



JCAP Scientific Advances

The Joint Center for Artificial Photosynthesis (JCAP) was established by the U.S. Department of Energy in 2010 as the Fuels from Sunlight Energy Innovation Hub to advance the science needed to convert sunlight, water and carbon dioxide into a range of commercially useful fuels. Since its founding, JCAP has addressed numerous scientific and engineering challenges necessary to meet its goals, including efficient use of sunlight, water, and carbon dioxide, discovery of abundant and effective light absorbers and catalysts, a better understanding of how catalysts function within their environment, and development of integrated systems. This document summarizes progress in several areas; JCAP's publications [<https://solarfuelshub.org/publications>] provide more detailed information.

Improved performance and durability

JCAP's goals have included demonstration of solar fuels generation with a solar-to-chemical conversion efficiency that exceeds that of plants. This has required improvements in all materials used in solar fuels systems, as well as the systems themselves. The optimum photoabsorbers¹ will be stable under illumination in the aqueous electrolyte supporting coupled water oxidation and fuel forming reactions, absorb the solar spectrum efficiently, have band edges aligned with the potentials required for water oxidation and proton or CO₂ reduction, and produce a photovoltage sufficient to overcome any electrocatalytic and other overpotentials. While the main effort has been to satisfy these requirements using thin films, JCAP has also investigated designs of semiconductor nanostructure arrays that enable near-unity absorption of light,² an additional route to improved efficiency. To accelerate the process of discovery of new materials, JCAP has developed a high throughput pipeline that couples experiment and theory,³ leading to exploration of complex compositions with the requisite physical and chemical attributes.

JCAP has also sought to understand factors that lead to instability in use, such as semiconductor corrosion,⁴ which results from formation of material phases at the liquid-solid interface that are soluble at the operating potentials and pH environment, and catalyst dissolution.⁵ One anti-corrosion strategy is stabilization through self-passivation, leading to identification of new photoactive materials such as n-FeWO₄.⁶ Alternatively, high performance protection layers⁷ can be deposited to mitigate corrosion while facilitating charge transport within the layer and at its interface with the electrolyte, as demonstrated with Ti oxide,⁸ Co oxide,⁹ and Sn oxide.¹⁰

Polyelectrolyte membranes are expected to be key components in solar fuels systems. They preserve efficiency by minimizing product crossover while conducting ions between the anode and cathode regions. There is a tradeoff between these two functions, and modeling¹¹ by JCAP has served to establish the associated device-driven specifications. Experiments¹² and simulations¹³ have been used to characterize membrane permeation by typical CO₂ reduction products far from steady state, which is unlikely to be achieved in real systems due to daily and seasonal variability in solar intensity. New anion-conducting polymer designs, desirable for CO₂ reduction conditions, have been investigated to identify the correlation between composition and permeability,¹⁴ and to confer polymer stability¹⁵ during operation in electrolytes with elevated pH.

Understanding the role of catalyst environment in catalytic activity and selectivity

