiency, and
scale up. There still remain many scientific and engineering challenges for this technology to truly penetrate the petrochemical market, but the advances in recent years suggests that these challenges can be overcome. The opportunity now rests with the chemical and energy companies that can capitalize on this technology to become early adopters, leaving the rest of the industry playing catch up.

7.3 Summary

Throughout this thesis I have presented four distinct cases of nanostructure engineering as strategies to increase CO$_2$RR activity from both an intrinsic and extrinsic view. The advances and ideas presented herein are described below:

- High local electric fields concentrate cations on the surface of nanoneedle catalysts which in turn stabilize reaction intermediates and speed up the reaction.

- Interfacing of two distinct materials offers challenges in ensuring electronic, structural, and catalytic cohesion between the two materials.

- Undercoordinated sites on sulfide-derived catalysts are particularly active for CO$_2$RR and nanoneedle morphologies can be used as current-increasing substrates.

- The oxidation state and morphology of copper both play an important role in controlling the selectivity of CO$_2$RR.

This thesis hopes to provide a few examples of how nanostructuring may impact reactivity. Nanostructured morphologies will certainly continue to play an important role in the design of next-generation CO$_2$RR catalysts. Looking forward, understanding how these nanostructures change during reaction, how these changes effect activity and selectivity, and how to control and stabilize active sites is essential to developing stable and selective catalysts.
Chapter 8 | Original Contributions

First and co-first authored contributions († indicates equal contributions)


Co-authored contributions († indicates equal contributions)


**Publications submitted, under review, or accepted** († indicates equal contributions)


References


100. Choi, K. M. *et al.* Plasmon-Enhanced Photocatalytic CO$_2$ Conversion within Metal–Organic


202. Kresse, G. From ultrasoft pseudopotentials to the projector augmented-wave method.


Appendix A Methods

Chapter 2 Methods

Techno-economic assessment

The techno-economic assessment model provides a total plant gate levelized cost of production in the units of $ per ton of product (ammonia, hydrogen, carbon monoxide, and ethylene). The costs are broadly categorized into capital costs and operating costs. The capital costs are limited to the cost of the electrolyzer and do not include the costs of infrastructure or other equipment costs. The plant lifetime is assumed to be 30 years. The operating costs consist of the electricity costs, separation costs, plant operation costs, and COGs costs which is mainly the cost of CO\textsubscript{2} gas.

A plant is assumed to convert 200 tons of CO\textsubscript{2} a day into carbon monoxide or ethylene, referenced to the production of ethylene from Bakken shale gas formations.\textsuperscript{179} Hydrogen is produced from a production capacity of 50 tons per day referenced to a central facility as outlined in the Department of Energy’s H2A Analysis.\textsuperscript{180} Ammonia production capacity is the largest at 1500 tons per day which is an average based on Haber-Bosch plants today.\textsuperscript{181} Plant lifetime is assumed to be 30 years, which is an average of the high (40 years) and low (20 years) H\textsubscript{2} volume projection scenarios as outlined in the DOE H2A Analysis.\textsuperscript{180} We assume a capacity factor of 80% which is an optimistic renewables scenario based primarily on nuclear and geothermal power generation.\textsuperscript{182} A separation constant of $0.001/kg, a capital recovery factor of 0.08, and a product fraction of 0.10 (kg/kg mixture) were all used to model the plant.

The spot price of ammonia is taken to be $500 per ton as defined as an average over the last 5 years taken from the USDA.\textsuperscript{183} The spot price of hydrogen is taken at $3.90/kg ($3900/ton) as defined in a International Energy Agency outlook report on hydrogen.\textsuperscript{184} The spot price of CO was $1200/ton\textsuperscript{185} and the spot price of ethylene is taken as $1000/ton.\textsuperscript{186} The spot price for CO\textsubscript{2} as a feedstock (COGS costs) is $30 USD per ton.\textsuperscript{187}
The Faradaic efficiency is assumed to be 90% and the electrolyzer system capital cost was chosen to be $300/kW which is 2020 DOE target for water electrolysis hydrogen production and corresponds to an electrolyzer operating at 600 mA/cm² current density. The energy conversion efficiency is defined as the ratio of the applied potential minus the over-potential over the applied potential. A separating constant of 0.001 $/kg and a product fraction of 0.1 kg product/ kg of mixture was used. The operational cost was taken to be 10% of the electricity costs.

The costs-of-goods-sold are defined as primarily the cost of CO₂. The COGs per ton of product sold is defined as:

\[
COGS(\$/ton) = \frac{\text{Cost of } CO_2 (\$)}{\text{Production Volume (ton)}}
\]

Where production volume is:

\[
\text{Production Volume (ton)} = \frac{CO_2 \text{ Converted} \times \text{Product Molecular Weight} \times \text{Faradaic Efficiency}}{CO_2 \text{ Molecular Weight} \times \text{Product Ratio} \times 100}
\]

The total electricity costs are:

\[
\text{Electricity cost (\$/ton)} = \frac{\text{Energy Consumed (kW)} \times \text{Electricity cost (cents/kW)} + 24 \text{hours}}{\text{Production volume (ton)} \times (100 \text{ cents/dollar})}
\]

Where the energy consumed is:

\[
\text{Energy consumed (kW)} = \text{Production volume} \times \text{Product energy density} \times \text{Energy conversion efficiency}
\]

The separation cost is:

\[
\text{Separation cost (\$/ton)} = \frac{\text{Separating Constant}}{\text{Product Fraction}}
\]

The capital cost is:

\[
\text{Capital cost (\$)} = \frac{\text{Energy consumed} \times \text{Electrolyzer cost} \times \text{Capital Recovery Factor}}{\text{Capacity Factor} \times 365 \text{ days} \times \text{Production Volume}}
\]

The total plant-gate levelized cost is then described as:
Total Cost \( \left( \frac{\$}{\text{ton}} \right) \) = CapitalCost + ElectricityCost + SeparationCost + OperationalCost + CostofCO2

An example calculation for carbon monoxide with an energy conversion efficiency of 30% and an electricity price of 2 cents/kWh is listed below:

**Production Volume (ton/day)** = \( \frac{200 \text{ ton/day CO}_2 \text{ converted} \times 28 \frac{g}{\text{mol}} \times 90\% \text{ FE}}{44 \frac{g}{\text{mol}} \times 100} \) = 114 tons/day

**Energy Consumed (kW)** = \( \frac{114 \frac{\text{ton}}{\text{day}} \times 1000 \frac{kg}{\text{ton}} \times 2.81 \frac{kWh}{kg} \times 100}{24 \frac{\text{hours}}{\text{day}} \times 30\% \text{ ECE}} \) = 44686 kW

**Capital Cost ($/ton)** = \( \frac{44686 \text{ kW} \times 300 \frac{\$}{\text{kW}} \times 0.8}{0.8 \times 365 \text{ days} \times 114 \text{ ton/day}} \) = $32.30 $/ton

**Electricity cost ($/ton)** = \( \frac{44686 \text{ kW} \times 24 \frac{\text{hours}}{\text{day}} \times 2 \frac{\text{cents}}{\text{kWh}}}{100 \frac{\text{cents}}{\$} \times 114 \frac{\text{tons}}{\text{day}}} \) = $187.26 $/ton

