



**JCAP**

JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

# Joint Center for Artificial Photosynthesis



**ENERGY INNOVATION HUB**

2010-2020



F127  
50 mL Ethanol

Cellulose  
45  
S-19

100 mL  
PYREX®  
1999



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# Director's Message



## Harry A. Atwater

Howard Hughes Professor of  
Applied Physics and Materials Science  
California Institute of Technology

*We are excited to have you join us for this reflection and outlook on a field of artificial photosynthesis to generate solar fuels, which has advanced over the last ten years from an embryonic science discipline. Solar fuels research now combines theory, modeling, accelerated materials discovery, insights about catalytic mechanisms, operando measurement and prototyping. First cohorts of solar-fuels generators for hydrogen production are now on a path towards reaching theoretical efficiency for model systems.*

*Many challenges remain, related to materials durability, achieving record efficiency with inexpensive, abundant materials, as well as generation of useful chemical products from carbon dioxide and nitrogen. Importantly, a big challenge for the solar fuels field is unlocking the combination of insights about catalysis, light-harvesting, and product separation that are scalable and durable, giving future technologists new options for generation of a portfolio of gaseous and liquid fuels, chemicals and materials.*

*Artificial photosynthesis is still a very young field, since we have just barely begun to understand and harness processes like the ones that nature uses in photosynthesis to generate products with exquisite selectivity in robust, repairable systems. We stand at a watershed moment where solar fuels has the opportunity to mature into a science field truly capable of harvesting sunlight for efficient and selective generation of desired products in durable systems.*

# Scientific Advancements

## Integrated systems design for high performance

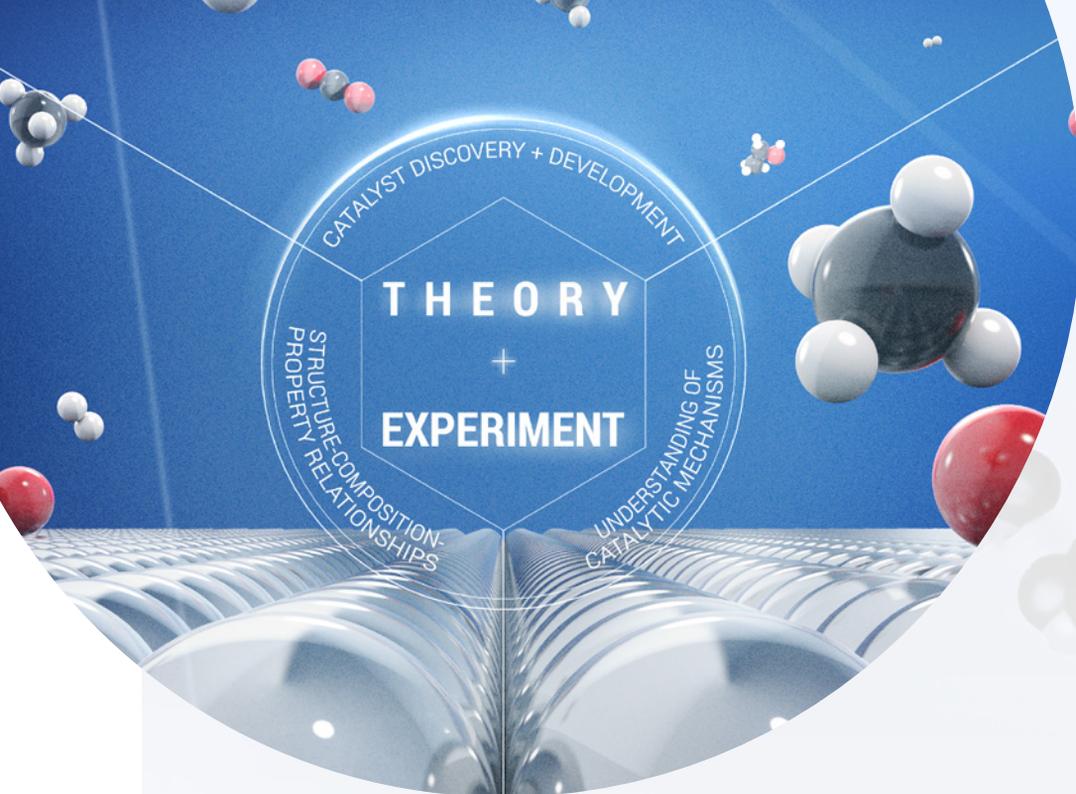
Solar fuels systems combine photoexcitation, chemical transformation, and transport processes to produce fuel. A fundamental challenge in creating these systems is how to design each component so that the resulting combination produces fuel as efficiently as possible. A typical system includes light absorbers, oxidation and reduction catalysts integrated with them, membrane separators, water, and CO<sub>2</sub> when carbon-based fuels are the target.