The surface structure of active sites and the surrounding chemical environment and electrochemical conditions comprise the major factors influencing the efficiency and selectivity of (photo)electrocatalysts for oxidation of water to form O₂ at an anode, and fuel formation at a cathode. JCAP has investigated combinations of materials, catalytic environments, electrolytes, and operating conditions that realize reduced overpotential (for efficiency) and improved selectivity for desired products while avoiding deactivation mechanisms. New catalysts have been developed for acidic electrolytes used in hydrogen generation systems, such as CoP¹⁶ for hydrogen evolution and Mn-Sb-O¹⁷ for oxygen evolution, and quinary lanthanide-Co-Fe-Ni oxide¹⁸ catalysts for oxygen evolution in basic electrolytes. The nanostructure¹⁹ of the quinary catalysts reduces overpotential²⁰ below those of the more widely used one- or two-metal catalysts such as Ni-Fe oxides. JCAP has evaluated metal electrodes for reduction of CO₂ using mechanistic theory and experiments, and has confirmed that copper and its alloys are the only materials that have sufficient activity to form fuel products by driving C-C coupling²¹ efficiently. The surface morphology²² of the catalyst plays a significant role in selectivity toward specific classes of products. JCAP has improved activity and selectivity by tandem electrocatalysis²³ schemes in which CO₂ is reduced to CO, and CO is further reduced to desired products. While efficient photoelectrochemical water splitting is most readily obtained with extreme acid or base electrolytes,²⁴ selective CO₂ reduction to liquid fuels by copper requires neutral to basic electrolytes.²⁵ JCAP has investigated how the concentration and identity of the cations²⁶ and anions²⁷ present in solution strongly influence the efficiency of CO₂ reduction. Water²⁸ also plays a role not only as a source of H, but also through its interactions with interfacial intermediates. Selectivity is also markedly affected by molecular additives²⁹ such as pyridiniums in the electrolyte, as well as polymeric overcoats³⁰ on copper surfaces. Because electrocatalysts change their structure when in contact with liquid and under an applied potential, JCAP has relied on *in situ* and *operando* measurements to characterize the actual catalytic environment. For example, JCAP has directly observed the dynamic evolution of Cu³¹ under bias and in contact with electrolyte, which influences activity and selectivity.³² JCAP has used these techniques to investigate the properties of interfacial double layers,³³ identify active sites in NiFeO_x,³⁴ and trace redox activity in IrO_x both with³⁵ and without³⁶ illumination.

Connecting photoexcitation and chemical reactions

Semiconductor photoabsorbers provide the electrons and holes required for artificial photosynthesis, and JCAP has performed studies that trace generation, relaxation and loss processes of charge carriers using transient absorption,³⁷ conversion efficiency³⁸ and photoemission³⁹ techniques. These studies provide information on how charge carrier generation is connected to photoabsorber composition and structure, particularly for metal oxides that may offer low cost alternatives to III-V semiconductors but typically suffer from low charge carrier mobility and photovoltage. The use of photoabsorbing cathodes to control selectivity for heterogeneous CO₂ reduction has been an important goal for JCAP. Because traditional photoelectrocatalytic materials such as Cu₂O are unstable, new materials have been sought using theory⁴⁰ as a guide. JCAP has investigated the use of photogenerated hot carriers,⁴¹ plasmonic⁴² and photonic⁴³ structures to couple light to chemical reactions and has found that this approach is a promising means to steer selectivity toward desired products.

Integrated systems design for high performance

Solar fuels systems function by integrating photoexcitation, chemical transformation and transport processes across broad length and time scales. A fundamental challenge is how to design system components so that the resulting combination of architecture and processes leads to optimum performance. A typical system will involve photoabsorbers, oxidation and reduction catalysts integrated with them, membrane separators, and water. JCAP has invested considerable effort in the design and fabrication of these components and test bed devices using them. Synthetic processes for integration of catalysts with photoabsorbers can be designed to optimize⁴⁴ interfacial structure and compositions. The challenge when both photoabsorber and catalyst are composed of multiple chemical elements is significant, and JCAP has developed high throughput techniques⁴⁵ to identify high-performing integrated systems. Selection of integrated components for full systems is guided by detailed multiphysics modeling,²⁴ which examines their performance characteristics within specified designs. JCAP has found that modeling is particularly important for CO₂ reduction systems due to performance constraints placed by internal transport⁴⁶ limitations and the variation of product distributions during a diurnal⁴⁷ cycle. JCAP has reported designs and demonstrations for solar-driven liquid electrolyte water splitting systems, progressively increasing solar-to-hydrogen efficiency performance by materials improvements from <1%⁴⁸ to 19.3%.⁴⁹ A sustainable technology⁵⁰ requires that a system be durable for years under the variable operational conditions. While this goal remains a challenge, JCAP has reported strategies for stabilizing systems while ensuring >10% solar-to-hydrogen efficiency with full product separation (for safety). These include use of TiO₂ protection layers⁵¹ and hybrid composite coatings⁵² to inhibit corrosion in electrolytes at extreme pH. High efficiency and stability has also been demonstrated in a vapor-fed photoelectrochemical system⁵³ using pure water, which minimizes corrosive conditions. The high overpotentials required for C-C coupling during photoelectrochemical CO₂ reduction pose additional challenges. JCAP has demonstrated a photocathode⁵⁴ design useful for liquid electrolyte systems, identified gas diffusion electrode⁵⁵ architectures as being particularly useful for CO₂ reduction, and exploited potential multistep strategies that reduce CO,⁵⁶ which can be formed as a reaction intermediate. These efforts establish technology-driven performance criteria for individual materials and integrated systems that guide materials discovery and development efforts.

