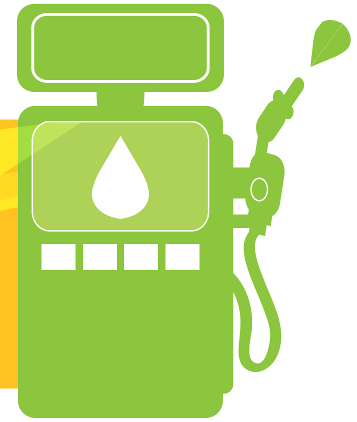
Pictured: Aniketa Shinde, materials instrumentation engineer at JCAP from 2013–19

Everything under the SUN

by Andrew Moseman



Within the Joint Center for Artificial Photosynthesis, researchers have spent the past decade pursuing breakthrough chemistry to convert sunlight into fuels capable of meeting humanity's growing energy needs.

Nature has had billions of years to perfect the marvel of photosynthesis, in which light energy from the sun powers a reaction between carbon dioxide and water inside plants (and certain bacteria) to create food. Of all the light plants receive, however, just 1 percent is used for this process. Although that may sound terribly inefficient, it is anything but: that smidgen of sunshine provides plants with 100 percent of the energy they require.

Humanity, on the other hand, has much more intensive energy needs. To meet those needs, the world continues to rely on dirty or dangerous sources including coal, oil, and nuclear to power the electricity grid, cars and airplanes, and industrial enterprises. And yet, every hour of the day, enough sunlight shines on Earth to power all of human civilization for an entire year. The challenge is the same one plants address through photosynthesis: to transform the light of the sun into viable forms of energy. To meet society's needs sustainably, however, we must convert a much larger percentage of that sunlight into fuel than plants do, on a vastly larger scale, all while creating a fuel that is more readily useable in our society.

That is why, a decade ago, the Department of Energy funded a new Energy Innovation Hub called the Joint Center for Artificial Photosynthesis (JCAP), led by Caltech and with primary sites both at Lawrence Berkeley National Laboratory (LBNL) and on campus. In JCAP, Caltech partners with researchers from LBNL, the SLAC National Accelerator Laboratory, UC Irvine, and UC San Diego. JCAP brought together a diverse team of chemists, physicists, materials scientists, engineers, and other researchers in the search for bold new ways to improve on nature's processes in the creation of "solar fuels" (products such as hydrogen fuel and hydrocarbons) using nothing more than sunlight and basic molecules such as water and carbon dioxide.

During their 10-year run, JCAP scientists have set new records for artificial photosynthesis by increasing solar-to-chemical energy efficiency performance from less than 1 percent to 19 percent and by designing highly stable solar-fuels generators. These efforts established performance criteria for individual materials and integrated systems that guide materials discovery. Together with the world's largest materials library, built by JCAP, these efforts laid the basic-science groundwork for a new energy economy.

"I think we have a real opportunity to draw up a blueprint and a scientific path for creating not only solar fuels but also essentially all of the processes that we use for industrial production," says Harry Atwater, Howard Hughes Professor of Applied Physics and Materials Science and director of JCAP.

Why Solar Fuels?

"At the California Institute of Technology, they're developing a way to turn sunlight and water into fuel for our cars." In that one line from his 2011 State of the Union address, President Barack Obama illuminated JCAP's mission: to discover renewable, solar-driven ways to create the kinds of liquid fuels, including hydrocarbons, that can be useful for powering cars, homes, and factories.

"When we burn fuels in a car or a jet engine or a boat, we start with hydrocarbons and we spit out carbon dioxide and water. Now we want to take that carbon dioxide and water and recycle it back into the fuel," says Tom Jaramillo, a JCAP team member and associate professor at Stanford University and SLAC.

Solar fuels promise to do what other renewable energy alternatives cannot. Liquid fuels can be easily stored and used anytime. Photovoltaic solar panels, by contrast, can soak up rays only when the sun shines, and they require major improvements to battery technology to store electricity for later use. An increasing number of electric cars have joined America's highways, but their batteries have a limited range to go with their long recharge times. The truth is, Atwater says, batteries generally cannot match liquid fuels in their ability to store a lot of energy in a small volume.