**Separation cost ($/ton)** = \( \frac{0.001 \frac{\$}{kg}}{0.01 \frac{kg}{\text{kg mixture}} \times 1000 \frac{kg}{\text{ton}}} \) = $10 $/ton

**Operational cost($/ton)** = 10% * \( \frac{187.26 \text{ $/ton}}{\text{ton}} \) = $18.73 $/ton

**COGS cost ($/ton)** = \( \frac{200 \text{ ton}}{114 \text{ tons/day}} \) = $0.26 $/ton

**Total cost ($/ton)** = \( \frac{32.20 \text{ $/ton}}{\text{ton}} + \frac{187.26 \text{ $/ton}}{\text{ton}} + \frac{10.00 \text{ $/ton}}{\text{ton}} + \frac{18.73 \text{ $/ton}}{\text{ton}} + \frac{0.26 \text{ $/ton}}{\text{ton}} = \frac{284.55 \text{ $/ton}}{\text{ton}} \)
The technology considered is a CO₂ conversion system which operates at room temperature and ambient pressure. The only energy requirements are in electrical energy to power the electrochemical conversion of CO₂. The carbon footprint of the conversion process itself is negligible, and the majority of emissions come from the capture process and the electricity generation. When coupled with renewable energy generation, this process has a net zero carbon footprint when the product is a fuel for long term energy storage. If the product generated is a plastic or chemical feedstock then the carbon footprint is net negative as the CO₂ is sequestered into a solid consumer good and can no longer be emitted into the atmosphere. Constants of the model are provided in Table 2.

The life cycle analysis seeks to provide a description of the technology process from material extraction to operations and end-of-life of the facility. In the case of this specific technology, the operation will account for the majority of the global warming potential (GWP). The GWP is defined as the ratio of mass of CO₂ (emitted) to mass of product.

Since there has been no CO₂ electrolyzer technology yet proven at scale, we reference the Life Cycle Analysis of an analogous technology, namely hydrogen electrolyzers. It was found that the GWP contribution of the eletrolyzer unit itself is relatively small (approximately only 4%) while the majority (~96%) is from the electricity generation and product compression/transportation. We expect similar numbers for CO₂ electrolyzer technologies. As CO₂ electrolyzer technologies rely heavily upon hydrogen electrolyzer architectures, we also find that the electrolytic technology is only more favourable from an emissions perspective if renewable energy is used. Furthermore, since the emissions related to building the electrolyzer is

<table>
<thead>
<tr>
<th>Table 8.1</th>
<th>Product specific constants</th>
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</thead>
<tbody>
<tr>
<td><strong>Ammonia</strong></td>
<td><strong>Ethylene</strong></td>
</tr>
<tr>
<td>Stoichiometric Ratio</td>
<td>0.50</td>
</tr>
<tr>
<td>Number of Electrons Transferred</td>
<td>8.00</td>
</tr>
<tr>
<td>Product molecular weigh (g)</td>
<td>17.00</td>
</tr>
<tr>
<td>Energy density of the product (MJ/kg)</td>
<td>18.60</td>
</tr>
<tr>
<td>Reactant Molecular weight (g/mol)</td>
<td>28.00</td>
</tr>
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</table>
minimal in comparison to the energy usage required for operation over a 20 year lifetime, we do not consider this in our LCA. Product constants are provided in Table 7.2. We assume a plant electricity capacity of 500 kW and a capacity factor of 0.9. The net CO₂ emissions are then calculated as a function of electrical-to-chemical conversion efficiency, simply called the conversion efficiency, and the grid intensity.

The calculations of the net CO₂ emissions are described below:

\[ \text{Net Emissions} = \text{Conversion Emissions per year} - \text{Baseline Emissions per year} \]  
\[ \text{Baseline Emissions} = \text{Production volume} \times \text{GWP of product} + \text{CO}_2 \text{ converted} \]  
\[ \text{CO}_2 \text{ converted per year} = \text{CO}_2 \text{ per kg product} \times \text{Production volume} \]  
\[ \text{Production Vol.} = \left( \frac{\text{Plant Electricity Cap.} \times \text{Conversion Eff.}}{\text{Product Energy Density}} \right) \times 8760 \text{h/yr} \times \text{Capacity Factor} \]  
\[ \text{Conversion Emissions} = \left( \frac{\text{Conversion Emission}}{\text{kg product}} \right) \times \text{CO}_2 \text{ converted per year} \]  
\[ \frac{\text{Conversion Emissions}}{\text{kg product}} = (\text{CO}_2 \text{ Conversion Em.} + \text{Prod. Sep. Em.}) \times \text{Grid Intensity} \]  
\[ \text{Product Separations Emissions} = \frac{\text{CO}_2}{\text{kg product}} \times \text{Cost of Prod. Sep.} \]  
\[ \text{CO}_2 \text{ Conversion Emissions} = \frac{\text{Product Energy Density}}{\text{CO}_2 \text{ per kg product} \times \text{Conversion efficiency}} \]

Table 8.2 | Product constants for the carbon emissions life-cycle assessment

<table>
<thead>
<tr>
<th>Constants</th>
<th>Ethylene</th>
<th>Carbon Monoxide</th>
<th>Formic Acid</th>
<th>Ethanol</th>
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</thead>
<tbody>
<tr>
<td>Product Energy Density (kWh/kg)</td>
<td>13.96</td>
<td>2.8</td>
<td>1.5</td>
<td>7.4</td>
</tr>
<tr>
<td>CO₂ per kg Product (kg CO₂ / kg)</td>
<td>1.57</td>
<td>1.57</td>
<td>0.957</td>
<td>0.95</td>
</tr>
<tr>
<td>Cost of CO₂/Product Separation</td>
<td>0.354</td>
<td>0.354</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(kWh/kg)</td>
<td>190</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GWP of Product (kg CO₂ / kg)</td>
<td>5.75</td>
<td>1</td>
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<td>5.75</td>
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Table 8.3 | Maximum reported FE over time

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<thead>
<tr>
<th>Year</th>
<th>Product</th>
<th>Faradaic efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1987</td>
<td>CO</td>
<td>35</td>
<td>43</td>
</tr>
<tr>
<td>1990</td>
<td>CO</td>
<td>80</td>
<td>44</td>
</tr>
<tr>
<td>2008</td>
<td>CO</td>
<td>85</td>
<td>45</td>
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<td>Year</td>
<td>Compound</td>
<td>Value</td>
<td>Page</td>
</tr>
<tr>
<td>------</td>
<td>--------------</td>
<td>-------</td>
<td>------</td>
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<tr>
<td>2012</td>
<td>CO</td>
<td>98</td>
<td>46</td>
</tr>
<tr>
<td>1987</td>
<td>Formic acid</td>
<td>87</td>
<td>43</td>
</tr>
<tr>
<td>1990</td>
<td>Formic acid</td>
<td>94</td>
<td>44</td>
</tr>
<tr>
<td>2016</td>
<td>Formic acid</td>
<td>97</td>
<td>47</td>
</tr>
<tr>
<td>1990</td>
<td>Ethylene</td>
<td>40</td>
<td>44</td>
</tr>
<tr>
<td>2005</td>
<td>Ethylene</td>
<td>65</td>
<td>48</td>
</tr>
<tr>
<td>2018</td>
<td>Ethylene</td>
<td>70</td>
<td>49</td>
</tr>
<tr>
<td>1995</td>
<td>Ethanol</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>2012</td>
<td>Ethanol</td>
<td>10</td>
<td>51</td>
</tr>
<tr>
<td>2016</td>
<td>Ethanol</td>
<td>63</td>
<td>53</td>
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</table>
Chapter 3 Methods

