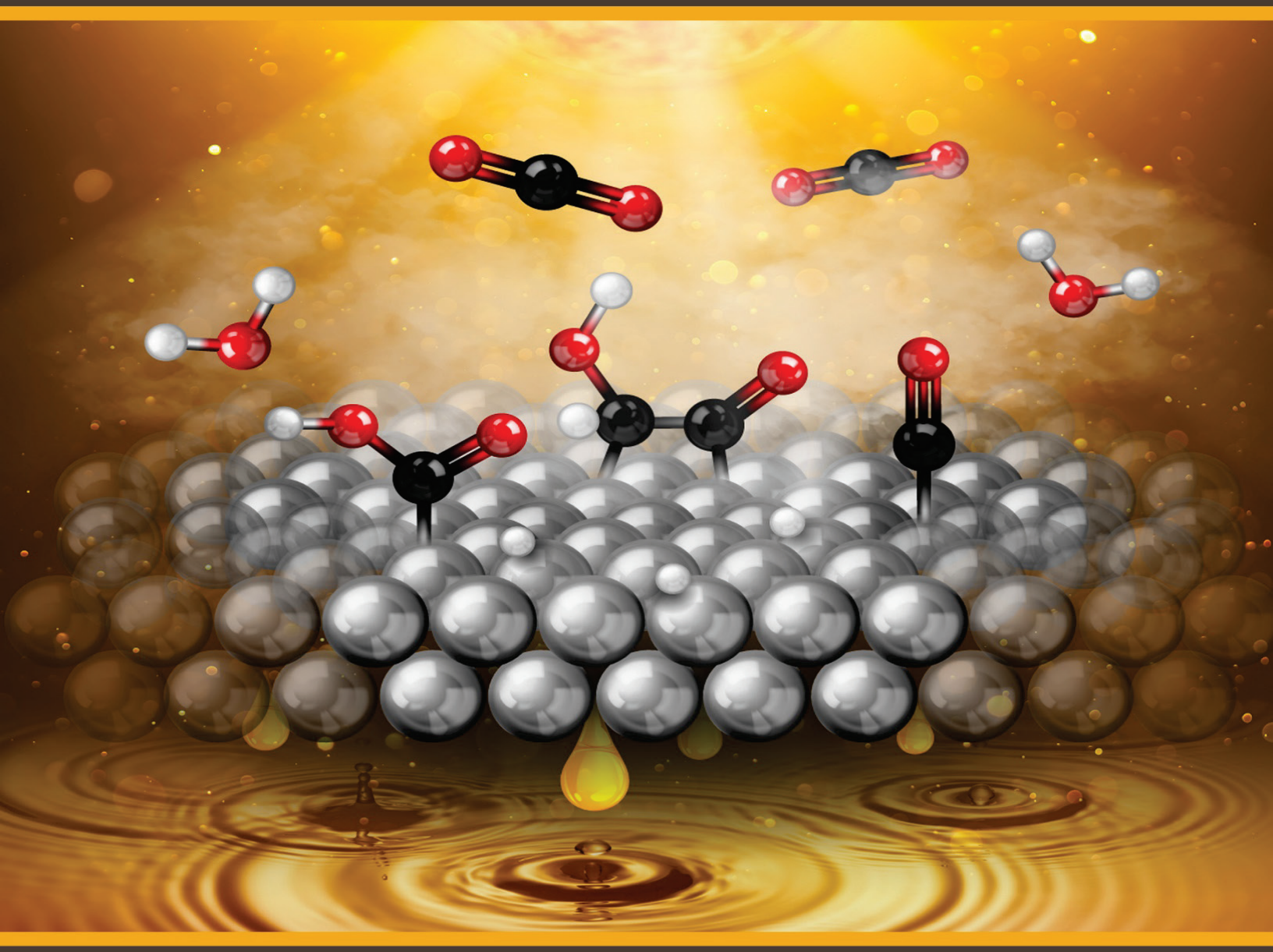
Basic Energy Sciences Roundtable

Liquid Solar Fuels



Report of the Basic Energy Sciences Roundtable on

Liquid Solar Fuels

August 20-21, 2019

The artwork on the cover portrays the generation of liquid solar fuels. Sunlight-driven processes transform carbon dioxide and water into liquid products through representative intermediates bound to a catalyst symbolized by the array of larger gray spheres. The red spheres symbolize oxygen, the black spheres symbolize carbon, and the white spheres symbolize hydrogen.

Cover image courtesy of National Renewable Energy Laboratory

Report of the Basic Energy Sciences Roundtable on Liquid Solar Fuels

August 20 – 21, 2019
Rockville, Maryland

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Abbreviations, Acronyms, and Initialisms

2e-	2-electron
2D	2-dimensional
3D	3-dimensional
4e-	4-electron
BES	Basic Energy Sciences
CO	carbon monoxide
CO_2	carbon dioxide
CO_2RR	carbon dioxide reduction reaction
Combi	combinatorial
DFT	density functional theory
DOE	US Department of Energy
EPR	electron paramagnetic resonance
EXAFS	extended x-ray absorption fine structure
FTIR	Fourier transform infrared
H_2	hydrogen
HER	hydrogen evolution reaction
HOMO	highest-occupied molecular orbital
IR	infrared
LUMO	lowest-unoccupied molecular orbital
MEA	membrane electrode assembly
MLCT	metal-to-ligand charge transfer
MOF	metal-organic framework
N_2	nitrogen
N_2RR	nitrogen reduction reaction
NMR	nuclear magnetic resonance

O_2	oxygen
OEC	oxygen-evolving complex
OER	oxygen evolution reaction
PRO	Priority Research Opportunity
PV	photovoltaic
QC	quantum chemical
QMC	quantum Monte Carlo
SECM	scanning electrochemical microscopy
SERS	surface enhanced Raman spectroscopy
STO	strontium titanate
TEM	transmission electron microscopy
TERS	tip-enhanced Raman spectroscopy
TRIR	time-resolved infrared
UV/Vis	ultraviolet/visible absorption
XANES	x-ray absorption near-edge structure
XFEL	ultrafast x-ray free-electron laser
XPS	x-ray photoelectron spectroscopy

Executive Summary

Harnessing the power of the sun—the world's most ubiquitous energy source—to produce liquid solar fuels promises a plentiful supply of sustainable, transportable, and storable energy to meet future US energy needs and help transform our global energy system. Anthropogenic liquid fuels generated directly from sunlight, water, and carbon dioxide or other abundant feedstocks (e.g. atmospheric nitrogen) using synthetic materials and chemical processes—often termed "artificial photosynthesis"—would provide novel economically and environmentally beneficial avenues toward energy-dense fuels. These fuels would be compatible with our existing fuel infrastructure and would complement fuels derived from fossil or biomass sources. Liquid solar fuels generated via artificial photosynthesis offer further benefits. Economically, they could also avoid the significant capital cost issues associated with the supporting components and auxiliary systems required for more indirect routes for carbon dioxide conversion, such as electrocatalysis powered by photovoltaics. Scientifically, advancing the fundamental understanding of liquid solar fuels provides knowledge that can also inform and improve these more indirect routes as well as related applications. Technologically, solar fuels generation offers new pathways for efficient chemical energy storage that could complement existing electrical energy storage. In addition to fuels, sunlight-driven chemical transformations of carbon dioxide and nitrogen could be used to produce diverse chemicals, products, and materials with low environmental impact.

The science underlying liquid solar fuels generation using an artificial photosynthetic approach builds on decades of sustained support for fundamental research by the US Department of Energy (DOE), Office of Basic Energy Sciences (BES). Important insights for artificial photosynthesis have been gained from the depth and breadth of BES-funded research programs by single principal investigators, small teams, and large multi-institutional, multi-disciplinary teams. The foundational progress in a number of areas—particularly hydrogen production from sunlight-driven water splitting—has brought us to a point where fundamental scientific and technical breakthroughs are now needed to create effective conversion systems for solar energy to liquid chemical fuels and to eventually establish a liquid solar fuels industry. Remarkable advances in theory and experimental methods for discovery, synthesis, and characterization of materials and molecular systems, including distinctive capabilities at DOE Office of Science user facilities, set the stage for new research that addresses remaining fundamental scientific challenges. These new avenues push the research community to think beyond the limits of current materials and approaches to achieve efficiency, selectivity, integration, and durability in liquid solar fuels components and systems. Specifically, new science is needed to enable researchers to understand, and ultimately control, individual processes; discover functionally active and robust molecules, materials, and components; identify competing processes that degrade components, as well as mechanisms that improve their durability; and advance the science of nano/meso/macroscale integration for assembly of components into complete systems.

BES hosted the Roundtable on Liquid Solar Fuels in August 2019 to assess basic science gaps, fundamental challenges, and research opportunities for generating energy-rich liquids from abundant feedstocks using sunlight as the only energy input. Four Priority Research Opportunities were identified to address critical physical and chemical phenomena required for efficient, selective, and stable production of liquid fuels directly from sunlight using an artificial photosynthetic approach. These opportunities, listed in the following paragraphs along with key questions, present new directions for fundamental chemistry and materials research needed to develop technologies for liquid solar fuels generation.

Priority Research Opportunities for Solar Fuels

Understand the mechanisms that underpin constituent durability and performance

Key question: *How can molecular-level knowledge of individual processes in solar fuels generation lead to predictive design of components with enhanced lifetime and desired activity?*

A current impediment to producing solar fuels is the limited lifetimes of components. Significant opportunities exist to design, discover, and develop high-performance and durable components, including robust light absorbers with sufficient photovoltages; efficient, stable catalysts with high selectivity; and tailored materials such as membranes and electrolytes to control transport and permeability. A detailed understanding of the thermodynamics, kinetics, and mechanisms of degradation will enable predictive science for durability at the molecular, material, and component levels. New science will also advance strategies to circumvent or counteract processes that reduce component lifetime and performance.

Control the catalyst microenvironment to promote selective and efficient fuel production

Key question: *How do we probe, understand, and tailor the structure, composition, and dynamics of the local region surrounding catalytic active sites to direct chemical reaction pathways?*

High selectivity and high activity in the light-driven production of energy-rich fuels present considerable challenges because of the complexity of chemically reducing carbon dioxide or nitrogen as well as oxidizing water. Advances require molecular-level understanding and control of the microenvironment around catalytic sites to direct reactions for key bond-making and bond-breaking steps. Research is needed to probe and control the interactions of catalysts with supports, light absorbers, electrolytes, and other components. It is also critical to understand how the microenvironment can mediate the transport of reactants, products, electrons, protons, and inhibitors to direct reaction pathways determining efficiency, selectivity, and degradation.

Bridge the time and length scales of light excitation and chemical transformations

Key question: *How can we enable and exploit the direct interaction of solar excitation with chemical change to achieve high selectivity and high efficiency of solar-to-chemical energy conversion?*

Most approaches to solar fuels generation decouple light absorption and chemical transformations. Significant opportunities exist to capitalize on the direct coupling of light-driven phenomena and chemical processes to enhance overall system performance. Exploiting light–matter interactions could open up new mechanisms to enable selectivity or efficiency that outperform conventional electrochemical reactions or use more of the solar spectrum. Fundamental research can realize advantages unique to light-driven fuels generation, such as strong electronic coupling or light-induced structural changes.

Tailor interactions of complex phenomena to achieve integrated multicomponent systems

Key question: *How can the fundamental science of integration advance the predictive design and control of interfaces and processes to enhance the performance, including durability, of solar fuels systems?*

Integration of individual molecular and material components presents challenges for generating solar fuels because individual elements may not perform the way they do in integrated systems. Fundamental research is needed to provide a mechanistic understanding of how individual multiscale processes interact and influence the function of integrated components. The resulting knowledge of how integration impacts performance, including durability, will guide the development of predictive models and enable the co-design of components for efficient, selective, and durable systems.

Introduction

Solar energy—the world's most abundant and ubiquitous energy source—has the potential to transform our future global energy system. Anthropogenic liquid fuels generated directly from sunlight, water, and atmospheric feedstocks (e.g. carbon dioxide (CO_2) and nitrogen (N_2)), termed *liquid solar fuels*, could provide novel economically and environmentally beneficial avenues to energy-dense fuels that would complement those derived from fossil-fuel or biomass sources. Using sunlight to directly produce energy-rich fuels promises a plentiful supply of sustainable, transportable, and storable energy to meet future US energy needs. Sunlight-driven chemical transformations can also be used to produce diverse chemicals, products, and materials with low environmental impact.

Remarkable progress has been witnessed in the conversion of sunlight into electrical and chemical energy since the publication of the US Department of Energy (DOE) Basic Energy Sciences (BES) report on *Basic Research Needs for Solar Energy Utilization* in 2005[1]. For example, scientific and manufacturing advances have put electricity generated by photovoltaics (PV) on par economically with traditional grid-scale electrical energy sources. Global installations of PV currently exceed 500 gigawatts[2, 3]. Although notable advances in the fundamental science of solar fuels have also been made[4-7]— particularly for efficient hydrogen production from solar-driven water splitting—solar fuels are much less mature than PV. As described below, fundamental scientific and technical breakthroughs are needed to create effective systems for converting solar energy to chemical fuel and to eventually establish a solar fuels industry.

As shown in **Figure 1**, solar fuels generation encompasses a wide range of processes to convert solar energy to chemical energy using man-made materials and chemical processes. Routes include electrolysis using solar electricity to make hydrogen or liquid fuels (electrolysis/electrocatalytic synthesis), as well as solar water splitting (e.g., photoelectrochemical, photocatalytic, or solar thermal), which generates hydrogen (H_2) that can could be used as fuel itself [8, 9] or be used to catalytically transform CO_2 or other feedstocks to liquid fuels (liquid fuels synthesis). This report focuses on the direct generation of ***liquid*** solar fuels (the upper green arc in **Figure 1**)—also termed *artificial photosynthesis*—which involves the direct conversion of sunlight, water, and CO_2 or other abundant feedstocks (e.g., N_2) to liquid fuels.

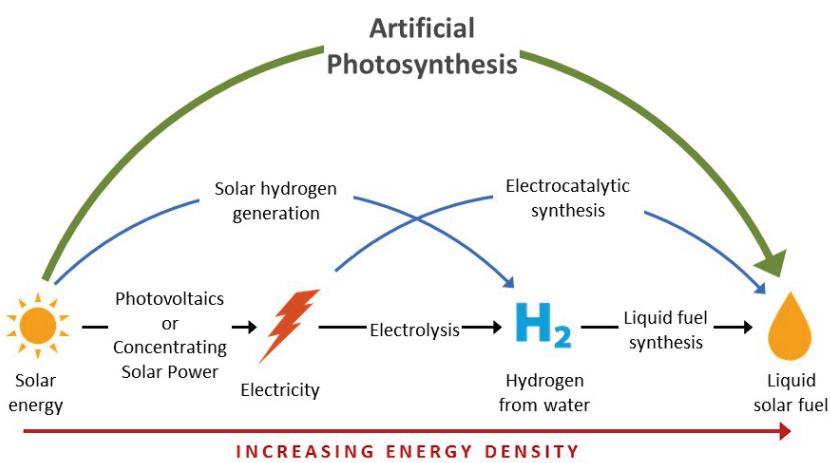


Figure 1. Illustration of solar fuels generation pathways including routes involving (a) H_2 generation directly from solar irradiation (via photoelectrochemical, photocatalytic, or solar thermal methods, left blue arc) or from electrolysis using solar electricity (straight arrows in the scheme), in which the H_2 is then used to make liquid fuels by subsequent reaction with CO_2 or other feedstocks; (b) electrocatalytic synthesis of liquid fuels from CO_2 and solar electricity (right blue arc in scheme) or (c) direct liquid fuels production from sunlight, CO_2 or other feedstocks via artificial photosynthesis (upper green arc).

For the purposes of this roundtable report, the term "liquid solar fuels" encompasses energy-dense chemicals that are liquid at or near ambient conditions (i.e., near room temperature at moderate or atmospheric pressure). They include methanol, hydrocarbons, oxygenated hydrocarbons, and nitrogen-containing compounds. Ammonia, dimethyl ether, and other chemicals that can be liquefied at moderate pressures, are also considered liquid solar fuels. The generation of energy-dense liquid solar fuels involves complex reaction schemes that involve more than two electrons in sequential reduction processes. Simple 2-electron reduction of CO_2, in the presence of water, yields gas-phase products CO and CO/H_2 mixtures or low–energy-density liquids such as formic acid and oxalic acid. Although these reduction reactions can provide important scientific insight, their products are not considered liquid solar fuels in the context of this workshop and report. As in photosynthesis, direct solar fuels generation uses the energy from sunlight to split water into oxygen (O_2), electrons, and protons. The electrons and protons can be combined to form hydrogen (a solar fuel by itself) or can be used to transform (i.e., chemically reduce) feedstocks such as CO_2 into promising liquid fuel targets, e.g. oxygenated hydrocarbons. For liquid solar fuels, sunlight is captured by molecular or solid-state photoabsorbers, which then create holes and electrons that can be transferred to catalysts that drive water oxidation (the oxygen evolution reaction, OER) and chemical reduction reactions, respectively. Reduction reactions include the hydrogen evolution reaction (HER), CO_2 reduction reaction (CO_2RR), and nitrogen reduction reaction (N_2RR). Sunlight-driven generation of liquid solar fuels requires the coordinated action of a number of phenomena that occur over a wide range of time and length scales, presenting challenges to understanding and using these processes in integrated systems for solar fuels production (see **Figure 2**).

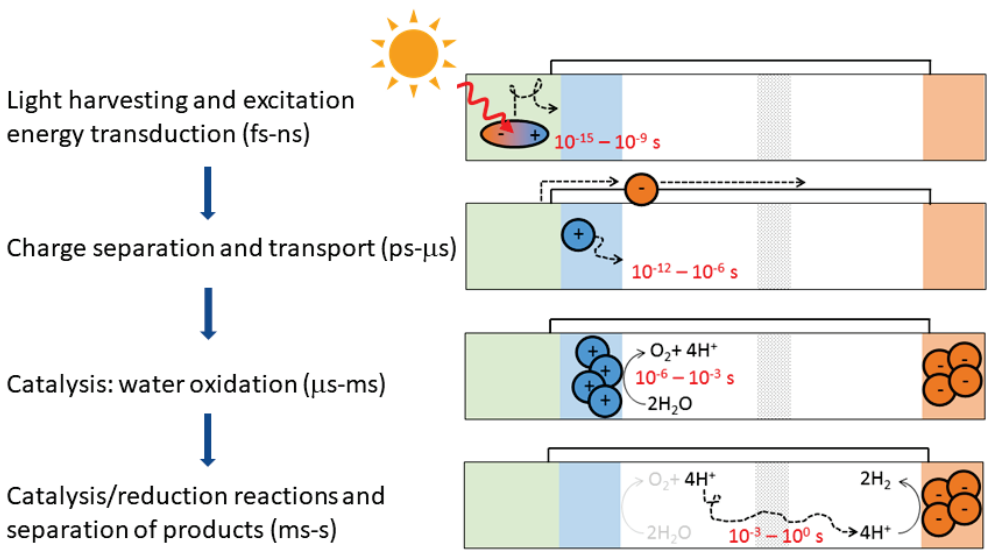


Figure 2. Illustration of the range of timescales for primary events in solar fuels generation that span from femtoseconds (fs) to picoseconds (ps) to microseconds (µs) to milliseconds (ms) to beyond seconds (s). In this system, the photoanode is irradiated to generate O_2 as well as protons and electrons, which are transported to the cathode to make H_2.

Natural photosynthesis can provide inspiration to the generation of man-made solar fuels, teaching researchers the importance of a number of concepts that could be applied to liquid solar fuels, including using Earth-abundant metals; storing reducing equivalents in transportable, stable chemical intermediates; orchestrating transport to control reaction pathways and hand-off of intermediates within a reaction environment; hierarchically arranging multiple chromophores for effective, broad-spectrum light harvesting; organizing chemical transformations into multi-step cascades that enable selective multi-electron, multi-proton transformations and cascading redox reactions; and using self-healing and repair to foster durability. The generation of liquid solar fuels via artificial photosynthesis has the potential to

capitalize on, and even mimic, a number of these concepts. Yet, artificial photosynthesis also can sidestep the constraints of biological systems and move beyond natural photosynthesis to create entirely synthetic systems that target specific fuels or demonstrate desired performance. Basic research on phenomena in organic and inorganic systems—as well as on the complex biological conversion of sunlight into chemical energy by natural photosynthesis—is advancing the molecular-level understanding of important physical and chemical phenomena such as light absorption, charge generation, electrocatalysis, thermal catalysis, ion and mass transport, and product separations.

Significant progress has been made in solar-driven hydrogen production, as illustrated in **Sidebar 1** and highlighted in the factual status document (and references therein) associated with this roundtable report [6]. For example, over the last several decades, the overall efficiency for photoelectrochemical water splitting to form H_2 (and O_2) has increased from less than 1% to almost 20% [10-13]. Advances for solar hydrogen include new homogeneous and heterogeneous catalysts for hydrogen production, more stable and even self-healing [14] water-oxidation catalysts (OER), and tandem photoabsorber approaches for high efficiency. Much has been learned about integrating photoabsorbers, catalysts, electrolytes, and even membranes into devices that generate solar hydrogen. A number of architectures and prototypes have been demonstrated, ranging from suspended photocatalysts to devices with PV-like photoabsorbers[10, 15-17]. Work in this area has highlighted not only the critical need for integration of individual components, but also for enhanced durability, revealing specific challenges with integration and durability at the level of components (e.g., catalysts, photoabsorbers), interfaces, and systems.

Much less progress has been made in the area of liquid solar fuels via artificial photosynthesis, where sunlight is used directly to chemically transform CO_2 and other small molecules into promising liquid fuel products. Advances have been made in understanding electrocatalytic CO_2 conversion [18], including the synthesis of C_1-based products (e.g., formic acid and methanol) and carbon-carbon bond-forming reactions (e.g., to ethylene and/or ethanol). To date, however, there is no solar fuels system that can selectively deliver a liquid fuel. The complex multi-electron, multi-proton transformations needed for liquid fuel production—in contrast to the 2-electron transformations needed to produce H_2 and carbon monoxide (CO) or formic acid (HCOOH) —give rise to major obstacles. The selective production of a liquid fuel remains a significant and persistent challenge. Conversion of CO_2 also must be promoted relative to the hydrogen evolution reaction (HER), which is often facilitated by the same catalysts. Moreover, product mixtures from >2-electron transformations are commonplace, adding to the challenges of catalytic selectivity and/or product separations.

The basic science underlying liquid solar fuels generation using an artificial photosynthetic approach builds on decades of sustained fundamental research. Important insights for artificial photosynthesis have been gained from the breadth of DOE BES-funded science, which includes research on other routes for solar fuels production supported by a range of BES funding modalities—from efforts of single principal investigators to large multi-institutional, multidisciplinary teams. Major opportunities exist as the research community thinks beyond current materials and approaches to address the scientific challenges impeding selectivity, integration, and durability in liquid solar fuels components and systems. There also are opportunities to link or merge scientific fields—e.g., electrochemistry with materials science, photochemistry with catalysis, molecular with solid-state approaches, soft with hard materials, and materials discovery with reliability. New science is needed to understand and ultimately control individual processes; discover functionally active and robust molecules, materials, and components; identify competing processes that degrade components, as well as mechanisms that increase their durability; and advance integration science at the nano/meso/macroscales for assembly of components into complete systems. Appendix A describes a number of advanced methods that can accelerate the needed science and discoveries for liquid solar fuels, including spectroscopy and imaging, theoretical modeling and scientific computation, high-throughput materials discovery and characterization, and state-of-the-art large-scale user facilities. Remarkable advances in theory and experimental methods for

discovery, synthesis, and characterization of materials and molecular systems set the stage to address critical fundamental scientific challenges in selectivity, efficiency, integration, and durability.

***Science of selectivity and efficiency*:** Efficient solar fuels systems must produce targeted liquid fuel molecules in sufficient quantity while limiting generation of unwanted molecules. The selective and efficient production of energy-rich liquid fuels is a considerable research challenge at the level of molecules, materials, and complex systems. Research must advance beyond simple 2-electron reduction chemistries (e.g., formation of CO) while suppressing the formation of hydrogen. Science gaps include how to harvest more of the solar spectrum to increase efficiency, how to uncover reaction mechanisms occurring in complex chemical and electrochemical processes [18], and how to design molecular-scale environments—processes, components, and materials—that direct reaction pathways to efficiently and reliably target higher molecular weight products. Many of these scientific challenges exist at the intersection of electrochemistry and photochemistry as well as materials and chemical science.

***Science of integration*:** Liquid solar fuels systems must operate across a wide range of temporal and spatial scales (e.g., **Figure 2**). Key challenges include understanding and controlling light harvesting, energy transfer, charge separation, catalytic reactions, product selectivity, and interfacial processes. The integration of molecular and material components—from solar energy capture to chemical conversions and separations—into multicomponent systems with controlled properties is critical to developing efficient systems to generate solar fuels under real-world conditions. Integration is much more than device fabrication from individually developed components. In addition to advancing novel processes and components, the discovery of the scientific principles underpinning integration is needed to enable the design and orchestration of complex systems with desired functionalities. Integration requires control (and exploitation) of the dynamic nature of the system, including fluxes, gradients, structures, and compositions that could mediate reaction pathways, transport, and stability. Additional challenges include how to control energy, mass, and charge generation and transport; and how to develop systems that can adapt to internal and external stresses. Scientific understanding is needed to control how the dynamics of multicomponent systems depend on their individual components and how functions and mechanisms of individual components may change when integrated into a system.

***Science of durability*:** Under operating conditions, the stability and degradation of components, such as electrodes, molecules, membranes, and catalysts, as well as multicomponent ensembles, limit the performance and ultimately the lifetime of solar fuels generating systems. Components and systems must operate effectively over a wide dynamic range of conditions and under intermittent solar radiation for extended periods of time. To date, solar fuels systems have not been demonstrated to operate stably beyond several weeks. As identified in the BES report *Transformative Opportunities for Discovery Science*[19],

> the challenge of degradation science is to identify, model, and predict the mesoscopic evolution of structure or function in a material over the appropriate timescales while monitoring the dynamic processes that arise in the materials' functional use and typically occur on daily timescales.

Sidebar 1: Progress in solar fuels: Solar photoelectrochemical water splitting to hydrogen

The solar-to-hydrogen (STH) efficiency is a critical figure of merit when evaluating the feasibility of a solar fuels device to produce hydrogen via photoelectrochemical water splitting. For a number of years, a 10% STH efficiency was considered a significant benchmark for the field. Technoeconomic analyses have suggested that the minimum STH efficiency needed was >10% to ensure positive energy return on energy invested[17] and near 25% to yield hydrogen at costs competitive with steam methane reforming[15]. As shown in **Figure S1**, the efficiency for solar hydrogen production has progressed from < 1% to devices that now approach 20%[11-13, 20].

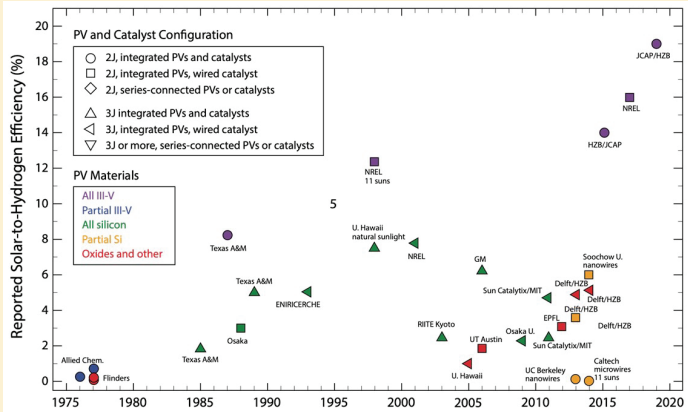


Figure S1. The progression of STH efficiency vs. time for various levels of absorber and catalyst integration.

Source: Used with permission of Energy Environ. Sci., from [Experimental demonstrations of spontaneous, solar-driven photoelectrochemical water splitting](), Ager, J. W., et al., 8, 2811–2824[20].

The first research exceeding 10% STH efficiency used a multijunction III-V semiconductor photoabsorber coupled to catalysts[12] (**Figure S2)**. The highest efficiencies continue to come from advances in tandem semiconductor photoelectrodes integrated with catalysts[11, 13, 20]. Note that this system suffered significantly from rapid corrosion, which dramatically highlights the need for *durability* as well as efficiency.

The highest currently reported STH efficiency for an immersed semiconductor with one of the water-splitting half reactions occurring on the light-absorbing surface is 19%[13] (**Figure S3**). The key advances that led to significantly improved STH efficiency beyond the 1998 "Turner cell"[12] are (1) absorber bandgaps that yield more favorable spectral splitting and (2) light management at the semiconductor/ electrolyte interface.

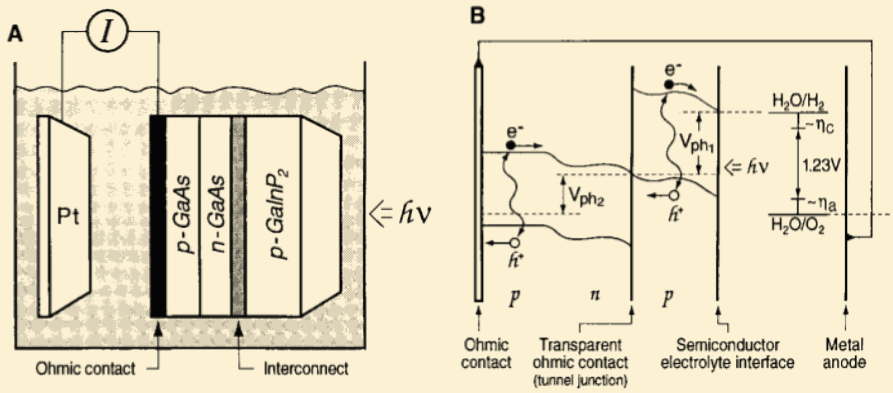


Figure S2. The stacked tandem III-V configuration that was first to break the 10% STH efficiency barrier.

Source: Reproduced with permission from Khaselev, O. and Turner, J.A.A. [Monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting](). Science 280, 425–427[12].

Although the Turner cell used two absorbing junctions optically and electrically in series, the lattice matching of the epilayers with the substrate restricts the materials, and consequently the bandgaps of the semiconductors that can be employed in a solar fuel device. The $Ga_{.52}In_{.48}P$ alloy has a bandgap of 1.82 eV, and the bottom GaAs *p/n* junction has a 1.42-eV bandgap. This combination of bandgaps inequitably splits the solar flux and results in limitation of the overall device current by the flux of photons absorbed in the bottom junction.

The 19%-efficient device[11] incorporates a metamorphic junction that translates the substrate lattice constant into one in which the lattice-matched GaInP (1.78 eV) and GaInAs (1.26 eV) epilayers can better use the solar spectral distribution. A high-activity rhodium nanoparticle catalyst was employed. This system reached 85% of the theoretical limited STH efficiency possible with this combination of semiconductor bandgaps. Applying a TiO_2 anti-corrosion barrier on the surface of this multijunction absorber also reduced the reflectivity at the semiconductor surface by 15%. A more optimized bandgap combination with an antireflective surface is likely to enable STH efficiencies in excess of 20%.