"I have a Tesla parked in my driveway, so I voted with my wallet that a battery vehicle is a good solution," Atwater says. "But if you look at the entire global vehicle fleet of 80 million vehicles, it's clear that they're not all going to go electric. And so we have to have some zero-carbon solution for all of them."

When JCAP launched in 2010, Atwater says, its scientists knew that to produce liquid fuels using only sunlight, they would need new catalysts (substances that speed up chemical reactions), new materials to carry electrical charges during the necessary chemical reactions, and new strategies to streamline the electrochemical reactions. "What we didn't know was which of these catalysts, materials, and strategies were the good ones," he notes.

To find out, JCAP built a multidisciplinary team of scientists and engineers to investigate every piece of the process. During its initial five-year run, from 2010 to 2015, which began under the leadership of Nathan Lewis (BS '77), Caltech's George L. Argyros Professor and professor of chemistry, JCAP refined the process of splitting water; breaking down H_2O into molecular oxygen and hydrogen is a critical step in the chemistry required to make solar fuels. During that time, Caltech researchers achieved a 10.5 percent efficiency in converting solar energy to hydrogen via water splitting, and then in 2018 bested this record with an efficiency of 19.3 percent. Over these subsequent five years, JCAP researchers have focused on reducing carbon dioxide to create the carbon-carbon bonds required to build energy-rich liquid fuels such as hydrocarbons.

"That's one of the reasons why Caltech is so great," says Kimberly See, assistant professor of chemistry. See's research on electrolytes (substances that create an electrically conducting solution when dissolved in a solvent like water) has focused on building better batteries, and now she's bringing some of the same strategies to research solar fuels. "That's where innovation comes from: when people come from one field and start working with experts in a different field. I think good things always happen."

One Piece at a Time

As he describes the record-breaking collection of new materials he and his colleagues have created, Caltech's John Gregoire, coordinator of one of JCAP's four research thrusts, points his finger straight up toward the second story of the Earle M. Jorgensen Laboratory, JCAP's home on the Caltech campus since 2012, where he built that materials library.

Artificial photosynthesis requires several essential steps. A device must be able to capture sunlight and transform the sun's rays into usable electrical voltage. That voltage would then provide the energy necessary to drive a variety of chemical reactions that covert existing molecules and use their ingredients to synthesize fuels.

Pictured: John Gregoire

For example, JCAP scientists want to be able to reduce CO_2 molecules, then combine the resulting individual carbon atoms into long chains to form energy-dense molecules. But they must do this entire process efficiently (so they do not put more energy into making fuels than they will ultimately get from burning them) and selectively (so the reactions do not produce a host of unwanted by-products), and that is not currently possible at the industrial scale.

Gregoire coordinates JCAP's efforts on photoelectrocatalysis: the use of materials that are activated by sunlight to create the electrical voltage to drive the necessary chemical reactions. Numerous materials already known to science, such as materials used in solar panels, can handle some of the tasks he requires. But such materials cannot survive and thrive in the harsh environment of an artificial photosynthesis device that splits water or reduces carbon dioxide.

That is why Gregoire and colleagues are still on the hunt for materials that can do it all. The chase takes place in the custom-built Jorgensen high-throughput experimentation laboratory right above Gregoire's office, where his team synthesizes different possible materials from the elements of the periodic table to see if the material has the needed properties. "We can synthesize and screen these materials a hundred times faster than anyone's ever been able to do before," Gregoire says. "But that still is not fast enough to make everything."

Given all the possible ways to combine the elements, there are billions if not trillions of possible candidates. Instead of relying on brute force or trial and error, Gregoire works with JCAP theorists to identify the types of materials that, based on their composition and structure, should have the kind of light-absorbing and conducting properties he seeks. But machines alone cannot do this job: computers will miss or dismiss some of the promising possibilities. The humans of JCAP, with their years of experience and intuition regarding what an auspicious material looks like, are also essential. Computers are great for reducing the size of the haystack, but sometimes you still need a human eye to find the needle.