References

1. Hu, S.; Xiang, C. X.; Haussener, S.; Berger, A. D.; Lewis, N. S., An Analysis of the Optimal Band Gaps of Light Absorbers in Integrated Tandem Photoelectrochemical Water-Splitting Systems. *Energy & Environmental Science* **2013**, *6* (10), 2984-2993, 10.1039/c3ee40453f.
2. Fountaine, K. T.; Cheng, W. H.; Bukowsky, C. R.; Atwater, H. A., Near-Unity Unselective Absorption in Sparse Inp Nanowire Arrays. *Acs Photonics* **2016**, *3* (10), 1826-1832, 10.1021/acsphotonics.6b00341.
3. Yan, Q. M.; Yu, J.; Suram, S. K.; Zhou, L.; Shinde, A.; Newhouse, P. F.; Chen, W.; Li, G.; Persson, K. A.; Gregoire, J. M.; Neaton, J. B., Solar Fuels Photoanode Materials Discovery by Integrating High-Throughput Theory and Experiment. *P Natl Acad Sci USA* **2017**, *114* (12), 3040-3043, 10.1073/pnas.1619940114.

4. Toma, F. M.; Cooper, J. K.; Kunzelmann, V.; McDowell, M. T.; Yu, J.; Larson, D. M.; Borys, N. J.; Abelyan, C.; Beeman, J. W.; Yu, K. M.; Yang, J. H.; Chen, L.; Shaner, M. R.; Spurgeon, J.; Houle, F. A.; Persson, K. A.; Sharp, I. D., Mechanistic Insights into Chemical and Photochemical Transformations of Bismuth Vanadate Photoanodes. *Nature Communications* **2016**, *7*, 10.1038/ncomms12012.
5. Ali-Loytty, H.; Hannula, M.; Valden, M.; Eilert, A.; Ogasawara, H.; Nilsson, A., Chemical Dissolution of Pt(111) During Potential Cycling under Negative Ph Conditions Studied by Operando X-Ray Photoelectron Spectroscopy. *Journal of Physical Chemistry C* **2019**, *123* (41), 25128-25134, 10.1021/acs.jpcc.9b05201.
6. Zhou, L.; Shinde, A.; Suram, S. K.; Stein, H. S.; Bauers, S. R.; Zakutayev, A.; DuChene, J. S.; Liu, G. J.; Peterson, E. A.; Neaton, J. B.; Gregoire, J. M., Bi-Containing N-Few4 Thin Films Provide the Largest Photovoltage and Highest Stability for a Sub-2 Ev Band Gap Photoanode. *Acs Energy Lett* **2018**, *3* (11), 2769-2774, 10.1021/acsenergylett.8b01514.
7. Hu, S.; Lewis, N. S.; Ager, J. W.; Yang, J.; McKone, J. R.; Strandwitz, N. C., Thin-Film Materials for the Protection of Semiconducting Photoelectrodes in Solar-Fuel Generators. *The Journal of Physical Chemistry C* **2015**, *119* (43), 24201-24228, 10.1021/acs.jpcc.5b05976.