Solar-driven water-splitting systems are used to generate hydrogen. Over time, JCAP has progressively improved liquid electrolyte-based systems to increase their solar energy-to-chemical energy efficiency performance from <1% to 19.3%. JCAP researchers have also demonstrated high efficiency and stability in a vapor-fed light-electrochemical system using pure water, which minimizes corrosive conditions. Other discoveries include designing a light-driven cathode useful for liquid electrolyte systems, identifying gas diffusion electrode architectures as being particularly useful for CO<sub>2</sub> reduction, and exploiting potential multistep strategies that reduce CO, which can be formed as a reaction intermediate. These efforts establish technology-driven performance criteria for individual materials and integrated systems that guide materials discovery and development efforts.

## Improved performance

One of JCAP's goals has been to demonstrate solar fuels generation with a solar energy-to-chemical energy conversion efficiency higher than that of plants. This has required improvements in all materials used in solar fuels systems, as well as in the systems themselves. The best light absorbers would be stable under illumination in the water and electrolyte environment around them, absorb the solar spectrum efficiently, and produce enough photovoltage. While the main effort has been to satisfy these requirements using thin films, JCAP has also investigated nanostructure assemblies that enable absorption of light across the spectrum, an additional route to improved efficiency. JCAP





has developed a high-throughput experiment-theory capability to identify the best-performing materials and integrated light absorber-catalyst systems, leading to the exploration of complex compositions with the needed physical and chemical attributes.

### **Improved durability**

Solar fuels systems must be designed to operate for years outdoors: their active components must be both long-lasting and able to withstand daily temperature cycling and seasonal weather. This requires preventing corrosion at the liquid-solid interface caused by the catalyst dissolving. JCAP has reported strategies for stabilizing systems while ensuring >10% solar energy-to-hydrogen conversion efficiency with full product separation for safety. These strategies include the use of protection layers and hybrid composite coatings to prevent corrosion in very acidic or basic electrolyte environments, including materials with the ability to recreate their own protective surface layer. Alternatively, high-performance protection layers can be deposited to prevent corrosion while facilitating charge transport within the layer and at its interface with the electrolyte.

### **Membranes for solar fuels**

Polyelectrolyte membranes separate the two regions of electrochemical devices, the anode and the cathode. For solar fuels systems to be efficient, these membranes must minimize crossover of electrochemical products. But the membranes must be permeable enough to conduct ions between the regions. JCAP has focused on three areas of this problem. First, JCAP researchers have studied anion-conducting membranes with polymers that are stable when operated in electrolytes in a basic



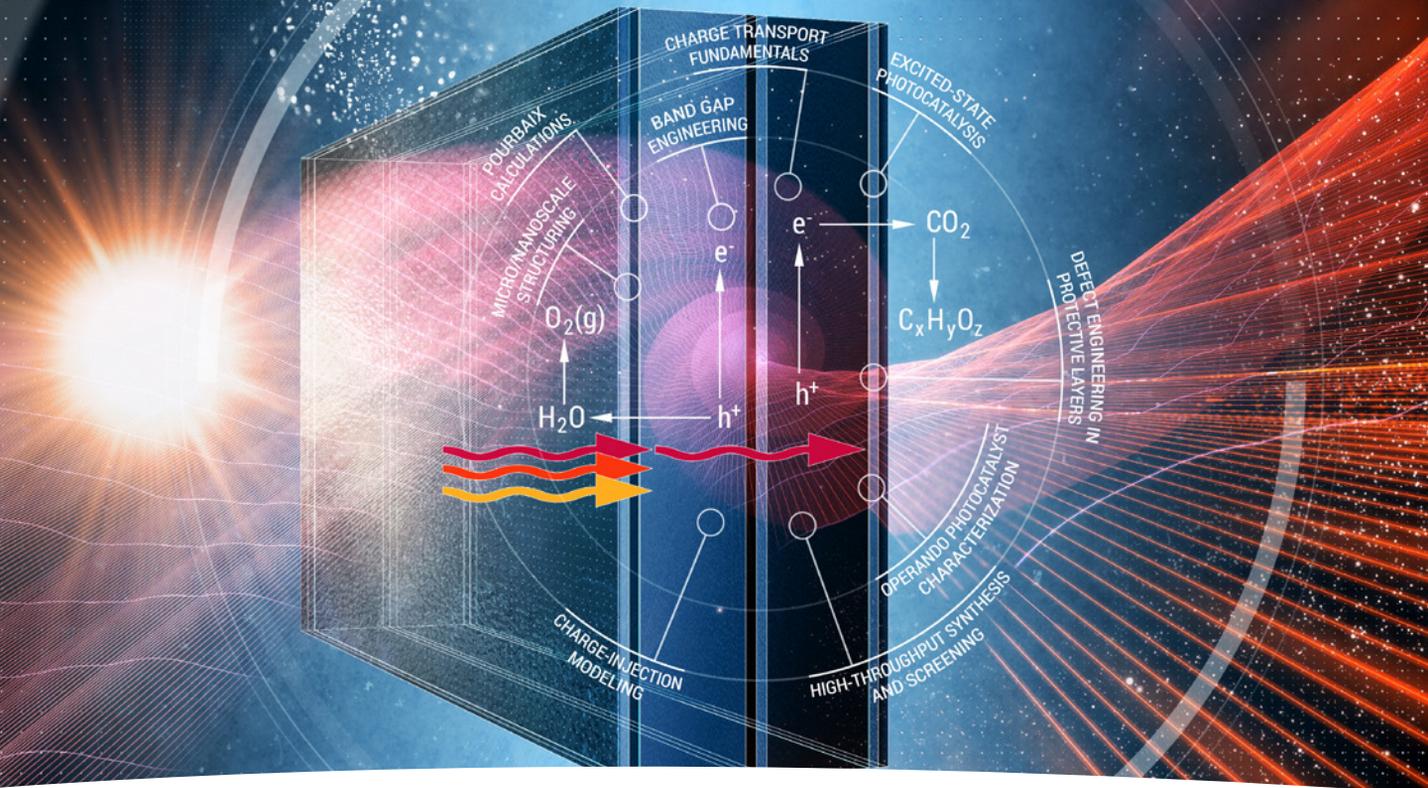
environment. Second, researchers have studied the correlation between polymer composition and permeability through synthesizing a series of related polymers and measuring their permeability and conductivity properties. Third, theories that explain permeability apply only to steady-state operation. But daily and seasonal variability in solar intensity means real systems will not operate this way. By studying time-dependent permeability, JCAP researchers have learned the membranes can behave differently when not operating in steady-state conditions.