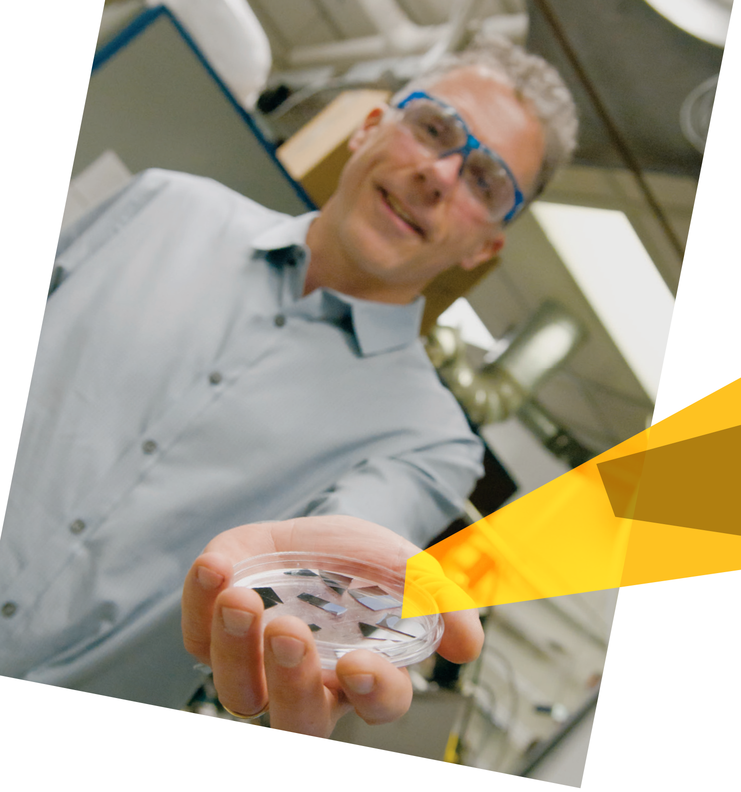
"You're looking for an outlier," Gregoire says. "An outlier is the answer."

This human/machine research collaboration has birthed the largest known library of materials, all of them metal oxides, useful for solar fuels. Of the 70 known metal oxides with any measurable photoelectric activity (the ability to turn sunlight into current), Gregoire says, 50 were discovered in the past decade and half of them by JCAP.

When it comes to understanding the materials developed within JCAP, Marco Bernardi, assistant professor of applied physics and materials science at Caltech, pursues the theoretical. Starting with only the atomic structure of a material and the equations of quantum mechanics, Bernardi computes how well electrons move through a semiconductor or oxide candidate. Bernardi describes this theoretical effort as complementary to the experimental side; it provides a framework to microscopically understand, down to the atomic level, the materials created in the lab and their performance. "I think we're bridging the gap between theory and experiments for these highly complex materials," Bernardi says.

Jaramillo at SLAC, meanwhile, is also building a library, but his is full of catalysts: compounds that can speed up the chemical reactions behind artificial photosynthesis and that have been at the heart of just about every advance in the chemical and fuel industries since their inception. Because of humanity's long experience with fossil fuels, the oil and gas industries have had decades to perfect the catalyst that helps to transform crude oil into the refined gasoline burned in car engines. Researchers investigating renewable alternatives, including solar fuels, are in a race to catch up.

Specifically, Jaramillo focuses on finding the ideal catalysts to accelerate and refine the reactions needed to break down water and reduce carbon dioxide. His goal is to create just the right arrangement of atoms, geometric structure, and electronic structure so that if, for instance,



Pictured: Harry Atwater

a CO_2 molecule encounters that catalyst, Jaramillo says, "the catalyst is ready to rip that thing apart into its constituent atoms and then re-form them into the molecule we want at the expense of the one that we dont."