Density Functional Theory Calculations

DFT calculations were performed on 3x3x3 slabs of Au(111), Au(110), Au(100), and Au(211) using the generalized gradient approximation (GGA) exchange correlation functional of Perdew-Burke-Ernzerhof. All DFT simulations were performed with the Vienna Ab Initio Simulation Package (VASP) using the projector augmented wave (PAW) method. PAW pseudopotentials were used to calculate the interaction between ions and electrons in a plane wave basis set with a cutoff energy of 500 eV and a 5x5x1 Monkhorst-Pack mesh used for k-point sampling and a fermi-level smearing of 0.1 eV. Spin polarization was included as it has previously shown to be important for binding energies on gold nanoparticles and surfaces. The surface slabs were modelled with 10 Å of vacuum and dipole corrections were implemented. Structural optimizations were performed with the BFGS algorithm until the maximum was less than 0.02 eV/atom with the surface slab being fully relaxed. Once the slab models were optimized all subsequent thermodynamic calculations were performed with the bottom two layers fixed.

All thermodynamic properties were calculated using the open-source atomic simulation environment (ASE) suite of programs. The Gibbs free energies were calculated at 298K and 1 atm as outlined below:

\[
G = H - T\Delta S = E_{DFT} + E_{ZPE} + \int_0^{298} C_v dT - T\Delta S
\]

where \( E_{DFT} \) is the DFT optimized electronic energy, \( E_{ZPE} \) is the zero-point vibrational energy, \( \int_0^{298} C_v dT \) is the heat capacity, \( T \) is the temperature, and \( \Delta S \) is the entropy. Gas phase molecules such as CO\(_2\) and H\(_2\) were treated using the ideal gas approximation while adsorbates were treating using a harmonic approximation. The DFT calculated energy for CO\(_2\) was corrected by 0.45 eV, commonly employed to account for an overestimation by DFT. The change in Gibbs free energy between reaction steps of the CO\(_2\) to CO reaction coordinate was calculated based on the computational hydrogen electrode model. Additionally, the binding energy was calculated from DFT optimized structures without K\(^+\) as follows, \( E_{\text{binding}} = E_{\text{CO}_2^*} - (E_{\text{Au}} + E_{\text{CO}_2}) \) where \( E_{\text{CO}_2^*} \) is the
energy of the system with CO$_2$ proximate to the Au surface, $E_{Au}$ is the energy of the gold surface (with and without K$^+$ for the respective cases), and $E_{CO2}$ is the gas phase energy of CO$_2$.

Charge density analysis was performed from the electron density as calculated from DFT. The volume slice was visualized in VMD with an isovalue of 0.5.$^{198}$ Bader partial atomic charges were calculated using the Bader Charge Analysis code as maintained by the Henkelman group.

**Ab Initio Molecular Dynamics (AIMD) Simulations**

All AIMD simulations on 6x6x5 slabs of Au(111), Au(110), Au(100), and Au(211) were performed within the DFT framework as mentioned above with a cutoff energy of 400 eV and gamma k-point sampling of the Brillouin zone. The electronic self-consistent loop was considered converged if the energy difference was lower than $10^{-5}$ eV at which point the MD would continue to the next time step. A canonical ensemble using a Nosé-Hoover thermostat was used with a constant temperature of 300 K. Fermi-smearing was used due to the presence of the Au(111) metal surface with 0.2 eV used as the width of smearing. A 5 ps total simulation run was performed with 1 ps equilibration and 4 ps production runs and a timestep of 1 fs for 5000 steps. An ensemble average of the RDF and MSD was obtained from 25 unique runs starting from the same initial configuration in order to better sample the binding event of CO$_2$ to Au.

**Preparation of gold needle, rod, particle and leaf electrodes**

Gold electrodes were prepared through an electrodeposition process using a solution containing HAuCl$_4$ (99.99% Sigma) and HCl (TraceSELECT) solution. The concentration of HCl was fixed at 0.5 mol l$^{-1}$ (M). Gold-coated slides (for characterization, EMF Corporation) and carbon paper (for CO$_2$RR performance measurement, Toray TGP-H-060, purchased from Fuel Cell Store) were used as substrates (0.1–0.3 cm$^2$). The Au needle electrode was formed using a 160 mM HAuCl$_4$ solution and direct current potential amperometry at $-400$ mV for 300 s. Au particle, rod and leaf electrodes were formed using direct current potential amperometry at $-250$ mV with 13 mM, 26 mM and 40 mM HAuCl$_4$ solutions for 1,200 s, 900 s and 600 s, respectively.

**Au secondary electrodeposition**
After washing with deionized water and drying, Au needles, rods and particles were coated with a thin layer of Au by electrodeposition in a solution of 20 mM HAuCl₄ and 0.5 M HClO₄. The secondary deposition was performed by using direct current potential amperometry at −400 mV for 30 s.

**Electric-field-induced adsorbed K⁺**

Electric-field-induced adsorbed K⁺ was performed in 0.5 M KHCO₃ solution. Au needles, rods and particles were run in the solution at −1 V. Once the running time reached 120 s, the electrode was directly raised above the solution. After removing the applied potential, the electrodes were immersed in 10 ml pure water and any adsorbed K⁺ on the Au needles was released into the pure water. Then, the amount of K⁺ in the water was checked using an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent Dual-View 720 with a charge-coupled device (CCD) detector for full wavelength coverage between 167 nm and 785 nm). The obtained results were normalized by using ECSA.

**Characterization**

The structural characteristics of the prepared samples were measured by powder X-ray diffraction at room temperature on a MiniFlex600 instrument with a copper target (λ = 1.54056 Å). The morphologies of the prepared Au electrodes were investigated using SEM on a Hitachi SU-8230 apparatus and TEM on a Hitachi HF-3300 instrument with an acceleration voltage of 200 kV. Compositions were studied by X-ray photoelectron spectroscopy (model 5600, Perkin-Elmer). The binding energy data were calibrated with reference to the C 1s signal at 284.5 eV. Kelvin probe atomic force microscopy images were obtained using an Asylum Research MFP-3D instrument. Electrostatic field \( \mathbf{E} \) around the electrodes was calculated to have the opposite gradient of the electric potential raw data \( \nabla V \) from Kelvin probe atomic force microscopy imaging: \( \mathbf{E} = -\nabla V \). Currents on single Au needle, rod and particle were measured by using a Cypher ES instrument with a conductive model. Before current measurement, a 10-nm-thick layer of TiO₂ was deposited on the surface of Au needles, rods and particles using a Picosun R200 atomic layer deposition system. Soft X-ray absorption measurements were performed at the Spherical Grating Monochromator beamline of the Canadian Light Source in Saskatoon.
Electrocatalytic reduction of CO\textsubscript{2}  

All CO\textsubscript{2} reduction experiments were performed using a three-electrode system connected to an electrochemical workstation (Autolab PGSTAT302N). Ag/AgCl (with saturated KCl as the filling solution) and platinum mesh were used as reference and counter electrodes, respectively. Electrode potentials were converted to the reversible hydrogen electrode (RHE) reference scale using $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197\,\text{V} + 0.0591 \times \text{pH}$.