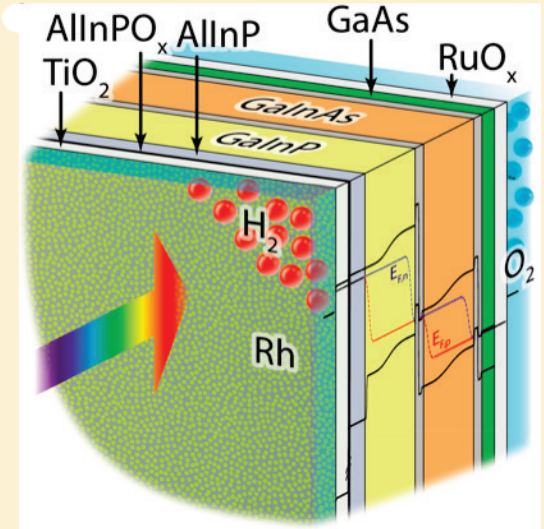


Figure S3. A schematic of the reported 19% STH device with more optimized absorber bandgaps and TiO_2 antireflective surface modification. *Source: Reprinted with permission from W.-H. Cheng et al., [Monolithic photoelectrochemical device for direct water splitting with 19% efficiency](), ACS Energy Lett. 3(8), 1795–1800, 2018. Copyright 2017 American Chemical Society[11].*

Degradation processes are caused by "slow and rare events," where the "mean behavior does not control the outcome." Design of more durable solar fuels systems requires the development of a molecular-level mechanistic understanding of the thermodynamics and kinetics of processes that lead to component and multicomponent system degradation. Chemical processes and materials properties are central to designing and developing solar fuel components and systems with the desired activity and functionality over extended periods of time and under diverse and dynamic operating conditions. Degradation mechanisms must be investigated and understood on multiple scales, along with the principles that underlie component reliability. Ultimately, predictive models will provide insights for understanding and controlling *durability* at the molecular, material, component, and systems level. Gaps exist, as well, in benchmarking and validation protocols. Novel concepts for repair of solar fuels components and systems also will play an important role in enhancing durability.

A DOE BES roundtable on liquid solar fuels was held in August 2019 to identify research opportunities for a coordinated, long-term research effort on liquid solar fuels. The workshop assessed the basic science gaps and fundamental research needed to overcome critical scientific and technical barriers in the generation of ***liquid solar fuels***. The scope of the roundtable focused exclusively on artificial photosynthesis approaches that can enable direct use of sunlight for liquid fuel production under mild temperature and pressure conditions. The intent of this roundtable was to take advantage of the strong foundation of current and past BES research by identifying and assessing the next critical steps in addressing the scientific and technical complexities of liquid solar fuels generation.

Four Priority Research Opportunities (PROs) were identified to provide the scientific foundation for the efficient, selective, durable and integrated production of liquid solar fuels. These PROs, which build on foundational studies of solar energy capture and conversion, present new horizons for fundamental chemistry and materials research needed to advance liquid solar fuels generation.

- **PRO 1:** Understand the mechanisms that underpin constituent durability and performance.
- **PRO 2:** Control the catalyst microenvironment to promote selective and efficient fuel production.
- **PRO 3:** Bridge the time and length scales of light excitation and chemical transformations.
- **PRO 4:** Tailor interactions of complex phenomena to achieve integrated multicomponent systems.

Ultimately, harnessing the power of the sun to produce liquid solar fuels can provide an abundant supply of sustainable, storable, and transportable energy to meet future US needs. Artificial photosynthetic approaches promise efficient and scalable generation of energy-dense liquid fuels (**Figure 3**). The importance of liquid fuels in the global economy cannot be overstated, since they can (1) enable commerce on a massive scale because of their high energy density and low storage cost; (2) use the vast, fully amortized capital infrastructure devoted to liquid fuels in industrialized countries; and (3) provide new pathways for delivering energy in developing countries. Carbon-based products continue to be the backbone of the US economy, with massive markets for transportation fuels, commodity chemicals, advanced polymers, plastics, and materials for buildings and infrastructure. The generation of ammonia and other nitrogen-containing species, which can be used as fuels, fertilizers, and other commodities, presents an opportunity to exploit an extremely abundant feedstock—atmospheric N_2. Artificial photosynthesis could avoid the significant capital cost issues associated with the supporting components and auxiliary systems required for indirect routes (e.g., PV-electrolysis and related approaches, **Figure 1**). Relative to electrochemical synthesis, artificial photosynthesis could provide alternative routes to liquid fuels. These processes require multiple electron transfer processes (e.g., more than the two electrons needed to produce H_2 or carbon monoxide, CO); so, different catalytic processes could potentially be made to have higher performance (e.g. more selective or efficient) at the effective low current densities in sunlight-driven processes (e.g., 20–30 milliamps per cm^2 for one-sun irradiation) relative to the high current densities employed by traditional electrolysis methods (e.g., > 1–2 amps per cm^2).

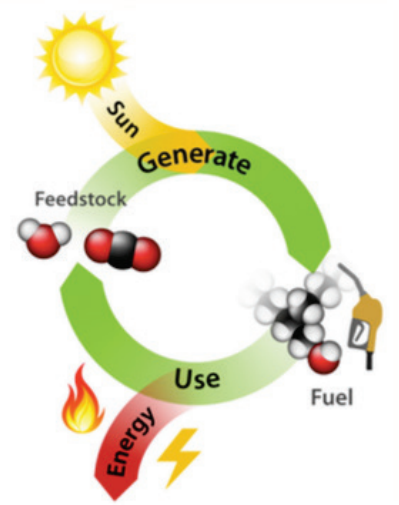


Figure 3. Liquid solar fuels offer the opportunity to create transportable and storable energy from feedstocks that are regenerated upon use.
For example, as shown here, reactions of CO_2 and water (left side) driven by sunlight could generate liquid fuels such as oxygenated hydrocarbons (right side). Subsequent use of the fuel to produce electricity or heat energy closes the cycle, regenerating the starting feedstocks of CO_2 and water. *Source: National Renewable Energy Laboratory.*

To realize efficient, durable, and selective liquid solar fuels systems, significant scientific challenges must be overcome. These obstacles will be surmounted only through fundamental research that achieves a more complete mechanistic understanding of solar energy capture and conversion, as well as integrated component and system performance. The breadth of this fundamental science will have impacts beyond solar fuels and can benefit a range of energy science needs, such as new concepts for chemical energy storage (transportation, grid-scale storage, and even seasonal storage); electrochemically driven synthesis of chemicals and materials to transform industries, as well as fuel synthesis from other renewable energy sources; membrane science for electrolysis, fuel cells, and advanced separations; innovative carbon

capture strategies; and solar and electrically driven processes for water purification. Advancing the fundamental science for liquid solar fuels via artificial photosynthesis can also have significant benefits to the indirect routes (**Figure 1**) to solar fuels. For example, considerable work is being done on PV-electrolysis processes, which use solar electricity to power electrochemical water splitting to produce hydrogen[8]—including a wide range of applied research and even large-scale demonstrations—that would benefit from increased efficiency, selectivity, and durability. Hydrogen will continue to play an increasingly important role in our future energy portfolio as a fuel, an energy carrier, and a reactant for chemical catalytic processes to produce methanol, ammonia, or other liquid fuels[12].

Addressing the research opportunities laid out in this report will be critical next steps in advancing liquid solar fuels as a new supply of sustainable, transportable, and storable fuels for future US energy needs. The wide range of time and length scales inherent in solar energy capture and conversion makes it exceptionally difficult to understand and control light harvesting, energy transfer, charge separation, catalytic reactions, product selectivity, and interfacial processes. As discussed in Appendix A, research will be bolstered by the application of major advances in multiscale theory and modeling, data science, chemical and materials synthesis, and state-of-the-art characterization—including ultrafast, high-resolution, and operando capabilities at DOE Office of Science user facilities.

Priority Research Opportunities

PRO 1: Understand the mechanisms that underpin constituent durability and performance

Summary

Liquid solar fuels generation requires the coordinated action of several components, including photoabsorbers, catalysts, and ion conductors—each of which serve key functional roles commensurate with the desired overall system performance (e.g., selectivity, efficiency) and durability (e.g., low degradation and stable operation on the time scale of decades). Significant advances have been made in materials, molecules, and their chemistries for liquid solar fuels. However, major opportunities exist to design, discover, and develop high-performance yet durable components to realize the promise of direct production of fuels from sunlight. These critical components (constituents) include (1) robust photoabsorbers with sufficient lifetimes and/or photovoltages (i.e., chemical potential); (2) stable catalysts that operate with high efficiency and selectivity; and (3) durable, tailored membranes, protective coatings, and electrolytes that help control transport and permeability.

Enhancing the performance of component-level processes requires advances in understanding photoabsorption (e.g., to capture more of the solar spectrum and increase efficiency), catalysis (e.g., to increase the selectivity or activity of catalysts for fuel formation and water oxidation), transport (e.g., to control locations of ions, reactants, and products), and interfacial phenomena. Increasing and predicting component durability requires a detailed understanding of the thermodynamics, kinetics, and molecular-level mechanisms of degradation for individual components. Developing the scientific principles for intrinsic and extrinsic stability is needed to advance strategies to circumvent or counteract processes that reduce lifetime and performance. It is imperative to characterize inherent stability as well as dynamic processes that compromise or enhance desired performance under actual solar fuels operating conditions.

Minimum best practices must also be established so that components and their integrated assemblies are consistently evaluated under the range of conditions and length scales relevant to liquid solar fuels generating systems. To ensure that component-level performance ultimately translates to integrated device performance, it is important to account for interactions between individual elements when designing individual components and chemistries.

Key Scientific Questions

- What are the molecular-level mechanisms of degradation for liquid solar fuels components (e.g., photoabsorbers, catalysts, ion conductors)? How can this mechanistic knowledge be used to develop solutions to circumvent or counteract these degradation pathways?
- How can advanced characterization methods coupled with first-principles theory and multiscale modeling be used to guide the discovery, design, durability, and performance of components? These components include:
  - Photoabsorbers that generate sufficient photovoltages under conditions relevant to liquid solar fuels devices, while absorbing significant amounts of sunlight
  - Catalysts that rapidly and selectively drive chemical transformations for forming intermediates and products that are relevant to liquid solar fuels devices
  - Membranes, ionomers, and separators with controllable levels of permeability for species that are present in liquid solar fuels devices.
- How can molecular-level knowledge of the processes in solar fuels generation lead to predictive models for durability and performance of components?

Scientific Challenges and Research Opportunities

Understanding the dynamic processes for individual components needed for liquid solar fuels generation (either isolated or within integrated assemblies) is paramount to designing durable systems with the desired activity. Advances in degradation science based on theory, simulation, and advanced characterization (including methods described in Appendix A) can provide insight beyond observable phenomenological properties of systems, such as time-dependent efficiency or selectivity, to move toward the development of a detailed molecular-level comprehension of the mechanisms of individual processes that lead to system failure. This insight is needed to enhance stability, prevent degradation, and enable the design, development and even repair (including self-repair) of molecules and/or materials, as well as develop operating conditions required for long-term performance and durability. In parallel, advances in the performance of individual components are needed to achieve target system metrics. As discussed in the following sections, research in the basic chemical and materials science for liquid solar fuels generation is needed to accomplish the following:

- Enhance the mechanistic understanding of the kinetics and thermodynamics of degradation processes to enable effective co-design of components, interfaces, and tailored electrolytes
- Design and discover stable molecules and materials for absorbing and channeling solar energy to provide the electrochemical potential for the generation of liquid solar fuels
- Expand the mechanistic understanding of the CO_2RR, the N_2RR, and the OER to guide the design of catalysts with controlled selectivity, reactivity, and durability
- Tailor the properties of interfacial materials such as polymers or ionomers to control the transport and permeability of species pertinent to liquid solar fuels generation.

Enhance mechanistic understanding of the kinetics and thermodynamics of degradation processes to enable effective co-design of components, interfaces, and tailored electrolytes

A mechanistic understanding of long-term degradation is needed for each constituent of a solar fuels system. Molecular-level mechanisms of degradation[21] that have been observed for individual liquid solar fuels components include, but are not limited to, the following: corrosion or passivation of photoabsorbers (e.g., **Figure 4)** and catalysts, ion intercalation in OER catalysts, surface reconstruction that alters the distribution of exposed facets in CO_2RR catalysts, electromigration of materials under prolonged polarization, and bond scission in polymer membranes and ionomers. For materials, the relatively fast surface diffusion of partially solvated surface atoms and additional mechanisms of solid-state migration underpin the challenges in obtaining long-term durability[22-24]. Even components that exhibit no apparent corrosion experience dynamic processes, including exchange of species with the electrolyte via dissolution and precipitation and via molecular dissociation and association of ligands and ions. These types of processes could also provide the opportunity for repair mechanisms, although re-precipitated atoms may not return to an equivalent surface site and may also infiltrate to other regions of devices. There is a significant research opportunity to develop protection schemes and new concepts for repair (or even self-healing) of solar fuels components.

As an example of changes in a component during operation, catalysts for multiple electron/proton-transfer reactions envisioned for the OER, CO_2RR, and N_2RR for liquid solar fuels can undergo compositional and structural changes that can be quite detrimental to product selectivity. In the case of a molecular catalyst, isomerization, ligand exchange, and decomposition can severely alter the performance of an active catalyst. For heterogeneous catalysts, the atomic distribution and structure at the surface can change with potential or chemical environment, which can sometimes be predicted from thermodynamic considerations[25]. In all cases, the performance of catalysts ultimately depends on the rates of

compositional and structural changes; therefore, it is important to understand which processes are critical to controlling catalyst function, stability, and repair.

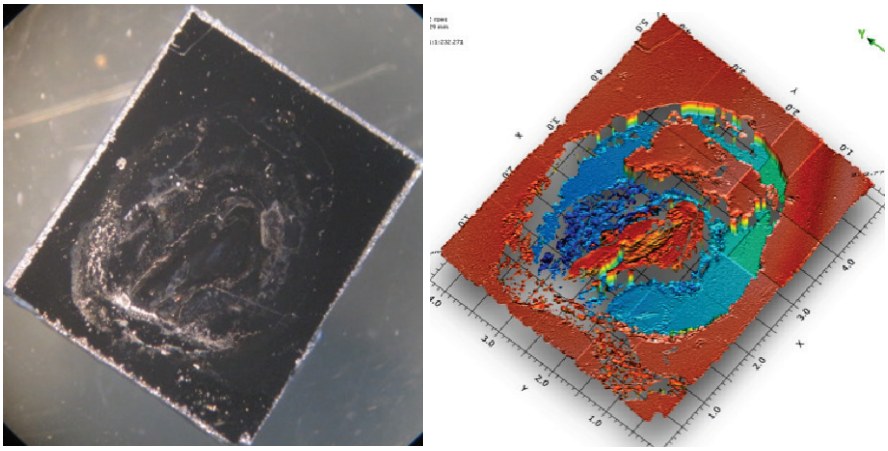


Figure 4. Photograph of nitrided p-$GaInP_2$ photoelectrode showing corrosion. The image on the right is from interference microscopy, with a z-scale that is about 2 µm between orange and blue. *Source: National Renewable Energy Laboratory.*

Experimental and computational approaches for studying dynamic processes that occur over a range of time and length scales need to be applied to solar fuels science. For example, first-principles theory can be used to probe the thermodynamics and pathways for corrosion, passivation, electrochemical stability, and other degradation processes for photoabsorbers[25], catalysts, and other components under a wide range of conditions. Theory can also provide insight into key intermediates, nucleation sites, or metastable materials. Advanced operando characterization methods (e.g., Appendix A) can deconvolute degradation pathways. Increased attention must also be given to processes that occur on longer time scales that will impact component performance over days, years, and decades after deployment. Methods for accelerated testing as well as forensics—e.g. analysis, imaging, spectroscopy—are also needed, along with predictive multiscale models, extensive databases of materials properties, informatics, and reliability principles to link physical models and statistical data.

Research is needed to probe and quantify changes in components as well as in the structure, composition, and properties of the interfaces that connect them. In addition, it is important to understand the differences in degradation mechanisms in electrolytes (aqueous and nonaqueous) as well as in the presence of other additives to enable the design of tailored electrolytes that control degradation and promote desired performance. Regeneration concepts are needed that restore activity of individual components and to develop new ideas for self-repair or self-healing. It should be noted that nature is expert at self-repair and regeneration, so it could provide additional insight for liquid solar fuels. Other opportunities may be afforded to solar fuels devices by taking advantage of the diurnal cycle to allow for productive solar fuels reactions during periods of illumination and using "dark" time to perform repair reactions.

Design and discover stable molecules and materials for absorbing and channeling solar energy to provide the electrochemical potential for the generation of liquid solar fuels

Photoabsorbers are an integral part of solar fuels systems because they convert solar radiation into chemical potential. Many proposed systems employ multiple photoabsorbers (in series or in parallel) to take advantage of more of the solar spectrum. Sequential light absorption, charge separation, and charge collection creates the driving force for thermodynamically unfavorable chemical transformations needed for oxidizing water (OER) and effecting reduction via CO_2RR and N_2RR. A number of arrangements of photoabsorbers comprising molecules, materials, or molecular hybrid materials have been demonstrated

in a number of different architectures for solar fuels generators—including semiconductor wafers, thin films, particle suspensions, membrane-bound absorbers, nanostructured materials, molecular chromophores, and molecular systems coupled to solid-state materials. A number of options could be explored to create the required chemical potential from solar radiation, depending on the bandgaps, band edges, hot-carrier energies, or HOMO-LUMO (highest-occupied and lowest-unoccupied molecular orbitals, respectively) of the photoabsorbers. The generation of multiple electrons and holes for the complex catalytic redox processes needed for liquid solar fuels production requires the absorption and utilization of multiple photons per reduced product.

Significant opportunities exist to improve known photoabsorbers and to discover new materials, molecules, and molecular hybrid materials with properties well suited for liquid solar fuels. In the design of new materials, durability must be considered at the outset—either intrinsic to the photoelectrodes themselves or extrinsic through, for example, incorporation of protective coatings, control of operating conditions, or development of repair mechanisms. Exploring how to control both optoelectronic properties (energetics, transport) and durability represents an important research area. For example, passivating defect sites or tuning trap state energies to lie outside the optical bandgap could decrease the rates of non-radiative recombination in semiconductor photoabsorbers. Research is needed to expand the coupling of first-principles theory with rapid synthesis and characterization methods to accelerate the discovery of stable single and tandem solid state and molecular-based photoabsorbers. Opportunities include not only well-studied oxide-based semiconductor materials but also many other materials such as nitrides, oxynitrides, and carbides as well as hierarchically assembled molecular systems and hybrid systems comprised of molecular complexes integrated with solid-state materials. Concepts involving multiple photoabsorbers (molecules or materials) could also be envisioned.

Opportunities exist to enhance the performance and durability of known solid-state photoelectrodes and molecular photoabsorbers by addressing their lack of intrinsic thermodynamic stability in the presence of water and/or under conditions relevant to liquid solar fuels generation. For example, fundamental understanding is required to effectively design and synthesize protective coatings and to elucidate their impact on performance. Mechanisms to protect electrodes, including passivation layers and other coatings, could be considered to protect semiconductor and dye-sensitized photoanodes.

Understanding the options for protection schemes, as well as the complexity of protective coatings, is still needed. As found for oxide coatings on semiconductors, the physics and chemistry of these coatings is complex. The Helmholtz potential drop for oxide coatings can exhibit a Nernstian dependence on the difference between the oxide isoelectric point and the solution pH, but the oxide can also passivate semiconductor surface states and be more catalytically active than the bare semiconductor surface[26-28]. Oxide overlayers can modulate surface energetics by hundreds of millivolts when oxides are deposited on semiconductor surfaces (see **Sidebar 2**). Research is needed to understand and control the physical and chemical processes for surface modifications of photoabsorbers. Photovoltage in semiconductors often depends on the surface recombination velocity and the magnitude of the built-in potential and flat-band potential of a semiconductor junction, so these parameters are important considerations in modifying surface properties. For example, adaptive junctions have been recently characterized where the chemical potential of electrons in the contacting metal-oxide/(oxy)hydroxide phase changes as a function of the current passed through it (see **Sidebar 3**). This bulk pseudocapacitive charging alters the oxide/oxyhydroxide phase that is in direct contact with the semiconductor to dynamically perturb the effective built-in potential across the interface during operation.

Sidebar 2: Energetic effects of oxide overlayers in photoelectrochemical systems

Oxide materials deposited onto semiconductor surfaces are passivating overlayers that can protect the underlying semiconductor from the electrolyte; however, their behavior and influence is complex. First, the oxides passivate semiconductor surface states, mitigating recombination that can lead to photovoltage losses. Second, depending on the nature of the oxide, they can serve a catalytic role to boost photovoltage. Third, oxide overlayers can create junctions at the semiconductor/oxide interface, which can enhance charge separation and provide another mechanism to increase photovoltage. Fourth, oxides can serve as a kinetic barrier to recombination by spatially separating charges in the oxide from the semiconductor/oxide interface. These effects are summarized in **Figure S4 a–c**.

The effect of the oxides on the system energetics is much less appreciated. To minimize energetic losses, it is essential to correctly position the semiconductor conduction and valence band edges relative to the redox potential of the fuel-forming reaction. Oxides can have a strong influence on the system flat-band potential (E_{fb}), which is the thermodynamic limit for driving both the fuel-forming reactions and corrosion reactions. It is well established that the Helmholtz potential drop (V_H) at the photoelectrode/electrolyte interface depends on the difference between the oxide isoelectric point (IEP)—defined as the point at which the surface has no net electrical charge (i.e., where there is an equal number of protonated and deprotonated hydroxyl groups on the oxide surface)—and the solution pH:

$$V_H = 0.059*(\text{IEP} - \text{pH}) .$$

Thus, the choice of oxide and electrolyte can conceivably shift the E_{fb} by up to 0.6 Volts for oxide IEPs ranging from 2-12. Catalysts, too, can impact not only the kinetics but also the thermodynamics of stability by modifying E_{fb}. **Figure S4d** shows the large positive shift observed in E_{fb} upon growth of native oxide onto a silicon photoelectrode surface, and the negative shift that occurs after platinum nanoparticles are deposited onto this oxide-covered surface. This makes sense because catalysts frequently lower activation energy, which reduces the barrier for both the forward (fuel-forming) and reverse (corrosion) reactions.

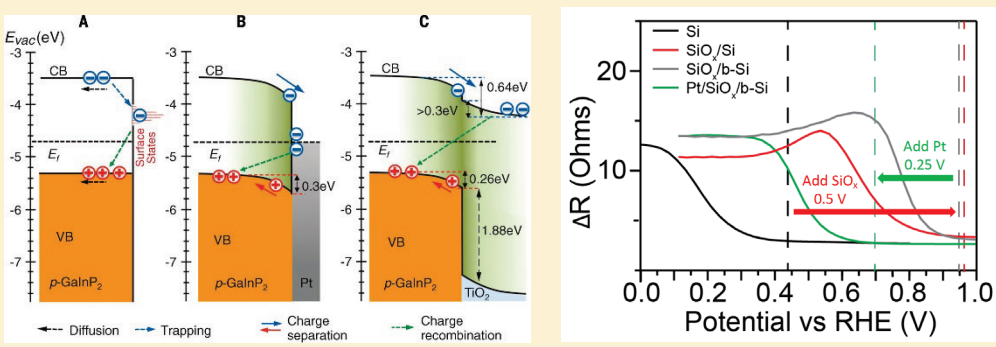


Figure S4. (a) Trapping of photogenerated carriers in a bare p-GaInP$_2$ photoelectrode by surface states. (b) Platinum metal on a p-GaInP$_2$ photoelectrode results in reduced recombination (cf. bare p-GaInP$_2$) due to passivation of surface states and band bending from the Schottky junction. (c) The oxide TiO_2 causes both a thermodynamic barrier of ~0.26 eV due to formation of a p-n junction with p-GaInP$_2$, and a kinetic barrier of >0.3 eV resulting from spatial separation of charges from the p-GaInP$_2$ interface. *Source: Yang, Y. et al., Semiconductor interfacial carrier dynamics via photoinduced electric fields, Science* ***350****, 1061–1065, 2015*[29]. (d) Growth of native oxide (SiO_x) onto planar (Si) or nanostructured black Si (b-Si) causes a positive shift in the thermodynamic flat-band potential of ~0.5 V; adding Pt nanoparticles to the surface of the SiO_x results in a negative shift of ~0.25 V, representing weaker resistance to corrosion. *Source: Reprinted from Anderson, N. C. et al., Silicon photoelectrode thermodynamics and hydrogen evolution kinetics measured by intensity-modulated high-frequency resistivity impedance spectroscopy, J. Phys. Chem. Lett. 8, 5253–5258, 2017. Copyright 2017 American Chemical Society*[30].

Sidebar 3: Adaptive junctions at photoelectrodes

Electrocatalysts are often integrated onto the surfaces of semiconductor photoelectrodes to reduce kinetic overpotentials for generating solar fuels. In addition to facilitating chemical reactions, the catalyst also forms an electronic interface with the underlying semiconductor that is responsible for building photovoltage by separating photoexcited electron-hole pairs. Thus, the nature of electronic charge transfer at this interface is of fundamental importance in determining photoelectrode performance and design principles.

The physical properties of the catalyst have dramatic effects on the electronic properties of the semiconductor/catalyst interface. If the catalyst material is a physically dense, electrically conducting solid (such as Pt metal), then the interface properties can largely be described by conventional Schottky-junction physics. In these cases, Fermi-level equilibration between catalyst and semiconductor drives band bending in the semiconductor to provide a minority-carrier-selective interface.

However, many catalysts, particularly those for the OER, are not physically dense metals; instead, they are electrolyte-permeable (oxy)hydroxides or hydrous oxides. These catalysts are often redox active and accumulate photogenerated holes through cation oxidation prior to the evolution of oxygen. Because the materials are typically disordered, porous, and permeated with electrolyte, the holes that accumulate are electrically compensated by ion motion in or out of the electrolyte phase, much like in a battery electrode. This hole-accumulation process increases the work function of the catalyst layer, therefore effectively creating a larger interfacial barrier height with the underlying *n*-type semiconductor (**Figure S5**, top).

Interfaces that create these interfacial barriers are termed "adaptive junctions" and are only possible for electrolyte-permeated catalysts in which mobile ions screen changes in electronic charge. Although dense metallic catalysts also can accumulate charge, that electronic charge must be compensated by ions in the double layer at the catalyst/solution interface, and the underlying "buried" semiconductor/metal junction interfacial energetics are uneffected. Practically, therefore, adaptive junctions provide a mechanism to generate, during operation, junctions with higher "effective" barrier heights—and thus, larger photovoltages than unoptimized buried junctions made with electrolyte-impermeable catalyst layers.

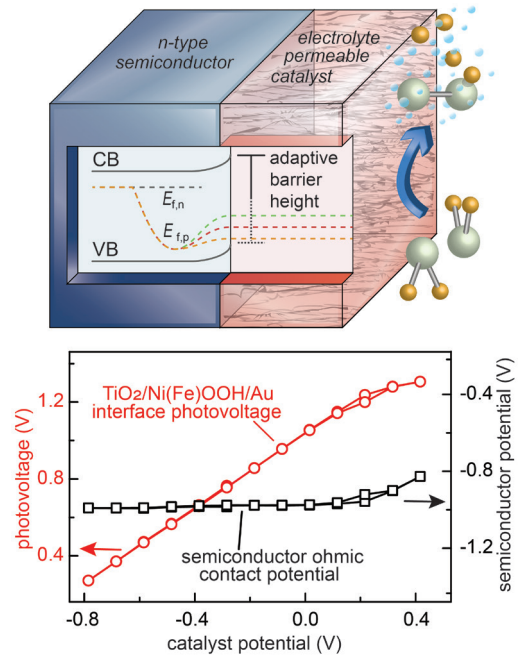


Figure S5. An electrolyte-permeable catalyst deposited onto an n-type semiconductor produces an "adaptive" junction. Top: During operation, the catalyst is charged with holes and accompanying ions from the electrolyte phase, leading to a lowering of the electron electrochemical potential in the catalyst and a larger effective interface barrier height. In contrast, a dense electrolyte-impermeable catalyst maintains a constant semiconductor/catalyst barrier height, which is not changed during operation. Bottom: Experimental data showing how the effective interface photovoltage is a function of the catalyst potential, which is not possible for a conventional buried junction. *Source: Used courtesy of Forrest Laskowski, Fuding Lin, and Shannon Boettcher, University of Oregon.*

Adaptive-junction behavior has been experimentally observed, for example, in *n*-TiO_2/Ni(Fe)OOH photoanodes using a so-called "dual-working electrode" approach. Here, the electron electrochemical potential (Fermi level) of the catalyst film is independently measured (or controlled) relative to the ohmic back contact with the semiconductor. The bottom panel in **Figure S5** shows how the effective photovoltage increases as the positive charge on the catalyst layer increases. However, many experimental systems are expected to exhibit behavior in between ideal adaptive and buried-junction behavior—for example, as a result of surface states at the semiconductor/catalyst interface or incomplete ionic screening of accumulated electronic charge in the catalyst layer.

Reaction kinetics for fuel formation and durability at coated semiconductors could also strongly depend on the charge transport ability of the coating layers (e.g., insulating vs. "leaky"), which can either inhibit or enhance reactivity. In addition, forming a high-quality junction between two materials—e.g., by spatially varying dopants in a semiconductor or protecting a semiconductor using a stable transparent conducting oxide or other material—may enable one to "bury" the electrostatic junction responsible for charge separation. Additional research is needed on decoupling the effectiveness of a material to generate a large photovoltage from its interfacial kinetic and thermodynamic properties. These concepts could offer more opportunities to increase durability yet retain the lifetime and functionality of known photoabsorbers. They may, however, require more complex or cost-intensive fabrication strategies, such as atomic layer deposition, for highly nanostructured materials or even molecular systems.

More understanding is needed to determine the balance of performance, durability, degradation mechanisms, and possible fabrication complexities. An important area of research that requires further investigation is the complex interplay of ionic and electronic permeability of coatings and their effect on performance and durability in liquid solar fuels devices. Repair mechanisms may be either inherent to the component itself (e.g., self-repair) or introduced via the addition or replenishment of chemicals (e.g., in the electrolyte or catalyst) as well as by externally controlled chemistry (e.g., electrochemical recycling). These repair mechanisms could play an important role in meeting technologically relevant metrics for long-term stability.

Expand the mechanistic understanding of CO_2RR, N_2RR, and OER to guide the design of catalysts with controlled selectivity, reactivity, and durability

Catalysts for liquid solar fuels have a number of important challenges related to both durability and selectivity. A mechanistic understanding of the detailed processes and elementary reactions is critical to prevent the undesired processes that degrade catalyst performance, structure and composition (see below). From a selectivity and reactivity standpoint, the main catalytic reactions of interest for producing liquid solar fuels are the OER—to generate O_2, protons, and electrons—and controlled CO_2RR and N_2RR to generate specific reaction products in high yields. As illustrated in **Figure 5,** the reaction scheme for CO_2 conversion consists of a complex reaction network with a wide range of potential pathways and intermediates[18]. CO_2RR proceeds via many steps that together require the transfer of multiple electrons and protons to form intermediates. Obtaining selective yields of liquid reaction products has proven challenging. For example, the unwanted HER is kinetically competitive with the desired liquid-fuel-forming cathodic reactions, especially at the large overpotentials required for the CO_2RR and N_2RR. Strategies must therefore be developed to slow the rate of the HER at overpotentials relevant to desired reduction reactions to enable product selectivity. An increased understanding of these pathways is needed to develop new catalysts. Clarification of active sites, reaction mechanisms, intermediates, and rate-determining steps are needed to enable the design and control of free-energy landscapes that funnel intermediates: (1) along reaction pathways toward the generation of specific products, (2) away from potential degradation processes, and/or (3) toward off-cycle intermediates that can readily be activated to re-enter the catalytic cycle. Advances are also needed in OER catalysts because of specific limitations of

current systems at various pH conditions. Low-pH operation requires the use of precious metal OER catalysts for stability, so opportunities exist to enhance the stability of non–precious metal catalysts or reduce the amount of precious metal content of catalysts. Independent of pH, more effective catalysts are needed for the OER to overcome scaling relations and enable both reversible and rapid rates of reactivity. Insights gleaned from studies of the OER can be leveraged to overcome similar limitations that exist for the CO_2RR and N_2RR, which are often more complex reactions that require the transfer of more electrons and protons.