### **Advances in catalytic activity**

Two catalysts are required for the water-splitting process: one for oxygen evolution, or separating the water, and typically one for hydrogen evolution, or assembling hydrogen from the separated water. Oxygen evolution must occur in either a very acidic or a very basic environment, but oxygen evolution catalysts are unstable in acidic environments. JCAP researchers have made progress in finding acid-stable oxygen evolution catalysts and in finding better functioning catalysts for basic environments.

JCAP has also made advances in using a carbon dioxide conversion catalyst in place of a hydrogen formation catalyst in order to make carbon-based fuels. Researchers have confirmed that copper and its alloys are the only materials able to function efficiently enough for this process and that the surface structure of the copper catalyst is important in being able to create desired products.

For the CO<sub>2</sub> conversion process, JCAP has explored using two different catalysts working in tandem, one to reduce CO<sub>2</sub> to CO and the other to reduce CO to the desired products, rather than relying on one catalyst for the full process. JCAP has also advanced the state of the art of using experimental techniques to look at catalysts and the catalytic process in operation.



## Selective catalytic environments

JCAP has investigated combinations of materials, catalytic environments, electrolytes, and operating conditions that improve efficiency and the ability to produce desired products while avoiding mechanisms that would deactivate catalysts. While water splitting occurs most efficiently in extremely acidic or basic electrolyte environments, reducing CO<sub>2</sub> using copper requires neutral to basic electrolytes. JCAP has investigated how the concentration and kinds of cations and anions present in a solution influence the efficiency of CO<sub>2</sub> reduction. Water plays a role not only as a source of hydrogen, but also through its interactions with interfacial intermediates. JCAP researchers have learned that molecular additives, such as pyridiniums in the electrolyte, as well as polymeric overcoats on copper surfaces, improve the ability to produce desired products.

## Connecting photoexcitation and chemical reactions

Semiconductor light absorbers provide the electrons and holes required for artificial photosynthesis. JCAP has performed studies that trace generation, relaxation, and loss processes of charge carriers using transient absorption, conversion efficiency, and light-emission techniques. These studies have provided information on how the composition and structure of light absorbers affect charge carrier generation. This may allow the use of lower cost alternatives to certain semiconductors, such as metal oxides that typically suffer from low charge carrier mobility and photovoltage. The use of light-absorbing cathodes to control selectivity for CO<sub>2</sub> reduction has been an important goal for JCAP. Because traditional materials that convert light into chemical energy efficiently, such as cuprous oxide, are unstable, new materials are being sought using theory as a guide. JCAP has investigated the use of light-generated hot carriers (holes or electrons with very high kinetic energy) and different structures to couple light to chemical reactions.

To learn more, see our publications [here](#).