8. Hu, S.; Shaner, M. R.; Beardslee, J. A.; Lichterman, M.; Brunschwig, B. S.; Lewis, N. S., Amorphous Tio2 Coatings Stabilize Si, Gaas, and Gap Photoanodes for Efficient Water Oxidation. *Science* **2014**, *344* (6187), 1005-1009, 10.1126/science.1251428.
9. Yang, J. H.; Cooper, J. K.; Toma, F. M.; Walczak, K. A.; Favaro, M.; Beeman, J. W.; Hess, L. H.; Wang, C.; Zhu, C. H.; Gul, S.; Yano, J. K.; Kisielowski, C.; Schwartzberg, A.; Sharp, I. D., A Multifunctional Biphasic Water Splitting Catalyst Tailored for Integration with High-Performance Semiconductor Photoanodes. *Nature Materials* **2017**, *16* (3), 335-+, 10.1038/Nmat4794.
10. Moreno-Hernandez, I. A.; Brunschwig, B. S.; Lewis, N. S., Tin Oxide as a Protective Heterojunction with Silicon for Efficient Photoelectrochemical Water Oxidation in Strongly Acidic or Alkaline Electrolytes. *Advanced Energy Materials* **2018**, *8* (24), 10.1002/aenm.201801155.
11. Berger, A.; Segalman, R. A.; Newman, J., Material Requirements for Membrane Separators in a Water-Splitting Photoelectrochemical Cell. *Energy & Environmental Science* **2014**, 10.1039/C3EE43807D.
12. Carter, B. M.; Dobyns, B. M.; Beckingham, B. S.; Miller, D. J., Multicomponent Transport of Alcohols in an Anion Exchange Membrane Measured by in-Situ Atr Ftir Spectroscopy. *Polymer* **2017**, *123*, 144-152, 10.1016/j.polymer.2017.06.070.
13. Soniat, M.; Houle, F. A., Swelling and Diffusion During Methanol Sorption into Hydrated Nafion. *J Phys Chem B* **2018**, *122* (34), 8255-8268, 10.1021/acs.jpcc.8b03169.
14. Carter, B. M.; Keller, L.; Wessling, M.; Miller, D., Preparation and Characterization of Crosslinked Poly(Vinylimidazolium) Anion Exchange Membranes for Artificial Photosynthesis. *J Mater Chem A* **2019**, DOI: 10.1039/C9TA00498J.
15. Cotanda, P.; Petzetakis, N.; Jiang, X.; Stone, G.; Balsara, N. P., Hydroxide-Ion Transport and Stability of Diblock Copolymers with a Polydiallyldimethyl Ammonium Hydroxide Block. *J Polym Sci Pol Chem* **2017**, *55* (13), 2243-2248, 10.1002/pola.28611.