Tools of the Trade

Scott Cushing, an assistant professor of chemistry at Caltech, is a self-described gearhead. "I grew up in West Virginia working on cars," he says. "I like working on mechanical systems. When I went to college, someone showed me a laser, and I fell in love. I've been working on laser-based instrumentation science ever since."

As evidence, Cushing spent his postdoctoral years working on a tabletop version of a synchrotron before joining the Caltech faculty in 2018. Typically seen in the form of a giant particle-accelerating ring, a synchrotron is a tool that takes advantage of fast-moving electrons' tendency to emit X-rays when they change direction. Cushing's downsized version fires a powerful laser to force electrons to change directions and emit X-rays. The X-rays then tell researchers how the electrons carry voltage through the ultrathin layers of a device. This is crucial for solar fuels research, Cushing says. "Our big goal is to try to measure these reactions all the way from when a material first absorbs sunlight until the product, a solar fuel, is made." Since artificial photosynthesis starts on a femtosecond timescale, or one-quadrillionth of a second, this pushes laser technology, and thus our ability to measure the electrons, right to its current frontiers.

The need for high-precision instruments including Gregoire's high-throughput characterization systems and ultrafast optoelectronic characterization at LBNL is one of the many reasons JCAP is a collaboration of researchers from scientific institutions across the state, says Frances Houle of LBNL, who serves as JCAP's deputy director for science and research integration. In addition to laboratory instruments, she says, the success of this research relies upon the large synchrotron rings at LBNL and SLAC.

Houle's focus on bringing together the many parts of JCAP requires that she also focus on another challenge: taking the fruits of the collaboration into the "real world." After all, when solar fuels are someday able to be manufactured on an industrial scale, they will not be made using simple test setups in a research laboratory. JCAP scientists are learning how to work at larger scales testing how their materials react under real operating conditions, which will include changes in light flux, temperature, and humidity. Gregoire's materials "will ultimately need to be able to sit out in the desert and work for one to three decades," he says.

"You just can't make technological advances without having a very deep science platform to work from," Houle says.

Carbon to Carbon

Tearing water or carbon dioxide into their constituent parts is only half the battle. Scientists then need to combine those parts to make a fuel, which brings a new set of chemical challenges.

Consider, Atwater says, the problem of cooking up a solar version of Jet A, the principal variety of jet fuel that commercial airliners burn. Jet fuel abounds in hydrocarbons, or compounds in which hydrogen is bound to long carbon chains; those bonds release ample energy when burned, which means that these compounds can store a huge amount of energy in a small volume. That is why a major JCAP focus is on synthesizing the building blocks of jet fuel. Using carbon dioxide, sunlight, and their own advances in chemistry, they could create a sustainable way to manufacture the kinds of fuel airplanes must burn.

"The airplane manufacturers are interested in this because they know there is just no way that they can electrify their fleets in any reasonable timeframe that is going to bend the curve for climate change," Atwater says. "So if they're going to make an impact on climate, it's going to be through solar fuels."

Those industry hopes depend in part on the work being done on the second floor of Jorgensen, where a team of researchers led by chemistry professors Jonas Peters and Theo Agapie (PhD '07) experiments with new tactics to tackle the problem of creating multiple-carbon bonds. Typically, Agapie says, breaking down carbon dioxide leaves behind single-carbon compounds such as carbon monoxide and formic acid. To build multicarbon compounds, such as those found in gasoline and other chemicals of interest, requires additional steps, and those steps require the right kind of electrode, a conductor that carries electrical charge into nonmetallic materials like carbon dioxide.

Scientists have found that the charge carried by copper electrodes, when applied to a solution of carbon dioxide, can create the desired carbon-carbon bonds. The problem is, it cannot do so "selectively," which is a chemist's way of saying that along with the carbon-carbon bonds, the reaction creates a host of extraneous molecules as well. To address that problem, over the past several years Agapie and Peters' team has pioneered a way to grow an organic film upon a copper electrode via electrolysis (the application of direct electrical current to drive chemical reactions); that electrode can then drive the conversion of CO_2 into products with two or three linked carbon atoms with very few undesired by-products.

