Accelerating Solar Conversion Science

Keynote speech delivered by

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at the first annual conference for Scialog: Solar Energy Conversion
held October 12 through 14, 2010 at Biosphere 2 in Tucson, Arizona

scialog

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Publisher's Note

On October 13, 2010, at the first Scialog Conference, Nathan Lewis provided a keynote presentation on *Accelerating Solar Conversion Science.* This booklet is a transcription of the presentation, edited by Jack Pladziewicz, former Vice President of Research Corporation for Science Advancement (RCSA) and professor emeritus of chemistry at University of Wisconsin – Eau Claire. This conference, held at Biosphere 2 in Tucson, Arizona, established a new methodology developed by conference sponsor RCSA. *Scialog: Solar Energy Conversion* began in 2010 with the funding of a three-year program aimed at breaking bottlenecks impeding greater efficiencies in solar energy conversion.

Solar, of course, is a leading alternative energy source, along with nuclear, wind and natural gas. For many decades, RCSA has strongly supported the physical sciences disciplines essential to advanced solar conversion research—chemistry, physics, optics, and, more recently, nanoscience.

With Scialog (science+dialog), RCSA is testing a singularly innovative process for generating ideas, as well as a programmatic approach to research funding designed to accelerate transformational science. Broadly, the funding program identifies individuals with highly innovative ideas, ideas that might produce breakthroughs relative to a key scientific challenge such as global climate change or solar energy conversion.

With those individuals, the program creates interdisciplinary research communities. Specifically, the convening process is a facilitated exercise of open, non-judgmental dialog. This allows normally argumentative scientists to achieve a common sense of clarity and, subsequently, to explore novel approaches to resolving a particular "bottleneck," or longstanding research problem. An example in the solar conversion arena includes how to make better use of the infrared portion of the sun's spectrum in photovoltaic power generation.

James M. Gentile
President & CEO
Research Corporation for Science Advancement

Introduction

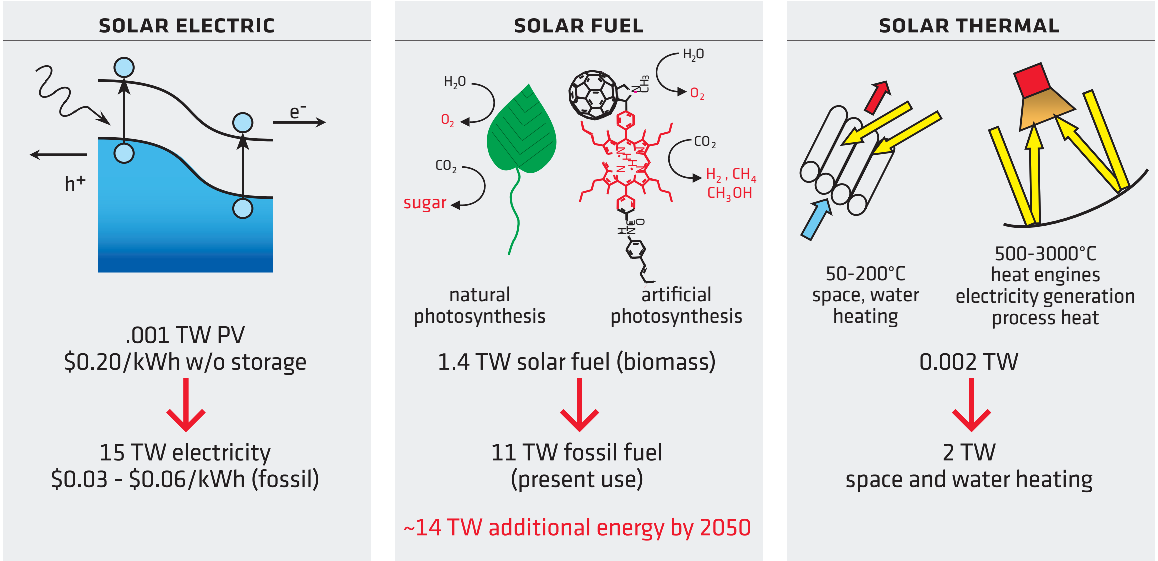
My goal is to stimulate dialog that will go beyond helping somebody with their short-term research tactics, but influence overall, longer-term strategy.