# New Research Tools and Capabilities

## High-throughput experimentation and theory capability for materials discovery

JCAP has established a high-throughput pipeline to discover new light absorbers, photocatalysts, and electrocatalysts using advanced mathematical techniques. Experiment and theory are combined to identify functional solar fuels materials. Rapid characterization using high-performance scanning instruments, such as the scanning droplet cell and online mass spectrometry, allows materials and interfaces with desired properties to be identified and then synthesized on a larger scale for in-depth study. An extensive, thorough, and searchable [Materials Experiment and Analysis Database \(MEAD\)](#) and associated big-data science techniques have resulted from the work and are available to the materials community.

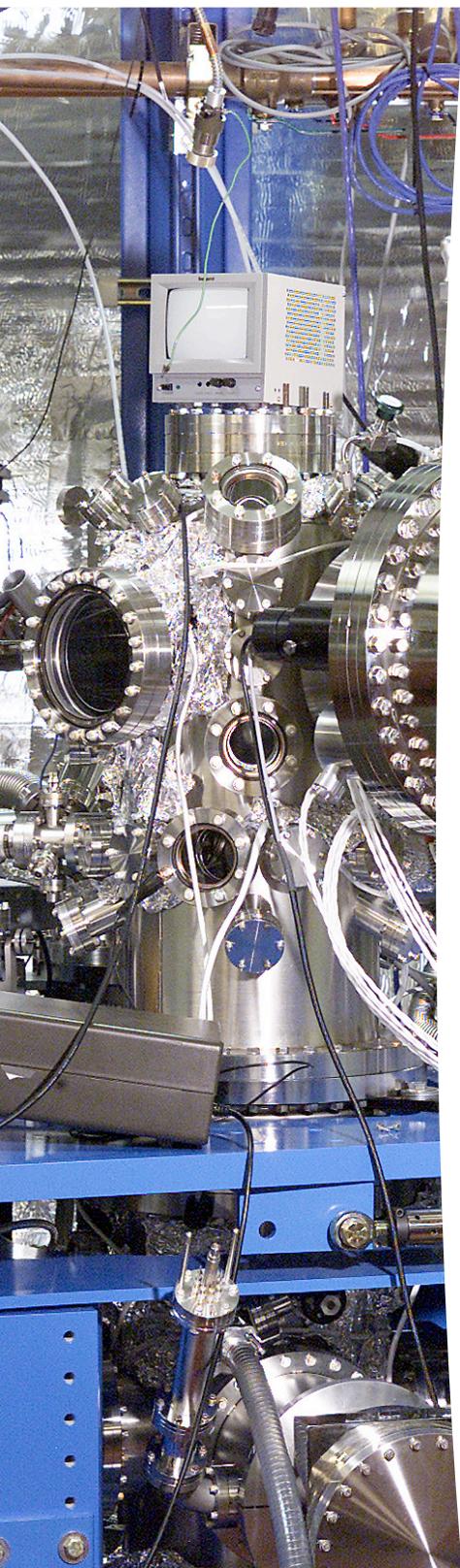
## Benchmarking

To help advance the field, JCAP has developed standardized measurement protocols for solar fuel generation reactions. Standard instrumentation, protocols for operating this instrumentation, and best practices for reporting and visualizing the resulting data have been detailed in several papers. These methods have been applied to establish an extensive database of benchmarked thin film and nanoparticulate electrocatalysts for water oxidation and hydrogen generation, essential parts of the process to generate solar fuels. JCAP has also developed standardized cells and analytical methods to quantify CO<sub>2</sub> reduction products. The cell designs and methods have been published for use by the scientific community.

## In situ and operando capabilities

JCAP researchers have expanded methods for laboratory- and synchrotron-based in situ and operando studies of electrocatalysis. Work at the synchrotrons (a particle accelerator that generates x-rays) involved partnerships with the Advanced





Light Source at Lawrence Berkeley National Laboratory and the Stanford Synchrotron Radiation Lightsource at SLAC National Accelerator Laboratory. New techniques developed through these partnerships include real-time studies of chemical transformations, and electronic characteristics of electrolyte-electrocatalyst interfaces and electrocatalyst structure while in contact with liquid electrolyte or humidified vapor. Each of these techniques is now available to the user community.

### **Prototyping**

JCAP's prototypes have provided platforms to study solar fuel systems and their components, including new catalysts and light absorbers, and to enable testing of durability over time under well-controlled conditions. They have also allowed additional factors affecting efficiency and performance to be identified and explored. Publications from JCAP researchers describe solar water splitting devices and CO<sub>2</sub> reduction systems using liquid electrolytes, vapor-fed systems, and membrane-electrode assemblies that improve efficiency and durability.