The electrolyte was 0.5 M KHCO\textsubscript{3} saturated with CO\textsubscript{2} with pH of 7.2. The experiments were performed in a gas-tight two-compartment H-cell separated by an ion exchange membrane (Nafion117). The electrolyte in the cathodic compartment was stirred at a rate of 300 r.p.m. during electrolysis. CO\textsubscript{2} gas was delivered into the cathodic compartment at a rate of 5.00 standard cubic centimeters per minute (s.c.c.m.) and was routed into a gas chromatograph (PerkinElmer Clarus 600). The gas chromatograph was equipped with a Molecular Sieve 5A capillary column and a packed Carboxen-1000 column. Argon (Linde, 99.999%) was used as the carrier gas. The gas chromatograph columns led directly to a thermal conductivity detector to quantify hydrogen and a flame ionization detector equipped with a methanizer to quantify carbon monoxide. The partial current densities of CO and H\textsubscript{2} production were calculated from the gas chromatograph peak areas as below:

$$
\dot{j}_\text{CO} = \frac{\text{peak area}}{\alpha} \times \text{flow rate} \times \frac{2Fp_0}{RT} \times (\text{electrode area})^{-1}
$$

$$
\dot{j}_\text{H}_2 = \frac{\text{peak area}}{\beta} \times \text{flow rate} \times \frac{2Fp_0}{RT} \times (\text{electrode area})^{-1}
$$

where $\alpha$ and $\beta$ are conversion factors for CO and H\textsubscript{2} respectively based on calibration of the gas chromatograph with standard samples, $p_0 = 1.013$ bar and $T = 300$ K.

Formate was quantified on a gas chromatograph with mass spectrometry (PerkinElmer Clarus 600 GC-MS System). Assuming that two electrons are needed to produce one formate molecule, the Faradaic efficiency was calculated as $2Fn_{\text{formate}}/Q = 2Fn_{\text{formate}}/(It)$, where $F$ is the Faraday constant, $I$ is the current, $t$ is the running time and $n_{\text{formate}}$ is the total amount of produced formate (in moles).
Chapter 4 Methods

Preparation of gold nanostructured microelectrodes (AuNME)

Gold nanostructured microelectrodes were prepared through an electrodeposition process using a solution containing HAuCl$_4$ (99.99% Sigma) and HCl (TraceSELECT) solution. The concentration of HCl was fixed at 0.5 mol l$^{-1}$ (M). Gold-coated slides (for characterization, EMF Corporation) and carbon paper (for CO$_2$RR performance measurement, Toray TGP-H-060, purchased from Fuel Cell Store) were used as substrates (0.1–0.3 cm$^2$). The Au needle electrode was formed using a 160 mM HAuCl$_4$ solution and direct current potential amperometry at $-400$ mV for 300 s.

Growth of thin film ZIF-8 by layer-by-layer method

The fabrication of ZIF-8 thin films on the SAM-functionalized Au-Needles substrate was achieved using the LPE method with an automated robot device. The Au substrate was firstly immersed in the 11-mercaptoundecanol (MUD) ethanolic solution to functionalize the surface with an OH-terminated SAM. The OH-functionalized Au-Needle substrate was immersed in a 0.1 mM zinc nitrate methanolic solution, then washed with methanol. Next the substrate is immersed in a 0.2 mM 2-methyl-imidazole (mIm) methanolic solution, and subsequently washed again with pure solvent, which we considered as one cycle. The same procedure was repeated to grow more cycles of the thin film to increase the thickness, which depends on the number of growth cycles.

Growth of thin film Cu(bdc)$_x$H$_2$O by layer-by-layer method

The method of growth for the Cu(bdc)$_x$H$_2$O thin film using the liquid-phase epitaxy method has previously been described in detail. In brief, the Au-needle substrate was first modified with COOH-terminated SAM by immersing the bare substrate for 24 h in ethanolic solution of 16-mercaptohexadecanoic acid, then the Cu(bdc)$_x$H$_2$O thin film was prepared by alternatively immersing of the modified sensor substrate into ethanolic solutions of the building components: 0.5 mM of copper acetates and 0.1 mM H$_2$bdc (bdc-benzene-1,4-dicarboxylic acid), and rinsing with pure ethanol in between. The thickness of the thin film was controlled by the number of growth cycles.
Growth of thin film RE-ndc-FCU-MOF by solvo-thermal method

Growth of thin films of the fcu-MOFs thin films were prepared solvo-thermally by heating a solution containing Naphthalene dicarboxylic acid (10.1 mg, 0.087 mmol), Y(NO$_3$)$_3$·6H$_2$O (33.4 mg, 0.087 mmol), 2-fluorobenzoic acid (195.0 mg, 1.392 mmol) DMF (2.7 mL), and deionized H$_2$O (0.5 mL) in a 20 mL scintillation vial. A pre-functionalized Au-needle with the MUD SAM was placed inside the vial and sealed and heated to 105°C for 36 h and then cooled to room temperature. The Au-needle substrate was collected and washed with about 10 mL of anhydrous DMF and immersed in 10 mL of ethanol for 3 days, during which time the ethanol was replaced three times per day.

Growth of thin film Al$_2$(OH)$_2$TCPP-MOF by solvo-thermal method

Growth of thin films of the Al$_2$(OH)$_2$TCPP-MOFs thin films were prepared solvo-thermally by heating solution containing the Tetrakis(4-carboxyphenyl)porphyrin (TCPP) (100.1 mg, 0.126 mmol), AlCl$_3$·6H$_2$O (60 mg, 0.25 mmol), DMF (5 mL), and deionized H$_2$O (5 mL) in a 23 mL autoclave. We chose to use DMF as a solvent to improve the solubility of the linker molecule, which allows us to work at a lower reaction temperature of 150 °C. A pre-functionalized Au-needle with the MUD SAM was placed inside the vial and sealed and heated to 150°C for 36 h and then cooled to room temperature. The Au-needle substrate was collected and washed with about 10 mL of anhydrous DMF and immersed in 10 mL of ethanol for 3 days, during which time the ethanol was replaced three times per day.

Characterizations

XRD measurements were performed on a PANalytical X’Pert PRO MPD X-ray diffractometer at 45 kV, 40 mA for CuKα (λ= 1.5418 Å). The SEM images were recorded on a Quanta 600 FEG scanning electron microscope at 30 kV. SCXRD data were collected on Bruker X8 PROSPECTOR APEX2 CCD diffractometers (CuKα, λ= 1.54178 Å). X. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a Thermo Scientific K-Alpha system with an Al Kα source with a 400 μm spot size, 50 eV pass energy, and energy steps of 0.05 eV. The C 1s, Cu 2p, N 1s and O 1s core level spectra were recorded with an overall resolution of 0.1 eV. The
core level spectra were background corrected using Shirley algorithm and chemically distinct species were resolved using a nonlinear least squares fitting procedure.