The aim of this paper is to provide a resource to others. As opposed to just telling you what we're doing in my laboratory—which normally I would be delighted and excited to do—my goal is to give a bigger picture perspective of solar energy conversion without making it sound too much like a TV beer commercial, i.e., "wouldn't it be great if we knew how to do X." I'd like to get above the day-to-day, in the trenches, tactical level of trying to take the next small step along our individual research paths and how to do this or that specific experiment. Instead, I'd prefer to examine some of the key system-level challenges and issues so that people can talk to other people in the room and say, well, maybe if you used a protein to somehow direct the assembly of these wires we could make them all stand up and face the sun. I'd like to address issues such as: after you make your wires, how do you make a real system out of it? My goal is to stimulate dialog that will go beyond helping somebody with their short-term research tactics, but influence overall, longer-term strategy.

Many of the figures that accompany this presentation come from the DOE Basic Energy Sciences workshop that some of you are probably too young to remember. It happened in 2005, but it remains essential reading for researchers in the field. I chaired the workshop. My co-chair was George Crabtree and we also had three panel chairs: Arthur Nozik, solar electricity; Mike Wasielewski, solar fuel; and Paul Alivisatos, solar thermal. The 200 scientists who participated in the workshop, including Tom Moore, Krishnan Rajeshwar and Neil Armstrong, who are participants at this Scialog Conference, produced a report entitled: "Basic Research Needs for Solar Energy Utilization." The report, which may be found at: *http://www.er.doe.gov/bes/reports/files/SEU_rpt.pdf,* identifies 14 priority research directions and includes: one sentence, one paragraph and two pages about what's involved in realizing those key headline visions.

Many solar scientists around the world still have this open on their lab benches, using it as the blueprint for what they should be doing. Although I was the lead author on the report, it reflected the insight and effort of the workshop group as a whole. The overarching message of the report was that we all know that the sun is the champion of all energy sources, but we have to figure out how to utilize the sun's energy cost-effectively. Doing so is a monumental challenge for interdisciplinary science.

Figure 1. Comparison of solar electric, solar fuel and solar thermal conversion.



From the Report of the Basic Energy Sciences Workshop on Solar Energy Utilization

In this paper, I will address, in this order, the challenges in solar electricity, solar thermal and finally solar fuels (Figure 1). We all know that solar energy has huge potential and that there are certain things that we can do right now and can extend out from existing technology. These issues are not the focus of this paper. Hence, I will not discuss, for example, how to move down the cost/learning curve on thin film cadmium selenide or telluride until we get to a dollar-a-watt by a particular date, because that's not primarily under our control. It's not where scientists can have the most impact. We can have the most impact, as our Secretary of Energy Steve Chu says, by creating disruptive technologies or doing new things in entirely new ways to change the equation entirely. In summation, we believe that science and technology can give us better choices than the ones we have now.

Nathan S. Lewis, Ph.D.
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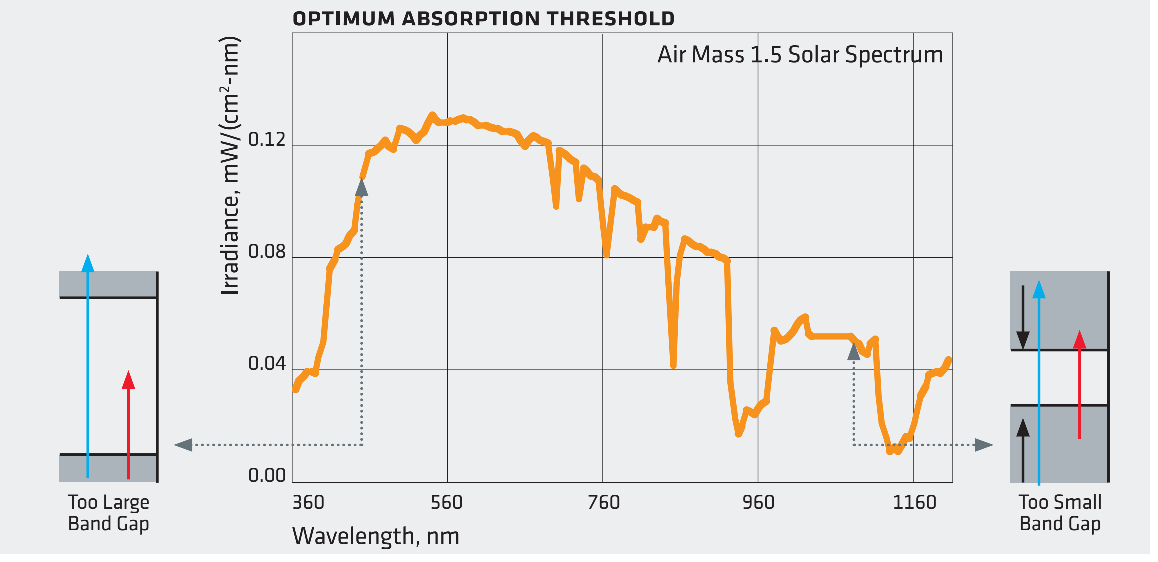
Solar Electric