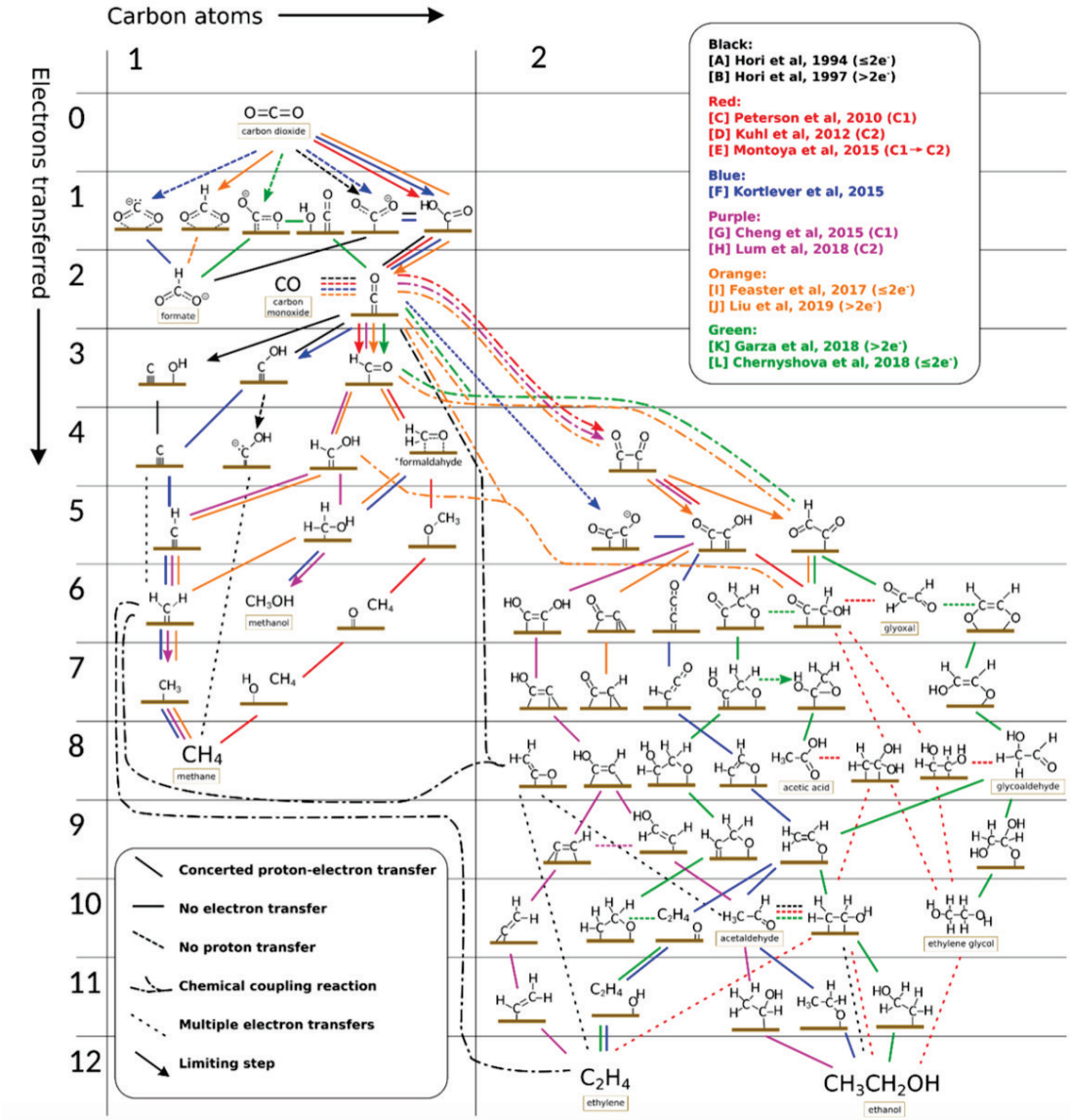


Figure 5. Possible mechanistic pathways of CO_2 conversion to C_1 and C_2 products on polycrystalline copper, grouped into different-colored reaction schemes taken from the works in the top-right legend. *Source: Nitopi, S. et al., Progress and perspectives of electrochemical CO_2 reduction on copper in aqueous electrolyte, Chem. Rev. 119, 7610–7672, 2019. Copyright 2019 American Chemical Society*[18].

For CO_2RR, multiple parallel reaction pathways can form C–H and C–C bonds and thus yield a mixture of products. It is critical to understand and delineate the factors that impact CO_2RR activity and selectivity, including catalyst composition, surface structure, morphology, choice of electrolyte ions, and local pH[31]. To date, polycrystalline copper is the most effective catalyst for the CO_2RR and is capable of

performing the series of steps required for carbon-carbon bond formation to generate C_2 products[18, 31, 32]. However, Cu-catalyzed reduction of CO_2 is complex because of the large number of copper facets that exhibit different reactivity (**Figure 6**). Most other heterogeneous catalysts form C_1 products such as CO, formate, methanol, or methane. A detailed mechanistic understanding of these catalytic pathways and the active sites of molecular and heterogeneous catalysts is required for control and selectivity and to discover other active catalysts for the CO_2RR.

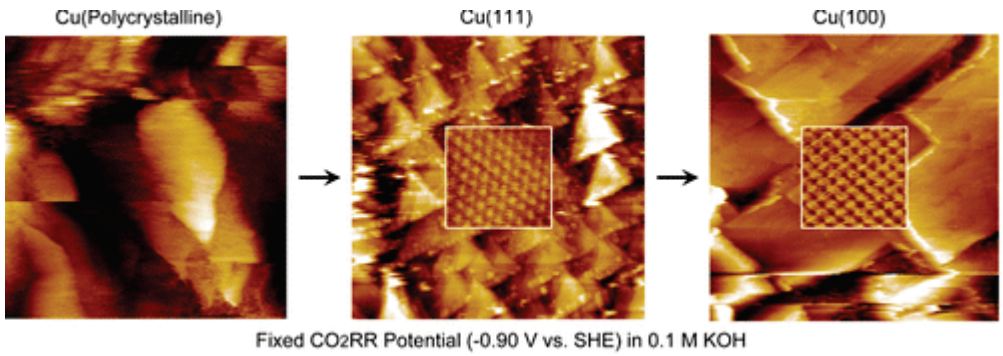


Figure 6. Operando electrochemical scanning tunneling microscopy (EC-STM) showing polycrystalline Cu electrode undergoes stepwise surface reconstruction—first to Cu(111) within 30 min, and then to Cu(100) after another 30 min—when held at a fixed negative potential, −0.9 V (vs. standard electrode potential), in the vicinity of CO_2RR in 0.1 M KOH. *Source: Reprinted with permission from Kim, Y.-G., et al., [The evolution of the polycrystalline copper surface, first to Cu(111) and then to Cu(100), at a fixed CO_2RR potential: A study by operando EC-STM](), Langmuir 30, 15053–15056, 2014. Copyright 2014 American Chemical Society*[22].

Although copper catalysts continue to be the only heterogeneous CO_2RR catalysts that form carbon-carbon bonds, nickel phosphide alloys[33] have recently been demonstrated to exhibit large overpotentials for the unwanted HER relative to the CO_2RR. Importantly, preliminary studies indicate that other catalysts can exhibit CO_2 conversion selectivity similar to that of Cu-based catalysts (see **Sidebar 4**). Examples of opportunities to discover new selective catalysts include new ligand design and surface-linking strategies for molecular catalysts, and understanding of the effects of alloying, surface reconstruction and modifications, and nanostructuring for heterogeneous catalysts.

Sidebar 4: Alloying makes Ni catalysts behave like Cu systems

Over the past decade, metal and metal alloy compounds have shown great promise for efficient and Earth-abundant electrocatalysts. Based on the binding of H atoms to surfaces, as well as descriptor and volcano plot analysis[34, 35] , Pt has long been established as the best catalytic metal for the HER. In contrast, nickel and other 3*d* transition metals bind H too strongly for optimal catalysis. Exploration of transition metal compounds—most notably, phosphides and sulfides—has shown that the binding of H can be tuned by binding to nonmetals and shifted very close to the peak of the volcano, thus offering effective catalysis with Ni and Co and other common metals[33, 36].

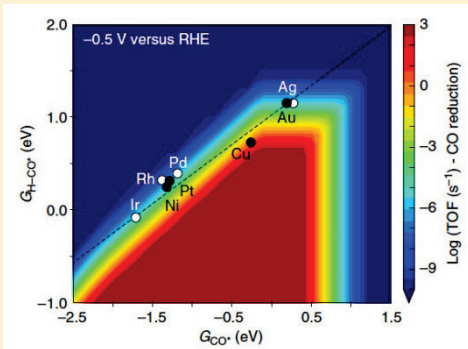


Figure S6. Two descriptors illustrate that Cu is the best monatomic metal for CO_2RR beyond CO; yet, it still operates with low activity and selectivity. *Source: Reproduced from Liu, X. et al., [Understanding trends in electrochemical carbon dioxide reduction rates](), Nat. Commun. 8, 15438, 2017*[37]. *Distributed under the Creative Commons license.*

Extending conductive compounds from HER to CO_2RR is a challenge. Because solar production of fuels involves hydrogenation of CO_2 and other oxidized carbon species, aqueous environments are common; this makes HER an undesired side product in the quest for multi-carbon products. For CO_2 conversion beyond CO, copper is considered the champion, supported by descriptor analyses (**Figure S6**). Notably, nickel phosphides offer better catalysis for CO_2RR than they do for H_2 (**Figure S7**).

Despite their known efficacy as active HER catalysts, these binary materials of the general formula Ni_xP_y favor CO_2 reduction over the kinetically facile HER at low overpotentials[33]. Product selectivity among the oxygenate products formate (C_1), methylglyoxal (C_3), and 2,3-furandiol (C_4) improves with increasing phosphorus content, and it is hypothesized that the binary material stabilizes oxygen-bound intermediates. A deeper understanding of the mechanisms by which liquid product can be produced—for example, the synergistic role of nickel and phosphorus—is needed to advance new binary materials for CO_2RR.

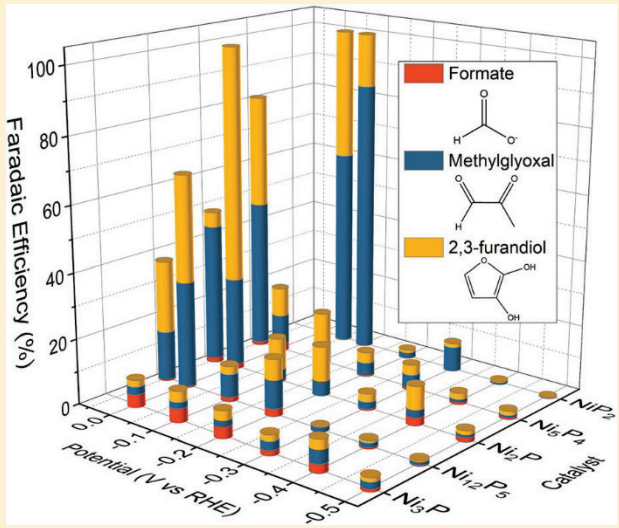


Figure S7. Selectivity of nickel phosphide catalysts for CO_2RR beyond CO. Phosphorus-rich Ni_xP_y compounds show high selectivity for converting CO_2 to multi-carbon organic products. While activity is low, selectivity of versus CO or H2 production is very high, making this class of catalytic compounds promising for fuel production. *Source: Reprinted from Energy Environ. Sci. 11, Calvinho, K.U.D. et al., Selective CO_2 reduction to C_3 and C_4 oxyhydrocarbons on nickel phosphides at overpotentials as low as 10 mV, 11, 2550–2559, 2018, with permission from Elsevier*[33].

Tandem and cascading catalysis concepts can also be envisioned whereby separate catalysts carry out selective elementary reaction steps (see also PRO 4 and **Sidebar 13**)[38, 39]. Catalytic activation and reduction of N_2 remains a grand challenge[40], and significant additional research is needed. Although several reports of electrocatalytic reduction of N_2 to NH_3 are available, no high-efficiency catalysts have been discovered to date, and it has been suggested that even these inefficient demonstrations are not reproducible and/or have artifacts[41]. As described in PRO 2, biological processes including nitrogenase could provide inspiration—which could lead to new artificial catalytic systems (see **Sidebar 8** in PRO 2).

Understanding the molecular mechanisms and processes that degrade activity or increase the durability of catalysts is critical. A strong overlap exists between catalysis for solar fuels and for electrochemical processes in the absence of light. Although many parallels, lessons learned, and challenges from electrocatalysis can be applied to solar fuels (e.g., see the recent BES *Catalysis Basic Research Needs* report[42]), it is important to note that commercial electrocatalysts operate at current densities several orders of magnitude larger than are possible in liquid solar fuels devices driven by unconcentrated sunlight, i.e., ~1–10 A/cm^2 vs. <~20-30 mA/cm^2, respectively. These differences suggest an opportunity for solar fuels lies in the area where the slower rates of solar-driven reactivity that produce lower current densities could

actually provide advantages over high current density applications. For example, design considerations could focus on enhancing catalyst durability and/or selectivity instead of (or even at the expense of) enhancing rates of reactivity without impacting the overall efficiency of generating liquid solar fuels. Dark electrochemical analyses also can be useful in benchmarking the durability, efficiency, and selectivity of homogeneous, heterogeneous, and hybrid catalysts. Depending on device architectures, catalysts may not even operate in regions of a solar fuels systems where they are irradiated by sunlight.

It is essential to identify the end products of solar fuels redox reactions as a function of operational conditions (e.g., applied potential, current density, electrolyte, light intensity including dark conditions). But one must also understand the pathways that result in the observed distributions of desired reaction products as well as undesired back reactions and degradation products. The ability to probe reaction intermediates nondestructively during electrocatalysis could be a key enabler leading to a better fundamental understanding of both the desired and the unwanted reaction pathways. Developing and applying operando and in-situ characterization techniques (e.g., Appendix A) is essential to improve the detailed understanding of reaction selectivity, efficiency, and durability and to facilitate theory-driven design and discovery of new homogeneous and heterogeneous catalysts.

Tailor membrane properties to control the transport and permeability of species pertinent to liquid solar fuels generation

Understanding and controlling the transport of mass, charge, and energy represents a critical challenge that must be addressed for liquid solar fuels generation. Photoabsorbers and catalysts require careful control over electron and hole transport processes, whereas solutions, electrolytes, and coatings can transport species including ions, reactants, and products that can exist in various phases. Research could create membranes and separators that could keep incompatible species apart from each other, avoid species crossover from the chemistry in one electrode to the other, control ion and mass transport, and maintain local pH environments[43]. These functions could be enabled by the specific design of the membrane or separator, including its ionic and water content, the chemical nature of its backbone and pendant groups, and structural characteristics such as crosslinking density and free volume.

To date, most membranes and separators used in solar fuels systems have been designed for other, albeit related, applications such as fuel cells (e.g., Nafion) or electrolyzers. Therefore, opportunities exist to better understand, design, and control the functionality, permeability, and stability of improved or new membranes and separators specific to solar fuels. For example, lower operating current densities for liquid solar fuels devices relative to electrolyzers could relax the demand for high ionic conductivity; but product crossover must be more highly controlled for solar fuels so that product yields remain high. Crossover of species resulting from CO_2RR and N_2RR could depend greatly on the chemical and physical structure of the polymer in a membrane, the nature of the products, and processes that control transport.

New polymer architectures could create the properties of membranes, separators, and ionomers needed for liquid solar fuels applications. Most of our understanding of polymer membranes and ionomers stems from (1) macroscopic observations made using experiments and multiscale modeling that characterize highly averaged steady-state conditions or (2) atomistic models that use molecular dynamics to gain insights into behaviors at very short length and time scales. The demands that liquid solar fuels place on membrane selective permeation and stability under intermittent use raise the need for a new understanding of detailed membrane physics and chemistry from a fundamental molecular-level perspective. Moreover, more needs to be known about the fundamental interfacial properties of complex membranes. Understanding how to evaluate and enhance membrane, ionomer, and separator stability, including operando measurements, remains a challenge. Further significant challenges include identifying stable and robust materials across a wide range of aqueous pH conditions, as well as understanding and controlling degradation mechanisms during operation.

Solar fuels generation systems have been developed that employ proton-conducting ionomers that support strongly acidic environments. If non–precious metal electrocatalysts are desired, their activity and stability can be enhanced by using non-acidic electrolytes; thus, anion-exchange membranes could be suitable choices for the ion-conducting medium. Moreover, by using anolyte and catholyte ionomers with different chemical structures, bipolar membrane function can present local conditions that are optimized for each catalyst and specific desired reaction products (see **Sidebar 5**).

There are a number of new materials and approaches that could be explored. Bipolar membranes are one example (**Figure 7**), which could enable long-term control and maintenance of differences in pH and control over local pH to afford optimal catalyst stability, product selectivity, and overall performance. These concepts could allow optimal conditions for operation of non–precious metal OER catalysts in strongly alkaline environments and CO_2RR or N_2RR catalysts under other conditions (see, for example, **Sidebar 5**). Membranes that contain fixed-charge groups or weak acid or weak base layers are also still relatively unexplored.

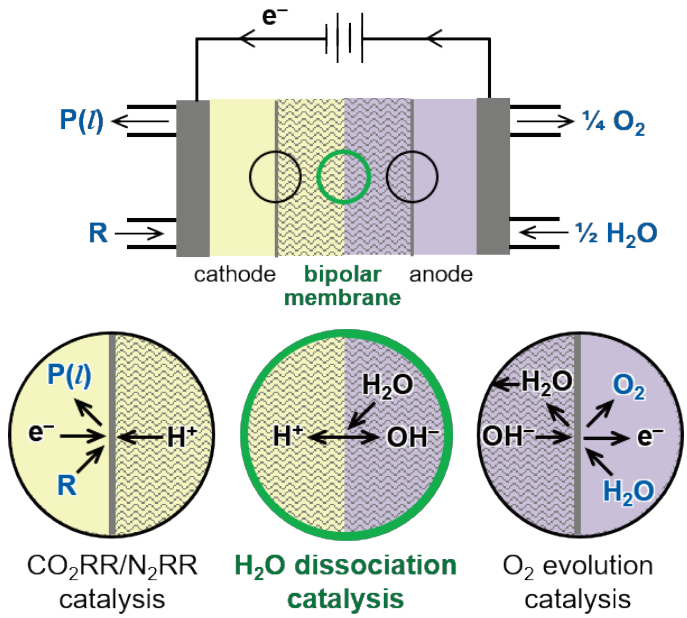


Figure 7. Simple illustration of a bipolar membrane that can use electropotential to create and maintain a pH gradient across it. *Source: Courtesy of Shane Ardo, University of California, Irvine.*

Scientific advances are needed to better explore the use of gas diffusion electrodes and membranes for solar fuels devices, which could enable gaseous reactant feeds that overcome solubility and mass transport limits of CO_2 and N_2 dissolved in water and aqueous electrolytes. Membrane–electrode–assemblies[23] could create a mesoporous network of mixed electronic and ionic phases coupled to gaseous and liquid species transport that meet at triple-phase boundaries at or near electrocatalyst active sites. These phases are very challenging to characterize at a fundamental level, yet they must be controlled to precisely enable desired functionality. A large knowledge gap exists in understanding and controlling the physicochemical properties of these highly structured and confined regions where electrocatalysis occurs (see also PRO 2). One could also envision the use of solid-electrolyte membranes in solar fuels devices that could be designed for gaseous reactant feeds and sufficient conductivity. From a durability standpoint, membranes and related components often have significant issues that need to be understood and mitigated.

Sidebar 5: Bipolar membranes enable the use of different anolytes and catholytes

(Photo)electrolysis cells require equal rates of electron and ion transport between the sites of oxidation and reduction. In conventional electrolyzers, the electrolyte is a strong acid or a strong base, and the ionic current is carried by protons or hydroxides. However, in the electrochemical reactions that produce hydrogen from water or reduced carbon-containing molecules from CO_2, the optimal catalytic performance at the anode and cathode may require different pH conditions. These can be achieved by using a bipolar membrane. Bipolar membranes contain fixed cationic groups on one side of the membrane to preferentially conduct mobile anions such as OH^-, and fixed anionic groups on the other side of the membrane to preferentially conduct mobile cations such as H^+.

An electrostatic space-charge layer forms at the junction between the anion-conducting and cation-conducting layers of a bipolar membrane. This junction imparts diode-like behavior to the flow of ions in the membrane. For electrolytic applications with the OER occurring in a base, the reverse-bias direction is of particular interest. Under an applied reverse bias, H^+ and OH^- ions that are generated by the autodissociation of water in the junction are driven through the cation-conducting and anion-conducting layers toward the cathode and anode of the (photo)electrolysis cell, respectively. Conceptually, the thermodynamic cost of generating a strong acid and a strong base from water is recovered at the anode and cathode, because reduction half-reactions are more thermodynamically favorable in acid and oxidation half-reactions are more favorable in base.

This principle is illustrated in the experiments of Luo et al.[44] (**Figure S8**), which demonstrated an efficient water electrolysis cell powered by two perovskite PV cells wired in series. Notably, this arrangement enabled the use of non–precious metal catalysts (cobalt phosphide and nickel-iron layered double hydroxide) that are optimized for operation in acid and base solutions, respectively. Ion flow outward from the bipolar membrane junction maintained a steady pH and an impressive solar-to-hydrogen efficiency of 12.7%. The decay in photocurrent over a period of 16 hours could be attributed primarily to the performance decay of the perovskite PV cells.

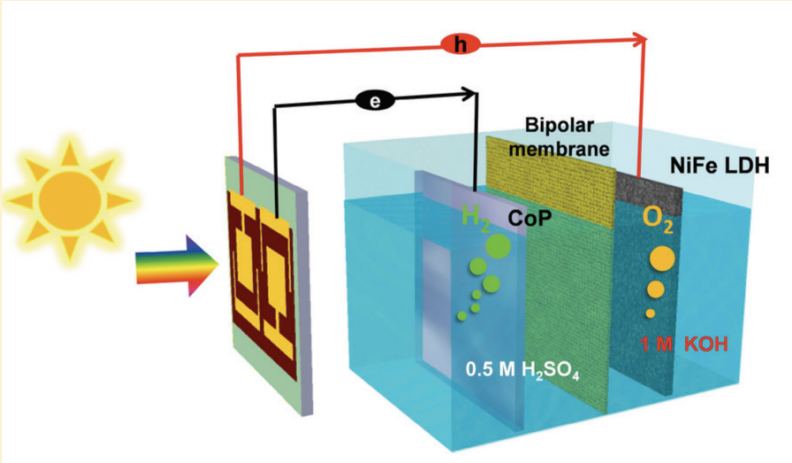


Figure S8. Schematic diagram of a photovoltaic-electrolysis device composed of perovskite light harvesters, Earth-abundant catalysts, and a bipolar membrane. *Source: Reproduced with permission from Luo, J., et al., Bipolar membrane-assisted solar water splitting in optimal pH, Adv. Energy Mater. 6(13), 1600100, 2016. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim*[44].

Potential Impacts

The long-term operation for liquid solar fuels generation relies on component stability, efficiency, and selectivity across various chemical, physical, electronic, and ionic phenomena. Only by identifying the mechanism(s) of operation and of degradation for each component, both in isolation and integrated in sub-assemblies with other components, can more durable, robust, and efficient liquid solar fuels processes

be developed. Furthermore, the fundamental understanding that can be gained from identifying degradation mechanisms and reaction pathways can have a direct influence on several other technologies that use the same or similar components and/or afford the same or similar functions. Since the most relevant chemistry, physics, and functionality of each component are different, the potential impact for developing new molecules and materials, and understanding the dynamics of each, will influence a wide range of applications.

Membranes and separators are at the core of multiple technologies including electrolyzers, fuel cells, and electrodialysis devices. Developing tools to fabricate and characterize polymer and solid-state membranes, separators, and ionomers will help enable improved performance and stability of parallel technologies needed to separate chemical reaction products and provide ionic transport between redox sites.

PRO 2: Control the catalyst microenvironment to promote selective and efficient fuel production

Summary

Selectivity remains a significant scientific challenge for liquid solar fuels as well as for related electrically driven processes. Challenges exist at multiple levels for the selective conversion of CO_2 (and other feedstocks such as N_2). The major challenges center around suppressing the HER and/or promoting CO_2RR relative to HER—which is a daunting challenge given that the concentration of water is often orders of magnitude higher than that of CO_2 in solar fuels processes. Accessing transformations beyond the simple 2-electron (>2e-) reduction (e.g., to CO or formic acid)[6, 45] presents further challenges, especially in controlling the selective formation of carbon-carbon bonds. There are also research opportunities to develop new science for the OER[6], such as reducing the required amounts of precious metal catalysts, promoting 4e- oxidation to O_2 over 2e- oxidation of H_2O_2, and mitigating catalyst damage under oxidative conditions.

As illustrated in **Figure 5**, selective generation of solar fuels necessitates understanding the catalytic pathways that lead to different products and controlling the branching among different pathways at key points in complex reaction networks, i.e., the relative rates of competing reactions. Much work remains to be done on catalyst design and discovery (as described in PRO 1), but these challenges also can be broadly addressed by controlling the microenvironment—a term that describes the local region around a catalytic center, i.e., beyond covalent interactions. The microenvironment around a catalytic active site can serve multiple functions, which include stabilizing the first coordination sphere structure, tuning the redox potentials, controlling the electrostatics around the active site, creating hydrogen bonding networks, and controlling transport and binding of reactants/intermediates/products.

The field of catalysis has seen major innovations in moving beyond the active site of a catalyst to understanding, controlling, and even designing the local environment over a range of length scales. The recent BES Basic Research Needs (BRN) report *Basic Research Needs for Catalysis Science to Transform Energy Technologies*[42] presented an entire Priority Research Direction on "*Design Catalysts Beyond the Binding Site*," addressing the key question of how to "elucidate the cooperative interactions among the binding site, reacting molecules, and the surrounding environment to enable the design of catalyst structures that precisely control chemical reactions." There are significant opportunities for solar fuels research to incorporate and even expand beyond the concepts codified in the catalysis BRN report to create and control the microenvironment to tune the energetics of intermediates, binding, and transition states for molecular, supported, and heterogeneous solid-state catalysts. Interactions within microenvironments can involve an ensemble of processes, including those that could have cooperative interactions and that can be transmitted over longer distances and time scales than the bond-breaking region around the active site.

Nature's catalysts—enzymes—execute many reactions relevant to liquid solar fuel production and provide excellent examples of controlling the microenvironment—in this case, with a complex biopolymer that positions functional groups around the metal active site with high precision. Lessons from biology on creating microenvironments include extending coordination through ancillary ligands, Lewis acid/bases, and Bronsted acid/bases; compartmentalizing reactions to create reaction media distinct from bulk water (e.g., creating hydrophobic reaction zones); creating and exploiting local electric fields; creating local pH environments and gradients; and controlling access to reactants and products (e.g., transport). At a metalloenzyme's core are one or more coordinated metal ions where catalytic transformation occurs. Metalloenzymes create an extended structure of ideally tuned and positioned atoms beyond the inner coordination sphere of the metal centers that create the perfect microenvironment (see **Sidebar 6**) for the given reaction, through ancillary functional groups, secondary and tertiary

Sidebar 6: Natural scaffolds for selective and efficient cascade reactions

In developing architectures for sequential reactions that convert CO_2 into liquid fuels, one must consider the catalyst environment across many length scales. Nature provides inspiration for developing such scaffolds, with highly selective and efficient cascade reactions being prevalent across natural enzyme systems. The CO dehydrogenase/acetyl coenzyme A synthase (CODH/ACS) enzyme complex is critical for metabolism in microbes such as methanogens, acetogens, and anaerobic bacteria, ultimately generating acetyl CoA. Ancestral versions of this enzyme have been implicated in primordial energy storage and conversion reactions. The CODH part of this enzyme converts CO_2 to CO with complete selectivity and at negligible overpotential at one active site, which features a modified nickel-iron-sulfur cluster (**Figure S9**). Electrons are shuttled in and out of the catalytic cluster through a molecular wire consisting of redox-active iron-sulfur clusters spaced appropriately to tune electron transfer rates; protons are managed through precisely positioned, positively charged secondary-sphere residues.

The CO, however, is just a short-lived intermediate and does not leave the protein scaffold. Instead, it enters a hydrophobic tunnel leading to the other part of the enzyme. Large protein conformational changes gate the access to this site, providing spatial and temporal control over the two distinct substrates—CO and a $-CH_3$ group—that must bind to the ACS active site, which features a different nickel-iron center. Once both substrates are bound, the metal center catalyzes methyl migration to generate a metal-bound acetyl species, forming a new carbon-carbon bond in the process. Ultimately, reductive elimination forms the carbon-sulfur bond of acetyl CoA, which is used as a biological fuel.

The combination of active-site electronic structure, secondary-sphere tuning, substrate channeling, and dynamic scaffold motion enables CODH/ACS to catalyze the completely selective, efficient generation of a C_2 species from one-carbon building blocks. Importantly, the CODH/ACS enzyme is fully reversible, indicating that it operates with high thermodynamic efficiency. Studies on understanding this dynamic interplay in the CODH/ACS enzyme offer a template for developing anthropogenic systems that carry out selective, sequential reactions to generate liquid solar fuels[46, 47].

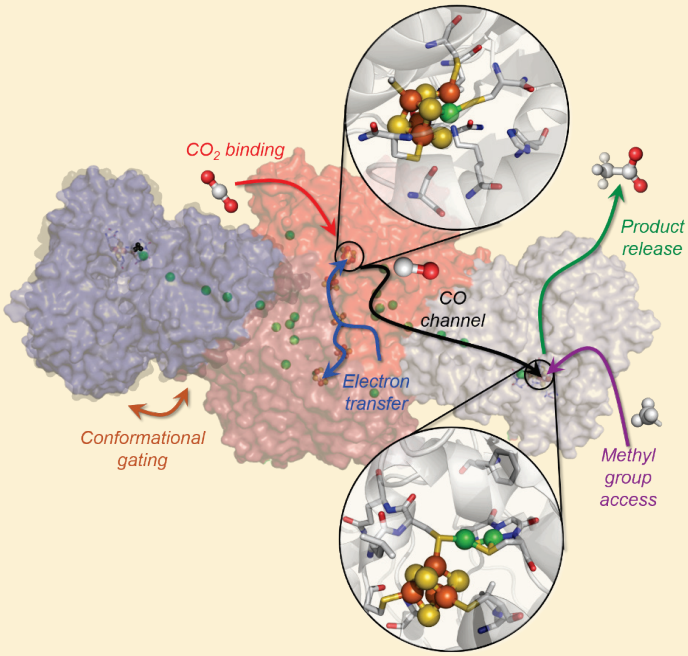


Figure S9. Structure of CODH/ACS (PDB: 2Z8Y/1OAO) with active sites and substrate binding sites indicated. *Source: Used courtesy of Hannah Shafaat, Ohio State University.*

structure of the protein, and co-factors. These functional groups can transfer protons, store electrons, stabilize products/reactants/intermediates, control hydrophobicity/hydrophilicity charge/electron transport, alter local reactant concentrations, and tune the redox potential—all with exceptional spatial and temporal control. There are a myriad of opportunities to mimic the features that create and control 3D microenvironments and to understand how these environments facilitate catalyst efficiency, rate, and selectivity in anthropogenic systems. Several recent studies[48-52] already show potential benefits of creating microenvironments for CO_2 conversion for solar fuels and electrocatalysis (see below). Many of the science opportunities are at the nexus of molecular and heterogeneous catalysis.

Key Scientific Questions

- What new approaches are needed to probe, understand, and tailor the structure, composition, and dynamics of the local region surrounding catalytic active sites to direct chemical reaction pathways?

- How do microenvironments control pathways/mechanisms/relative rates for key bond-making and bond-breaking steps and activation of catalytic intermediates for H_2 production, H_2O oxidation, CO_2 reduction, and N_2 reduction?