**Electrochemical Measurements**

The CO$_2$RR activity was investigated by performing electrolysis in a gas-tight two-compartment H-cell separated by an ion exchange membrane (Nafion 117) using CO$_2$ saturated 0.1 M potassium bicarbonate (KHCO$_3$) electrolyte. The three-electrode set-up was connected to a potentiostat (Autolab PGSTAT302N). Ag/AgCl (saturated KCl) was used as the reference electrode and platinum foil was used as the counter electrode. The reaction was performed at constant iR-corrected potential and the products were taken after at least 1 hour of continuous run time. Potentiostatic electrochemical impedance spectroscopy (PEIS) with a potential range of -5 to 5 V, 100 kHz frequency and sinus amplitude of 10 mV was used to calculate the iR correction. The resistance values were 34 Ohms for H-cell. Reaction products were quantitatively determined using gas chromatography and nuclear magnetic resonance (NMR) for gas and liquid products respectively. The NMR results showed no liquid products from CO$_2$RR. Electrode potentials were converted to reversible hydrogen electrode (RHE) using the following equation, $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{V} + 0.0591 \times \text{pH}$.

The electrolyte in the cathodic compartment was stirred at a rate of 300 rpm during electrolysis. CO$_2$ gas was delivered into the cathodic compartment at a rate of 20.00 sccm and was routed into gas chromatograph (GC, PerkinElmer Clarus 600). The GC was equipped with a Molecular Sieve 5A capillary column and a packed Carboxen-1000 column. Argon (Linde, 99.999%) was used as the carrier gas. The GC columns led directly to a thermal conductivity detector (TCD) and a flame ionization detector (FID). The number of moles of gas product were calculated from GC peak areas with conversion factors for CO, H$_2$, and ethylene based on calibration with standard samples at 1.013 bar and 300 K. The Faradaic efficiency was calculated as follows: Faradaic efficiency $= eF \times n/Q = 2F \times n/(I \times t)$, where $e$ is the number of electrons transferred, $F$ is the Faraday constant, $I$ is the current, $t$ is the running time and $n$ is the total amount of product (in moles).
Chapter 5 Methods

DFT Calculations

Initially, we started by simulating a SnS slab. It is characterized by an orthorhombic herzenbergite structure where the Sn$^{2+}$ ion adopts a tetrahedral geometry coordinating three S$^{2-}$ ions with the Sn 5s$^2$ lone pair occupying the fourth position. We then gradually increased the Sn content in the SnS crystal structure by randomly replacing S atoms with Sn atoms such that the resultant structures had 37.5%, 25%, and 12.5% sulfur content. The atomic positions and unit cell parameters of all structures were relaxed and fully optimized using DFT. The optimized structural parameters for SnS served as a benchmark for the validity of further calculations. The (100) facet was used for all slabs with a $4 \times 4 \times 4$ atom slab and 20 Å between mirror images in the z axis in the unit cell. To justify the facet choice, we calculated the surface energies for the (100), (110), (111), (211), and (311) facets of SnS. It was found that the (100) facet has the lowest surface energy and is thus expected to be the most stable surface. Bader charge analysis shows electron density of the bound oxygen atoms is slightly higher on slightly doped Sn(S), suggesting a stronger Sn–O intermediate bond.

X-Ray Absorption Measurements

The Sn K-edge spectra were collected at the 06ID-1 Hard X-ray MicroAnalysis (HXMA) beamline and soft X-ray Microcharacterization (SXMRB) beamline from Canadian Light Source. In situ Sn-L$_3$ edge and S K-edge XANES spectra were collected at the soft X-ray Microcharacterization (SXMRB) beamline from Canadian Light Source. Ex situ Sn L$_3$-edge spectra were collected at Beamline 10.3.2 from the Advanced Light Source.

Preparation of Sn(S) on Au Needles

Gold electrodes were prepared through an electrodeposition process using a solution containing HAuCl$_4$ (99.99%, Sigma) and HCl (TraceSELECT) solution. SnS$_x$ was deposited at 90°C using tetrakis(dimethylamino)-tin(IV) (TDMASn, 99.99% Sn; Strem Chemicals) and H$_2$S at a constant growth rate of 0.035 nm per cycle measured by ellipsometry. TDMASn was held at 65°C. Nitrogen was used as a carrier gas (99.9999% pure, Carbagas) with a flow rate of 10 sccm. Cyclic
voltammetry measurements from 0.4 V to −1.0 V versus RHE at 50 mV/s were performed in CO₂ saturated 0.1 M KHCO₃ electrolyte for three cycles to activate and partially remove sulfur atoms from the as-prepared SnSₓ/Au electrode. The CO₂ reduction performance was then carried out in the same electrolyte.

**Preparation of Sn Nanoparticles on Au Needles**

Electrophoretic deposition was implemented to uniformly deposit Sn NPs on nanostructured Au electrode. Specially, 10 mg/L Sn NPs in ethanol were placed in the ultrasonic bath for 50 min and centrifuged for 30 min at 4,000 rpm to remove large NPs from the suspension. Finally, a DC power supply of 20 V was applied for 20 min to deposit Sn NPs.

**Electrocatalytic Reduction of CO₂**

All CO₂ reduction experiments were performed using a three-electrode system connected to an electrochemical workstation (Autolab PGSTAT302N). Ag/AgCl (with saturated KCl as the filling solution) and platinum mesh were used as reference and counter electrodes, respectively. Electrode potentials were converted to the RHE reference scale using \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.0591 \times \text{pH} \). The potentials were iR corrected using electrochemical impedance spectroscopy. The electrolyte was 0.1 M KHCO₃ saturated with CO₂. Formate was quantified on gas chromatography with mass spectrometry (PerkinElmer Clarus 600 GC-MS System). Assuming that two electrons are needed to produce one formate molecule, the Faradaic efficiency was calculated as follows: Faradaic efficiency \( = \frac{2F \times n_{\text{formate}}}{Q} = \frac{2F \times n_{\text{formate}}}{I \times t} \), where \( F \) is the Faraday constant, \( I \) is the current, \( t \) is the running time, and \( n_{\text{formate}} \) is the total amount of formate produced (in moles).

**Characterization**

High-resolution TEM (HRTEM) images were taken on an FEI monochromated F20 UT Tecnai microscope operated at 200 kV. STEM elemental mapping of samples were taken on a FEI Titan 80–300 environmental (scanning) electron microscope (E(STM)), with a spot size of 6 and a C2 aperture size of 70 μm. Scanning electron microscopy (SEM) was performed on a Hitachi SU8230 scanning electron microscope operated at 1.0 kV. Powder X-ray diffraction patterns were
obtained with a MiniFlex600 instrument. XPS measurements were carried out on a Thermo Scientific K-Alpha system, with a 300 μm spot size, 75 eV pass energy, and energy steps of 0.05 eV, and aluminum anode X-ray excitation. The Shirley algorithm was used to fit the background. Then the atomic ratio was computed by summing over the curves over the background and taking into account the absorption cross-section of Sn and S to determine relative ratios from their intensities. The *in situ* spectroelectrochemical (ATR-FTIR) measurements were performed on a Bruker IFS 66/S spectrometer. For the *in situ* technique, a sealed electrochemical cell with Pt as counter electrode, Sn(S) as working electrode, and Ag/AgCl reference electrode was mounted in the spectrometer. The system was continuously flushed with CO₂ saturated 0.1 M KHCO₃. Sn(S) was deposited onto a germanium crystal (1 × 1 × 0.2 cm parallelepiped, angle 45°C) as reflection element. During the spectroscopic recording, a constant potential was applied (−0.3 V, −0.5 V, and −0.7 V versus RHE, respectively).