We know that the key steps for more effective solar electric are to better capture sunlight while creating long-lived excited states so that the electrons and holes can be separated, make it to the external circuit and generate electricity. Sounds easy and it is easy if you're willing to pay the price to make very, very high purity silicon or other materials so that separated charge carriers can travel the required distances to get to wires before recombination occurs. It is also easy if you want to do it for a small part of the solar spectrum. But if you want to do it for a large part of the solar spectrum at optimal efficiency with impure or inexpensive materials, it's not so easy. Let's look at this in a little detail.

The standard solar spectrum, the so-called air mass 1.5 spectrum (Figure 2), shows the distribution of wavelength and intensity of light available on earth from the sun.

Figure 2. Air mass 1.5 solar spectrum and relationship to large and small band gap materials.



The challenge is that if you have a single band gap light absorber of very high band gap energy, you can't absorb much sunlight because all of the photons of energy below the band gap are lost and all of the photons above the band gap are thermalized down to that band gap. For large band gaps, you get a lot of voltage per photon absorbed but not many photons are absorbed. If you move the band gap to the infrared, you can absorb a lot of photons but all of those with energy above the band gap thermalize down to that band gap, so you get a lot of photons absorbed but not as much voltage per absorbed photon, and much of the energy is lost as heat. If one considers losses by accounting for the photons too low in energy for a particular band gap and balances this against thermalization losses for photons with energy above the band gap, one finds that the optimum band gap to minimize the aggregate energy loss is about 1.4 electron volts. This is the so-called Shockley-Queisser limit (SQL) and it yields an efficiency of 32% at one sun at standard concentration. So now one can ask: a) are there really cheap ways to get something close to that efficiency, or b) are there other physical principles or approaches that can be employed to circumvent the SQL and produce much more efficient devices. Then tactical implementations flow from one or the other of these two strategies.

The fundamental operating constraints of all current solar modules go back to 1955 and the first solar cells constructed at Bell Labs, which are still working today. In those systems, one makes a single crystal thick enough to absorb all the light—for silicon that's about 200 microns thick. Any thinner silicon wastes photons, since some go through without absorption. Any thicker silicon wastes expensive silicon. That limitation, in turn, dictates the needed purity, because the excited states have to last long enough to make it all the way back to the surface to get the charge separation and current to the wire. The purity needed for silicon is about one part per billion. When you touch a single crystalline silicon solar panel, it is probably the purest thing you will ever touch. To get silicon this pure requires multiple zone refining, which is both expensive and energy intensive. This relationship between absorber thickness and charge transport distance must be faced by all solar conversion systems. It's great to think about having a beaker or a membrane that, by itself, might separate charge across the membrane in a mono-molecular layer, but that may not be sufficient to absorb all of the sunlight. Furthermore, you're going to have to think about how to assemble many of these together into a macroscopic system that effectively directs charge carriers, separating them from one another, while still fully absorbing the light. This is fundamentally harder than putting one little molecular unit into a PowerPoint slide or getting it even into a membrane in the laboratory. There's a systems level construct that needs to be addressed.

The fundamental operating constraints of all current solar modules go back to 1955 and the first solar cells constructed at Bell Labs, which are still working today.

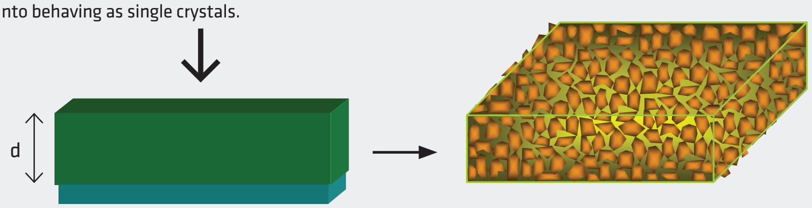
An inorganic solids approach to get around this is to make small grain size materials. The problem with small grain size materials is that the atoms at the surface know that they're not in the bulk. For example, silicon atoms in the bulk have the requisite electronic structure because every silicon atom is surrounded by four others exactly like it. That environment produces the electronic bands that facilitate electron movement to the surface and prevents recombination with holes. There's no law of physics that says that we can't fool those atoms at the surface of small grain size materials into thinking they're in the bulk by producing terminating bonds on surface silicon atoms as strong or stronger than in the bulk. If these bonds are strong enough, molecular orbital theory predicts that the relevant wave functions are split below the valence band and above the conduction band and surface silicon atoms think they're in the bulk. There's no law of physics or chemistry that says that this cannot be done.