### **Theoretical methods for electrochemical systems**

Computational code and techniques developed by JCAP's theory researchers have been used extensively in the Hub's science programs. These have been placed in open source or open access for use by the community. They include codes for nonadiabatic molecular dynamic simulation, codes for calculating Pourbaix energetics and electronic excitation and dynamics in solids, and a suite of electronic structure and dynamics tools using quantum embedding and machine learning methods.

[To learn more, see our publications here.](#)

# Alumni News



*Many of JCAP's scientific advancements were realized by the hard work of excellent early career scientists and engineers: graduate students, postdocs, and staff. JCAP alumni can now be found working at US and international universities and US National laboratories, as well as in industry.*



**Ivonne Ferrer** is an analytical chemist, who came to JCAP to work in the catalyst benchmarking laboratory at Caltech. As part of the benchmarking team, Ivonne helped develop standardized methods to analyze different chemical and physical properties of solar fuels materials. After completing her work at Caltech, Ivonne joined Dow Chemical as an analytical chemist. She has recently moved to become the Associate Analytical Manager at Corteva Agriscience, where she is using her technical training as well as team collaboration skills she learned in JCAP.

When asked about her memories from the time in the Hub, Ivonne recalls the beautiful open labs in the Jorgensen building, Caltech's turtle pond, as a "Zen place" to think, and the JCAP nightcaps that brought "the family together" at 5 PM on Friday nights in the Jorgensen lobby: "we have built this community where we were all helping each other, trying to figure out...all working towards the same goal." She also has fond memories of the All Hands meetings: "I love the All Hands Meetings. I love the All Hands Meetings so much, that when I got hired at Dow, I asked to start after the All Hands Meeting, so that I could go to my last one."

Now at Corteva, Ivonne leads a team of 10 scientists, who are charged with running a large analytical laboratory. Ivonne has been developing and improving analytical methods, creating new analytical tools to identify impurities, and making on-line tools available. She says, "I really like industry because it allows me to bring my knowledge into real life." As part of her job, she works with many different people and tackles various technical problems. One of the lessons learned from the Hub and that helps her in the current job is that "where you have a bunch of different backgrounds and a bunch of different brains working together, (it) pushes you to find something that doesn't yet exist out there."

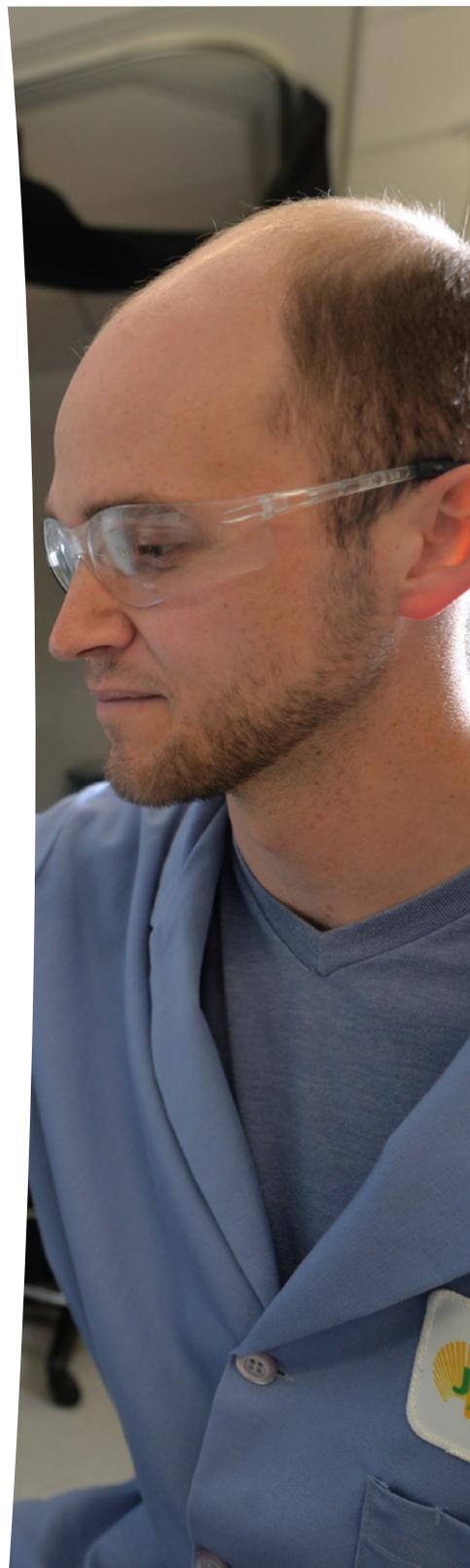
[You can learn more about Ivonne's work here.](#)

**Kurt Van Allsburg** is a Research Scientist at the National Renewable Energy Laboratory (NREL). He went to NREL as a postdoc after completing his doctoral work at UC Berkeley with Prof. T. Don Tilley. Kurt worked at LBNL and JCAP for approximately six years and was one of the first JCAP graduate students. As a synthetic inorganic chemist, he recalls that working in JCAP “was exciting and fun,” in part because he and other chemists were “exposed to the broad range of applied research, as well as to device physics and assembly.” Since Kurt’s JCAP research focused on transplanting catalyst units from delicate biological settings to the often harsh conditions of artificial photosynthesis, this exposure was key to his success. JCAP gave Kurt “the opportunity to work in a translational way, bringing together fields of expertise and practicing talking to different groups.” He continued to apply these skills when he moved from JCAP to NREL.