Chapter 6 Methods

**Computational Details**

All density functional theory (DFT) calculations were carried out with the Vienna Ab Initio Simulation package (VASP)¹⁹³. The projector augmented wave (PAW) method¹⁹⁴ was used with the Perdew-Burke-Ernzerhof (PBE)²⁰¹ generalized gradient approximation (GGA) exchange correlation functional. All-electron frozen-core PAW pseudopotentials with a plane wave basis set as described by Blöchl²⁰² were used with a cutoff energy of 500 eV, and fermi smearing width of 0.1 eV and dipole corrections were employed. Monkhorst-Pack mesh¹⁹⁵ was used for k-point sampling with 6x6x6 k-points sampled for the optimization of all bulk structures and 5x5x1 k-points sampled for all vacuum slabs of Cu and Cu/Cu₂O. The (111) and (211) facets were used with a 4x4x4 atom slab and 20Å between mirror images in the z-axis in the unit cell. Structural and unit cell optimizations were performed with the Broyden-Fletcher-Goldfarb-Shanno (BFGS)²⁰³ algorithm until the maximum cutoff was less than 0.02 eV/atom with the structures being fully optimized. Once the slab models were optimized all subsequent thermodynamic calculations were performed with the bottom two layers fixed.
For the calculation of all thermodynamic quantities, the open-source atomic simulation environment (ASE) code was used. The Gibbs free energies were calculated at 298K and 1 atm as outlined below:

\[
G = H - TS = E_{DFT} + E_{ZPE} + \int_0^{298} C_v dT - TS
\]

where \( E_{DFT} \) is the DFT calculated electronic energy, \( E_{ZPE} \) is the zero-point vibrational energy, \( \int_0^{298} C_v dT \) is the heat capacity, \( T \) is the temperature, and \( S \) is the entropy. Gas phase molecules such as \( \text{CO}_2 \) and \( \text{H}_2 \) were treated using the ideal gas approximation while adsorbates were treated using a harmonic approximation. The computational hydrogen electrode model (CHE) was used to calculate the Gibbs free formation energy for methane and ethylene intermediates \( \text{COH}^* \) and \( \text{OCCOH}^* \). The Gibbs free energy of formation for \( \text{OCCOH}^* \) is calculated as \( G_{\text{Form}}(\text{OCCOH}^*) = G_{\text{OCCOH}^*} - (G_{\text{CO}^*} + G_{\text{H}_2}/2) \). The Gibbs free energy of formation for \( \text{COH}^* \) is calculated as \( G_{\text{Form}}(\text{COH}) = G_{\text{COH}^*} - (G_{\text{CO}^*} + G_{\text{H}_2}/2) \). The binding energy of \( \text{CO} \) is calculated as \( E_{\text{bind}}(\text{CO}) = E_{\text{CO}^*} - (E_{\text{slab}} + E_{\text{CO}}) \).

**Chemicals**

Copper (II) chloride dihydrate (99.999%, CAS 10125-13-0), copper powder (99.999% trace metal basis, CAS 7440-50-8), copper (II) oxide powder (CAS 1317-38-0), copper (I) oxide power (99.99% CAS 1317-39-1), (±)-Propylene oxide (ReagentPlus®, >99%, CAS 75-56-9), and ~5% Nafion 117 solution (CAS 31175-20-9) were purchased from Sigma-Aldrich. Toray TGP-H-060 carbon paper was purchased from Fuel Cell Store.

**Experimental Synthesis**

In a typical synthesis, 3 mmol of copper (II) chloride dihydrate (Sigma-Aldrich) is dissolved in 2 mL 2-propanal (Sigma-Aldrich, anhydrous, 99.5%) to yield a transparent green solution. Next, 2 mL of epoxide (Sigma Aldrich, (±)-Propylene oxide ReagentPlus®, >99%) and 0.2 mL of deionized water were slowly added with under constant stirring resulting in a blue solution. The solution was then allowed to age in room temperature for >24 hours to promote network formation and gelation. After aging, the gels were repeatedly washed and centrifuged with acetone (3 x 15 mL) to remove any 2-propanol and then dried under vacuum for 24 hours. The resulting sol-gel was
then ground into a fine powder using a mortar and pestle. To prepare the deposition ink 10 mg of this powder was dispersed in a mixture of 0.5 mL ethanol, 0.5 mL water, and 50 μL 5% Nafion 117 solution (Sigma-Aldrich) and then sonicated for at least 30 minutes. The ink was air-brushed onto 0.25 cm² carbon paper (Toray TGP-H-060, purchased from Fuel Cell Store) with a loading of 0.65 mg/cm² and dried to form the copper sol-gel working electrode. The loading was determined by measuring the weight of the carbon paper before and after deposition. The active catalyst was then formed by reduction at specific applied potential in CO₂ saturated 0.1 M KHCO₃ electrolyte (pH 7.2). The colour of the catalyst began to change from blue to black within 5 minutes and was completely black by 10 minutes regardless of potential applied, resulting in the active SGD-Cu catalyst. The copper nanoneedle catalysts (NN-Cu) were electrodeposited on carbon paper from a deposition solution of 0.15 M CuCl₂ in 0.5 M HCl using an applied potential of -0.7 V vs. Ag/AgCl for 1000s.

**Synthesis of ERD-Cu and NN-Cu Catalysts.**

The sol-gel precursor was prepared using an epoxide gelation synthesis (Details in Supporting Information). The active catalyst was then formed by reducing the sol-gel at specific applied potential in CO₂ saturated 0.1 M KHCO₃ electrolyte (pH 7.2). The colour of the catalyst began to change from blue to black within 5 minutes and was completely black by 10 minutes regardless of potential applied, resulting in the active ERD-Cu catalyst. The copper nanoneedle catalysts were synthesized following a modified procedure. NN-Cu were electrodeposited on carbon paper from a deposition solution of 0.15 M CuCl₂ in 0.5 M HCl using an applied potential of -0.7 V vs. Ag/AgCl for 1000s.