There's no fundamental law that says we can't do it in a way that not only passivates the particle surface features that lead to charge recombination, but also lets the electrons and holes hop from particle to particle, like stepping stones, as conductively as in pure solid, but a hundred times cheaper. However, no one knows how to do this yet, so it remains a challenge worth serious thought. There are other related issues here. Many of us have talked about "solar paint," but how do you make sand-like solar collectors that can be imbedded in a polymer and wired? There are system-level issues to address. For example, one would need multiple layers to separate charge and physical asymmetry, otherwise the system never knows top from bottom and left from right, and photo-driven charge separation is simply followed by recombination. Once the particle boundary issues are solved, I think the system-level issues can be done because we know how to layer materials and use chemical kinetics to selectively extract charge carriers from one side or the other. However, all of this is necessary in order to implement an imaginative idea like a solar paint or coating (Figure 3).

Figure 3. Top: Solar paint from granular solids; Bottom: PPV bulk heterojunctions.

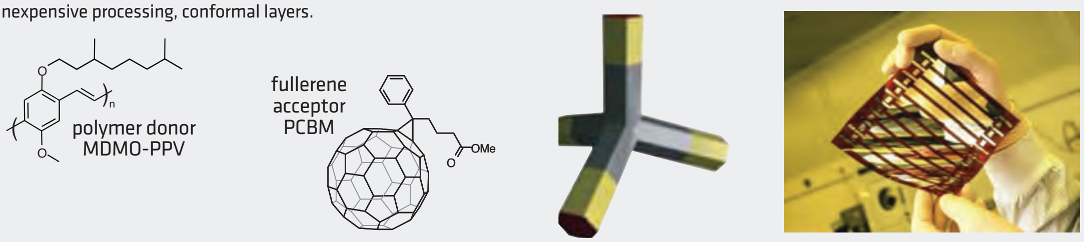
SOLAR PAINT

"Fooling" inexpensive particles into behaving as single crystals.



PPV BULK HETEROJUNCTIONS

Inexpensive processing, conformal layers.

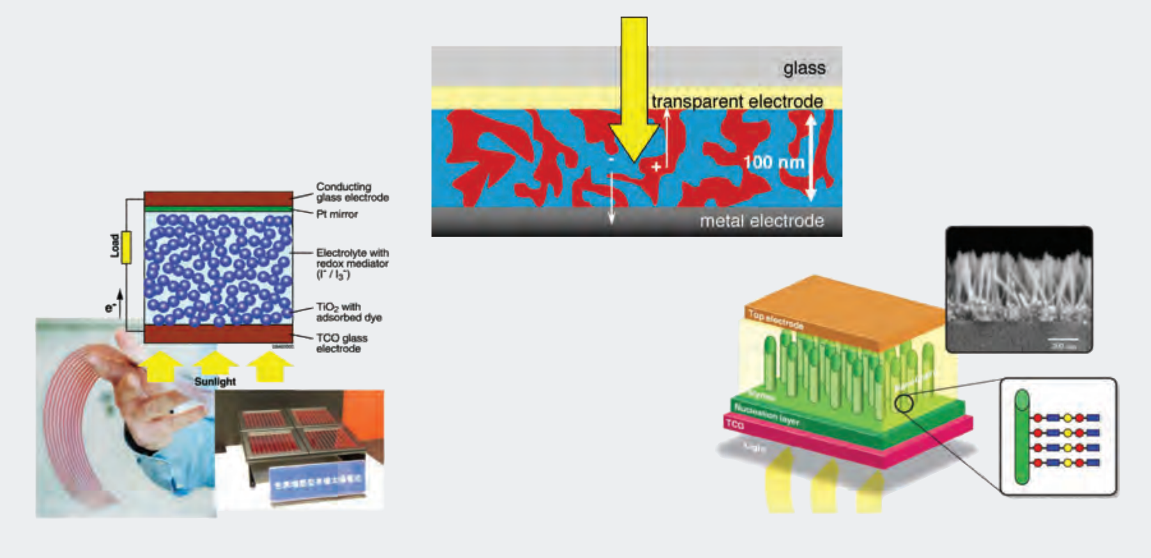


From the Report of the Basic Energy Sciences Workshop on Solar Energy Utilization