16. Saadi, F. H.; Carim, A. I.; Verlage, E.; Hemminger, J. C.; Lewis, N. S.; Soriaga, M. P., Cop as an Acid-Stable Active Electrocatalyst for the Hydrogen-Evolution Reaction: Electrochemical Synthesis, Interfacial Characterization and Performance Evaluation. *Journal of Physical Chemistry C* **2014**, *118* (50), 29294-29300, 10.1021/jp5054452.
17. Zhou, L.; Shinde, A.; Montoya, J. H.; Singh, A.; Gul, S.; Yano, J.; Ye, Y. F.; Crumlin, E. J.; Richter, M. H.; Cooper, J. K.; Stein, H. S.; Haber, J. A.; Persson, K. A.; Gregoire, J. M., Rutile Alloys in the Mn-Sb-O System Stabilize Mn³⁺ to Enable Oxygen Evolution in Strong Acid. *Acs Catalysis* **2018**, *8* (12), 10938-10948, 10.1021/acscatal.8b02689.
18. Haber, J. A.; Cai, Y.; Jung, S. H.; Xiang, C. X.; Mitrovic, S.; Jin, J.; Bell, A. T.; Gregoire, J. M., Discovering Ce-Rich Oxygen Evolution Catalysts, from High Throughput Screening to Water Electrolysis. *Energy & Environmental Science* **2014**, *7* (2), 682-688, 10.1039/c3ee43683g.
19. Haber, J. A.; Anzenburg, E.; Yano, J.; Kisielowski, C.; Gregoire, J. M., Multiphase Nanostructure of a Quinary Metal Oxide Electrocatalyst Reveals a New Direction for OER Electrocatalyst Design. *Advanced Energy Materials* **2015**, *5* (10), 10.1002/aenm.201402307.
20. McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F., Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *Journal of the American Chemical Society* **2015**, *137* (13), 4347-4357, 10.1021/ja510442p.
21. Garza, A. J.; Bell, A. T.; Head-Gordon, M., Mechanism of Co₂ Reduction at Copper Surfaces: Pathways to C-2 Products. *Acs Catalysis* **2018**, *8* (2), 1490-1499, 10.1021/acscatal.7b03477.
22. Hahn, C.; Hatsukade, T.; Kim, Y. G.; Vailionis, A.; Baricuatro, J. H.; Higgins, D. C.; Nitopi, S. A.; Soriaga, M. P.; Jaramillo, T. F., Engineering Cu Surfaces for the Electrocatalytic Conversion of Co₂: Controlling Selectivity toward Oxygenates and Hydrocarbons. *P Natl Acad Sci USA* **2017**, *114* (23), 5918-5923, 10.1073/pnas.1618935114.
23. Lum, Y.; Ager, J. W., Sequential Catalysis Controls Selectivity in Electrochemical Co₂ Reduction on Cu. *Energy & Environmental Science* **2018**, *11* (10), 2935-2944, 10.1039/c8ee01501e.
24. Xiang, C. X.; Weber, A. Z.; Ardo, S.; Berger, A.; Chen, Y. K.; Coridan, R.; Fountaine, K. T.; Haussener, S.; Hu, S.; Liu, R.; Lewis, N. S.; Modestino, M. A.; Shaner, M. M.; Singh, M. R.; Stevens, J. C.; Sun, K.; Walczak, K., Modeling, Simulation, and Implementation of Solar-Driven Water-Splitting Devices. *Angew Chem Int Edit* **2016**, *55* (42), 12974-12988, 10.1002/anie.201510463.
25. Liu, X. Y.; Schlexer, P.; Xiao, J. P.; Ji, Y. F.; Wang, L.; Sandberg, R. B.; Tang, M.; Brown, K. S.; Peng, H. J.; Ringe, S.; Hahn, C.; Jaramillo, T. F.; Norskov, J. K.; Chan, K. R., Ph Effects on the Electrochemical Reduction of Co(2) Towards C-2 Products on Stepped Copper. *Nature Communications* **2019**, *10*, 10.1038/s41467-018-07970-9.
26. Resasco, J.; Chen, L. D.; Clark, E.; Tsai, C.; Hahn, C.; Jaramillo, T. F.; Chan, K.; Bell, A. T., Promoter Effects of Alkali Metal Cations on the Electrochemical Reduction of Carbon Dioxide. *Journal of the American Chemical Society* **2017**, *139* (32), 11277-11287, 10.1021/jacs.7b06765.