As recent example, Kurt and his NREL colleagues “built a catalyst costing tool (CatCost) that allows researchers to understand what it would look like to produce their material at industrial scale.” To build the tool, Kurt, the CatCost Lead Developer, had to engage potential users, scientists, industry partners, and web development teams. He really liked “being in that role where you’re helping all these groups understand each other and getting science done.” When asked why he chose to work at the DOE lab, Kurt said that “what attracted me to that position (was that) I’ve been able to get involved in a huge range of projects from building computational databases to allow theoretical catalysis researchers to better collaborate, to making and testing catalysts via new methods in the lab.”

As for many JCAP alumni, when asked about the most memorable and interesting time in JCAP, Kurt said “definitely the All Hands” meetings: “I really enjoyed the forced discussion and sometimes things would ignite into heated debate. I think it is really helpful in doing this sort of team science effort to feel that you had a personal connection to the other people on the team.” Overall, Kurt feels that his positive experience in JCAP helped lead him to his current role in the Catalytic Carbon Transformation and Scale-Up Center at NREL, where large groups of researchers pitch in on grand challenges facing the world of energy catalysis.

[You can learn more about Kurt’s work here.](#)



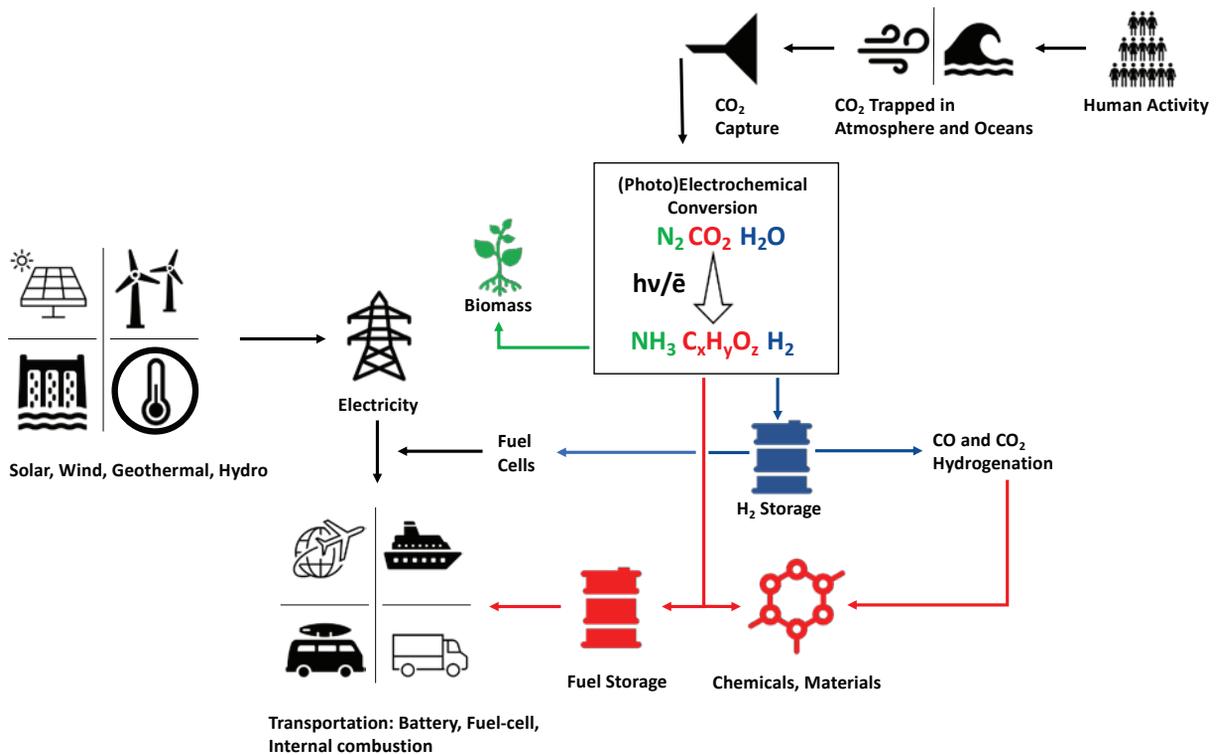


**Jenny Yang** is a chemist who came to Caltech to be a lead staff scientist in JCAP's Molecular Catalysis project from Pacific Northwest National Laboratory (PNNL), where she was a key investigator in a DOE EFRC and the Lab's Directed Research and Development Project in electrocatalysis. In JCAP, Jenny's work focused on synthesis and analysis of molecular electrocatalysts. When asked about what she remembers fondly about JCAP, she mentions JCAP nightcaps and working together with students, postdocs and staff. She stays connected with people from JCAP.