If you don't think this can be done from a cheap inorganic solids approach, you could turn to the molecular scale with organic systems. The poster child for this approach is the organic bulk heterojunction solar cell (Figure 3). In these cells, a conducting polymer, such as poly-phenylenvinylene (PPV), serves as the photon absorber and electron donor, and is imbedded with a fullerene (C_{60}) derivative that functions as the electron acceptor. The polymer absorbs visible light, producing excitons resulting in electron injection into the fullerene and concomitantly producing holes in the polymer. The holes and injected electrons separate and migrate to opposite conducting surfaces to produce the external current. My Ph.D. advisor, Mark Wrighton, used to say, "there are a million reasons not to do the experiment; none are compelling". That is, you could have listed many reasons why this approach couldn't possibly work—for example, once the electrons holes are injected onto the fullerene, they can't move very far and they should recombine with one of the holes. If they don't annihilate by recombining with a hole right there, then as they percolate through this whole biphasic solid they should surely recombine with another hole somewhere along the way to the wire. The bulk material is a complex mixture of donors, acceptors and defects, and it is not clear why it works, but it does. While the current world record is only six or seven percent efficiency, they clearly are very promising. The fact that the way they work is so poorly understood is a classic example of opportunity imbedded in challenge. Understanding how they work is the obvious key to improving the efficiency. All of these systems have this property: that they must have these two interpenetrating, network-percolative domains, one of which allows one charge carrier to magically make it out without somehow recombining with the opposite charge carrier that's migrating in the other direction. How do you control this beyond just making one molecule and another and another and trying them? How do you facilitate the migration of the charge carriers, while at the same time limiting charge recombination? Control of interfaces and charge transport is going to be critical if we're going to get beyond systems that mysteriously work at low efficiency and progress to systems that somebody can put on their roof.

Another approach might be to alter the system structure in the first place. Instead of hoping that you get a system like C_{60}–PPV, that magically bi-phase separates this way, it might be good if we did it on purpose. There have been two approaches to this. One is essentially a dye-sensitized solar cell. At its core is a monolayer of dye on an interpenetrating network of TiO_2 particles (Figure 4 lower left).

Figure 4. Interpenetrating nanostructured networks.



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Somehow, nearly magically, the excited electron in the particle network makes it to the back conductor preferentially, rather than recombining with the hole that makes it all the way to the front. Now, this actually only works well when the iodide–triiodide couple is the redox mediator. All other redox couples that have been tried don't work, even if the electrons are injected in the TiO_2, even if they're femtosecond quenched, To get optimum light absorption, we have to combine structure with orientation.

even if we have the seemingly right dyes. In spite of research that has led to over 10,000 papers aimed at improving this system, very little improvement has been achieved. If you don't have iodide–triiodide, the cell doesn't work because the electrons don't make it all the way to the back to the conductor. Instead, they recombine with holes and you get nothing. So at its core, we don't understand how to make these cells work better because we don't understand how iodide–triiodide works and, therefore, how to design improvement.

Grätzel has tried over 3,000 dyes and, yet, the third one he tried is the one most people still use. One approach to improving the system has been to nanostructure the particle absorber to maximize the absorber length, while minimizing the charge transport distance. Scialog award winner Joan Redwing has done this, as has my collaborator Harry Atwater and my group. You can do this in two ways. In one approach, you create nanostructured "pogo sticks" from silicon, so that light comes in over the long axis of the rods and is absorbed, but separated charge moves only the short distance, sideways, to be collected (Figure 4 lower right). That's a pretty good idea in my view, because it's a game changing paradigm shift. This departs from the 50-year-old assumption that the absorption path length defined the charge migration distance. Now, light goes in a long distance, but charge goes out a short distance. This is but one example of the games one can play with the physics via clever synthetic chemistry and materials science.