- How can the design principles learned from the study of enzymes be translated to create specific reactivity or improve catalyst efficiency and/or rate? How can these principles be used to tailor and control the microenvironment around homogeneous and heterogeneous catalysts?

- How can the microenvironment be used to control competitive reaction pathways for CO_2 and N_2 reduction, including avoiding H_2 generation, in order to target high-value products with high selectivity?

- How do microenvironments influence the transport of reactants, products, electrons, and potential inhibitors to control reactivity and selectivity while avoiding catalyst degradation?

- What design elements allow integration of homogeneous and heterogeneous catalysts and catalyst supports with the rest of a solar fuels generation system?

Scientific Challenges and Research Opportunities

High selectivity and high activity in the light-driven production of energy-rich fuels present considerable challenges because of the complexity of chemically reducing CO_2 and N_2 as well as oxidizing H_2O. Advances require molecular-level understanding and control of the microenvironment around catalytic sites to direct reactions for key bond-making and bond-breaking steps. Research is needed to probe and control the interactions of catalysts with supports, light absorbers, electrolytes, and other components. It is also critical to understand how the microenvironment can mediate the transport of reactants, products, electrons, protons, and inhibitors to direct reaction pathways determining efficiency, selectivity, and degradation (**Figure 8**). The local environment can be influenced by a number of effects through a wide range of mechanisms. Significant research is needed to probe, understand, computationally model, and manipulate microenvironments for solar fuels. Major opportunities exist in several areas for solar fuels:

- Designing electrolytes to enable microenvironment control
- Controlling the second/outer coordination sphere
- Creating local structure through supports, scaffolds, nanostructures, and porous materials

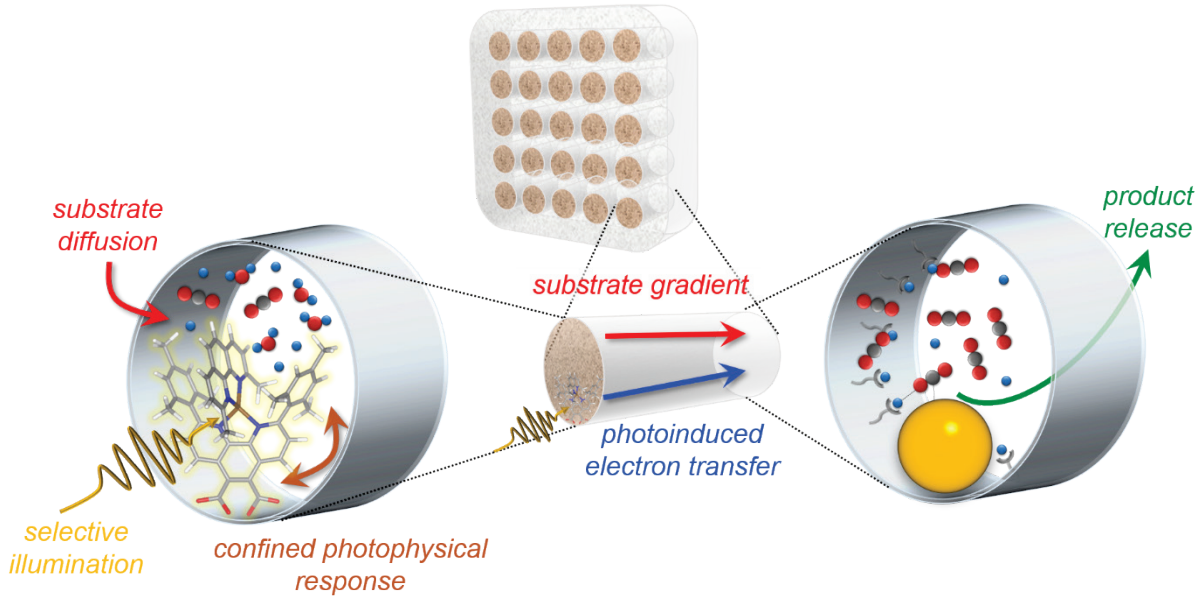


Figure 8. Generation of liquid solar fuels will require an integrated system, and success may require mimicking many features found in biological systems. For instance, pores can result in modified interfacial effects due to confinement, such as gradients and controlled dynamics (left). Physically separating the photoabsorber from the catalyst requires the delivery of electrons and substrate to the catalyst (metal, gold ball, right), which can take advantage of functional groups to control energetics, with the potential of benefits from the confinement effects of a small pore structure. *Source: Used courtesy of Karen Mulfort, Argonne National Laboratory.*

Designing electrolytes to enable microenvironment control

Solvents have a significant impact on catalyst performance, so one approach to controlling the microenvironment is achieving control of the solvent or electrolyte. For solar fuels, water is a reactant but can also be a solvent or a constituent of a solvent. There are still opportunities to probe and understand the effects of solvents on homogeneous and heterogeneous catalyst reactivity—not only effects in bulk complex mixtures, but also the properties and effects of electrolyte solutions near surfaces, at interfaces, in pores, and under confinement conditions. As an example of understanding bulk solvent effects, metal hydrides are a key intermediate in forming C-H bonds in the conversion of CO_2 to generate formate at both heterogeneous and homogeneous catalysts. The relative thermodynamic favorability for hydride transfer to CO_2 is highly dependent on the bulk solvent, and the relative stability of formate compared with organometallic hydride donors increases in hydrogen bond donating solvents, such as water[48, 50, 53-56]. It is important to understand and control solvent-dependent reactivity. **Figure 9** illustrates six different homogeneous transition metal hydride complexes in which CO_2 reduction is endergonic in acetonitrile but exergonic in water.

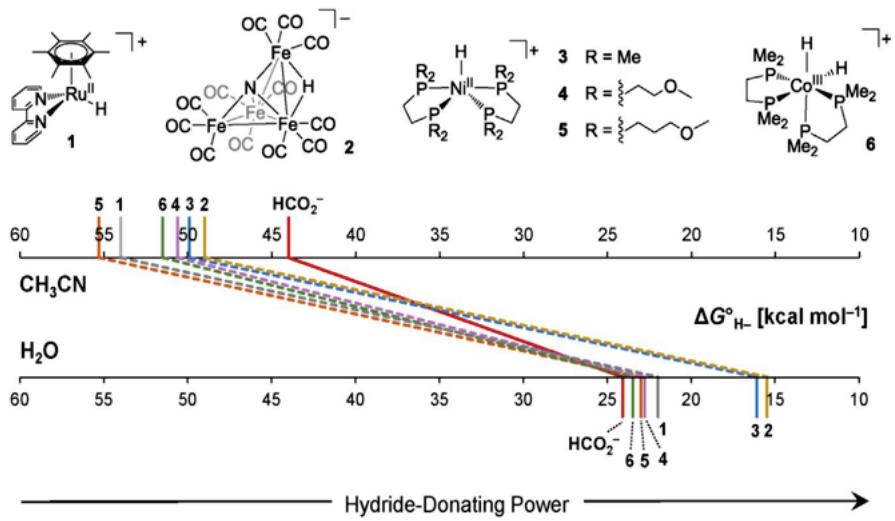


Figure 9. Solvent-dependent hydricity for select metal complexes and formate. *Source: Reproduced from Wiedner, E. S., and Linehan, J. C., 2018, Making a splash in homogeneous CO_2 hydrogenation: Elucidating the impact of solvent on catalytic mechanisms, Chem. Eur. 24(64), 16964–16971,. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim*[57].

Protons and pH deserve special attention in both bulk and local environments because the oxidation and reduction reactions in solar fuels generation involve multiple proton transfers coupled with electron transfers. Understanding, measuring, and controlling pH is critical because local pH as well as pH changes and gradients can have a significant influence on reactivity. It has been shown for electrocatalytic reduction that nano- or mesostructuring of Au, Ag, and Cu catalysts can increase the local pH at the catalyst surface by restricting mass transport, which serves to suppress hydrogen evolution, leading to a higher preference for CO_2RR over HER[58, 59]. In other work[60], high selectivity for electrocatalytic CO_2 reduction to ethylene at a copper catalyst was obtained by using very concentrated KOH as the electrolyte (**Sidebar 7** highlights Cu-catalyzed CO_2 reduction). Mechanistic studies suggest that kinetic branching between C_1 and C_2 product formation on copper can be determined by the proton donor environment around the catalyst. Related strategies have been used to generate ethanol from CO_2 at copper alloys. Understanding how to manage proton availability is key to coupling proton and electron transfer in homogeneous systems as well, where sluggish proton movement or sequential proton and electron transfers can lead to high-energy transition states or intermediates[61]. Dissecting and understanding the elementary steps and fundamental effects of local pH in microenvironments[51, 62] on reaction pathways requires additional research. Furthermore, the design of systems that enable precise control over the local proton concentration is critical for improving the selectivity of liquid solar fuels production. A particular challenge in aqueous systems is that the nature of the proton donor is often ill-defined, with many possible different water/hydronium clusters present that depend on a multitude of structural and chemical conditions. Through a combination of theory and experiment, a frontier opportunity exists for the rational design of precise proton donors and electrolyte media that target delivery of protons only along the desired sequences that lead to selective reduction pathways.

Sidebar 7: Understanding and tuning the selectivity of copper-based electrocatalysts for carbon dioxide conversion

Copper surfaces are unique in being able to catalyze the electrochemical conversion of CO_2 to a wide variety of multi-carbon fuels, including ethylene, ethanol, and acetate. However, production of these multi-carbon fuels is typically in competition with the production of hydrogen, CO, and methane. Initial observations of the potent electrocatalytic potential of copper were documented in the mid-1980s[32, 63, 64], but significant advances have been made in improving product selectivity for multi-carbon fuels over the past decade[18].

The strategies employed to increase selectivity include varying the pH and composition of the electrolyte, increasing the surface area and altering the surface structure of the catalyst through nano- and mesostructuring, chemically modifying the surface with molecular additives, and integrating the catalyst into a gas-diffusion electrode that increases the flux of CO_2 to the surface (**Figure S10**). These studies have allowed for a steady improvement in product selectivity for multi-carbon products from 34%[65] to greater than 70%[66]. Depending on the catalyst, these selectivity improvements can result from an increase in the rate of formation of multi-carbon products; an inhibition in the rate of formation of methane, hydrogen, and CO; or both.

Copper electrocatalysts generate higher-order products by first reducing CO_2 to CO and then reducing CO further to methane, ethylene, and other C_2^+ products. Mechanistic insights indicate that (1) C_2^+ product formation is uniquely promoted by cations in the electrolyte[67, 68] and (2) methane and hydrogen production proceed via a common adsorbed H intermediate that is in competition with adsorbed CO[69]. These mechanistic insights suggest that catalyst active sites with high CO affinity, and catalyst microenvironments with elevated local pH, elevated CO concentrations, and proximal cation promoters will all contribute to enhanced selectivity for multi-carbon fuel formation.

Unfortunately, despite the long-standing observation that multi-carbon product formation is favored in alkaline environments, hydroxide ions react with CO_2 to form carbonate, eroding the carbon balance of liquid fuel production[62]. Additional mechanistic understanding and new strategies for tuning copper active-site structure and microenvironment will be essential for the rational design of improved electrocatalysts that are tailored for selective liquid fuel production.

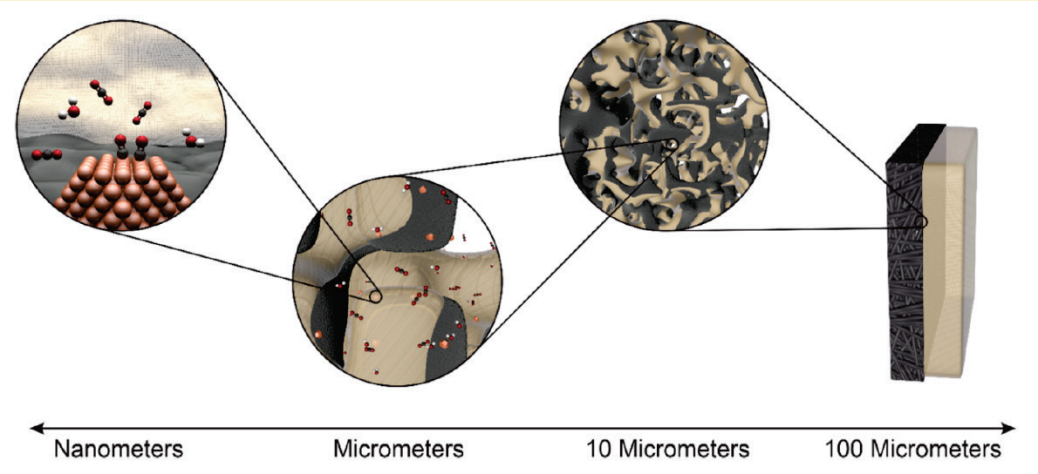


Figure S10. Copper-based CO_2 reduction catalysis is a multiscale phenomenon that requires understanding and control of catalyst surface structure, local environment, mesoscale transport, and device integration. *Source: Reprinted from Higgins, D., et al., Gas-diffusion electrodes for carbon dioxide reduction: A new paradigm, ACS Energy Lett. 4, 317–324, 2019. Copyright 2019 American Chemical Society*[70].

With the addition of ions to create an electrolyte—and in the presence of an applied potential—the solution environment becomes extremely complex, particularly in the double-layer region, which continues to present challenges to study[71]. The chemistry and physics of solvents and electrolytes are rich at both flat and confined electrode interfaces. There are significant opportunities in considering the design, study, and control of the electrolyte; determining how it can influence catalysis; and understanding limitations in using solvent effects in local environments. Solvation structure and dynamics, along with ion activity (including H^+/OH^-), can be markedly different at the catalyst/catalyst support/electrode interface. The chemistry and physics of these interfaces are poorly understood and not well controlled. Many potential effects to a microenvironment can be imparted by solvents near surfaces or interfaces. Further understanding in this area could be enhanced by exploring a number of effects, including, for example, local pH and gradients; gradients of ions or solvent molecules; localized structuring of solvent molecules, including hydrophobic effects or extensive hydrogen bonding; very strong local electric fields; and significant non-equilibrium effects. The application of light or an applied potential could modulate these types of effects; but in addition, it could likely increase their complexity. Moreover, altering ion concentration to break or alter the water superstructure on a moistened surface can greatly change solvation structure, dynamics, and the electrode interface, and thus the reaction selectivity and activity. This highly variable interface, even during one catalytic turnover, creates challenges in understanding and controlling catalyst reactivity; but it also creates opportunities for control if it is correctly understood. A key challenge facing the selective generation of liquid solar fuels is learning to measure, probe, and control solvent structure, dynamics, and the ion-solvent interface, on non-flat surfaces. It is critical to understand the properties of the solvent (e.g., proton activity, polarity, dielectric, polarizability, local structure/solvation, viscosity) at an interface or in confined spaces. Challenges still remain to define—let alone measure and eventually model—the local pH or proton activity in complex mixtures and microenvironments. This understanding will help us to control elementary charge-transfer reaction steps of electrochemical reactions at the electrode interface. The use of model surfaces, advances in interfacial characterization methodology, and the development of computational methodologies may be required for advances in this area (see, for example, Appendix A).

Controlling the second/outer coordination sphere

The second and outer coordination spheres can be critical to catalysis by impacting selectivity through (but not limited to) electrostatics, binding of reactants/products/intermediates, coupling of proton and electron transfers, and cooperativity. Electrostatic effects can selectively stabilize intermediates, direct competitive reaction pathways, or tune redox potentials. Large electrostatic effects have been invoked in enzymatic active sites, and can in principle be generated in synthetic catalysts by structuring functional groups or other metal ions around the active site, and possibly further refined by structuring the solvent to modulate the local dielectric constant. These effects have been shown in bioinspired homogeneous catalysts[72] with covalently attached microenvironments, and with both homogeneous and heterogeneous systems with added cations—resulting in effects varying among destabilizing hydrogen bonding, stabilizing intermediates, influencing product distribution, and increasing the local CO_2 concentration by field or pH effects[71, 73-77]. These electrostatic effects are often not fully understood, and there is significant promise in being able to control them based on the configuration of atoms surrounding the active site. Fully exploiting electrostatic effects requires materials design as well as experimental and modeling tools to fully understand and implement these effects. Note that these effects are also present at electrode interfaces, where the electrochemical potential gradient can be impacted by solvent or electrolyte selection.

Opportunities also exist to design microenvironments around catalysts that can direct the binding of reactants, release of products, and stabilization of intermediates. Targeted interactions in the microenvironment can selectively lower the relative energetics or barriers of competitive pathways to steer selectivity toward desired products.

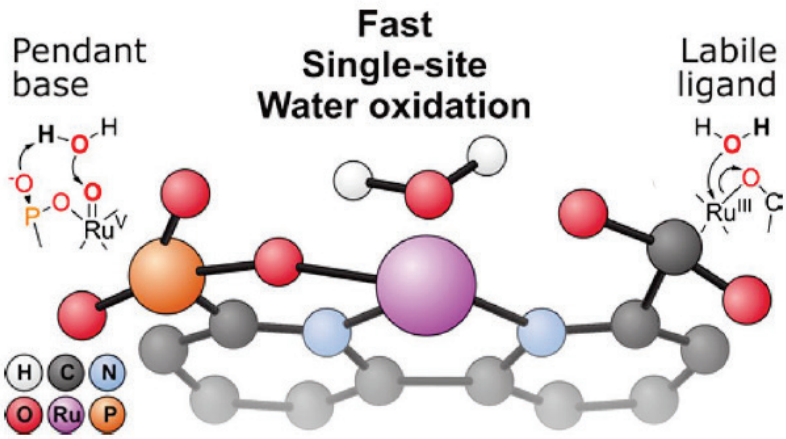


Figure 10. In a synthetic ruthenium catalyst for water oxidation, phosphonate groups were strategically positioned as pendant bases on a tetradentate ligand to put them in close proximity to the active site (left), with the immediate proton delivery resulting in a decrease in ΔG^{++} of more than 10 kcal/mol over the system without the pendant phosphonate (right). The consequent O_2 generation had a turnover frequency >100 s^{-1} at pH 1. Overcoming the entropic barrier resulted in the fastest catalyst reported to date under these conditions, on par with the oxygen evolving complex in Photosystem II and well above any heterogeneous system on a per-atom basis. *Source: Reprinted with permission from Shaffer, D. W., et al., Lability and basicity of bipyridine-carboxylate-phosphonate ligand accelerate single-site water oxidation by ruthenium-based molecular catalysts, J. Am. Chem. Soc. 139, 15347–15355, 2017. Copyright 2017 American Chemical Society*[78].

The use of fixed-proton relays in the secondary coordination sphere has become a well-accepted practice in homogeneous and bioinspired catalysts[79-81]. The complexity of these interactions is illustrated in a case for CO_2 hydrogenation to formate, in which a pendant amine ligand that is not basic enough to deprotonate a ruthenium homogeneous catalyst (**Figure 10**) still modulates the catalytic turnover frequency by one to two orders of magnitude[78]. Basic (or acidic) catalyst supports have been used extensively for heterogeneous catalysts; however, heterogeneous systems become even more complex because our current understanding and control is even less mature. Cooperative interactions can stabilize intermediates and disrupt scaling relationships that would otherwise exist for single-site catalysts, as has been shown for homogeneous catalytic H_2 production[82]. Extending these concepts beyond simple 2e- processes remains a significant challenge.

Direct electrocatalytic or photocatalytic reduction of nitrogen (N_2) to ammonia or other nitrogen-containing products remains a major challenge. There are a number of examples in the literature using hydrogen derived from electrocatalytic water splitting to form ammonia using Haber-Bosch catalysis. There is also a growing literature using lithium-mediated nitrogen reduction, where, for example, lithium metal is used stoichiometrically to react with nitrogen to form lithium nitride (Li_3N), which can be protonated to ammonia while the lithium ions are reduced back to lithium metal electrochemically[83, 84]. Unlike the CO_2RR, however, there are no viable electrochemical pathways for direct reduction of N_2 (N_2RR). As called out in recent reports, research in this area has been hampered by potential artifacts whereby small amounts of observed ammonia production could stem from contamination, ligand degradation, or other processes[41]. Proper controls, standards, and experimental methods, including the development of protocols such as ^{15}N-labeling experiments, therefore need to be broadly employed. A 2016 BES roundtable report providing an excellent summary of the status and challenges for homogeneous, heterogeneous, and enzyme catalysis concludes that new science is needed to discover and develop catalysts for sustainable ammonia synthesis[85]. **Sidebar 8** provides a brief overview of nitrogenase in biological systems for N_2 reduction, which could provide inspiration for new anthropogenic catalyst systems.

Sidebar 8: Inspiration from nitrogenase for N_2 activation

In nature, nitrogenase enzymes convert atmospheric nitrogen to ammonia. While the overall process is actually quite energy inefficient—e.g., it uses 16 adenosine triphosphate per reduced N_2 molecule, corresponding to an energy expense of almost 5 eV per turnover of one N_2 molecule (~500 kJ/mole of N_2)[85]—these biological processes can provide considerable insight into possible synthetic approaches to address the grand challenge of activating and reducing the N≡N triple bond in N_2. Many aspects of the mechanism for nitrogenase have been uncovered and have been codified in the Lowe and Thornley kinetic model. A key feature of the mechanism is the accumulation of multiple electrons and protons at the nitrogenase catalyst center comprising Fe, Mo and S (FeMo-co) as a requirement for N_2 binding. Bridging metal hydrides have been directly observed, and these hydrides can reductively eliminate H_2. This H_2 release is not simply a competitive process; recent computational and experimental work has confirmed that the reductive elimination of H_2 provides the energy to initiate the binding and first 2-electron reduction of N_2[86]. Quantum chemical calculations on enzyme models coupled with experimental work (**Figure S11**) show that the generation of H_2 bound from the FeMo site and its displacement by N_2 provides a mechanism to couple exothermic hydrogen formation with endothermic N_2 triple-bond activation, thereby providing the thermodynamic driving force to initiate nitrogen reduction. Whether these steps can be replicated in anthropogenic systems remains to be seen.

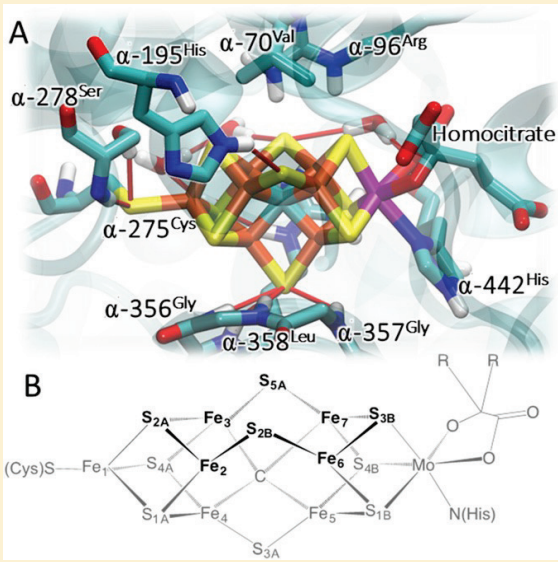


Figure S11. Structure of the FeMo-co binding pocket in nitrogenase (obtained from molecular dynamic simulations (A) and schematic representation of FeMo-co (standard atom numbering (B). For simplicity, only the polar H atoms are shown. Atom color coding: rust, Fe; yellow, S; cyan, C; purple, Mo; red, O; blue, N; light gray, H. Hydrogen bonds are shown as thin red sticks. *Source: Taken from S. Raugei, et al., Critical computation analysis illuminates the reductive-elimination mechanism that activates nitrogenase for N_2 reduction, Proc. Nat. Acad. Sci. 115, E10521, 2019*[86].

Designing features that work cooperatively or synergistically with one another can result in significant rate enhancement, reduced overpotential, or overall increased efficiency. Theoretical studies on single heterogeneous electrode surfaces suggest that activation of CO_2 is limiting because of the instability of the resulting carboxylate species, but it could potentially be stabilized by additional groups. Cooperative interactions, such as hydrogen-bond donors or acceptors, may be particularly useful in CO_2 and N_2 reduction because they are likely to interact with many of the proposed catalytic intermediates. For example, Lewis acids are known to influence CO_2RR catalysis in homogeneous and heterogeneous systems (**Figure 11**). Recently, Lewis acid adducts of CO_2 were shown to enhance proton-induced C-O bond cleavage in a homogeneous molybdenum complex[87]. Although several studies describe the

incorporation of Lewis acids into ligand scaffolds to activate CO_2, much room remains to explore and understand the potential for Lewis acids or bases to create cooperativity. Despite the Lewis basicity of water, note that there are Lewis acids that remain active in water for other chemical reactions[88].

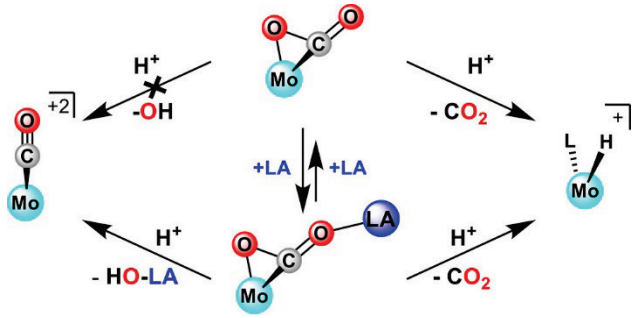


Figure 11. A Mo(0) CO_2 complex forms adducts with Lewis acids (LAs). C-O cleavage upon proton addition is achievable in these LA adducts, whereas protons displace the CO_2 in the absence of LAs. *Source: Reprinted with permission from J. A. Buss, et al., Lewis acid enhancement of proton induced CO_2 cleavage: Bond weakening and residence time effects, J. Am. Chem. Soc. 140(32), 10121, 2018. Copyright 2018 American Chemical Society*[87].

Designing and building multisite systems to create new cooperative catalysts presents an important opportunity for solar fuels[42]. Model studies that can help overcome synthetic, experimental, and computational challenges are critical to effectively and rationally developing strategies for reactant/product binding to contribute to controlling catalytic pathways. It is important to develop computational tools with higher precision to enable the prediction of highly coupled systems down to the level of 1 pK_a unit or 2–4 kcal/mol, for example. In addition, experimental techniques are needed that can resolve rapid complex processes, such as intramolecular proton transfer, with high resolution.

An additional route to control catalysis is introducing molecules onto a catalytic surface that can assist in transporting protons or modulating electrostatics. Building on earlier work[89, 90], it was recently shown[48, 52] for Cu-catalyzed CO_2 reduction that cationic organic additives can increase the selectivity for >2e-reduced products, including those from carbon-carbon bond-forming reactions (**Sidebar 9**). Understanding the spatial arrangement of solvent molecules, co-adsorbates, and reactants on catalytic surfaces could provide access to new approaches for selectivity using molecular/material hybrids. It is also important to sort out the detailed mechanisms (e.g., blocking sites, inhibiting reactions, activating reactions) and characterize these systems under solar fuels operating conditions.

Sidebar 9: Enhanced selectivity of copper-catalyzed reduction of CO_2 achieved with additives

Small-molecule additives have long been known to influence the reactivity and selectivity of heterogeneous catalysts through various mechanisms, including inhibiting substrate diffusion, stabilizing surface-bound intermediates, and mediating charge transfer. The abundant structural diversity of molecular additives presents numerous opportunities to tune and optimize the effects of these small molecules on selectivity and durability. In the context of CO_2 conversion, copper electrodes are effective catalysts; but untreated nanocrystalline copper electrodes produce a mixture of hydrocarbon products. The addition of molecular additives has presented a highly tunable approach for enhancing selectivity for $C_{\geq 2}$ hydrocarbons.

Building on previous work[89, 90], adding N-substituted arylpyridinium salts to polycrystalline copper electrodes impacts the selectivity of C–C coupled products by effectively suppressing hydrogen evolution reaction and CH_4 production—with ratios of $C_{\geq 2}$ products to CH_4 exceeding 800 under optimized conditions[52] (**Figure S12**). The additives serve as precursors for a film that deposits on the copper electrode when polarized. In the case of *N*-tolylpyridinium chloride, characterization of the film that coats the electrode surface reveals it is the reductive

coupling product of the N-substituted pyridinium (N-tolyl tetrahydrobipyridine), which precipitates onto the copper surface. Studies probing the mechanism by which the adhered N-aryl-substituted tetrahydro-bipyridines influence selectivity indicate that the nitro atom of the pyridine ring enhances the binding of a top-bound CO, which leads to effective C–C coupling[52]. Enhancing the number of these stabilizing nitrogen atoms leads to CO_2-to-ethylene conversion with a 72% Faradaic efficiency.

Additives may not influence selectivity through a single mechanism. For example, *N*,*N*′-ethylene-phenanthrolinium dibromide promotes restructuring of the copper surface into cube-like nanostructures, which are known to have product ratios distinct from those of polycrystalline copper. In parallel, the reductive coupling product of this additive stabilizes the nanostructures formed and likely influences binding of key CO intermediates through a mechanism similar to N-substituted arylpyridinium salts[66]. To fully exploit the beneficial effects of molecular additives to optimize product selectivity and enhance catalyst durability, their mechanisms of action must be fully understood.

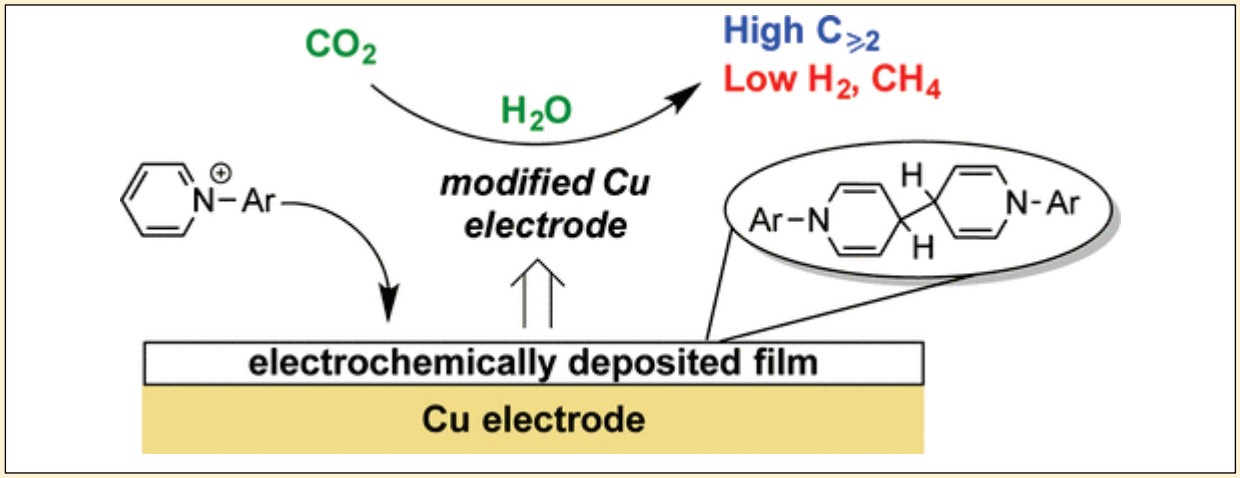


Figure S12. Electroreduction of N-substituted arylpyridinium salts generates a film of N-aryl-substituted tetrahydro-bipyridine on the copper electrode, which substantially promotes $C_{\geq 2}$ product generation over CH_4 and H_2. *Source: Reprinted from Han, Z., et al., [CO_2 reduction selective for C≥2 products on polycrystalline copper with N-substituted pyridinium additives](), ACS Cent. Sci. 3, 853–859, 2017. Copyright 2017 American Chemical Society[52].*

Creating local structure through supports, scaffolds, nanostructures, and porous materials

For homogeneous catalysis, essential elements of the microenvironment can be distilled down to carefully controlling the extended environment through synthetic design, in concert with changing the solvent system. Further development of microenvironments for both homogeneous and heterogeneous catalysts is needed to realize the desired increases in performance and stability. Zeolites are a quintessential example of using manmade hierarchical assembly to create microenvironments in porous materials that can dramatically affect catalytic selectivity[91, 92]. Several reports have explored metal-organic frameworks (MOFs)[93] for electrochemical reduction of CO_2, including nano-sized MOFs as electrocatalysts[94-97]. Although the 3D environment offers more control over the catalytic reaction, characterizing solvent and electrolyte interfaces in a 3D environment is significantly more complex and will likely require the development of additional methods. An example could be well-defined 3D catalytic sites or cavities within which organometallic or metalloclusters can be placed. Flat surfaces are currently being studied and still offer rich opportunities for understanding interfacial effects at electrified surfaces. But 3D sites add a complexity of structure that introduces additional control over the microenvironment. Although significant advances have been made in 3D materials, in general, they suffer from challenges in one or more areas, including stability, scale-up, the introduction of asymmetry around the active site, transport of

reactants/products, and characterization. To continue to develop materials for liquid solar fuels, catalysts in 3D scaffolds are needed that are stable, can be characterized to an atomic level, and allow the introduction of diverse functional groups[98]. Understanding how systems like these can be developed into catalysts, photocatalysts, or electrocatalysts (e.g., through tuning of metal centers and framework ligands) could impact CO_2RR in solar fuels and accrue benefits from both heterogeneous and homogeneous catalysts.