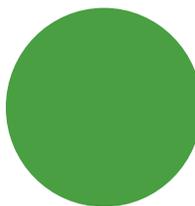
Jenny left Caltech for UC Irvine, where she is an Associate Professor of Chemistry leading a group of 15 young researchers. "I still work in the area of solar fuels, from electrocatalyst development to immobilizations onto electrodes." In addition, "a new area for us is electrochemical CO<sub>2</sub> capture and concentration." Although becoming a professor may not have always been her plan, it awards the academic freedom and opportunity to do innovative research: "I can work on problems I think are important and determine the best way to solve them." In 10 to 15 years, Jenny sees this field moving towards "using a more diverse set of feedstock materials to make both fuels and materials, for example replacing petroleum as a feedstock for plastics (manufacturing)."

**You can learn more about Jenny's current research and her research group [here](#).**

# Into The Future



Many scientific achievements have been made in the search to develop chemistries to generate solar fuels through artificial photosynthesis. But a number of crucial challenges remain to be overcome in order to build a robust system that transforms sunlight, water, and carbon dioxide into transportation fuels for the nation.



## **Durability**

Solar fuels systems must be designed to operate for years outdoors. That means their active components must be both long-lasting and able to withstand daily temperature cycling and seasonal weather. Current components of solar fuels systems have limited lifetimes, and corrosion remains a problem. New work is needed to design, discover, and develop high-performing and durable components. New research is also needed to mitigate corrosion and circumvent other processes that reduce components' lifetimes.

## **High-performing Systems and Components**

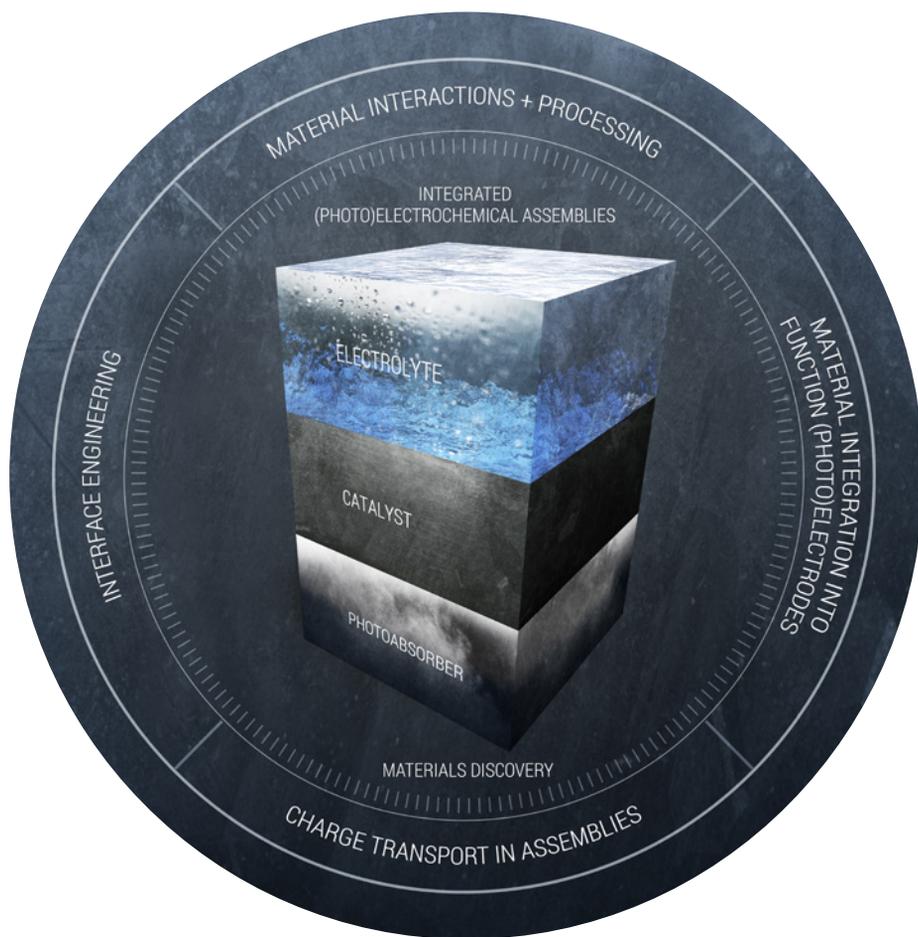
Integrating individual components into solar fuels systems is a challenge because these components can perform differently within a system than on their own. Fundamental research is needed to provide a mechanistic understanding of how individual components and processes interact. This will allow better design of both components and systems for high performance.