27. Resasco, J.; Lum, Y.; Clark, E.; Zeledon, J. Z.; Bell, A. T., Effects of Anion Identity and Concentration on Electrochemical Reduction of Co₂. *Chemelectrochem* **2018**, 5 (7), 1064-1072, 10.1002/celec.201701316.
28. Cheng, T.; Xiao, H.; Goddard, W. A., Reaction Mechanisms for the Electrochemical Reduction of Co₂ to Co and Formate on the Cu(100) Surface at 298k from Quantum Mechanics Free Energy Calculations with Explicit Water. *J Am Chem Soc* **2016**, 10.1021/jacs.6b08534.
29. Han, Z., Kortlever, R., Chen H.-Y., Peters, J. C., and Agapie, T., Co₂ Reduction Selective for C₂ Products on Polycrystalline Copper with N-Substituted Pyridinium Additives. *ACS Central Science* **2017**, 10.1021/acscentsci.7b00180.
30. Buckley, A. K.; Lee, M.; Cheng, T.; Kazantsev, R. V.; Larson, D. M.; Goddard, W. A.; Toste, F. D.; Toma, F. M., Electrocatalysis at Organic-Metal Interfaces: Identification of Structure-Reactivity Relationships for Co₂ Reduction at Modified Cu Surfaces. *Journal of the American Chemical Society* **2019**, 141 (18), 7355-7364, 10.1021/jacs.8b13655.
31. Kim, Y. G.; Baricuatro, J. H.; Javier, A.; Gregoire, J. M.; Soriaga, M. P., The Evolution of the Polycrystalline Copper Surface, First to Cu(111) and Then to Cu(100), at a Fixed Co₂ Potential: A Study by Operando Ec-Stm. *Langmuir* **2014**, 30 (50), 15053-15056, 10.1021/la504445g.
32. Tsang, C. F.; Javier, A. C.; Kim, Y. G.; Baricuatro, J. H.; Cummins, K. D.; Kim, J.; Jerkiewicz, G.; Hemminger, J. C.; Soriaga, M. P., Potential-Dependent Adsorption of Co and Its Low-Overpotential Reduction to CH₃CH₂OH on Cu(511) Surface Reconstructed from Cu(Pc): Operando Studies by Serial Stm-Eqcn-Dems. *Journal of the Electrochemical Society* **2018**, 165 (15), J3350-J3354, 10.1149/2.0451815jes.
33. Favaro, M.; Jeong, B.; Ross, P. N.; Yano, J.; Hussain, Z.; Liu, Z.; Crumlin, E. J., Unravelling the Electrochemical Double Layer by Direct Probing of the Solid/Liquid Interface. *Nature Communications* **2016**, 7, 10.1038/ncomms12695.
34. Friebel, D.; Louie, M. W.; Bajdich, M.; Sanwald, K. E.; Cai, Y.; Wise, A. M.; Cheng, M. J.; Sokaras, D.; Weng, T. C.; Alonso-Mori, R.; Davis, R. C.; Bargar, J. R.; Norskov, J. K.; Nilsson, A.; Bell, A. T., Identification of Highly Active Fe Sites in (Ni,Fe)OOH for Electrocatalytic Water Splitting. *Journal of the American Chemical Society* **2015**, 137 (3), 1305-1313, 10.1021/ja511559d.
35. Li, L.; Yang, J. H.; Ali-Loytty, H.; Weng, T. C.; Toma, F. M.; Sokaras, D.; Sharp, I. D.; Nilsson, A., Operando Observation of Chemical Transformations of Iridium Oxide During Photoelectrochemical Water Oxidation. *ACS Appl Energ Mater* **2019**, 2 (2), 1371-1379, 10.1021/acsaem.8b01945.
36. Sanchez Casalongue, H.; Ling, N. M.; Sarp, K.; Daniel, F.; Hirohito, O.; Anders, N., In Situ Observation of Surface Species on Iridium Oxide Nanoparticles During the Oxygen Evolution Reaction. *Angewandte Chemie International Edition* **2014**, 10.1002/anie.201402311.
37. Cooper, J. K.; Reyes-Lillo, S. E.; Hess, L. H.; Jiang, C. M.; Neaton, J. B.; Sharp, I. D., Physical Origins of the Transient Absorption Spectra and Dynamics in Thin-Film Semiconductors: The Case of BiVO₄. *Journal of Physical Chemistry C* **2018**, 122 (36), 20642-20652, 10.1021/acs.jpcc.8b06645.
38. Segev, G.; Dotan, H.; Ellis, D. S.; Piekner, Y.; Klotz, D.; Beeman, J. W.; Cooper, J. K.; Grave, D. A.; Sharp, I. D.; Rothschild, A., The Spatial Collection Efficiency of Charge