There is ample opportunity to create cooperativity at the convergence of homogeneous and heterogeneous catalysis through the "heterogenization" of homogeneous catalysts in mesoporous structures—wherein the synergy of the microenvironment and the tunable properties of the molecular catalysts, in combination with activation of the substrate in the microenvironment, could provide enhanced performance, durability, and selectivity. Attempts have been made to attach molecular electrocatalysts or metal clusters onto electrode surfaces or into mesoporous structures[99-102], but a decrease in rate or selectivity often occurs upon immobilization. For continued advances in this area, new synthetic methods and/or catalysts are essential whose functions are preserved or ideally enhanced upon binding. Supports can offer acid/base properties, specific binding (e.g., through heteroatoms or Lewis basic/acidic sites), and stereoelectronic effects (through structure and composition). Better characterization of catalysts on surfaces, including in situ methods, are needed.

Creating nanostructured and/or mesoporous features in catalysts and catalyst supports can have a strong influence on selectivity through a wide range of physical and chemical effects. These concepts have been applied to copper catalysts for electrochemical CO_2RR[52]. The understanding of the effects of confinement within zeolite-catalyzed reactions conducted in the gas phase is relatively good, theoretically and experimentally. However, the understanding of confined processes for solution-phase reactions is still at an early stage. Probing and controlling the effects of nanostructuring, confinement[103], and surface interactions within pores to create microenvironments represent a significant challenge in solar fuels and related electrochemistry. A recent example of a confinement effect[104] shows how confining CO at the buried interface between a Pt electrode and a semi-permeable SiO_2 layer significantly alters the peak potential associated with CO oxidation (**Figure 12**). The shift in CO oxidation peak potential to more negative values was interpreted to reflect the weakening of CO binding in the presence of the overlayer. For increasing the understanding of confinement effects on electrocatalysis, general challenges include (1) deconvoluting different influences of the confined environment on reactivity (steric/physical, electronic, chemical) and (2) advancing both state-of-the-art atomistic modeling and in situ characterization tools that will enable doing so—while establishing the design rules or structure-property-performance relationships that can guide the design and optimization of active sites in confined environments.

Additional research is also needed to control transport phenomena of all reactants and products—elements that are a critical aspect in addressing the rational design of microporous or 3D structured materials for liquid solar fuels. If properly accounted for, transport of reactants and products, in general, can be an important control knob for tuning selectivity. Diffusion is often very slow compared with many other phenomena occurring in (photo)electrochemical devices and can be even slower within microporous environments. If transport is not controlled or directed, then it can very easily limit the overall reaction rate, thus resulting in significant overpotential requirements, lack of selectivity, and/or large undesirable pH gradients that adversely affect reactivity and the stability of the catalyst/material. Developing design rules to account for transport can help inform the selection of maximum/optimal pore lengths and other features of the catalyst and support.

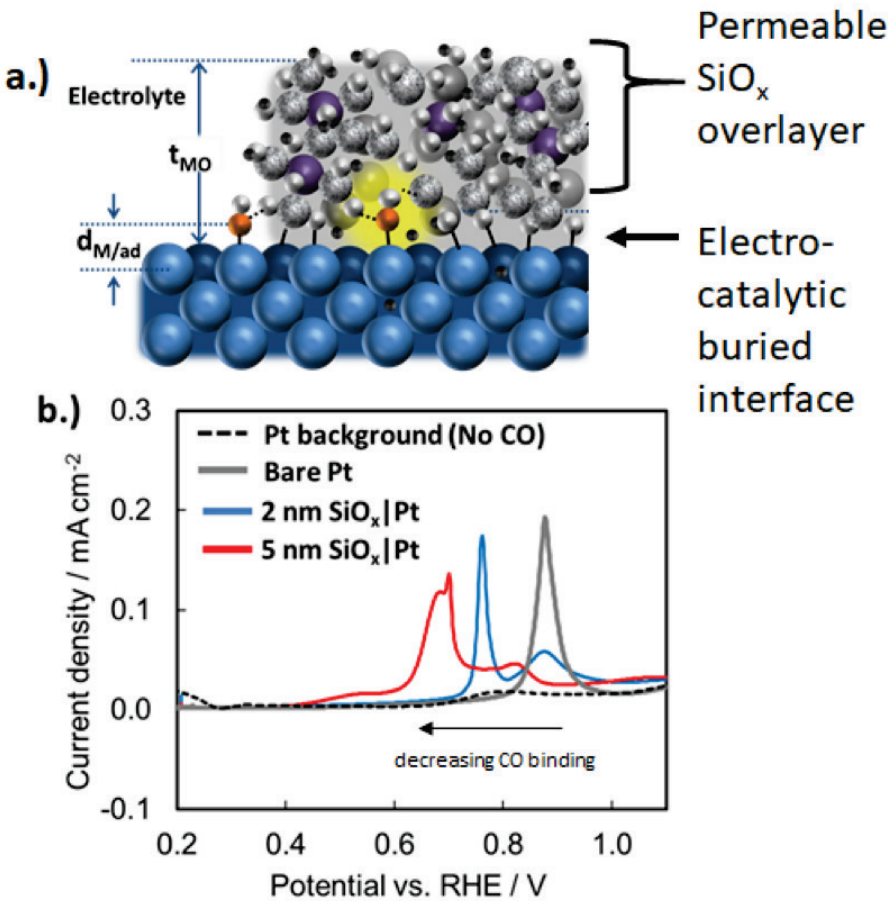


Figure 12. (a) Schematic side view of reactants at the buried interface between a permeable overlayer and substrate. (b) CO-stripping voltammetry of bare platinum and silicon-oxide-encapsulated platinum films. *Source: Robinson, J. E., et al., Silicon oxide-encapsulated platinum thin films as highly active electrocatalysts for carbon monoxide and methanol oxidation, ACS Catal. 8, 11423–11434, 2018. Copyright 2018 American Chemical Society*[104].

For advanced electrochemical systems such as fuel cells and water electrolyzers, the catalyst, support, ionomer, and membrane in membrane electrode assemblies (MEAs) can create microenvironments that could alter intermediate binding energies, surface coverages, and adsorbate interactions among other contributions. These interactions vary for each pair of catalyst/support materials used, including both hard and soft supports, the specific chemical transformation of interest, and the phase of the reactants/products. Such a correlation between the activity and the structure/composition of catalyst/supports has not been rigorously evaluated for the production of liquid solar fuels. There may be important prospects for incorporating catalyst supports—including porous materials—into solar fuels systems, which could create new microenvironments. The production of liquid solar fuels could benefit from better understanding of catalyst/support interactions, especially the coupling of light-absorbing semiconductors and selective "dark" electrocatalysts. A significant opportunity exists for hybrid systems comprising catalysts, catalyst supports, and polymeric ionomers in solar fuels systems, even creating MEAs for solar fuels[23]. The interaction of catalysts, ionomers, membranes, catalyst supports, and gas-diffusion electrodes could create new microenvironments. The requirements for a solar fuels system could be more stringent than for electrolyzers or fuels cells, given the need for at least one electrode in a solar fuels system to be exposed to solar light and the need for energy/charge transfer. At the same time, there may be beneficial effects for solar fuels relative to the high current densities in electrolyzers. Understanding the properties of these

complex systems and their interfaces remains a significant challenge. Significant opportunities exist to extend many concepts for creating and controlling microenvironments for homogeneous and heterogeneous catalysts to solar fuel generation. Of course, ensuring the stability and durability of supports, scaffolds, and membranes is also critical.

Potential Impacts

Selectivity, durability, efficiency, and specificity are all needed elements in catalysts to enable the practical development of liquid solar fuels. Controlling the microenvironment offers the potential for revolutionary impacts in each of these areas. Understanding the fundamental science of how to control each of these aspects will enable the application of the resulting principles to a variety of situations, depending on the chemistry and the need. This understanding requires advances in synthesis, characterization, and modeling, as described above and in Appendix A. But appropriate advances in each of these areas could launch unprecedented advances in the generation of liquid solar fuels. Furthermore, the microenvironment, in many cases, involves a scaffold of some kind. Although this scaffold creates the microenvironment, its presence also provides the ability to integrate with the rest of the system. Therefore, with atomically developed design, the resulting catalyst can address the needs of the catalytic reaction and could also facilitate the overall function of a solar fuels generation system.

PRO 3: Bridge the time and length scales of light excitation and chemical transformations

Summary

A signature challenge of liquid solar fuels production is to accrue distinct benefits from the interoperation of light-induced processes and chemical catalysis. Charge carriers excited by sunlight exist at short time scales in a non-equilibrated (i.e., non-thermalized or non-Boltzmann) energy distribution and offer the possibility of accessing chemical transformation pathways that would be inaccessible for thermalized carrier distributions generated via applied potentials in dark electrocatalysis. However, approaches for designing solar fuel generation processes generally decouple the processes of light absorption and chemical transformations—potentially missing distinct prospects for solar fuels to capitalize on light-driven processes to enhance overall catalytic efficiency, selectivity, or even system performance. While many early experiments in solar fuels used semiconductors that served as both the photoabsorber and the catalyst, much of solar fuels research since then has moved to the independent development of solar light absorbers and fuel-forming catalysts that are subsequently integrated[7, 105-107]. Therefore, the catalytic activity of a solar fuel catalyst typically mimics that of a dark electrocatalyst under similar conditions (e.g., in electrochemical parlance, similar voltage/driving force and/or current density). These catalysts therefore likely operate via the same reaction mechanisms, whether under irradiation or driven by electrochemistry in the dark. A major opportunity exists to realize systems in which solar radiation specifically influences the reactivity (i.e., activity, selectivity) for fuel-forming catalysis via temporal changes in the active site or its microenvironment. A significant research challenge is to understand specifically how to induce and exploit the coupling of photoexcitation and catalytic transformations to create new mechanisms that direct light-matter interactions for increased selectivity or efficiency that exceeds the performance limits imposed by conventional electrochemical reactions.

Coupling photoexcitation with chemical reactions for solar fuels requires new scientific understanding and approaches to enable access to alternate chemical pathways that can confer enhanced catalytic reactivity. A significant disparity exists in the time scales of photon absorption, carrier relaxation, and chemical events. Photoexcitation of solid-state and molecular absorbers occurs on the femtosecond time scale (e.g., **Figure 2)**. Photogenerated carrier relaxation can occur in several stages via multiple decay channels[108, 109]. For solid-state systems, excited carriers generated by photoexcitation typically establish quasi-Fermi levels through direct or disorder-assisted phonon emission on the time scale of 1–100 picoseconds. Molecular systems typically relax to the lowest thermalized excited state within hundreds of picoseconds, as well. By contrast, redox reactions involving proton-coupled electron transfer processes and other catalytic reactions typically occur on a much longer time scale, e.g., microseconds or longer[110, 111]. It is particularly important to note that the complex chemistries needed to generate liquid fuels from CO_2, N_2, and H_2O require reactions that involve multiple electron and proton transfer processes that necessitate the absorption of more than one solar photon to generate products.

Photoelectrochemical and photocatalytic reactions for solar fuels production also generally occur long after carriers have thermalized to the band edge in solid-state systems (or to the lowest unoccupied molecular orbital, LUMO, states in molecular systems). Research is needed to bridge these length and time scales through exploration of molecular assemblies and materials that can either (1) access fundamentally different chemical pathways for optically excited hot carriers than for thermalized carriers, (2) drive chemical transformations on much shorter time scales, or (3) induce longer-lived effects from excitation to effectively "park" excitation energy into photoresponsive or metastable states. Understanding the fundamental photophysical and photochemical properties—including energy transfer and relaxation/recombination processes that set the excited-state lifetime and limit conversion efficiency—is critical for controlling the energy and chemical pathways. The development of a mechanistic framework for these photoelectrochemical processes and the design of novel materials and

paradigms both depend on understanding the time and length scales of photocarrier generation, relaxation, transport, and coupling with chemical processes. Modern materials discovery methods, advanced theory, synthesis, and characterization, including operando analyses (e.g., Appendix A), can now enable complex design schemes with multiple objectives.

Key Scientific Questions

- How can the direct interaction of solar excitation with chemical change be enabled and exploited to achieve high selectivity and high efficiency of solar-to-chemical energy conversion?

- How can charge transfers from the locus of optical excitation be tracked and directed to a catalytically active site?

- How can electronic or atomic structural changes upon photoexcitation be made to persist on the order of catalytic reaction times to create non-equilibrium conditions within the catalyst or its locale as a result of solar radiation? What fundamental physics and chemistry in molecular systems, surfaces (e.g., hot-carrier injection, plasmon-mediated resonant energy transfer, transient local heating), and in bulk materials needs to be uncovered to understand, create, and control mechanisms to couple photoexcitation, carrier transport, and selective catalysis?

- How can electronic processes, such as interfacial plasmon excitation or atomic structural changes, at interfaces occurring upon photoexcitation be used to control multi-electron and multi-atom (electro)chemical transformations essential to solar fuels production?

- How can photo-responsive materials and processes be developed and incorporated into solar fuel systems to couple photo-excitation and catalysis?

- What new insight for coupling light absorption to catalytic chemical change can be provided by new theory and advanced spectroscopy, including operando experiments?

Scientific Challenges and Research Opportunities

The prospect of capitalizing on the direct coupling of light-driven phenomena and chemical processes to enhance overall system performance centers around understanding and controlling electronic or atomic structural changes from photoexcitation. Photoexcitation would need to persist on the order of catalytic reaction times or to create non-equilibrium conditions within a catalyst or its local environment to alter its reactivity. Gaining an advantage from light-driven chemistry in solar fuels will require the discovery of new mechanisms for strong electronic coupling of photoabsorbers, electron donors/acceptors, and catalysts, including the co-design of optoelectronic and chemical functionalities. Exploiting light-matter interactions could open up new mechanisms to enable selectivity or efficiency that outperforms conventional electrochemical reactions, or to use more of the solar spectrum. Fundamental research can realize advantages unique to light-driven fuels generation that could arise from strong electronic coupling, light-induced structural changes, or other phenomena. Research in this area can capitalize on significant advances in designing and controlling the optoelectronic properties of a wide range of molecular systems, hierarchical assemblies, solid-state materials, modified surfaces, nanoscale systems, and low-dimensional materials. Key research opportunities include the ability to accomplish the following:

- Exploit light-matter interactions to effect catalytic transformations
- Increase relaxation times beyond bulk materials to couple multiple-photon photochemistry to catalysis
- Develop light-stimuli-responsive molecules and materials for catalysis
- Create metastable surfaces and systems.

Exploit light-matter interactions to effect catalytic transformations

Light-matter interactions provide an opportunity to influence catalytic outcomes by coupling photochemical and (electro)chemical events. The links between photoexcitation and (electro)chemical activity are important for controlling selectivity and reactivity, and an enhanced understanding of the physical and chemical characteristics is critically needed.

Surface plasmons are known to influence photocatalytic outcomes. Specifically, surface plasmons provide a pathway to absorb and confine light in metallic nanostructures (**Figure 13***)* leading to an orders-of-magnitude increase of local electromagnetic fields[112-114], which has been shown in several cases to alter catalytic activity and selectivity for photoelectrochemical reactions[115]. The energetic carriers derived from the decay of surface plasmons can drive chemical reactions for nanoscale photochemical energy conversion. "Semiconductor-free" water-splitting structures using only plasmonic hot carriers have been recently demonstrated[116].

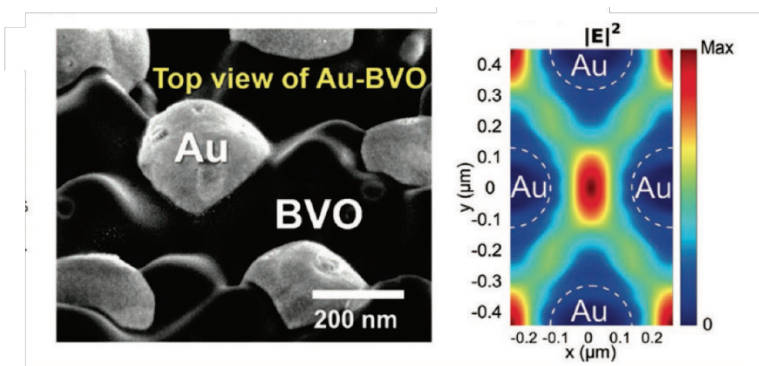


Figure 13. Top view scanning electron micrograph plasmon generated from ordered gold nanosphere patterned array embedded in a Mo:$BiVO_4$ photoanode (left) and corresponding simulated $|E|^2$ field distribution at 500 nm (right). *Source: Reproduced from Mascaretti, L. et al., [Plasmon-enhanced photoelectrochemical water splitting for efficient renewable energy storage](), Adv. Mater. 31, 1805513, 2019. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim*[114].

Plasmonic structures have been reported for photoelectrochemical CO_2 reduction[117, 118] demonstrating enhanced chemical selectivity for product generation relative to dark electrocatalysis under similar conditions (see **Sidebar 10**). Catalytic ammonia synthesis has also been reported[119]. These and other reports highlight the potential for novel plasmonic hot-carrier materials and architectures to drive photoelectrochemical reactions for solar fuel production[120]. However, the complexity of the underlying processes has limited the ability to gain a detailed understanding of the mechanisms underpinning these reactions, and this knowledge gap makes it difficult to articulate design considerations.

Research is needed to understand the fundamental physics and chemistry of plasmonic processes and systems[121]. Current experimental and theoretical evidence suggests several mechanisms by which charge transfer and chemical reactions can be coupled to surface plasmons. Yet new approaches are still needed to sort out these mechanisms. To explain the change in rates in selectivity of plasmon-driven fuel production, proposed mechanisms invoke hot electrons/holes, transient ionic states induced by the plasmons, transient bond weakening by coupling of the strong local electrical and magnetic fields associated with the plasmon, and transient phase changes in the catalysts. Plasmonic systems also convert sunlight into heat. The role of local heating induced by the plasmon resonances has not been fully determined in these types of systems, e.g., whether and how local heating effects could be influencing the conversion efficiency and selectivity. To advance applications of surface plasmons for liquid solar fuels, research is critical to enhance the fundamental understanding of the roles of excited-carrier injection, the

mechanisms of molecular excitation or substrate activation by an interfacial plasmon, and the influence of thermal processes.

Sidebar 10: Plasmonic-promoted selectivity in catalysis

Conventional solar fuels generators use light absorption in semiconductor photoelectrodes to generate a photovoltage used to drive redox reactions, such as water oxidation and hydrogen evolution. By contrast, harvesting non-equilibrium hot carriers from plasmonic-metal nanostructures offers unique opportunities for driving photochemical reactions at the nanoscale. Hot-electron photogeneration processes—and, more recently, hot-hole photogeneration processes as well—have been shown to drive photoelectrochemical water splitting and CO_2 conversion, sparking the nascent field of plasmonic photocatalysis.

Plasmons are hybridized light-matter excitations that couple collective oscillations of the free-electron gas in a conductor with the generated electromagnetic field. Plasmons give rise to high local electric fields that greatly enhance the sensitivity of chemical spectroscopies, such as Raman and infrared spectroscopy, and can be used to sensitively detect changes in the local refractive index near metallic interfaces.

At the Au/*n*-type TiO_2 interface depicted in **Figure S13a**, hot electrons generated in Au are injected into the conduction band of TiO_2. In **Figure S13b**, holes generated via interband transitions in Au are sufficiently hot to inject above the 1.1 eV interfacial Schottky barrier at the Au/*p*-GaN heterojunction. The hot-hole injection balances hot-electron transport, which is used to chemically reduce adsorbed species at the Au/electrolyte interface in the photoelectrochemical device (far right of **Figure S13**). In photoelectrochemical CO_2 reduction with the Au/*p*-GaN photocathodes, improved selectivity for CO production is observed with respect to H_2 evolution in aqueous electrolytes, as compared with dark electrocatalysis in a similar environment. Future challenges for plasmonic photocatalysis include the use of new theoretical methods to predict how to improve chemical selectivity for excited-state processes and to design hot-carrier photoelectrode motifs that enable improved energy efficiency.

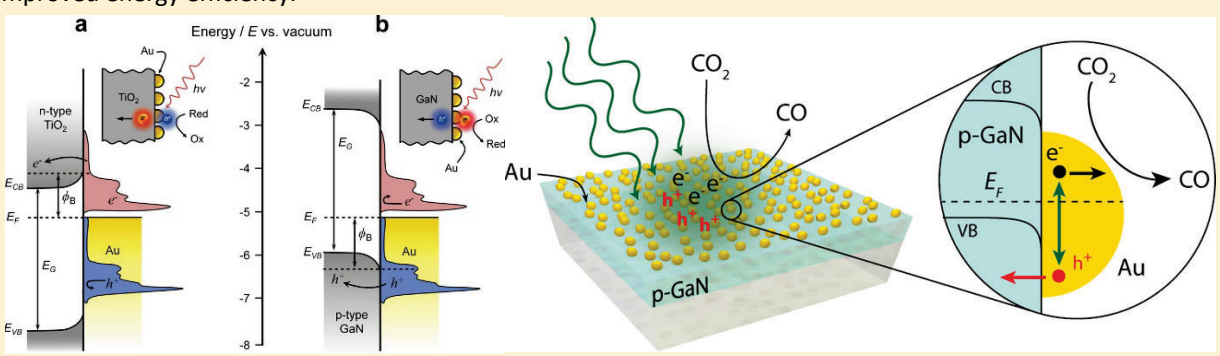


Figure S13. Hot-carrier collection across an interfacial Schottky barrier at metal/semiconductor heterojunctions. (a) Energy band diagram of a plasmonic metal (e.g., Au) contacting an n-type semiconductor (e.g., TiO_2). Plasmon excitation creates hot electrons (red) and hot holes (blue) above and below the Fermi level (E_F) of Au, respectively, with an energy distribution governed by the metal band structure and incident photon energy. Only hot electrons with sufficient energy above Φ_B (indicated by dashed line) surmount the interfacial barrier and populate empty conduction states of the n-type semiconductor. (b) Energy band diagram of Au in contact with a p-type semiconductor, p-GaN. Hot holes with sufficient energy below Φ_B (indicated by dashed line) surmount the interfacial barrier and populate available valence levels of the p-type semiconductor. Shown at right, Au/p-GaN photocathodes perform photoelectrochemical CO_2 reduction with enhanced selectivity for CO with respect to H_2, as compared with dark electrochemical CO_2 reduction. (Far-right scheme) Hot-hole injection balances hot-electron transport, which is used to reduce adsorbed species at the Au/electrolyte interface in the PEC device. *Source: Reprinted from DuChene, J. S. et al., [Hot hole collection and photoelectrochemical CO_2 reduction with plasmonic Au/p-GaN photocathodes](), Nano Lett. 18, 2545–2550, 2018. Copyright 2018 American Chemical Society*[117].

Complementary approaches employing ultrafast and time-resolved spectroscopies, advanced characterization of surface chemistries using spectroscopy and chemically sensitive imaging techniques, and first-principles theory are needed to achieve this understanding—which could lead to needed gains in the efficiency of plasmonic processes. Research could also lead to a much broader materials design envelope for plasmonic effects on chemical reactions including, but not limited to, metallic structures or metallic/dielectric structures.

Other processes to couple photochemical events with chemical reactivity can also be considered. For example, light-matter interactions could induce changes in the local electric fields at a semiconductor electrode/solution interface, which can modify the electrical field experienced by a surface-anchored catalyst, the distribution of ionic species (including protons and hydroxide ions), or the binding energy and conformation of substrates (e.g., CO_2 or N_2). Differences between the interfacial environment and the bulk solution are apt to influence chemical reactivity. Understanding the effect of the local electric field on (photo- and electro-) chemical transformations represents a research opportunity that would be enabled by theoretical and experimental methods to measure and model complex interfacial environments[122, 123].

Increase relaxation times beyond bulk materials to couple multiple-photon photochemistry to catalysis

The design and development of light-harvesting compounds and materials that support long-lived excited states (including excitonic systems) could lead to new pathways to induce excited-state effects on chemical reactivity. With both inorganic and organic molecules, excited-state lifetimes in the range of tens to hundreds of microseconds have been achieved. Long-lived metal-to-ligand charge-transfer (MLCT) excited states can provide sufficient time for efficient charge transport/injection and could even be commensurate with time scales of fuel-forming reactions. Chromophores with long-lived MLCT excited states are typically based on rare 4d and 5d metals, so research is needed to identify new long-lived chromophores based more on Earth-abundant elements (**Figure 14**)[124, 125]. More understanding is needed to determine how to incorporate light-harvesting materials that have long lifetimes and long carrier diffusion lengths—such as the metal halide organic/inorganic hybrid perovskites and other systems—into solar fuels generation.

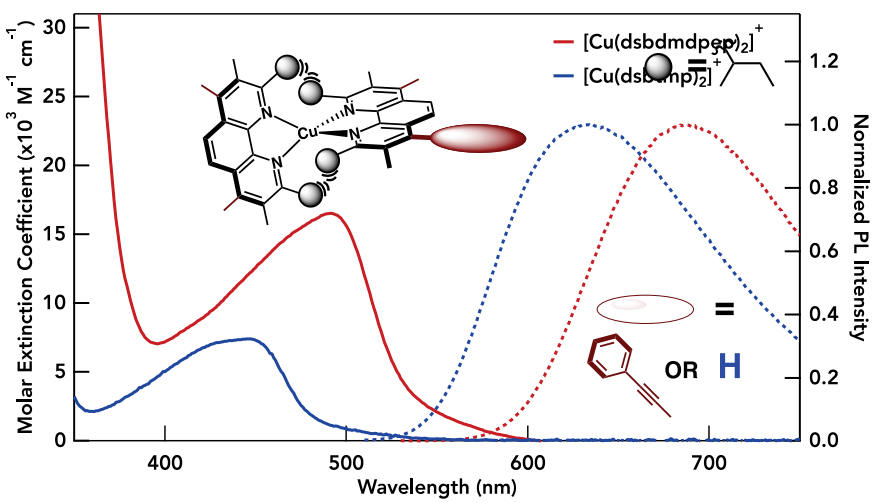


Figure 14. First-row transition metal complex featuring a metal-to-ligand charge-transfer state. This Earth-abundant cuprous phenanthroline photosensitizer features broadband visible light absorption, long excited-state lifetime, and favorable excited-state redox properties representing a viable alternative for second- and third-row transition metal sensitizers. *Source: Reprinted with permission from Garakyaraghi, S. et al., Enhancing the visible-light absorption and excited-state properties of Cu(I) MLCT excited states, Inorg. Chem. 57, 2296–2307, 2018. Copyright 2018 American Chemical Society*[125].

A free-energy cost is typically incurred when long-lived excited states are accessed via intersystem crossing from an excited singlet state to triplet states. The trade-off between free-energy loss and charge-separation lifetimes is common in natural photosynthetic systems that involve multi-step electron transfer cascades and coherent energy transport. Research can build on this understanding to probe and control the evolution of excited states and to elucidate the factors that can lead to long-lived, molecular excited states that could influence catalytic reactions.

Research is needed to understand how to integrate molecular light-harvesting chromophores and catalysts into other elements of a solar fuels system, such as membranes or molecular scaffolds—thereby leading to systems that have the light absorber and catalyst functionality in intimate contact[126]. Essential to this research is an understanding at the atomic scale of how to integrate light-harvesting, charge-separating, charge-accumulating, and liquid fuels catalytic functions into an efficient ensemble. This will necessitate that components not simply be placed in discrete modules, but rather be linked using tuned, performance-enhancing electronic connections. Understanding and controlling multiple, sequential charge- and energy-transfer processes in these synthetic assemblies will be critical. This knowledge could also lead to the design of hierarchical assemblies that can carry out multiple, light-driven electron transfers to charge-accumulating acceptor sites. Analogous to the oxygen-evolving complex (OEC) of photosystem II, these systems may co-localize multiple redox-active sites that enable rapid successive electron transfers to activate substrates. Further, opportunities exist to advance the science of light-harvesting systems/chromophores and their coupling to catalytic sites, in part through deeper study of photosynthesis and donor-acceptor complexes.

Long-lived excited states could also open up additional approaches to solar fuels—e.g., in photoredox catalysis, in which small molecules such as CO_2 are activated by single-electron transfers from photo-excited molecular metal complexes to enable bond-making processes[127]. Application of this concept to solar fuel-forming catalysis involving multiple electron transformations requires the understanding of how multiple light-driven redox processes can be induced to work in concert.

X-ray, electron, and optical spectroscopic approaches to resolve atomic coordinates and electronic structures of complex materials and interfaces under operando conditions can be used to follow atomic and electronic state conversions—across the full time-scale of initial light-harvesting to final fuels catalysis. Opportunities abound to develop and apply these techniques. For example, a fundamental feature of interfacial, thin-film catalysts and semiconductor or metal electrode-supported molecular (heterogenized) catalysts is the merging of charge-transport properties of conductive supports, with discrete sites for charge accumulation and multi-step catalysis. Recent work has demonstrated opportunities to combine soft x-ray emission spectroscopy with high-energy x-ray scattering to resolve both atomic and electronic structures with high resolution and to show how the atomic structural features determine bulk catalytic properties in amorphous oxide thin films. More generally, milestone advances in x-ray, electron, and neutron light sources, as well as transient optical techniques, offer radically new opportunities to probe structures and photochemical mechanisms at a fundamental level. Results in these areas could establish the foundation to design optimized, integrated photochemical systems exploiting light-excited states to drive liquid fuels catalysis.

It is not yet clear how to design excited states in nanostructures and other low-dimensional materials that couple excitations to catalytic reactions that form liquid fuels. An understanding of the photochemistry of polymers, nanoparticles, 2D and low-dimensional materials, and hybrid systems is rapidly developing. A significant opportunity could be to develop more precise synthetic approaches as well as analytical methods to understand and control the coupling of excited states with charge separation and catalysis in nanoscale systems and other materials. For example, research could capitalize on the significant body of knowledge of nanoscale semiconductor materials, in which optoelectronic properties may be significantly different from those in the bulk. Hot carriers in these systems represent an opportunity to access new

light-driven reactivity from non-equilibrium states; recent spectroscopic studies indicate that capture of hot carriers is feasible. Multiple-exciton generation (MEG) has also been demonstrated in quantum-dot–based PV cells[128], and recent work has shown that MEG can be exploited to drive photoelectrochemical reactions such as H_2S splitting (see **Sidebar 11**)[129].