**In-situ X-ray absorption.**

X-ray absorption measurements at the copper L-edge and K-edge were performed at the spherical grating monochromator (SGM) beamline 11ID-1 and soft x-ray microcharacterization beamline (SXRMB) at the Canadian Light Source. All **in-situ** fluorescence yield mode measurements were performed using a custom flow cell with the catalyst immersed in CO₂ saturated 0.1 M KHCO₃ electrolyte at open-circuit potential (OCP) for at least 30 minutes before applying a potential. The window of the sample cells was mounted at an angle of roughly 45°.
with respect to both the incident beam and the detectors. The bodies of the sample cells were fabricated on an SLA NEXT 3D printer. Silicon nitride membrane windows (1 mm × 1mm × 100 nm) in Si frames (5 mm × 5mm × 525 μ m) were purchased from SPI Supplies. 20 μL of catalyst ink was drop-casted onto the windows and allowed to dry in air. For electrochemical flow cells, the windows were treated by HF, and then coated by electron-beam evaporated titanium (10 nm) and gold (30 nm) which served as the working electrode. Silver and platinum wires were used as reference and counter electrodes respectively. The calibration of Ag wire reference electrode was conducted in the standard three-electrode system (the same system as that for performance measurements) as reference electrodes, using Pt foil as working and counter electrodes. The 0.5M H₂SO₄ electrolyte (pH = 0.3) was pre-purged with Grade 4 H₂ overnight and continuously bubbled with H₂ with a flow rate of 25 ml min⁻¹ during calibrations. LSV was run around +/− 100 mV between hydrogen evolution and oxidation, and the potential of zero current was recorded. The potential of zero current was around 0.2198 V (including pH correction of 0.3 * 0.0591 = 0.0177 V) for Ag/AgCl electrode and 0.3306 V (including pH correction) for Ag wire electrode, resulting in a calibration of \( E_{Ag/AgCl(KCl, sat)} + 0.1108V = E_{Ag\ wire} \), which is the same as the previous reported value.²⁰⁴ The windows were then screwed onto the cell forming an air-tight electrolyte chamber of ∼1 mm height.

All measurements were made at room temperature in the fluorescence mode using Amptek silicon drift detectors (SDDs) with an energy resolution of approximately 120 eV. Four SDDs were employed simultaneously. The scanning time was one minute and repeated five times. The sample measurement spot was moved 0.1 mm between measurements at different applied potentials to minimize the effect of the x-ray beam on the sample. The scanning energy range of the Cu L-edge was from 920 to 960 eV. The partial fluorescence yield (PFY) was extracted from all SDDs by summation of the corresponding Cu L emission lines.

To determine the concentration of different copper species, the XAS spectra of copper standards (Cu, Cu₂O and CuO representing copper’s 0, 1+ and 2+ oxidation states respectively) were measured. Each \textit{in-situ} XAS measurement was then decomposed into a linear combination of these three copper standards with a simple linear least squares script written in MATLAB. An \( R^2 \) value is obtained as a metric for the quality of the fitting. To determine the magnitude of each
species’ XAS spectrum, the standards were normalized by matching the pre-edge and post-edge values simultaneously to account for potential changes in the cross-section of the material throughout the measurement. In addition, to account for self-absorption and other measurement artifacts that lead to the appearance of a linear term in the XAS spectrum, a linear term was subtracted from the signal prior to fitting. Despite all measures taken, it is worth noting that changes in the density of the material could occur potentially distorting the fitting, these effects are considered to be negligible however.

X-ray fluorescence mapping was performed on the SGM beamline by rastering the sample across the beam while collecting X-ray fluorescence spectra. The sample is slewed across the beam and the detectors are read out continuously. For the microscopy the beamspot size was focused to approximately 50 microns using a Kirkpatrick-Baez mirror system.

Characterization

Scanning electron microscopy (SEM) images were acquired using a Quanta FEG 250 or JEOL FE-SEM. Transmission electron microscopy (TEM) images were taken with a Hitachi H-7650 microscope. Dark field microscopy images were taken with an Olympus BXFM microscope. Powder X-ray diffraction (XRD) patterns were obtained with MiniFlex600 instrument. Data were collected in Bragg-Brentano mode using 0.02° divergence with a scan rate of 0.1° s\(^{-1}\). X-ray photoelectron spectroscopy (XPS) measurements were carried out in a Thermo Scientific K-Alpha system with an Al K\(\alpha\) source with a 400 \(\mu\)m spot size, 50 eV pass energy, and energy steps of 0.05 eV. Auger Spectroscopy imaging was performed with the PHI 710 Scanning Auger Nanoprobe system, with a cylindrical mirror analyzer and a 25 kV coaxial field emission electron gun.

Electrochemical Reduction of CO\(_2\)

The CO\(_2\)RR activity of the ERD-Cu catalysts was investigated by performing electrolysis in a two compartment H-cell in CO\(_2\) saturated 0.1 M potassium bicarbonate (KHCO\(_3\)) electrolyte. The three-electrode set-up was connected to a potentiostat (Autolab PGSTAT302N). Ag/AgCl (saturated KCl) was used as the reference electrode and platinum foil was used as the counter electrode. The reaction was performed at constant iR-corrected potential and the products were taken after at
least 1 hour of continuous run time. Potentiostatic electrochemical impedance spectroscopy (PEIS) with a potential range of -5 to 5 V, 100 kHz frequency and sinus amplitude of 10 mV was used to calculate the iR correction. The resistance values were 34 Ohms and 4.5 Ohms for H-cell and flow-cell configurations respectively. Reaction products were quantitatively determined using gas chromatography and nuclear magnetic resonance (NMR) for gas and liquid products respectively. Electrode potentials were converted to reversible hydrogen electrode (RHE) using the following equation, \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \, V + 0.0591 \times \text{pH} \).

The experiments were performed in a gas-tight two-compartment H-cell separated by an ion exchange membrane (Nafion 117). The electrolyte in the cathodic compartment was stirred at a rate of 300 rpm during electrolysis. CO\(_2\) gas was delivered into the cathodic compartment at a rate of 20.00 sccm and was routed into gas chromatograph (GC, PerkinElmer Clarus 600). The GC was equipped with a Molecular Sieve 5A capillary column and a packed Carboxen-1000 column. Argon (Linde, 99.999%) was used as the carrier gas. The GC columns led directly to a thermal conductivity detector (TCD) and a flame ionization detector (FID). The number of moles of gas product were calculated from GC peak areas with conversion factors for CO, H\(_2\), and ethylene based on calibration with standard samples at 1.013 bar and 300 K. NMR was used to determine the liquid products. 1H NMR spectra were collected on Agilent DD2 500 spectrometer in 10% D2O using water suppression mode, with DMSO as an internal standard. 10 second relaxation time between the pulses was used to allow for complete proton relaxation. The Faradaic efficiency was calculated as follows: Faradaic efficiency = \( eF \times n / Q = 2F \times n / (I \times t) \), where \( e \) is the number of electrons transferred, \( F \) is the Faraday constant, \( I \) is the current, \( t \) is the running time and \( n \) is the total amount of product (in moles).
# Appendix B DFT Tables

## Chapter 3 DFT Tables

### Table 8.4 | Summary of simulation parameters as calculated from DFT

#### A) Free Energy Corrections for gas-phase species (eV)

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_{DFT}$</th>
<th>ZPE</th>
<th>$\int CvdT$</th>
<th>$T\Delta S$</th>
<th>$G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>-14.214</td>
<td>0.564</td>
<td>0.806</td>
<td>0.67</td>
<td>-14.218</td>
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<tr>
<td>CO$_2$</td>
<td>-22.946</td>
<td>0.306</td>
<td>0.099</td>
<td>0.622</td>
<td>-23.204</td>
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<tr>
<td>H$_2$</td>
<td>-6.771</td>
<td>0.268</td>
<td>0.091</td>
<td>0.434</td>
<td>-6.848</td>
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<td>CO</td>
<td>-14.775</td>
<td>0.132</td>
<td>0.091</td>
<td>0.668</td>
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<td>HCOOH</td>
<td>-29.87</td>
<td>0.891</td>
<td>0.348</td>
<td>-1.047</td>
<td>-29.914</td>
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#### B) Free Energies for CO$_2$RR Reaction (eV)