## **Fuel Generation**

Two essential parts of the artificial photosynthesis process, carbon dioxide reduction and water splitting, need to be improved for future solar fuels systems. Goals include the ability to efficiently control for and select a single desired fuel product, to ensure water splitting occurs efficiently and with a rate matched to the fuel production rate, and to ensure catalytic surfaces do not degrade or become inactive.

## **Using Sunlight Effectively**

Current systems separate the process of light absorption from the catalytic reactions that generate fuels. Overall system efficiency could be improved by directly coupling diverse light-driven phenomena and chemical processes. Exploiting light-matter interactions could open up new mechanisms to outperform conventional electrochemical reactions or use more of the solar spectrum.

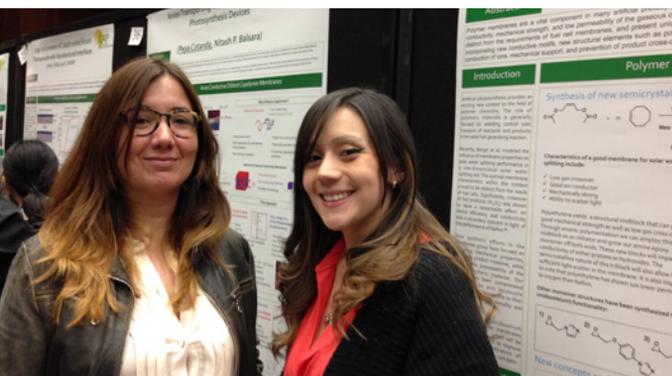
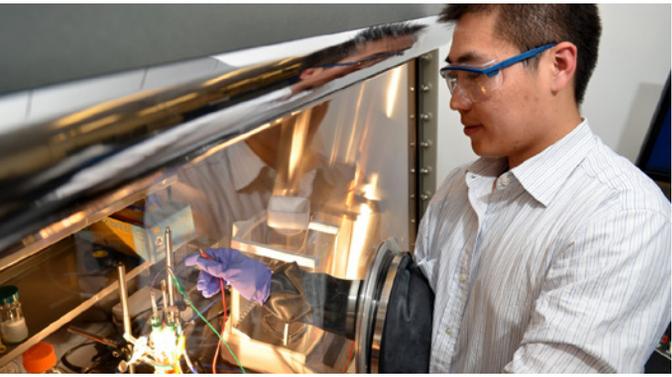


## Development of Standards

Early-stage applied research invariably reveals problems with once-promising materials and assemblies that limit their usefulness. This necessitates a return to fundamental science to solve these problems, and then back to applied science to test the solutions, creating a cycle of learning. The combination of fundamental science in an applied context, and applied science in a strong fundamental science organization, provides the best opportunity for making rapid progress toward a technology for solar fuels. This approach could also play an important role in developing and validating the testing and analysis of components and systems resulting from solar fuels research. This would establish common standards for the field and provide a way to confirm claims made about solar fuels systems prototypes.

## Methods and Tools

Improvements in methods and tools used to develop solar fuels are needed to advance the field. Examples include finding new measurements to enable mechanism discovery and validation through in operando observations, developing accurate theoretical methods for large multiphase electrochemical assemblies, and learning whether systems that do not require large flat areas to capture and use sunlight are possible.



**Editors:** Xenia Amashukeli, Frances Houle,  
Mabby Howard

**Art Direction and Design:** Xenia Amashukeli,  
Berkeley Lab Creative Services

**Writers:** Jessica Scully, Frances Houle,  
Xenia Amashukeli

**Photography:** Robert Paz, Weilai Yu,  
Xenia Amashukeli, Julianne Just

**Artwork:** Darius Siwek, Xenia Amashukeli

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## CONNECT WITH US

[solarfuelshub.org](http://solarfuelshub.org)

[info@solarfuelshub.org](mailto:info@solarfuelshub.org)

### JCAP @ Caltech

California Institute of Technology  
Jorgensen Laboratory, Mail Code 132-80  
1200 East California Boulevard  
Pasadena, CA 91125

### JCAP @ LBNL

Lawrence Berkeley National Laboratory  
1 Cyclotron Road, Mail Stop 30R0205  
Berkeley, CA 94720



**Caltech**



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**UCI**