Sidebar 11: Hot-carrier utilization for solar hydrogen production: Harvesting multiple carriers

The efficiency of any solar energy converter based on semiconductors is limited by the loss of excess photon energy—that is, the energy greater than the minimum amount that the semiconductor needs to absorb. In most solar energy converters, that excess energy generates heat. But in quantum dots (QDs), which are small semiconductor nanocrystals, the excess energy can be used to generate two electron-hole pairs (reduction/oxidation equivalents) that can participate in chemical reactions[129] (**Figure S14**). Such a process in semiconductor QDs is termed MEG or carrier multiplication[130, 131]. Such an approach can enhance the overall efficiency and make better use of the solar spectrum. In the ideal limit, the power conversion efficiency for a water-splitting reaction reaches ~47% at 1-sun concentration and rises to >50% when solar concentration (>10×) can be employed[132].

Recently, this concept has been demonstrated in a PbS QD-based photochemical cell able to drive an HER with an external quantum efficiency for H_2(g) generation of greater than 100% when the absorbed photons have an energy > ~2.7x the PbS QD bandgap[129]. The system consists of two separated electrodes and is constructed so that hydrogen generation is accomplished with no external voltage bias. One electrode consists of a conductive PbS QD layer deposited on top of an FTO/TiO_2 dielectric stack; the second electrode consists of a Pt mesh and is kept in the dark. Light is absorbed at the photoanode within the QD layer, which produces free electrons and holes. Photogenerated holes oxidize sulfide to sulfur ($nS^{2-} + 2(n-1)h^+ \rightarrow S_n^{2-}$) at the QD/solution interface (1M Na_2S aqueous solution), while electrons make their way to the Pt electrode where they can reduce H^+ to H_2(g) ($2H^+ + 2e^- \rightarrow H_2$). Therefore, the overall reaction is to directly photo-split H_2S to H_2 and S (which further reacts to form S_n^{2-}).

Photo-splitting H_2S requires much less energy than splitting water and thus can be achieved with a single low-bandgap photoelectrode. For a water-splitting system, two semiconductor layers in a tandem configuration with bandgaps of ~1.25 eV and ~0.5 eV could generate the appropriate voltage. When coupled with MEG, it can achieve power conversion efficiencies of >50% at 10× solar concentration[132].

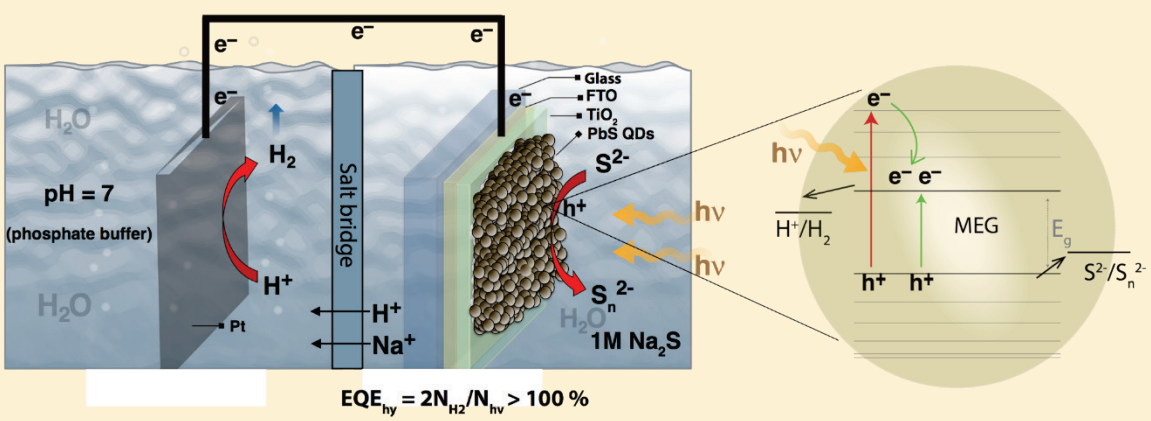


Figure S14. QD photoelectrodes were fabricated with bandgaps (E_gs) of 0.85, 0.92, and 1.08 eV by depositing the QDs from solution using a layer-by-layer approach on top of a patterned sol-gel TiO_2/FTO-coated glass slide. The highest hydrogen external quantum efficiency ($EQE_{h\nu}$) was 114±1.3% for E_g of 0.85 eV at incident light of 380 nm. *Source: Modified by permission from Springer Nature, Nat. Energy 2, 17052, Multiple exciton generation for photoelectrochemical hydrogen evolution reactions with quantum yields exceeding 100%, Yan, Y. et al., 2017*[129].

Reactivity from electronic excited states accessed through light absorption could substantially differ from catalytic reactions driven from electronic ground states, which are restricted by the Boltzmann distribution of states and thermally equilibrated reaction landscapes. Few examples provide direct evidence for excited-state effects on catalysis. However, carrying out catalysis on light-excited-state landscapes will create opportunities to escape the limitations existing in thermal catalysis by (1) exploiting far-from-equilibrium electron-density distributions such as ligand-to-metal, metal-to-ligand, and other charge-transfer excited states; (2) using localized energy deposition such as selective vibronic mode activation; and (3) capturing (not dissipating) energy from "hot electrons and holes" to drive new reaction pathways. A number of examples of molecular complexes that capture photons and drive H_2 generation have recently emerged[133-135]. New research is needed to identify unique proton-coupled electron transfer reactivity from electronic excited states that will enable fuel-forming reactions to be driven from single-component absorber-catalysts that can access reaction trajectories unavailable to thermal catalysts. Separately, bond-localized energy capture has recently been observed, suggesting that energy-transfer processes that funnel excitation to selective bonds can, in principle, provide mechanisms for liquid fuels catalysis not accessible by thermal catalysis[136]. Research is needed to determine if bond activation can be promoted from these vibronically excited states. A long-standing challenge in PV and solar fuels is that solar energy absorbed above the bandgap or HOMO-LUMO level is generally lost as heat. A significant scientific challenge remains in understanding how to harness the excess excitation energy in hot carriers and molecular excited states to drive chemical bond-breaking and -forming processes, photoredox reactions, or catalytic surface reconstructions. Recently, organic polymeric photoabsorbers like those employed in organic PV (thin films and nanoparticles) have been used for water splitting[137, 138]. Yet to be demonstrated is whether other novel processes such as singlet fission (conversion from a singlet excited state to two triplet excited states), upconversion (combination of multiple excited states to a single highly excited state), or bulk photovoltaic effects can be applied advantageously to solar fuels.

Develop light-stimuli-responsive molecules and materials for catalysis

A vast body of synthetic chemistry has been centered around developing molecules and materials with the ability to modulate their structure in a well-defined fashion using heat, pH, light, ion concentrations, and environmental polarity. Integrating these elements into photoactive systems could, in principle, enable better control of catalytic properties by solar radiation. This approach has the further advantage that many stimuli-responsive molecules and materials have been developed that offer different and complementary functionalities, charting a suite of novel mechanisms to promote selectivity.

Fundamental research is needed to incorporate photoresponsive concepts into solar fuels by effectively integrating light absorbers and catalysts into multi-functional, dynamic materials. An archetypal example of this principle is the light-driven *cis-trans* isomerization of retinal that is a vital part of animal vision and also the photoprocess that drives a proton pump in bacteriorhodopsin. In the latter case, light absorption and the torsional motion of the retinal are coupled on the sub-100 fs time scale[139], storing energy in the form of a transmembrane proton gradient. Research is needed to connect the design principles of molecular machines with light-driven motion to effect proton pumping and, possibly, proton-coupled electron transfer in solar fuel systems. Research also is needed to determine how to use light-driven molecular conformational changes to alter the ligand environment of molecular and nanoscale catalysts in a dynamic manner, creating high-energy states that can drive energetically demanding chemical transformations. Other photoinduced modifications could include direct alterations of an active site or structural changes due to photoexcitation, such as alterations in the surface chemistry of facets of a heterogeneous catalyst (or ligand modification in molecular systems).

Ultimately, photochemical generation of structural or chemical changes in the microenvironment could provide new mechanisms to influence chemical reactivity. Research exploring and understanding these

mechanisms could impact several areas, including (1) changes in catalyst, catalyst support, and supporting membrane structure (and even functionality); (2) control of transport by creating pH or other gradients (active transport); and (3) photo-driven conformational changes that could work in concert with ion transfer after electron transfers.

Several stimuli-responsive materials[140] interconvert one form of energy to another and adapt to changing conditions; but these materials—including ferroelectrics[141], phase-change materials, nonstoichiometric compounds, shape-memory, and metamaterials—have not been explored for solar fuels. External stimuli beyond light and the catalytic chemical environment could effect meaningful change, thus augmenting catalytic functionality. For example, the polar order of ferroelectrics can be reoriented with electric fields or light pulses or, since all ferroelectrics are piezoelectric and pyroelectric, by stress or temperature change. Nonstoichiometric materials can undergo metal-insulator transitions and serve as reservoirs of ions for Mars-van Krevelen-type catalysis. Phase-change materials can reversibly offer different surface terminations for reactions. Applying strain or a voltage to a surface can deform the active sites and change their charge distribution. This could favor certain reaction steps and disfavor others. Any of these systems could be harnessed as part of a well-designed light-absorber and photocatalyst system.

Create metastable surfaces and systems

A specific area of light-induced compositional, structural, or functional changes that could benefit from new research and concepts is the creation of metastable phases at surfaces or even simple reconstructions, which could open up new ways to bridge the time scales of photoexcitation and chemistry. Work is needed to delineate what kinds of longer-lived structural changes (metastable systems) could be created distinctly in solar fuels systems from solar radiation. Additional research can provide insight into how surface reconstruction occurs and how it impacts reaction processes[126, 142]. For example, nanoscale systems could offer opportunities to co-design optical and surface catalytic responses. Many studies have documented that size-selected nanoparticles—because of surface-volume effects—can favor one phase or another for the same nominal composition. This result can lead to fluxional systems in which external conditions such as light could favor nanoparticle phase transitions, offering different surface terminations at different times. Research into this category of responsive systems will benefit from recent research characterizing the favorable catalytic properties of each phase of nanoparticles (e.g., titania/anatase/brookite). In some cases, a single facet of a single surface can host different reconstructions with different compositions based on the environment (temperature T, chemical potentials μ_i, pH). Recent work (**Figure 15**) demonstrated that control of the surface reconstruction of strontium titanate via pH and substrate electric potential changes[143, 144] can enhance hydrogen evolution catalysis in water splitting.

Understanding and harnessing nonstoichiometric reconstructions could create new design principles for catalyst activity and selectivity. In addition, the undesired evolution of surface structure under reaction conditions is a key feature of catalyst degradation; so understanding these processes is crucial to forming favorable and avoiding unfavorable surfaces. Temporal and spatial variations in the reaction conditions (e.g., pH change) could favor different surface structures and compositions, leading to shifts in binding energies for reactants, intermediates, and products. This alteration in reaction pathway energetics can accelerate overall solar fuel reaction rates by shifting peaks in volcano curves, enhancing activity, and ameliorating poisoning[145]. For 2D materials, the design of the catalytic functionality includes understanding defect formation (e.g., anion vacancies in transition metal dichalcogenides) as well as adherence of additional co-catalytic functionalities.

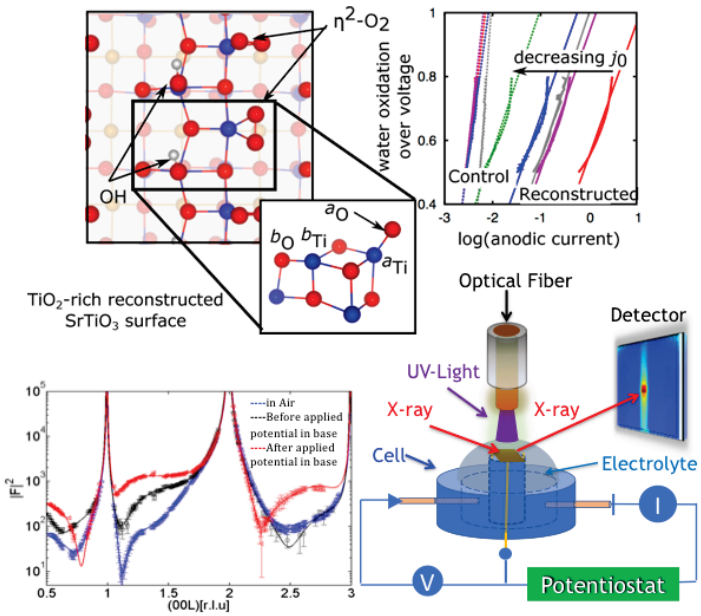


Figure 15. Design of novel reconstructed surface photocatalysts. (Top left) The surface of $SrTiO_3$ (STO) offers a variety of reconstructions including a TiO_2 double layer. (Top right) The reconstructed surface gives a much lower Tafel slope (better HER catalysis) than the same STO material with bulk-like surface. *Source: Reprinted with permission from Martirez, J.M.P. et al., Synergistic oxygen evolving activity of a TiO_2-rich reconstructed $SrTiO_3$(001) surface, J. Am. Chem. Soc. 137, 2939–2947, 2015. Copyright 2015 American Chemical Society*[143]. (Bottom left) Operando spectroscopy (bottom right) enables detailed correlation between catalyst cell conditions, surface reconstruction, and catalytic properties. *Source: Reprinted with permission from Plaza, M. et al., Structure of the photo-catalytically active surface of $SrTiO_3$, J. Am. Chem. Soc. 138, 7816–7819, 2016. Copyright 2016 American Chemical Society*[144].

Potential Impacts

Research addressing these opportunities will lead to greater understanding of how light excitation drives chemical transformations with improved selectivity and efficiency. Coupling strategies will more closely mesh light excitation with chemical reactions—with the possibility of exceeding the energy conversion efficiency achievable in conventional photoelectrochemical systems. This research will uncover opportunities for using light to control chemical product distributions to align with future liquid fuel needs. The research will spur the co-design of a new generation of thin absorber materials, 2D materials, and molecules that can integrate photoabsorber and photocatalyst functionality for simplified design and high efficiency of solar-to-fuels conversion.

PRO 4: Tailor interactions of complex phenomena to achieve integrated multicomponent systems

Summary

The development of systems for solar fuel generation has seen notable successes—in particular, for water splitting to produce hydrogen, where energy conversion efficiencies for H_2 production approaching 20% have been reported (**Sidebar 1**) in several systems[11-13, 20]. However, considerable challenges remain with durability, even for solar H_2 generation. There are also major challenges for the overall system efficiency and selectivity for liquid solar fuels. Addressing these challenges requires fundamental understanding of the scientific factors that impact the performance and durability of integrated constituents. Creating effective systems for generating liquid solar fuels requires careful consideration of the delicate interplay among the numerous processes that operate in parallel but are also interdependent. In turn, the intentional integration of the materials and molecular species that comprise individual components is necessary to effectively convert solar energy into chemical energy.

Understanding the fundamental science required to effectively integrate components is both a major challenge and a significant opportunity because numerous processes that occur on multiple length and time scales must be coordinated, including (1) photon absorption, charge separation, and transfer of electrons and holes; (2) transport of ions in liquid or solid electrolytes; and (3) delivery of reactants to active catalytic sites for fuel-forming reactions or water oxidation, followed by separation and collection of products. These processes typically involve multiple phases. The coupling is controlled by gradients and fluxes of the species present, as well as the energetics and molecular structures of interfaces and interfacial materials. Integration is particularly important because liquid solar fuels generation requires the absorption of multiple photons from sunlight and complex multi-electron and multi-proton processes—all processes that may be spatially and temporally distributed, as illustrated in **Figure 16**. Note that a number of solar fuels system architectures have been developed, including those that incorporate molecular absorbers and/or catalysts.

The durability of integrated solar fuel systems is another critical factor in their ultimate use. Systems must display high efficiency and selectivity over broad temperature ranges and under intermittent solar illumination for periods ranging from many years to decades. To date, however, successful operation beyond a number of weeks has not been demonstrated. Thus, a significant need exists to understand the science of degradation and durability. Making progress toward this long-term goal requires a fundamental understanding of the thermodynamics, kinetics, and mechanisms of processes that lead to degradation of components and loss of couplings in solar fuels assemblies.

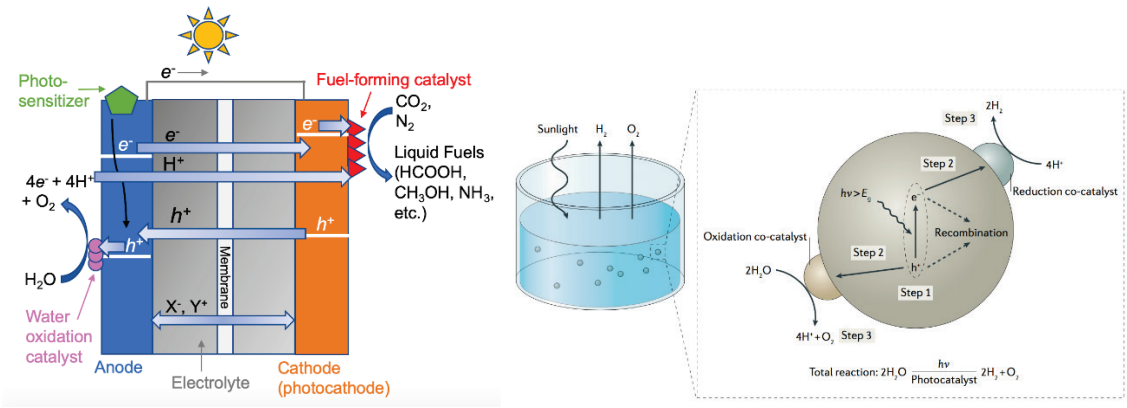
Key Scientific Questions

- How can the fundamental science of integration advance the predictive design and control of interfaces and processes to enhance the performance and durability of solar fuels systems?

- How can the function of systems be understood, designed, and controlled to support multiple-photon, multiple-electron, multiple-proton reactivity?

- How can the impact of fluxes of water/solvents, molecules in vapor and condensed phases, and ions in integrated systems and the resultant impacts on component and system performance be comprehended, designed, and controlled?

- How can predictive methods be developed to provide insights for understanding and controlling durability at the molecular, material, component, and systems level?



(a) (b)

Figure 16. Schematic of integrated systems for solar fuel production that illustrates photon capture to generate electrons and holes, electron and ion transfer/transport, and fuel-producing catalysis: (a) flat-panel system showing Z-scheme system with a dye-sensitized anode and a photocathode in an electrolyte separated by a semi-permeable membrane that facilitates ion flow and maintains product separation. *Source: Used with permission from University of Rochester*; (b) schematic of suspended-particle system for hydrogen production. *Source: Chen, S., et al., Particulate photocatalysts for overall water splitting, Nat. Rev. Mater.2, 17050, 2017* [10]. A number of device architectures are provided in the references in the factual status document associated with this report. *Source: Neale et al., Factual Status Document Associated with the Liquid Solar Fuels Roundtable Report, 2019* [6].

Scientific Challenges and Research Opportunities

Integration of the individual components presents challenges for generating solar fuels because the stand-alone performance of individual elements may not translate to comparable performance in full systems. Fundamental research is needed to provide a mechanistic understanding of how individual micro- and macroscopic processes interact and affect the function of other integrated components. The resulting knowledge will reveal how integration impacts performance and durability, guide the development of predictive models, and enable the co-design of components for efficient, selective, and durable systems. The following are several research opportunities to gain the needed fundamental scientific understanding and advances at the systems level for liquid solar fuels that go beyond system demonstration and testing:

- Enable complex light-driven fuel-forming reactions by coordinating physical and chemical steps
- Understand the interactions of components and processes in integrated liquid solar fuels systems
- Understand, control, and design transport of water and solutes in integrated systems
- Identify and understand degradation mechanisms in systems and at interfaces.

Enable complex light-driven fuel-forming reactions by coordinating physical and chemical steps

Solar fuel systems exhibit complexity over a wide range of temporal and spatial scales. Linking multiple-photon absorption events to multiple-electron (and multiple-proton) catalytic transformations represents an outstanding challenge that is further complicated by the time scales over which multiple redox equivalents are accumulated and the competing kinetics of energy-wasting charge-recombination processes[146], as well as other deleterious reactions. Multiple-photon, multiple-electron, and multiple-proton reactions necessitate robust photon-driven charge-transfer processes because the sequential nature of catalytic transformations (see **Figure 5**) presents an evolving state such that driving force, electronic coupling, and chemical coupling (e.g., proton-coupled electron transfer, bond making/breaking) are distinct in each step. In systems that integrate photochemical and catalytic processes, strategies need to be developed to favor productive and selective reactions over nonproductive and non-selective ones.

Coupling photon absorption events to single-electron events can place stringent limitations on reaction pathways, because processes that proceed through single-electron events often involve high-energy charged intermediates. Catalysts are employed in solar fuels systems because they can modulate this landscape by coupling proton and electron transfer processes or by proceeding through transformations involving multiple electron (typically at least two) and proton transfers[147, 148]. New approaches for integration of liquid solar fuels systems can provide novel mechanisms to accumulate redox equivalents for catalysis. For example, electron/hole buffering components could serve to accumulate charges that are subsequently delivered to the catalytic sites in unison (instead of sequentially). Molecular redox agents could also be employed to store redox equivalents, as biological systems do in storing hydride equivalents in the form of nicotinamide adenine dinucleotide hydride, NADH, or its phosphate, NADPH. New concepts could be developed that employ and integrate multiple light absorbers to capture different parts of the solar spectrum and/or to drive different elementary steps in multi-step catalytic reaction pathways. There are also research opportunities to develop the science needed to create new architectures for synchronizing photoabsorption, catalysis, and ion/mass transport. To date, most solar fuels systems use architectures that comprise either (1) a photoabsorber semiconductor supporting the system that mimics a solar panel or (2) suspended particles in an electrolyte solution (**Figure 16**). Developing other approaches—including membranes, ionomers, or molecular scaffolds (e.g., MOFs) as the integrating framework—could provide new concepts and research directions for solar fuels. Haussener and coworkers recently published a device that integrated a concentrator multijunction III-V PV cell with an electrolyzer for water splitting to produce hydrogen and oxygen (see **Sidebar 12**). This example is more akin to a tightly integrated PV-electrolysis approach, but it does show that a number of novel concepts and architectures could potentially lead to direct solar fuels production.

Sidebar 12: Thermal integration and process intensification in photoelectrochemical systems

Thermal integration is one way to uniquely benefit from the synergies of interacting components in a photoelectrochemical (PEC) system. Understanding the coupled charge, mass, and heat transfer in the PEC system is key in taking advantage of these synergies and increasing efficiency, selectivity, and longevity. Specifically, multi-mode heat transfer can be used to evacuate the thermalization energy from the photoabsorber, keeping it at a lower temperature so as to reduce recombination; one possible design is shown in **Figure S15a**. At the same time, the evacuated heat can be used to pre-heat the reactant—which fulfills a double function as cooling fluid and reactant—increasing the operational temperature of the electrochemical reaction while reducing reaction overpotentials.

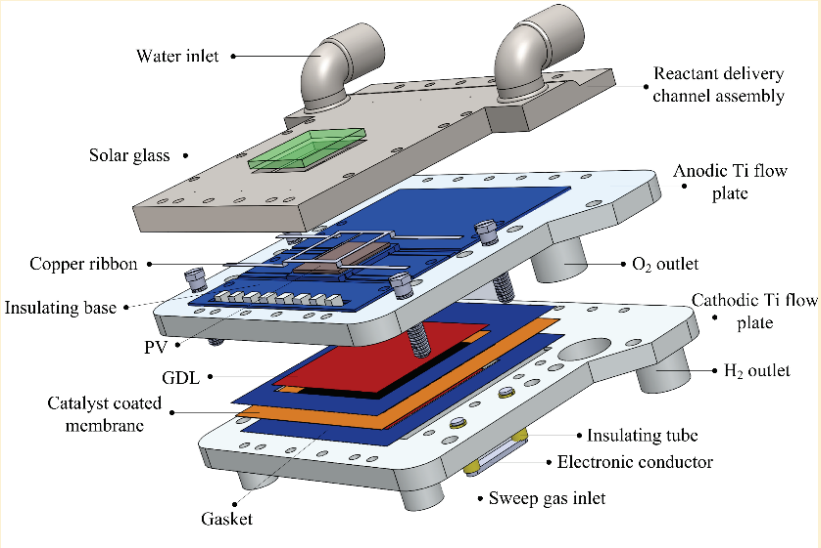


Figure S15a. Illustration of the integrated photo-electrochemical device. *Source: Reprinted by permission from Springer Nature, Nat. Energy 4399–407, A thermally synergistic photo-electrochemical hydrogen generator operating under concentrated solar irradiation, Tembhurne, S. et al., 2019*[149].

This thermal integration enhances the maximum possible efficiencies (**Figure S15b**) and enables operation at higher current density. Large operational current densities are desired because they ensure process intensification, a high–power-density device, and an increase in economic competitiveness. High current densities can be achieved through irradiation concentration (concentrations >100), but this also requires even more careful management of the heat. PEC demonstrations of high efficiency and high power density are essential to advance PEC pathways and cost-effective production of solar fuels and commodities.

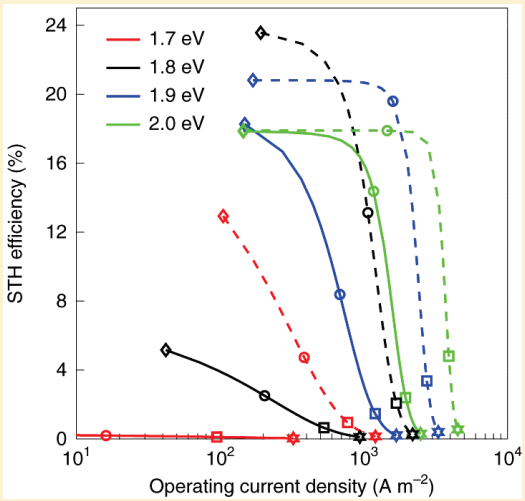


Figure S15b. Single junction limiting efficiency as a function of operating current density for four bandgaps without thermal integration (solid lines) and with thermal integration (dashed lines). *Source: Reprinted by permission from Springer Nature, Nat. Energy 4399–407, A thermally synergistic photo-electrochemical hydrogen generator operating under concentrated solar irradiation, Tembhurne, S. et al., 2019*[149].

The multi-step reactions required for synthesizing liquid solar fuels from small-molecule reactants such as CO_2 and N_2 can, in some cases, be subdivided into a series of 2-electron reaction steps. Although a single catalyst may enable these transformations, there are also opportunities to develop cascading or tandem catalysis schemes. For example, the 6-electron, 6-proton reduction of CO_2 to methanol can be subdivided into three 2-electron reactions for reduction of CO_2 to formic acid, formic acid to formaldehyde, and the final reduction of formaldehyde to methanol (**Figure 17**)[38]. Each of these 2-electron transformations has a similar reduction potential; so, in principle, a series of three catalysts tailor-made for each 2-electron conversion can be co-localized to allow for a tightly coupled reaction cascade that furnishes the methanol product with enhanced selectivity and efficiency[150]. This concept borrows from nature's blueprint, in which reaction cascades are ubiquitous, e.g., conversion of CO_2 to carbohydrates. Additional concepts could be developed for tandem or cascade catalysis (see **Sidebar 13**). The discovery of highly selective and efficient liquid solar fuels systems will benefit from developing the basic science around cascade catalysis and learning how to integrate cascade catalysis with photo-absorber/charge-separating materials in full systems. The primary challenge is developing and integrating catalysts that are optimized to perform the sequential reduction reactions. To achieve "one-pot sequential" catalysis, the catalyst and reaction conditions must also be compatible. A detailed understanding of the kinetics of intermediate production and transfer must be mastered to develop highly selective and efficient solar-to-liquid-fuel electrolytic cells (PRO 1).

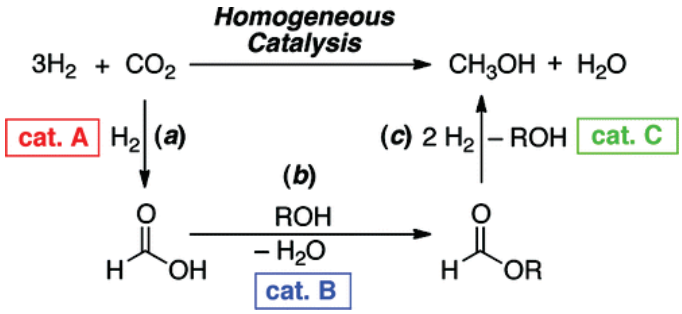


Figure 17. Example of a reaction cascade for converting CO_2 to CH_3OH. *Source: Reprinted with permission from Huff, C. A. and Sanford, M. S., Cascade catalysis for the homogeneous hydrogenation of CO_2 to methanol, J. Am. Chem. Soc. 133, 18122–18125, 2011. Copyright 2011 American Chemical Society*[38]*. From Scheme 3 "Cascade Catalysis for the Homogeneous Hydrogenation of CO_2 to Methanol."*

A central challenge for implementing cascade catalysis in liquid solar fuels production hinges on the spatial and functional integration of multiple catalysts to achieve rapid hand-off of intermediates and tight kinetic coupling of reaction steps. The tight coupling of highly efficient catalysts is a frontier direction for homogeneous, heterogeneous and hybrid catalyst design. Sequential catalysis has been demonstrated for the hydrogenation of CO_2 to methanol[38]. As shown in **Figure 17** the first 2-electron reduction by catalyst A produces formate. Formate is then activated by a Lewis acid (catalyst B) and an equivalent of methanol to form the more easily reduced methylformate ester, which is then reduced to methanol using catalyst C (and releases the equivalent of methanol used to form the ester). Use of the ester intermediate both activates a thermodynamically stable product (formate) and avoids the isolation of chemically unstable intermediates (such as formic acid or paraformaldehyde). Although both catalyst A and B are hydrogenation catalysts, the sequential route illustrates a viable chemical pathway that could also be used in electrocatalytic reduction.

Examples of possible approaches include attaching catalysts to structured supports, including particles; nanofabricating materials for heterogeneous catalysts (see **Sidebar 13**); and facilitating the arrangement of molecular catalysts. Established approaches for integrating molecular catalysts with photosensitizers help lay the groundwork for these directions (e.g., see **Figure 18**) [151]. Ultimately, integrating cascading catalysis into liquid solar fuels systems could result in products with much greater selectivity and efficiency than can be achieved by a single catalyst.

Sidebar 13: Cascade catalysis

Developing a single catalyst to navigate the intricate reaction pathways required for >2e- reductions can be a tricky task. Another approach is to develop multiple catalysts for sequential reactions that ultimately lead to complex product(s). This approach is particularly advantageous for chemically reducing CO_2 to hydrocarbons because of the large number of potential products and relative stability of potential intermediates. For example, there are many selective catalysts optimized for the 2e- reduction of CO_2 to CO or HCO_2^-.

However, both CO and HCO_2^- can be more challenging to activate toward further reduction. Furthermore, catalyst properties important for CO or HCO_2^- reduction are often orthogonal to those needed for CO_2 activation. As a result, optimizing a single catalyst for sequential reactions may not be possible.

In contrast, several catalysts can each be tailored to perform highly selective sequential reactions that lead to reduced products. A few examples using sequential catalysts to access unique product selectivity have been demonstrated using molecular catalysts (e.g., **Figure S16**) and heterogeneous solid-state catalysts.

Gold and Ag heterogeneous catalysts are highly selective electrocatalysts for the chemical reduction of CO_2 to CO. Copper electrodes can directly convert CO_2 to form > C_2 hydrocarbon products. However, co-production of CO from CO_2 from interspersed Au and Ag catalysts increases the local concentration of CO as a substrate,

leading to a higher proportion of oxygenate products from subsequent Cu-catalyzed processes while maintaining a high Faradaic efficiency for C_2 and C_3 products[39].