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<tr>
<th>Surface</th>
<th>Rxn Coordinate</th>
<th>$\Delta E$</th>
<th>Au(111)</th>
<th>Au(100)</th>
<th>Au(110)</th>
<th>Au(211)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>CO$_2$ + $^*$ + 2(H$^+$ + e$^-$)</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
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<tr>
<td></td>
<td>COOH$^*$ + H$^+$ + e$^-$</td>
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<td>1.28</td>
<td>0.97</td>
<td>0.92</td>
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<tr>
<td></td>
<td>CO$^*$ + H$_2$O</td>
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<td>0.74</td>
<td>0.29</td>
<td>0.34</td>
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<tr>
<td></td>
<td>CO + $^*$ + H$_2$O</td>
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<td>0.61</td>
<td>0.61</td>
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<tr>
<td>K$^+$</td>
<td>CO$_2$ + $^*$ + 2(H$^+$ + e$^-$)</td>
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<td>0.61</td>
<td>0.28</td>
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<tr>
<td></td>
<td>COOH$^*$ + H$^+$ + e$^-$</td>
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#### C) Free Energy Corrections for Surfaces and Adsorbates

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<tr>
<th>Facet</th>
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<th>Species</th>
<th>$E$</th>
<th>ZPE</th>
<th>$\int CvdT$</th>
<th>$T\Delta S$</th>
<th>$G$</th>
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</thead>
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<td></td>
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<td>Au(211)</td>
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<tr>
<td></td>
<td></td>
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<td>-122.06</td>
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<tr>
<td></td>
<td></td>
<td>COOH$^*$</td>
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<td>0.09</td>
<td>-0.16</td>
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<tr>
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<tr>
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<td>0.07</td>
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<td>-0.19</td>
<td>-106.32</td>
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<td>K$^+$</td>
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<td>-0.19</td>
<td>-109.65</td>
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### Chapter 5 DFT Tables

#### Table 8.5 | Optimized structural parameters

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<th>Material</th>
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<th>b</th>
<th>c</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>Ref</th>
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<td>90</td>
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<tr>
<td>Sn</td>
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<td></td>
<td></td>
<td>Nature 166, 482 (1950)</td>
</tr>
<tr>
<td>Sn16S16</td>
<td>4.02</td>
<td>4.43</td>
<td>11.41</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>Calc.</td>
</tr>
<tr>
<td>Sn16S16</td>
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<td>11.43</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>APL Materials, 2013, 1(1), 011002.</td>
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<tr>
<td>Sn28S4</td>
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<td>91.1</td>
<td>Calc.</td>
</tr>
<tr>
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<td>93.3</td>
<td>91.1</td>
<td>Calc.</td>
</tr>
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</table>

#### Table 8.6 | Gas phase molecules and their thermodynamic quantities (eV)

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<tr>
<th>Molecule</th>
<th>$E_{\text{DFT}}$</th>
<th>ZPE</th>
<th>$\int CvdT$</th>
<th>TS</th>
<th>$G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>-14.21</td>
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<td>0.10</td>
<td>0.67</td>
<td>-14.22</td>
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<tr>
<td>CO$_2$</td>
<td>-22.95</td>
<td>0.31</td>
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<td>0.66</td>
<td>-22.79</td>
</tr>
<tr>
<td>H$_2$</td>
<td>-6.77</td>
<td>0.27</td>
<td>0.09</td>
<td>0.43</td>
<td>-6.94</td>
</tr>
<tr>
<td>CO</td>
<td>-14.78</td>
<td>0.13</td>
<td>0.09</td>
<td>0.67</td>
<td>-15.22</td>
</tr>
<tr>
<td>HCOOH</td>
<td>-29.87</td>
<td>0.89</td>
<td>0.11</td>
<td>1.05</td>
<td>-29.71</td>
</tr>
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#### Table 8.7 | Adsorbate molecules and their thermodynamic quantities (eV)

<table>
<thead>
<tr>
<th>Adsorbates</th>
<th>$E_{\text{elec}}$</th>
<th>ZPE</th>
<th>$\int CvdT$</th>
<th>$(-T\Delta S)$</th>
<th>$G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn16S16 (100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slab</td>
<td>-136.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHOO*</td>
<td>-162.40</td>
<td>0.62</td>
<td>0.10</td>
<td>-0.21</td>
<td>-161.89</td>
</tr>
<tr>
<td>COOH*</td>
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<td>0.60</td>
<td>0.12</td>
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<td>-161.21</td>
</tr>
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<td>CO*</td>
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<td>H*</td>
<td>-138.53</td>
<td>0.16</td>
<td>0.01</td>
<td>-0.02</td>
<td>-138.38</td>
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</tbody>
</table>

| Sn20S12 (100) |
| Slab       | -128.25         |     |             |                 |     |
| CHOO*      | -153.90         | 0.61| 0.11        | -0.26           | -153.44|
| COOH*      | -154.01         | 0.62| 0.11        | -0.24           | -153.78|
| CO*        | -143.29         | 0.18| 0.09        | -0.20           | -143.22|
| H*         | -131.55         | 0.16| 0.01        | -0.01           | -131.39|
### Table 8.8 | Theoretical limiting potential (V vs. RHE, pH=0, 273 K, 1 atm).

<table>
<thead>
<tr>
<th>% Sulfur</th>
<th>HCOOH</th>
<th>CO</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.22</td>
<td>-1.08</td>
<td>-1.06</td>
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<tr>
<td>3.8</td>
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<td>-0.46</td>
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<tr>
<td>50.00</td>
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### Table 8.9 | Calculated bader partial atomic charges in units of e

<table>
<thead>
<tr>
<th>Atom</th>
<th>Sn16S16</th>
<th>Sn20S12</th>
<th>Sn24S8</th>
<th>Sn28S4</th>
<th>Sn</th>
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<tr>
<td>O1</td>
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<td>O2</td>
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<td>7.81</td>
<td>7.99</td>
<td>8.14</td>
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<tr>
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<td>4.19</td>
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<td>4.00</td>
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<td>Sn2</td>
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<td>3.53</td>
<td>3.34</td>
<td>4.01</td>
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</table>

### Table 8.10 | Surface energies for various facets of SnS slab models
Chapter 6 DFT Tables

Table 8.11 | Thermodynamic quantities used in DFT calculations

<table>
<thead>
<tr>
<th>Facet</th>
<th>Energy/FU (eV)</th>
<th>Surface Energy (eV)</th>
<th>Relative Surface Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk SnS</td>
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Table 8.12 | Gibbs free energy of formation for reaction intermediates and CO binding energies
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<th>Catalyst</th>
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<th>$G_{form} OCCOH^*$ (eV)</th>
<th>CO $E_{binding}$ (eV)</th>
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<td>Abbreviation</td>
<td>Description</td>
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<td>flame ionization detector</td>
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