- Carriers in Photovoltaic and Photoelectrochemical Cells. *Joule* **2018**, 2 (2), 210-224, 10.1016/j.joule.2017.12.007.
39. Borgwardt, M.; Omelchenko, S. T.; Favaro, M.; Plate, P.; Hohn, C.; Abou-Ras, D.; Schwarzburg, K.; van de Krol, R.; Atwater, H. A.; Lewis, N. S.; Eichberger, R.; Friedrich, D., Femtosecond Time-Resolved Two-Photon Photoemission Studies of Ultrafast Carrier Relaxation in Cu₂O Photoelectrodes. *Nature Communications* **2019**, 10, 10.1038/s41467-019-10143-x.
 40. Singh, A. K.; Montoya, J. H.; Gregoire, J. M.; Persson, K. A., Robust and Synthesizable Photocatalysts for CO₂ Reduction: A Data-Driven Materials Discovery. *Nature Communications* **2019**, 10, 10.1038/s41467-019-08356-1.
 41. DuChene, J. S.; Tagliabue, G.; Welch, A. J.; Cheng, W. H.; Atwater, H. A., Hot Hole Collection and Photoelectrochemical CO₂ Reduction with Plasmonic Au/P-GaN Photocathodes. *Nano Letters* **2018**, 18 (4), 2545-2550, 10.1021/acs.nanolett.8b00241.
 42. Kim, Y.; Creel, E. B.; Corson, E. R.; McCloskey, B. D.; Urban, J. J.; Kostecki, R., Surface-Plasmon-Assisted Photoelectrochemical Reduction of CO₂ and NO₃⁻ on Nanostructured Silver Electrodes. *Advanced Energy Materials* **2018**, 8 (22), 10.1002/aenm.201800363.
 43. Gauding, E. A.; Liu, G.; Chen, C. T.; Lobbert, L.; Li, A.; Segev, G.; Eichhorn, J.; Aloni, S.; Schwartzberg, A. M.; Sharp, I. D.; Toma, F. M., Fabrication and Optical Characterization of Polystyrene Opal Templates for the Synthesis of Scalable, Nanoporous (Photo)Electrocatalytic Materials by Electrodeposition. *Journal of Materials Chemistry A* **2017**, 5 (23), 11601-11614, 10.1039/C7TA00512A.
 44. Yang, J.; Cooper, J. K.; Toma, F. M.; Walczak, K. A.; Favaro, M.; Beeman, J. W.; Hess, L. H.; Wang, C.; Zhu, C.; Schwartzberg, A.; Sharp, I. D., A Multifunctional Biphasic Water Splitting Catalyst Tailored for Integration with High-Performance Semiconductor Photoanodes. *Nat. Mater.* **2017**, 16, 335-341,
 45. Guevarra, D.; Shinde, A.; Suram, S. K.; Sharp, I. D.; Toma, F. M.; Haber, J. A.; Gregoire, J. M., Development of Solar Fuels Photoanodes through Combinatorial Integration of Ni-La-Co-Ce Oxide Catalysts on BiVO₄. *Energy Environ. Sci.* **2016**, 9, 565-580, 10.1039/C5EE03488D.
 46. Weng, L. C.; Bell, A. T.; Weber, A. Z., Towards Membrane-Electrode Assembly Systems for CO₂ Reduction: A Modeling Study. *Energy & Environmental Science* **2019**, 12 (6), 1950-1968, 10.1039/c9ee00909d.
 47. Chen, Y., Lewis, N. S. & Xiang, C., Modeling and Simulation of the Spatial and Light-Intensity Dependence of Product Distributions in an Integrated Photoelectrochemical CO₂ Reduction System. *Acs Energy Lett* **2016**, 10.1021/acsenergylett.6b00134.
 48. Walczak, K.; Chen, Y. K.; Karp, C.; Beeman, J. W.; Shaner, M.; Spurgeon, J.; Sharp, I. D.; Amashukeli, X.; West, W.; Jin, J.; Lewis, N. S.; Xiang, C. X., Modeling, Simulation, and Fabrication of a Fully Integrated, Acid-Stable, Scalable Solar-Driven Water-Splitting System. *ChemSuschem* **2015**, 8 (3), 544-551, 10.1002/cssc.201402896.
 49. Cheng, W. H.; Richter, M. H.; May, M. M.; Ohlmann, J.; Lackner, D.; Dimroth, F.; Hannappel, T.; Atwater, H. A.; Lewerenz, H. J., Monolithic Photoelectrochemical Device for Direct Water Splitting with 19% Efficiency. *Acs Energy Lett* **2018**, 3 (8), 1795-1800, 10.1021/acsenergylett.8b00920.