The key to this tandem reactivity is the use of interdigitated bimetallic electrodes, which permits independent control of CO production through the relative electrode area of Au or Ag vs. Cu, as well as control of the diffusion length for CO transport. Integration of the sequential catalysts exhibited additional advantages over isolating intermediate products for further reduction. Generation of CO in situ results in a supersaturated (non-equilibrium) concentration near the Cu electrode, leading to a unique product profile that could not be achieved using mixtures of CO_2 and CO.

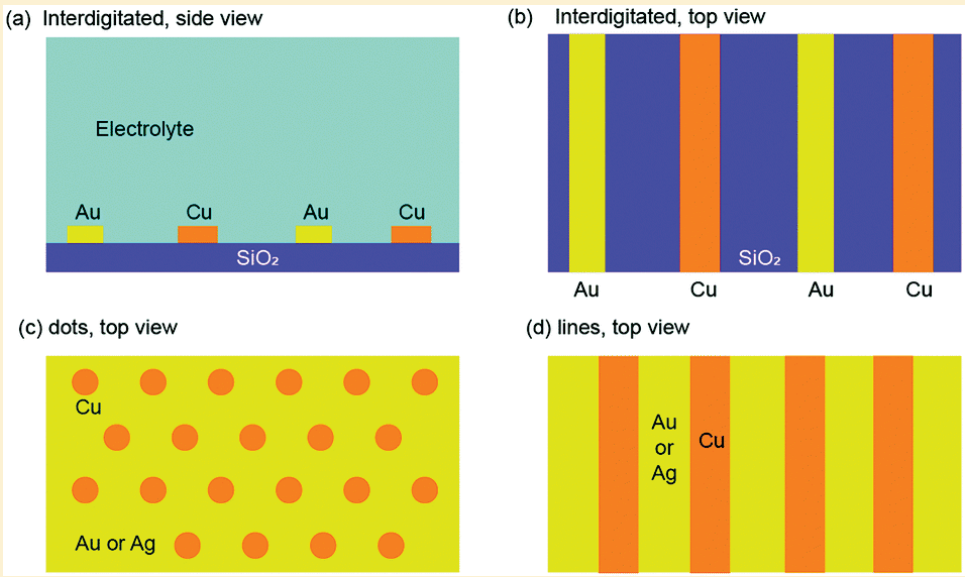


Figure S16. Micropatterned electrodes interface Au and Ag catalysts with Cu catalysts. The Au or Ag electrocatalysts reduce CO_2 to CO. Non-equilibrium concentrations of CO build up near the Cu electrodes, where the mixture of CO and CO_2 is reduced to $>C_1$ hydrocarbons and oxygenates. These tandem processes enable access to unique product distributions for the CO_2 reduction reaction. *Source: Reprinted from Energy Environ. Sci. 11, Lum, Y. and Ager, J. W., Sequential catalysis controls selectivity in electrochemical CO_2 reduction on Cu, 2935–2944, 2018[39], with permission from Elsevier.*

Advancing the design and understanding of integrated liquid solar fuels systems raises opportunities to develop and implement sophisticated modeling approaches. Advances in kinetic simulations of reaction networks can inform the design of cascade reaction sequences with optimal arrangements of active sites to maximize selectivity and energetic efficiency. Likewise, the bottom-up design of cascade reaction sequences requires mechanistic insight into the catalyst design parameters that allow for selective conversion of intermediates along a sequence.

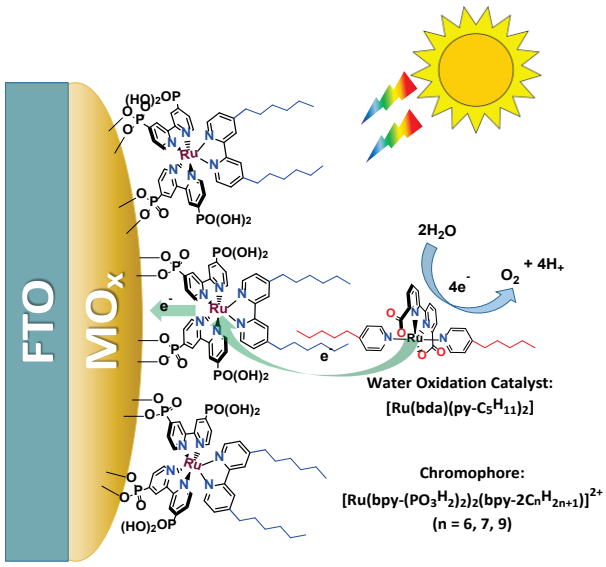


Figure 18. Illustration of photoanode for water oxidation based on a molecular chromophore-catalyst assembly anchored on a mesoporous metal-oxide electrode using the self-assembled bilayer strategy. *Source: Reprinted from Wang, D. et al., Self-assembled chromophore–catalyst bilayer for water oxidation in a dye-sensitized photoelectrosynthesis cell, J. Phys. Chem. C 123, 30039–30045, 2019. Copyright 2019 American Chemical Society*[151].

Understand the interactions of components and processes in integrated liquid solar fuels systems

Successfully integrating various components in a functional liquid solar fuels system requires the control and balance of light, energy, charge, and molecular and ion fluxes. This challenge stems from the variety of coupled physical phenomena and fluxes that require coordination. Coupled fluxes are a means to match dynamics across the system. The charge-carrier flux provides chemical potential to the catalytic sites, which convert the charge carriers and reactants (charged and neutral species) into products along catalytic pathways that depend on the local environment. These phenomena occur on a broad range of temporal and spatial scales. Spatial variation in the types of transport involved needs to be resolved, including bulk transport, transport across boundary layers, and transport across Helmholtz layers. Furthermore, local temperature changes resulting from waste heat and external factors will likely be nonuniform, which will impact local rates of reaction and transport. Moreover, an operating system will necessarily not be at equilibrium, thus yielding gradients of heat, molecules, and ions that change over time. It is also critical to avoid deleterious crossover of reactants, intermediates or products from the oxidation and reduction processes occurring in different regions, e.g. protect the chemistry of one electrode from the chemistry of the other. Finally, as shown in **Figure 19,** product distributions in solar fuels systems could be highly nonuniform and depend on a number of factors, including electrode dimensions as well as the illumination intensity. Steady-state situations may likely not be attained. Additional complexities could arise under diurnal cycling, as well as seasonal fluctuations in irradiation and temperature. Taken together, these variations demand an understanding of the full time-dependence of the system. These challenges are familiar within battery, electrolyzer, and fuel cell technologies; and some of the same modeling, diagnostic tools, and design solutions may inform the development of robust solar fuel systems[152].

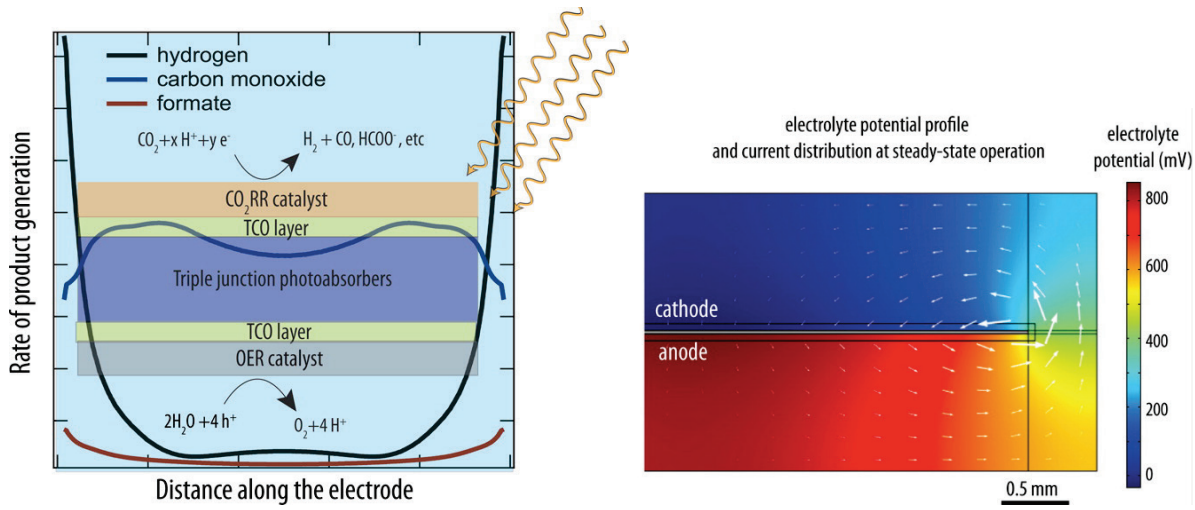


Figure 19. Left: Schematic of an integrated photoelectrosynthetic CO_2 reduction cell that incorporates a silver cathode catalyst and an optimized triple-junction light-absorber structure (2.1 eV/1.6 eV/1.2 eV). The calculated partial current densities for hydrogen, CO, and formate production are shown for 60 mW cm^{-2} of simulated AM 1.5G illumination. Right: Snapshot of the electrolyte potential profile and ionic current distribution (white arrows) from the center to the edge of the electrode. The simulated product distributions are highly nonuniform and depend on the electrode dimensions as well as the illumination intensity. *Source: Reprinted from Chen, Y., et al., Modeling and simulation of the spatial and light-intensity dependence of product distributions in an integrated photoelectrochemical CO_2 reduction system, ACS Energy Lett. 1, 273–280, 2016. Copyright 2016 American Chemical Society*[153].

Variations in operating conditions could influence the selectivity of CO_2RR and N_2RR. For example, electrocatalysis studies of these reactions typically indicate that the product distribution varies with applied potential. Thus, the spatial or temporal variations in photovoltage (arising from position in the device, time of day, season of year) is anticipated to change the distribution of fuels produced. These variations, therefore, present several opportunities for separation and storage of fuels as well as system efficiency.

In liquid solar fuels systems, components are integrated through interfaces that connect materials, molecules, fluids, and processes. Examples include interfaces between electrodes and catalysts, between catalysts and electrolyte, and between electrolyte and membrane (**Figure 16**). Properties of interfaces must be considered on a range of scales—from individual bonds between molecules and materials (**Figure 18**) to bulk junctions. These features will influence transport kinetics as well as local chemical and physical phenomena such as the properties of photoexcited immobilized molecules and the catalyst microenvironment. Interfaces also may be focal points for energy and transport efficiency losses. Understanding and characterizing these effects over multiple length and time scales is a critical need. Another clear research opportunity is to design interfaces to enhance system performance—e.g., by developing innovative coatings to improve durability or transport selectivity. Furthermore, interfaces involving catalytically active surfaces may be modified to tune catalyst activity through microenvironment control or to enhance durability by promoting self-healing processes or inhibiting degradation pathways.

The characterization and quantification of gradients and spatial heterogeneities in a working system must account for its multiscale nature—spanning nanometers at interfaces to centimeters and beyond in the full assembly. Multiscale modeling[152] and detailed spatially resolved operando spectroscopic characterization[154] of the systems are essential to understand how all these components are coupled. Whether such gradients are beneficial or not must be understood in the specific location and context.

Developing advanced experimental in situ/operando methods with high chemical specificity and spatial and temporal resolution is highly important.

Understand, control, and design transport of water and solutes in integrated systems

Water plays a special role in liquid solar fuels systems because it is an essential participant in the desired chemistry and in ion transport, as well as in undesired chemical processes such as corrosion. There are two major classes of systems with respect to how water is integrated: water-immersed and moistened.[155] In water-immersed systems, the availability of water is never rate-limiting, but passivation of components could be required; also, the transport of sparingly soluble molecules such as H_2, O_2, N_2, and CO_2 can be rate-limiting. In moistened systems—which include vapor-fed systems and nonaqueous electrolytes with low concentrations of water—corrosion could be suppressed, but water availability can become rate-limiting. Management of the water distribution within such a system is critical to maintaining ionic conductivity and reaction pathways within the cell (see **Sidebar 14**).

Sidebar 14: The science of water management and impact on cell performance

Water plays a critical role in most solar fuels devices, as both a reactant and a solvent within the cell. A schematic of the relevant components is shown in **Figure S17**. Flow fields allow bulk transport of reactants and products through the cell and are typically channels formed in a carbon or metallic plate, with varying channel geometries depending on the cell pressure and type of fluid being transported. Porous transport layers—also commonly referred to as *gas diffusion layers* in fuel cells in which the reactants are gaseous—allow fluid access to and from the catalyst layer while also providing mechanical support and electrical contact between layers. The porous transport and catalyst layers are a collection of layers with varying pore sizes and shapes, in which modeling fluid flow is complex, even geometrically. It is even more difficult to include effects of the relative affinity of each surface for water absorption, or to simulate the electrochemical transformations occurring at the electrode interfaces, which involve water consumption or production. All of these factors impact the distribution and local activity of water across the cell.

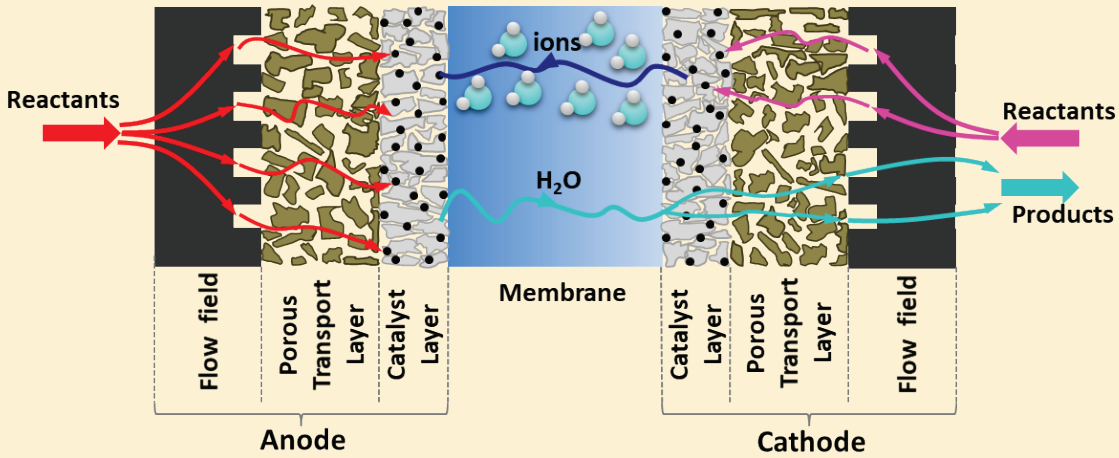


Figure S17. Schematic of a typical low-temperature electrochemical energy conversion cell. The flow fields and porous transport layer manage fluid transport to and from the catalyst layers, while water and ions flow through the membrane to balance the chemical transformations. *Source: Reprinted from Cur. Opin. Electrochem. 12, Mustain, W. E., Understanding how high-performance anion exchange membrane fuel cells were achieved: Component, interfacial, and cell-level factors, 233–239, 2018*[156]*, with permission from Elsevier*.

Insufficient water can cause permeant transport issues and inhibit reactions at the electrode surface that require water as a mediator or reactant; too much water can also be harmful to performance. Liquid water can have negative effects, serving as a barrier layer to gaseous reactant transport to catalyst surfaces, or acting as a source of mechanical stress within the electrode structure. For example, hydrodynamic forces caused by membrane swelling can deform porous transport-layer (PTL) components, causing issues such as pore blockage or loss of mechanical integrity. **Figure S18** compares an electrode at optimal humidity conditions (water vapor is in the PTL) to higher dew points (at which the liquid water begins to encroach into the PTL from the membrane and cause undesirable flooding).

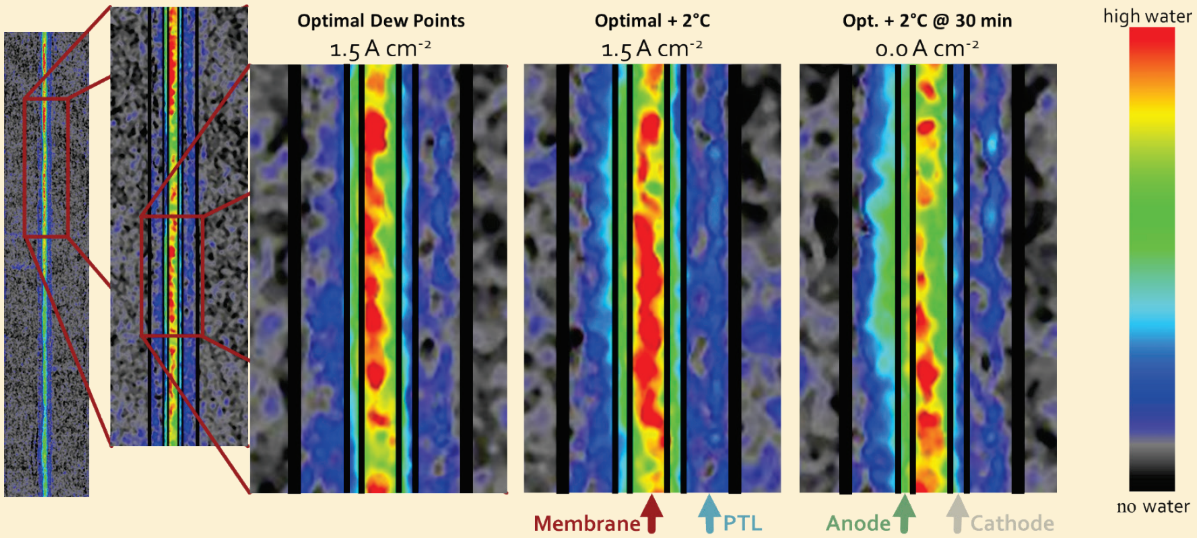


Figure S18. Operando in-plane neutron radiographic images of water transport in a fuel cell illustrate the sensitivity to cell geometry and operating conditions. The first magnified image shows the optimal dew point for the selected current density, with liquid water in the membrane but low water content in the porous transport layer. As the dew point is increased by 2°C, the water content begins to increase and migrate to the porous transport layer. The reaction cannot be sustained because of anode flooding, and the current drops to zero. *Source: Adapted from Eng. Environ. Sci. 11. Omasta, T. J. et al., Beyond catalysis and membranes: Visualizing and solving the challenge of electrode water accumulation and flooding in AEMFCs, 551–558, 2018*[157]*, under a Creative Commons license.*

Thus, controlling the water distribution by balancing transport and consumption of water is an important technical challenge to be resolved for durability and consistent performance over time. Therefore, high-performance, stable devices can be enabled by modulating the water transport rate through membranes and porous materials; this can be done through (1) designing the pore size and structure for capillary action and liquid transport, (2) modifying hydrophobicity and hydrophilicity of the layers by coatings or surface functionalization, and (3) managing operating conditions such as dew point, flow rate, and backpressure. However, science efforts such as multiscale modeling of water transport, spectroscopic measurements of water distribution in real time, and kinetics of water transport along surfaces are needed to intelligently design electrode and cell structures.

Sufficient water is required to transport species (including water itself) to and from the catalytic surfaces, as well as to conduct ions between the reduction and oxidation centers; low water content can increase ohmic loss due to poor ionic conductivity and can limit the supply of reactants to the catalyst interface. When systems are vapor-fed, too much local water can result in condensation and flooding, which can block reactant access to the catalyst and trap product at the electrode surface. Research is needed to explore macroscopic phenomena and to understand molecular-level and nanoscale structural changes within systems—e.g., the structure of electrolytes at the interfaces in systems and, for instance, how ion and other concentrations affect it. Understanding how water affects individual component performance

such as catalyst activity (PRO 2) or membrane durability (PRO 1) is also critical. For example, dehydration of membranes and solid electrolytes can result in local temperature variation and mechanical stresses. It also important to understand how the catalyst environment can be affected in water-limited systems.

Research opportunities at the system level include learning how to (1) quantify very low concentrations of water with full spatial and temporal resolution, (2) understand water-transport rates within the different phases/domains of the system (membrane vs. free liquid vs. porous layers), and (3) monitor local consumption or production of water. In nonaqueous electrolytes, diffusion and convection are the primary water-transport processes. In vapor-fed systems, water used in the reaction can be supplied on the opposite side of the membrane from where it is being consumed; in that case, the system relies on transport of water through the membrane to balance its consumption. The local fluxes of water across the membrane, within the catalyst electrode, and within the pores and channels of the system need to be balanced simultaneously for durable and stable performance.

Identify and understand degradation mechanisms in systems and at interfaces

As called out in the BES report *Transformative Opportunities for Discovery Science*[19], "the challenge of degradation science is to identify, model, and predict the mesoscopic evolution of structure or function in a material over the appropriate timescales while monitoring the dynamic processes that arise in the materials' functional use and typically occur on daily timescales." Degradation processes are caused by "slow and rare events" in which the "mean behavior does not control the outcome." Advanced characterization tools and predictive models (including those described in Appendix A) are an essential starting point to understanding the thermodynamics and kinetics of physical and chemical processes that occur in a liquid solar fuels system as it loses efficiency or selectivity over time. Research needs include predictive multiscale models, extensive databases, informatics, accelerated testing protocols, and reliability principles to link physical and statistical models. Opportunities exist to examine the modes of degradation[158], as well as self-passivating and self-healing processes that can potentially stop, mitigate, or even reverse degradation[14]. It is also important to elucidate how the operation of integrated systems impacts durability. Overall, there is a significant research opportunity to develop systems for enhanced durability, as well as predictive models for lifetime and durability.

The last decade has seen remarkable advances in understanding and enhancing the durability of PV and fuel cell systems. Extensive studies of PV system degradation at the device and panel level, as well as of semiconductor device failure due to electromigration phenomena, provide an excellent starting point to design experimental, theoretical, and computational tools and techniques for liquid solar fuels systems (**Figure 20**). A wide range of mechanisms have been identified, including mechanical stressors, chemical stressors, corrosion, and interfacial processes. The photocorrosion literature provides insights into specific electrochemical and photochemical processes that can occur in illuminated systems. In all cases, gradual movement of atoms and ions from initial to new locations in solid structures and at interfaces is at the heart of the relevant physics.

Identifying and understanding degradation pathways in integrated liquid solar fuels systems is crucial in developing durable components and systems. These systems operate in widely varying chemical environments. For example, understanding and mitigating corrosion (e.g., of catalysts and photoelectrodes) is particularly challenging in liquid solar fuels systems because of the corrosivity of systems using high and/or low pH. Full identification and characterization is needed of the nature, rates, and mechanisms of degradation processes, along with development and use of new experimental and computational methods to measure, understand, and predict the lifetimes of materials and material assemblies within the system. For example, new operando experimentation methods over multiple length and time scales under realistic operating conditions will be highly valuable to directly observe subtle

changes, such as catalyst restructuring during operation, that accumulate over time and impact performance.

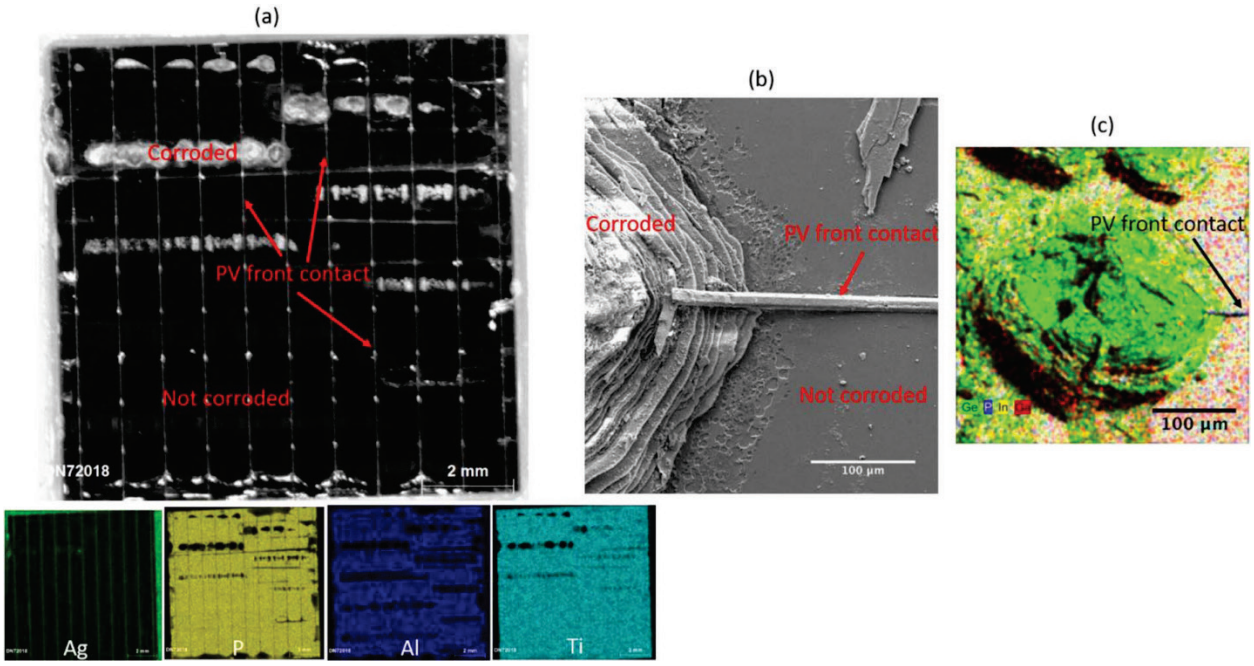


Figure 20. Failure analysis characterization of photovoltaic material after durability testing. (a) X-ray fluorescence (XRF) with insets, (b) scanning electron microscopy (SEM), (c) energy-dispersive x-ray images after 100 hours. Corrosion occurs on only some parts of the photovoltaic material, whereas other parts remain unaffected as seen in the XRF and SEM images. *Source: Reproduced from Kistler, T. A. et al., Integrated membrane-electrode-assembly photoelectrochemical cell under various feed conditions for solar water splitting, J. Electrochem. Soc. 166, H3020–H3028, 2018*[23]*. Covered under Creative Commons License: http://creativecommons.org/licenses/by/4.0/.*

Understanding the roles of extrinsic parameters—such as compositional impurities and current density inhomogeneities—in system lifetimes will reveal what level of perfection must be achieved for optimal system performance. Degradation and self-healing processes may occur independently at various locations, or they may be coupled by emergent phenomena; but multiscale modeling will help distinguish and characterize them. Developing a deep scientific understanding of the degradation processes that occur over months and years and constructing validated predictive models for them will allow the design of realistic accelerated tests and long-lasting systems, as well as the reliable prediction of lifetimes using short-term measurements. Furthermore, a detailed understanding of factors that determine the thermodynamics and kinetics of degradation will provide a foundation for developing approaches to prevent degradation or even reverse it if it occurs. Research is needed to develop new concepts for repair mechanisms of solar fuels components and systems—either during operation or during times they are not in use, such as when the sun is not shining.

Potential Impacts

The design, prediction, construction, and analysis of integrated liquid solar fuels systems presents opportunities and challenges at the forefront of fundamental energy science. Achieving the absorption of multiple photons to provide multiple redox equivalents to catalysts that use coupled phenomena within a reaction cascade will yield efficient liquid solar fuels systems. Making progress in this area demands the development and use of multiscale modeling and operando experimental methods able to predict and interrogate a range of phenomena that span orders of magnitude in time and space. Considering the

system as a whole—as well as subsystems and interfaces—is expected to spur new research directions that will ultimately yield liquid solar fuels systems that are more durable and efficient.

Scientific knowledge and experimental and theory/modeling methods gleaned from liquid solar fuels research can, in turn, be applied to understanding and potentially quantifying degradation and durability for a range of other energy technologies, including fuel cells, electrolyzers, and batteries.

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Appendix A: Advanced Characterization and Computational Methods for Solar Fuel Systems

Transformative discoveries in science often follow closely on the heels of breakthroughs in experimental and computational methods. The science that underpins the realization of efficient and durable liquid solar fuel systems involves understanding and controlling processes that occur on timescales from femtoseconds to decades and on length scales from angstroms to meters, so characterization and predictions are required that can span these time and length scales. The performance of these systems depends on complex reaction pathways at multicomponent interfaces that remain challenging to characterize in molecular-level detail. The science of this problem will thus advance most rapidly by developing and using analytical methods that push the frontiers of *in situ* spectroscopy and imaging, advances in theoretical modeling and scientific computation, and high-throughput materials discovery and characterization, including leveraging of DOE investments in large-scale user facilities.

Ultrafast spectroscopies. A powerful methodology to resolve the mechanisms of multi-step solar fuel catalysts is ultrafast transient optical and vibrational spectroscopies. These approaches are foundational for establishing light-driven reaction pathways and identifying the sequence of charge-accumulating multi-step events (analogous to photosynthetic "S-states") in the complex cascade of reactions that lead to chemical products.

Beyond these foundational spectroscopic approaches is a critical need for new methods to resolve atomic and electronic structures along the full timescale of the photons-to-fuels reaction coordinate. Dynamic atomic and electronic structural information is needed for correlating transient structures with photochemical and catalytic function and for identifying excited-state mechanisms that control branching points and recombination pathways. These experimental investigations will also provide databases of atomic and electronic structure benchmarks for quantitative testing and development of quantum electronic structure theory and mechanisms, while guiding the understanding and cultivation of next-generation solar fuels systems.

New enabling capabilities for direct atomic and electronic structure resolution and imaging are emerging with the development of the ultrafast x-ray free-electron laser (XFEL) and "benchtop" x-ray light sources, coherent x-ray synchrotron light sources, diffraction with in situ, liquid operando capabilities, and advanced neutron sources. The combination of photochemical excitation with x-ray scattering on ultrafast timescales opens a new window to studying molecules that undergo light-driven reactions (see **Sidebar 15**). XFEL-based time-resolved crystal structures, extended x-ray absorption fine structure (EXAFS), and other spectroscopic measurements have combined to produce the highest-resolution picture of photosynthetic oxygen evolution, which requires successive single-photon, charge-accumulation steps in Photosystem II. A key challenge now lies in achieving comparable resolution of light-driven solar fuels processes in artificial photosynthesis.

Identifying the nature of the reactive excited state(s) through measurement and theory is still a significant challenge, and methods need to be developed to accurately establish the structures and lifetimes of excited states (excitons). Opportunities exist to advance and develop new time-resolved spectroscopies capable of mapping excited-state electronic structures during photoexcitation and subsequent reactivity. Recent advances in coherent transient optical and infrared spectroscopies have provided critical new approaches for experimentally detecting excited-state lifetime dynamics, motions, and the electronic and vibronic coupling mechanisms that underlie long-range energy transfer within an electronically coupled array of chromophores[159]. These methods provide new opportunities to measure atomic and electronic structure and dynamics with sub-angstrom spatial and femtosecond temporal resolution in parallel with quantum theoretical mapping of excited states. This work is generating new understanding for designing or

managing energy flow through electronically coupled arrays of oscillators. New opportunities exist to exploit these concepts and designs.

Sidebar 15: Watching the oxidation of water in Photosystem II

The development of liquid solar fuel technologies is guided by an understanding of the mechanisms by which photosynthesis occurs in plants. In Photosystem II, four photons captured by key pigments in the protein drive the 4-electron redox chemistry at the Mn_4CaO_5 cluster (the oxygen-evolving complex, OEC) to oxidize water to oxygen. As the OEC cycles through five intermediate states, water is activated, temporary metal-oxygen bonds are formed then broken, and the key oxygen-oxygen bond forms. Until recently, the reactivity between the inorganic OEC subunit and water was poorly understood. To which metal atom(s) does water bind? Between which two oxygen atoms is a bond formed?

Serial femtosecond x-ray crystallography and simultaneous emission spectroscopy using pulses from an XFEL at the SLAC National Accelerator Laboratory have provided time-resolved images of the water oxidation process, capturing four of the five reaction states and two transient moments between reaction states (**Figure S19**)[160]. These images reveal how the protein stretches and shifts and how metal-oxygen bonds are made and broken during the water oxidation process. Complementary studies using ammonia as a surrogate for water helped affirmatively identify the metal-based binding sites[161]. These data provide new insight into how water binds to the OEC and how oxygen is formed, showing that water binds to calcium and then bridges calcium and the Mn_1 unit between the S_2 and S_3 states. Subsequent O-O bond formation occurs between oxygen atoms in this intermediate open cubane and not through a nucleophilic attack mechanism of another water molecule. These atomic-level details advance the understanding of how nature effectively oxidizes water at an inorganic reaction core. The design of new, effective water oxidation catalysts could be guided by this mechanistic insight. Further, a key research opportunity is represented by the application of linear accelerator capabilities at DOE national laboratories to gain analogous insight into the pathways by which artificial systems operate.