What the Future Holds

In addition to leading JCAP, Atwater heads up one of four main initiatives within Caltech's Resnick Sustainability Institute (RSI), an effort called Sunlight to Everything. It is an apt phrase, he says. The basic chemical processes and new materials discovered during this decade of JCAP efforts have laid the foundation for the next phase of solar fuels research, which will include more affordable materials and efforts to test prototypes under real-world conditions, giving industry new starting points for tomorrow's sustainability solutions. Future research also will focus on seizing CO_2 from sources such as power-plant flue gas or capturing it from the atmosphere or seawater and using it for solar fuels reactions.

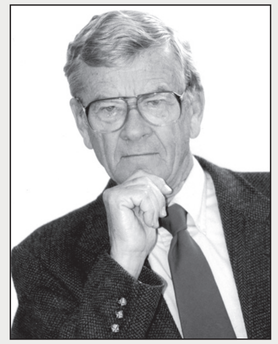
For solar fuels to be made at useful levels for society and industry, researchers must continue to find better photoactive materials, more efficient catalysts, and new ways to build fuels at the molecular level. That quest energizes Atwater. "I tell my students: when I started as a grad student, solar photovoltaics were in the same stage of development that solar fuels are today," he says. "During my professional lifetime, I've seen solar photovoltaics grow from something that was done as a curiosity in research labs to a global industry that's having an impact on the world's energy transformation."

Solar fuels hold the same promise. And as the JCAP team well knows, this kind of technological sea change begins with, and requires, basic research.

"We're focused on the fundamental science, and we recognize that that fundamental science will have broad-reaching implications," Jaramillo says. "The periodic table is our playground."

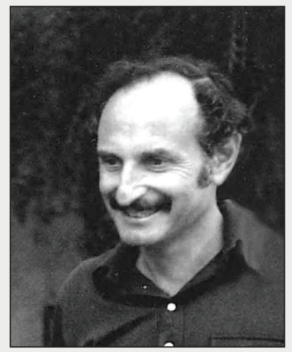
In Memoriam

Read more about their lives at **magazine.caltech.edu/post/in-memoriam**



Allan Acosta
(BS '45, MS '49, PhD '52), 1924–2020

Allan Acosta, Caltech's Richard L. and Dorothy M. Hayman Professor of Mechanical Engineering, Emeritus, who spent 50 years at Caltech and helped launch the Institute's present-day mechanical engineering option, passed away on May 18, 2020. He was 95 years old. Acosta was a faculty member at the Institute in the Division of Engineering and Applied Science from 1954 until his retirement in 1993. He taught courses on fluid flow and heat transfer. His research group was a small collection of faculty with similar interests, including pioneering Caltech mechanical engineer Rolf Sabersky (BS '42, MS '43, PhD '49), with whom he published the textbook *Fluid Flow: A First Course in Fluid Mechanics* in 1963. Acosta was recognized as an exceptional teacher and mentor, and was highly influential in shaping the education and training of many generations of students. He was an elected member of the National Academy of Engineering and a Fellow of the American Association for the Advancement of Science.



Louis Breger 1935–2020

Louis Breger, a professor of psychoanalytic studies, emeritus, at Caltech, and a psychotherapist who authored several books, passed away on June 29, 2020. He was 84 years old. Breger joined Caltech in 1970 and retired in 1994. His research centered on dreams, reformulations of psychoanalytic theory, psychotherapy process and outcome, personality development, and the application of psychoanalysis to literature. He authored numerous books, including two biographies of Sigmund Freud. His research on dreams used techniques to monitor people's sleep throughout the night and showed that dreams are symbolic attempts to master emotional conflicts rather than wish fulfillments as Freud proposed.