50. Sathre, R.; Scown, C. D.; Morrow, W. R.; Stevens, J. C.; Sharp, I. D.; Ager Iii, J. W.; Walczak, K.; Houle, F. A.; Greenblatt, J., Life-Cycle Net Energy Assessment of Large-Scale Hydrogen Production Via Photo-Electrochemical Water Splitting. *Energy & Environmental Science* **2014**, 10.1039/C4EE01019A.
51. Verlage, E.; Hu, S.; Liu, R.; Jones, R. J. R.; Sun, K.; Xiang, C.; Lewis, N.; Atwater, J. H. A., A Monolithically Integrated, Intrinsically Safe, 10% Efficient, Solar-Driven Water-Splitting System Based on Active, Stable Earth-Abundant Electrocatalysts in Conjunction with Tandem Iii-V Light Absorbers Protected by Amorphous Tio₂ Films. *Energy & Environmental Science* **2015**, 10.1039/C5EE01786F.
52. Walczak, K. A.; Segev, G.; Larson, D. M.; Beeman, J. W.; Houle, F. A.; Sharp, I. D., Hybrid Composite Coatings for Durable and Efficient Solar Hydrogen Generation under Diverse Operating Conditions. *Advanced Energy Materials* **2017**, 7 (13), 10.1002/aenm.201602791.
53. Kistler, T. A.; Danilovic, N.; Agbo, P., A Monolithic Photoelectrochemical Device Evolving Hydrogen in Pure Water. *Journal of the Electrochemical Society* **2019**, 166 (13), H656-H661, 10.1149/2.1151913jes.
54. Gurudayal; Beeman, J. W.; Bullock, J.; Wang, H.; Eichhorn, J.; Towle, C.; Javey, A.; Toma, F. M.; Mathews, N.; Ager, J. W., Si Photocathode with Ag-Supported Dendritic Cu Catalyst for Co₂ Reduction. *Energy & Environmental Science* **2019**, 12 (3), 1068-1077, 10.1039/c8ee03547d.
55. Higgins, D.; Hahn, C.; Xiang, C. X.; Jaramillo, T. F.; Weber, A. Z., Gas-Diffusion Electrodes for Carbon Dioxide Reduction: A New Paradigm. *Acs Energy Lett* **2019**, 4 (1), 317-324, 10.1021/acseenergylett.8b02035.
56. Han, L. H.; Zhou, W.; Xiang, C. X., High-Rate Electrochemical Reduction of Carbon Monoxide to Ethylene Using Cu-Nanoparticle-Based Gas Diffusion Electrodes. *Acs Energy Lett* **2018**, 3 (4), 855-860, 10.1021/acseenergylett.8b00164.