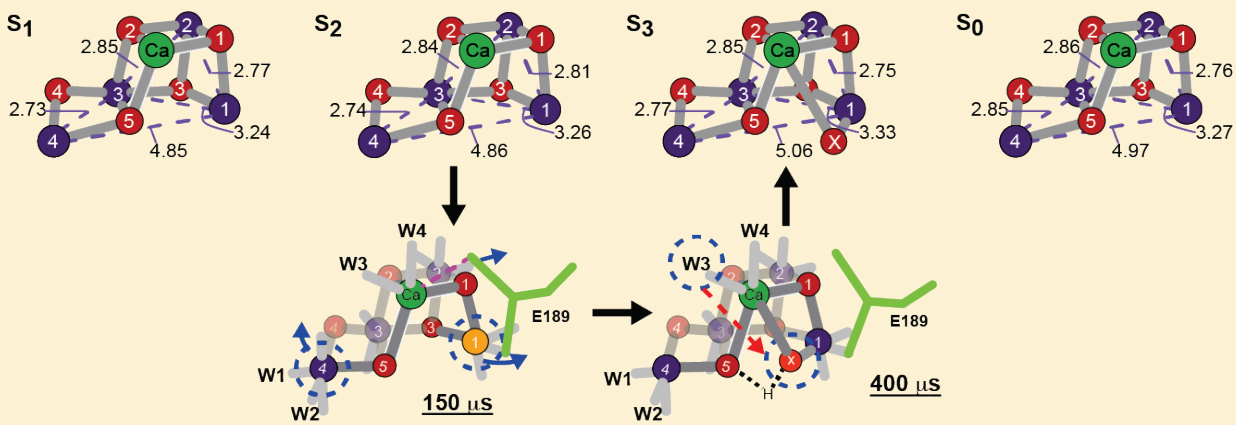

Figure S19. Structures of the reaction and intermediate states of the Mn_4CaO_5 cluster in the O_2-evolving complex of Photosystem II were elucidated through ultrafast x-ray crystallography and spectroscopy employing an XFEL. *Source: Springer Nature, Nature 563, 421–425, Structures of the intermediates of Kok's phytosynthesic water oxidation clock, J. Kern et al., 2018*[160].

Operando spectroscopy and microscopy. Beyond the standard techniques for characterizing catalyst structures—e.g., EXAFS, x-ray absorption near-edge structure (XANES), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), circular dichroism, electron microscopy, nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and more—in their isolated forms, in situ characterization will be essential to probe the structural environments of liquid solar fuel systems under operating conditions. Developments in infrared (IR)

spectroscopy with high-pressure, high-temperature, and electrochemical cells provide unprecedented insight into the nature and structure of adsorbed species on electrode surfaces, key reaction mechanism details, and information on the concentration, species orientation, and double-layer structure at the electrode/liquid interface. In addition, IR enables access to higher-energy pathways that, although thermodynamically favorable, might not be accessible under normal conditions because of kinetic limitations. In solvents, ultraviolet/visible (UV/Vis) absorption and IR spectroscopies can be used to probe local electric-field effects by monitoring Stark shifts or broadening, and IR spectroscopy has been used to observe changes in water structure close the electrode/electrolyte interface. In situ surface enhanced Raman spectroscopy (SERS) is similar to IR, but its sensitivity to different vibrational features/species provides complementary information; tip-enhanced Raman spectroscopy (TERS) provides an opportunity to carry out these measurements with high spatial resolution for immobilized or heterogeneous catalysts under electrochemical conditions[162-164]. Advances in high-pressure, high-temperature solution or solid-state magnetic resonance spectroscopies enable the detection of products as they form and information about the catalyst, providing key insight into reaction mechanisms and catalytic active sites[165-167]. Mass spectroscopy coupled to (photo)electrochemical measurements provides real-time detection of reaction intermediates[168]. Dynamic nuclear polarization NMR dramatically enhances the sensitivity of NMR to probe interfacial structures, and the advent of electrochemical NMR/EPR extends this capability to redox catalysis[169].

In situ x-ray spectroscopies and diffraction methods provide direct information about the atomic structure and oxidation states of elements involved in photo- and electrocatalytic cycles. The coupling of these synchrotron-based x-ray techniques to transient electrochemical methods is particularly powerful for understanding the details of multi-electron, multi-proton electrocatalytic reactions such as hydrogen evolution[170], oxygen evolution, and oxygen reduction[171] (**Figure A1**).

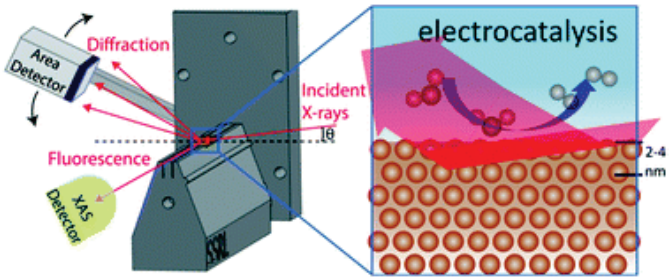

Figure A1. An electrochemical flow cell enables operando x-ray characterization of the structure and metal oxidation states of a thin electrocatalyst during the reduction of protons to hydrogen at high current density. *Source: Reprinted from Farmand, M. et al., Electrochemical flow cell enabling operando probing of electrocatalyst surfaces by x-ray spectroscopy and diffraction, Phys. Chem. Chem. Phys. 21, 5402–5408, 2019. Copyright 2019 American Chemical Society*[170].

Increasingly, laser flash photolysis and pulse radiolysis[172] are being coupled to optical detection in regions beyond the visible, including IR absorption and x-ray absorption[173, 174], for the direct observation of high-energy transient catalytic intermediates. For example, the recent coupling of time-resolved infrared (TRIR) spectroscopy with pulse radiolysis using high-power quantum cascade lasers[175] has enabled improved characterization of radiolytically generated redox species[172]. Advances in cell design and vacuum systems have also allowed for x-ray spectroscopic techniques such as photoemission spectroscopy to probe the potential profiles at semiconductor/electrolyte and electrocatalyst/liquid[176, 177] interfaces as a function of applied potential in the presence of a liquid electrolyte. Ultrafast electron microscopy promises a new approach to characterize the structure and dynamics of microenvironments with nanoscale resolution at relatively high temporal resolution for heterogeneous systems[178].

In situ microscopy—including transmission electron microscopy (TEM), scanning electron microscopy, scanning tunneling microscopy, and atomic force microscopy—is no longer confined to high-vacuum conditions; it can now be conducted in gas-controlled environments that model environmental conditions. Also, potentiostatic control of samples in liquid sample holders now enables hybrid electrochemical TEM measurements. Cryo-EM has recently been used to obtain high-resolution snapshots of soft electrochemical interfaces[179]. Fluorescence microscopy enables the investigation of local pH within electrochemical microenvironments with tens of nanometers spatial resolution, and field-emission microscopy has been demonstrated to enable direct investigation of synergistic effects[180] between different crystal facets of catalytic surfaces. Recent advances in scanning electrochemical microscopy (SECM) have enabled the in situ characterization of electrocatalyst structure and activity at 15 nm resolution, and SECM can also probe local photoelectrochemical reactivity[181, 182]. Collectively applying these new advances in operando methods, as well as continuing to advance the methods themselves, has the potential to advance our knowledge significantly in the reactivity, pathways, and degradation mechanisms of liquid solar fuels.

High-throughput discovery and data science. The high-throughput synthesis and screening of photoactive and catalytic materials, which began in the 1990s with inspiration from methods developed in biological and pharmaceutical research, has taken on new life in partnership with predictive and data-driven computational materials discovery. Advances in robotic synthesis, 3D printing, and automated (photo)electrochemical testing methods now enable fast screening of material arrays containing hundreds to thousands of samples, as well as automated synthetic process optimization. High-throughput synthesis (see **Sidebar 16**) is often coupled with high-throughput characterization, such as electrochemical and diffraction methods. The exploration of composition spaces made very large by the inclusion of multiple components (e.g., light absorbers, electrocatalysts, and surface modifying groups), each containing several constituent elements, can be dramatically simplified by first computationally screening the components for properties such as bandgap, redox potential, and electrochemical stability. Theory-guided, high-throughput experimental discovery has recently been applied successfully to complex materials discovery problems in both photoelectrochemistry[183] and flow batteries[184]. The large data sets that are emerging from these studies now offer opportunities for machine learning and prediction of new material combinations with enhanced properties[185].

Theory and simulation. A persistent challenge for artificial photosynthesis is the fundamental difficulty in understanding the time evolution of many-atom-many-electron photoexcited systems—from the moment that solar irradiation excites electrons, through and up to the point that electrons cool to the band edge or LUMO states. Methods for quantum-mechanical time evolution are highly developed, but each has critical shortcomings in terms of efficiency and accuracy, which make the simulation of excited-state reaction dynamics via first-principles methods difficult. A better understanding of photochemical dynamics can be achieved by developing and applying novel theoretical approaches that can capture the coupling between the excited electronic states and chemical dynamics—both at long timescales, with relevant system complexity, and with chemical accuracy. Progress can be achieved here by bridging methods that treat local "active" sites, such as density functional theory (DFT), quantum Monte Carlo, and quantum chemical (QC) calculations; atomistic simulations that account for hot-carrier dynamics; and continuum scale models that can effectively model the macroscopic behavior of plasmonic excitations and implicit solvent effects.

For electronic structure, further development is required to better understand the non-equilibrium structural and functional changes that occur as results of excited-state carriers. Methods are needed to improve the accuracy of predicting excited-state phenomena and to account for the dynamics induced by electronic excitations. Recent progress employing real-time time-dependent DFT shows promise for exploring the chemical dynamics of plasmon-driven systems at metal surfaces[186]. Expanding these

approaches to novel photocatalytic systems may provide new insights into how to use light to control chemical-reaction pathways, thereby enabling control of reactivity and selectivity.

Sidebar 16: Accelerated and AI-assisted discovery

The challenge of discovering multifunctional solar fuels materials has motivated advances in accelerated computational and experimental screening techniques, thus helping to elevate high-throughput screening from an optimization strategy to a framework for scientific discovery. The functionalities of a photoelectrocatalyst span from bulk electronic to surface chemistry properties, so a multifaceted search strategy is required.

A prolific discovery workflow summarized in **Figure S20** integrates theory and experiment to screen mutually compatible properties to guide the search to new photoanodes. Deploying such strategies uses and expands the capabilities of the Materials Project, a computational database of materials properties (https://materialsproject.org/) and has also been enabled by the development of a suite of high-throughput experimental methods specifically designed for solar fuels materials. The increasing role of data science in extracting fundamental knowledge from large data sets has added value to the high-throughput methods. The deployment of machine-learning techniques in computational catalysis has notably enhanced the speed and accuracy of catalyst screening. The emerging vision of autonomous materials discovery[187] offers a complementary approach to efficiently explore a materials search space by actively learning the performance trends. Generative models[188], which have yet to be sufficiently developed for solid-state materials, will further expand the purview of active learning to design materials based on desired properties.

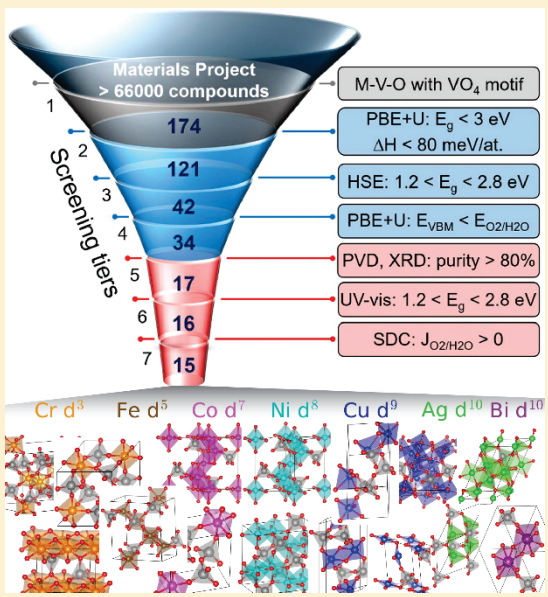

Figure S20. High-throughput screening with complementary theory and experimental methods rapidly identifies a breadth of candidate photoanodes. *Source: Taken from Q. Yan et al., Solar fuels photoanode materials discovery by integrating high-throughput theory and experiment, Proc. Nat. Acad. Sci. 114, 3040–3043, 2017*[189].

In addition, solar fuel chromophores, photoelectrodes, and catalysts often incorporate transition metals, benefiting from the complexity of the spatially localized and strongly correlated *d*-orbital electronic energy levels that provide vital moderate-strength bonds to enable both visible-light absorption and catalysis. Capturing the physics and chemistry of correlated electrons and of excited-state phenomena has long been a challenge for electronic structure theory[190, 191]. The time evolution of electronic excited states is less advanced, yet important progress has been made. Furthermore, the motions of ions on excited-state potential-energy surfaces (nonadiabatic dynamics/chemical dynamics) are often reduced to model systems in order to extract governing insights; but the applicability of these predictions to complex liquid solar

fuel systems is limited. Furthermore, the explicit incorporation of photon states in electronic structure modeling has led to intriguing insights in some demonstrations, but this approach is also not widespread. A pressing research need is to increase efficiency—and concurrently, incorporate all these elements of complexity (correlated electrons, excited states, chemical dynamics, photon-electron states)—and develop accurate methods for quantum modeling of photoelectrocatalysis.

Another fundamental aspect of exploring photocatalytic reactions is the need to understand complex molecule surface interactions in 3D architectures that can address reactivity and selectivity across multiple length and time scales. Pragmatically, methods such as DFT and QC calculations enable detailed insights into molecular-level interactions at active sites. However, there is growing evidence that implicit solvent models are not adequate. In this regard, approaches are needed that can efficiently include solvent interactions with the level of accuracy of electronic structure methods.

A second level of complexity is introduced by mid- and long-range interactions with second and outer coordination spheres. Hybrid approaches are unlikely to be adequate; these approaches include quantum mechanical / molecular mechanics, in which the active site is modeled with high-level electronic structure methods such as DFT and the second sphere is modeled with empirical potentials that are ultimately embedded within a continuum matrix. However, the expense of doing a full-atom calculation is also unrealistic with current computing platforms. Understanding how to connect molecular dynamics, interactions, and reactivity across scales is an ongoing challenge. Thus, advances are needed in both theoretical modeling of dispersion interactions at the level of DFT and fine-tuning of the connection across the relevant length scales of the simulation. Recently, a deep potential molecular dynamics model—a neural-network representation of the ab initio potential energy surface—has been developed to accurately model isotope effects in liquid water at a small fraction of the computational cost of conventional ab initio molecular dynamics simulations. This suggests a potentially promising path forward by applying data science approaches to more complex modeling problems[192].

A final question concerns understanding fluid flow within pores and at surfaces. Fluid dynamics simulations are critical to the introduction of feedstocks and removal of products from the active sites; yet, they couple poorly with electronic structure methods such as DFT. New techniques that help to bridge the domains of both these simulation techniques may be crucial to understanding selectivity. In this regard, efforts to understand the stochastic nature of reactions at an active site, along with kinetic Monte Carlo methods, may be useful for providing a link between the two disparate approaches.

Major research facilities. The DOE Office of Science operates a wide range of user facilities providing distinguishing capabilities, including x-ray and synchrotron sources, free electron lasers, high-intensity neutron scattering, and high-performance computing. For example, the Spallation Neutron Source (**Figure A2**) and the High Flux Isotope Reactor enable a broad range of techniques such as diffraction, reflectometry, quasi-elastic and inelastic scattering, and imaging that can provide unique insight into the structure and dynamics of materials.

The scattering cross sections of neutrons (see **Sidebar 17**) have different elemental dependencies from those of x-rays and are sensitive to nuclear spin. So neutron diffraction experiments are particularly valuable for determining the positions of light atoms and the ordering of spins in solid materials. The coherent neutron scattering lengths of protons and deuterons have opposite signs, which means that the contrast between water and other components of hydrated structures in neutron scattering experiments can be tuned by adjusting the hydrogen/deuterium ratio. This effect is especially useful in studying aqueous interfaces and composite materials that contain water, which are ubiquitous in solar fuel systems.

Figure A2. The Spallation Neutron Source at Oak Ridge National Laboratory. *Source: Oak Ridge National Laboratory.*

Sidebar 17: Neutron scattering for operando water measurement

Numerous experimental methods have been applied to the study of water, and these have, in turn, generated an extensive knowledge base. Among these methods, neutron scattering techniques are especially valuable for the in situ/operando study of both bulk and interfacial water as a result of the high penetration depth of neutrons. In addition, neutron scattering cross-sections can exhibit significant variations—in magnitude and sign—across specific nuclei. An especially important and relevant case is the difference between protons and deuterons. In essence, they have not only different coherent scattering lengths but also different signs, opening up numerous opportunities. For example, one can study water distribution and transport in operating devices; in addition, by varying the volume fractions of H_2O and D_2O, the water can be contrast-matched with other materials, making interfaces between these materials and water effectively invisible to neutrons. Thus, one can characterize the interfacial structure without contributions to the scattering by interfaces that are not of interest.

These studies can be extended to interfacial water via neutron reflectivity measurements at grazing incidence. At small angles above the critical edge, the specular neutron reflectivity is modulated by the interference of waves reflected from interfaces between materials of differing scattering length densities (SLDs) at different depths. Analysis of the reflected intensity yields a depth profile in the surface normal direction and, with the use of isotopic contrast variation, it can reveal water distribution in interfacial layers. **Figure S21** illustrates how this technique can be used to determine the structure of a thin film of hydrated Nafion—a perfluoroalkyl sulfonate ionomer widely used as a polymer electrolyte in electrochemical and photoelectrochemical energy-conversion devices. The high conductivity of protons in hydrated Nafion is thought to involve nanoscale water channels that are lined by anionic sulfonate groups. These channels percolate through a hydrophobic polymer phase that contains the perfluoroalkyl chains. Neutron SLD profiles recorded from the dehydrated film can be compared with those measured in films humidified by H_2O and D_2O to constrain a molecular-level model of the structure of the hydrated polymer thin film.

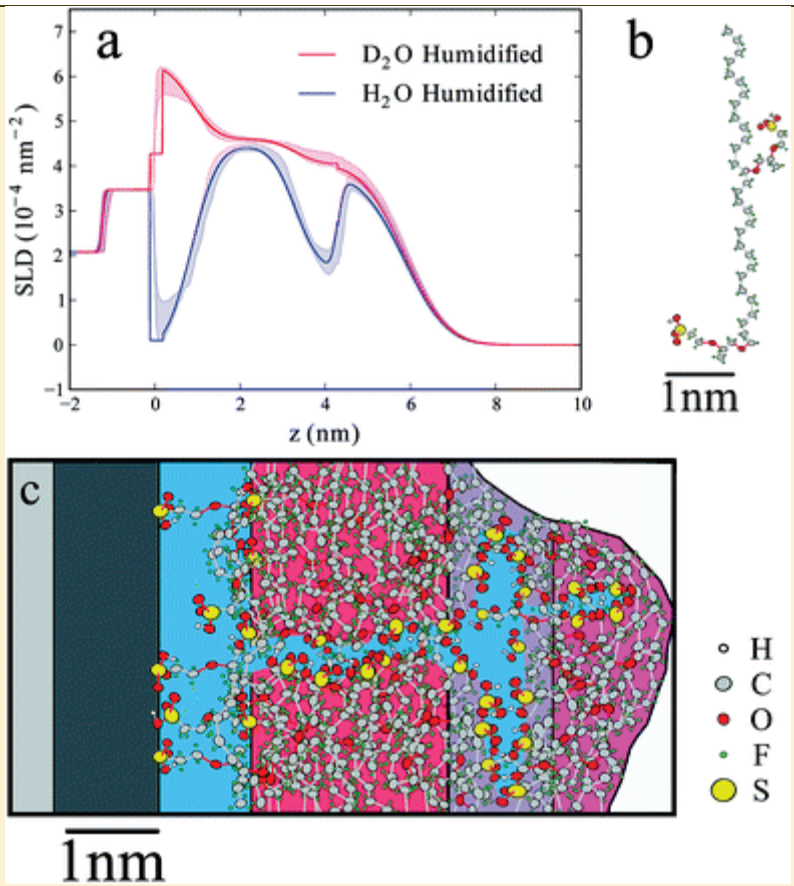

Figure S21. Proposed atomistic physical model for a Nafion film in a humidified environment based on a composition depth-profile determined using neutron reflectometry. *Source: National Institute of Standards of Technology Center for Neutron Research.* ***(a)*** *Neutron scattering length density (SLD) profiles for a partial fit to the physical model (solid lines) and 68% confidence intervals (shaded regions) for fits to H_2O- and D_2O-humidified vapor.* ***(b)*** *Nafion 1100 repeat unit, including both folded and unfolded side-chain morphologies.* ***(c)*** *Illustration of the physical model. Source: Reproduced from DeCaluwe, S. C., et al., Phase segregation of sulfonate groups in Nafion interface lamellae, quantified via neutron reflectometry fitting techniques for multi-layered structures, Soft Matter 10, 5763–5776, 2014*[193]*. Reproduced by permission of The Royal Society of Chemistry.*

Emerging soft, tender, and hard x-ray spectroscopies are being developed to probe transient electron-density changes at heteroatom, C, N, O, S ligand atom K-edges and transition metal L- and K-edge sites, respectively, within inorganic materials and metal coordination complexes. Atomic x-ray absorption edge energies directly measure and dynamically respond to shifts in excited-state electron densities at the spectroscopically selected atomic positions. In each case, sophistication in technique development has revealed milestone advances in the resolution of selective features of atomic and electronic structural dynamics in molecular modeling and simplified surrogate components of functional liquid solar fuel architectures. Advances in x-ray total scattering analysis, enabled by synchrotron x-ray sources, can provide atomic-level information about the structure of poorly crystalline materials. Combined with other synchrotron techniques, these methods yield insight into the molecular structure and electronic properties of an electrodeposited cobalt phosphate (CoPi) OER catalyst, as shown in **Figure A3**. Advances in materials development for liquid solar fuel systems will be enabled by further development of these synchrotron-based techniques.

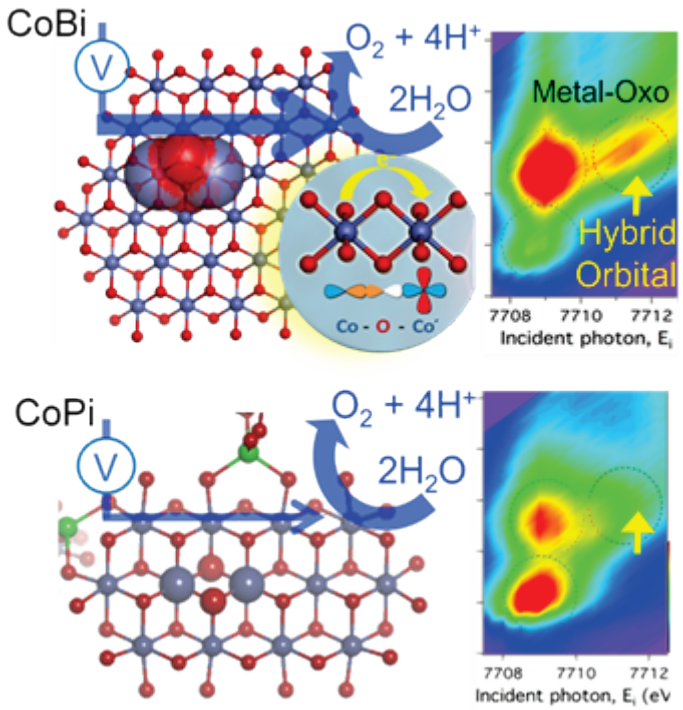

Figure A3. A combination of L-edge synchrotron x-ray absorption, resonant x-ray emission, resonant inelastic x-ray scattering, resonant Raman scattering, and high-energy x-ray pair distribution function analyses that identify electronic and structural factors correlated to the charge-transport differences of Co-oxide OEC thin films in the presence of borate (CoBi) and phosphate (CoPi). *Source: Reprinted from Kwon, G. et al., Resolution of electronic and structural factors underlying oxygen-evolving performance in amorphous cobalt oxide catalysts, J. Am. Chem. Soc. 140, 10710–10720, 2018. Copyright 2018 American Chemical Society*[194].

Parallel and high-speed calculations are the lifeblood of theoretical research in the physical sciences. For complex multicomponent, multiple length- and time-scale problems such as solar fuels generation, a suite of computational tools is required; all of these tools are computationally extremely intensive, and many of them are also intensive with regard to internal memory and/or disk memory. Many others rely crucially on extremely fast interconnects between processors. Some of these calculations (e.g., QC, molecular dynamics) have been successfully ported to emerging graphics processing unit architectures, and this trend could greatly accelerate progress in these fields. For all of these research directions, the concentrated investment; expert installation, maintenance, and consultation; and collaboration with DOE theoretical scientists are vital contributions to the success of endeavors such as solar fuel understanding and discovery. Furthermore, DOE supercomputer facilities lead innovation in scientific computation approaches and the dissemination of the benefits of these computations to the wider scientific computing community.

Appendix B: Liquid Solar Fuel Roundtable Attendees

Invited Roundtable Participants

Selectivity Panel (Lead: Wendy Shaw, Pacific Northwest National Laboratory)

John Gregoire, California Institute of Technology
Leif Hammarström, Uppsala University
Hannah Shafaat, Ohio State University
Yogi Surendranath, Massachusetts Institute of Technology
Jenny Yang, University of California–Irvine

Integration Panel, (Lead: Kara Bren, University of Rochester)

Harry Atwater, California Institute of Technology
Curtis Berlinguette, University of British Columbia
Javier Concepcion, Brookhaven National Laboratory
Sophia Haussener, École Polytechnique Fédérale de Lausanne (EPFL)
Wilson Smith, University of Colorado/National Renewable Energy Laboratory

Durability Panel (Lead: Shane Ardo, University of California–Irvine)

Héctor Abruña, Cornell University
Kathy Ayers, Nel Hydrogen
Frances Houle, Lawrence Berkeley National Laboratory
Daniel Esposito, Columbia University

Cross-Cut Panel (Lead: Andrew Rappe, University of Pennsylvania)

Valentino Cooper, Oak Ridge National Laboratory
Suljo Linic, University of Michigan
Yang Shao-Horn, Massachusetts Institute of Technology
David Tiede, Argonne National Laboratory

Chair:

Bill Tumas, National Renewable Energy Laboratory

Co-Chairs:

Jillian Dempsey, University of North Carolina–Chapel Hill
Tom Mallouk, University of Pennsylvania

Speakers:

Harry Atwater, California Institute of Technology
Leif Hammarström, Uppsala University

Invited Observers

Aaron Appel, Pacific Northwest National Laboratory
Chris Bradley, Office of Basic Energy Sciences
Chris Fecko, Office of Basic Energy Sciences
Bruce Garrett, Office of Basic Energy Sciences
Chris Hahn, SLAC National Accelerator Laboratory
Craig Henderson, Office of Basic Energy Sciences
Stephen Herbert, Office of Basic Energy Sciences
Linda Horton, Office of Basic Energy Sciences
Jim Horwitz, Office of Basic Energy Sciences
Refik Kortan, Office of Basic Energy Sciences
Jeff Krause, Office of Basic Energy Sciences
George Maracas, Office of Basic Energy Sciences
Alex Martinson, Argonne National Laboratory
Daniel Matuszak, Office of Basic Energy Sciences
Gail McLean, Office of Basic Energy Sciences
Eric Miller, Office of Energy Efficiency and Renewable Energy
Raul Miranda, Office of Basic Energy Sciences
Nate Neale, National Renewable Energy Laboratory
Sunita Satyapal, Office of Energy Efficiency and Renewable Energy
Viviane Schwartz, Office of Basic Energy Sciences
Michael Sennett, Office of Basic Energy Sciences
Grigorii Soloveichik, ARPA-E
Andrew Sutton, Los Alamos National Laboratory
Javier Vela-Becerra, Ames National Laboratory
Kevin Wilson, Lawrence Berkeley National Laboratory
Brandon Wood, Lawrence Livermore National Laboratory
Zili Wu, Oak Ridge National Laboratory
Brenda Wyatt, Oak Ridge National Laboratory

Appendix C: Liquid Solar Fuels Roundtable Agenda

BES Roundtable on Liquid Solar Fuels
Hilton Rockville
1750 Rockville Pike, Rockville, MD
August 20–21, 2019

Tuesday, August 20, 2019

7:00 – 8:00 a.m.	**Registration/Continental Breakfast – Plaza II and III**
8:00 – 8:15 a.m.	Welcome and Roundtable Charge (BES leadership)
8:15 – 8:30 a.m.	Introduction of Chairs, Panel Members, Participants
8:30 – 8:50 a.m.	Roundtable Goals and Logistics, Bill Tumas (Chair), NREL
8:50 – 9:30 a.m.	Plenary Lecture: Harry Atwater, Caltech
	Joint Center for Artificial Photosynthesis: Approaches/Remaining Challenges for Solar Fuels
9:30 – 10:10 a.m.	Plenary Lecture: Leif Hammarström, Uppsala University
	Solar Fuels in Europe: Perspective on Strategies, Approaches and Vision of Challenges
10:10 – 10:25 a.m.	**Break**
10:30 – 11:20 a.m.	High Level Overview of Liquid Solar Fuels (Roundtable co-Chairs)
	Tom Mallouk, University of Pennsylvania and Jillian Dempsey, University of North Carolina
11:20 – 11:30 a.m.	Discussion on Clarity of Scope, Processes and Logistics
11:30 – 12:00 a.m.	*Breakout Session I*: Convene panel breakouts
	Panel lead introduction—10 minutes
	Panel 1: Selectivity, Wendy Shaw, PNNL—Plaza II and III
	Panel 2: Integration, Kara Bren, University of Rochester—Plaza I
	Panel 3: Durability, Shane Ardo, University of California–Irvine—Regency
	Cross-Cut Panel, Andrew Rappe, University of Pennsylvania—Wilson
Noon–1:00 p.m.	**Working lunch**
1:00 – 2:45 p.m.	*Breakout Session I (cont.):* Development of key science challenges and draft PROs
2:45 – 3:00 p.m.	**Break**
3:00 – 4:00 p.m.	Report-outs from each panel by panel leads (15 minutes each)
	– Key ideas/challenges/approaches; first draft of PROs from panels
4:00 – 5:30 p.m.	*Breakout Session II:* Revise, refine, prioritize, integrate (across panels) PROs based on report-outs
5:30 – 7:30 p.m.	**Dinner on your own [panel leads and chairs meet to develop evening presentation]**
7:30 – 8:30 p.m.	Debrief to roundtable and discussion of PROs, agenda for next morning, and possible reconfiguration of panels: Bill Tumas, Jillian Dempsey, Tom Mallouk

Wednesday, August 21, 2019

7:00 – 8:00 a.m.	Continental Breakfast
7:30 – 8:00 a.m.	Panel leads and chairs meet over breakfast (Regency)
8:00 – 9:00 a.m.	Panel leads present new PROs (10 min each), 20 minute discussion
9:00 – 10:45 a.m.	Reconvene breakout groups to revise, refine, and finalize draft PROs
10:00 – 11:00 a.m.	**Break**
10:45 – 11:15 a.m.	Panelists work on sidebars, graphics, etc. and chairs/panel leads meet
11:15 – Noon	Presentation of final PROs and discussion
Noon	Roundtable adjourns

Noon–5 p.m. ***Writing team assembles (by invitation only)***

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