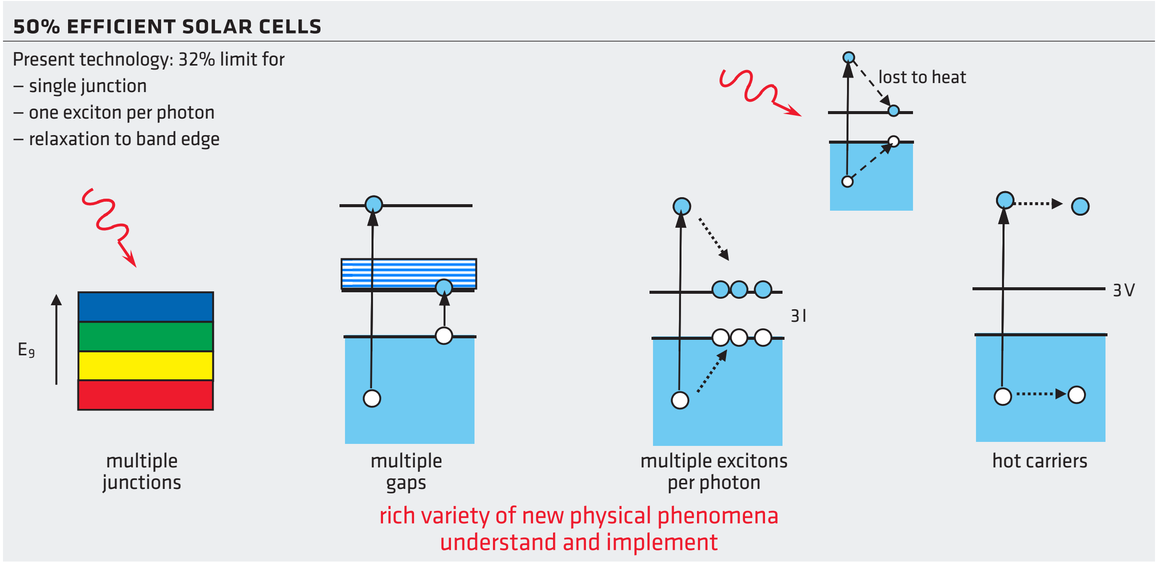
A second approach, developed by Mike McGehee at Stanford University, is to fill a TiO_2 porous nanostructure with organic polymer light absorbers, like PPV. In this instance, it's the organic polymer fill that is the absorber and the exciton moves a short distance before an electron is injected into the TiO_2. While these devices do work pretty well, the problem of controlling the interfaces remains. While greater interfacial area per unit area has been achieved and the charge transport distances have been decreased, if you don't do something about the dangling bonds at the surfaces, charge recombination at the surface will plague photo conversion efficiency. It will work in PowerPoint, lots of papers will be published, but you will fall short of a good working device.

So, thinking about this is more than just thinking about what materials systems you use. It's the question of how you orient or structure the system for maximum light absorption with light coming in at various angles. Nature solved this by having blades of grass pointing up in all sorts of directions. So it's really important to think about how to pattern this from the bottom up. For example, if you are a nanoscientist, like Paul Alivisatos, who has a beaker full of nanowires, how would you paint them on a substrate and get them to mostly orient up towards the sun like blades of grass? It's a pretty neat problem. You can think about hydrophobic ends and hydrophilic tails. You can think about interactions that are repulsive along the sidewalls. Nature has learned how to build from the bottom up with the optimal structure and orientation. Can we emulate that in synthetic systems?

To get optimum light absorption, we have to combine structure with orientation. Nature's solution is highly branched structures, trees, for example. In fact, pine trees have branches optimally radiating from the trunk in Fibonacci series. The first one is at one distance and the next one is half the way around, the next one is a third of the way around, etc. Leonardo Fibonacci discovered this a long time ago. This arrangement favors optimum light absorption and minimal shading from the top branches down. So it makes sense that if that's the way to get optimal transmission and minimal light shading, that that's what we should do. How do you direct structured growth with light to get optimal light absorption on the micro and nano scale and still collect carriers along the trunks and branches of the trees? This is another really interesting problem that holds a key to systems for efficient conversion of solar energy.

Now, let's suppose that we've done all the structural optimization just described, but want to beat the SQL of 32% for a single band gap system. How do we think about that? One approach is to consider limiting thermalization of hot excitons (Figure 5). In my assessment, that hasn't shown too much promise in a real-world device yet. Even if we demonstrate the physics in principle on the picosecond time scale for a process to convert excitons with energy well above the band gap, there is still a very short distance with which to make that contact to collect those carriers before they're going to thermalize and then you've got to collect them in their excited state and then move them through that whole percolative network in the presence of all the holes going the other way with which they can recombine. How do we think about strategies that let us do this?

Figure 5. Revolutionary photovoltaics: beating the Shockley Queisser Limit of 32%.



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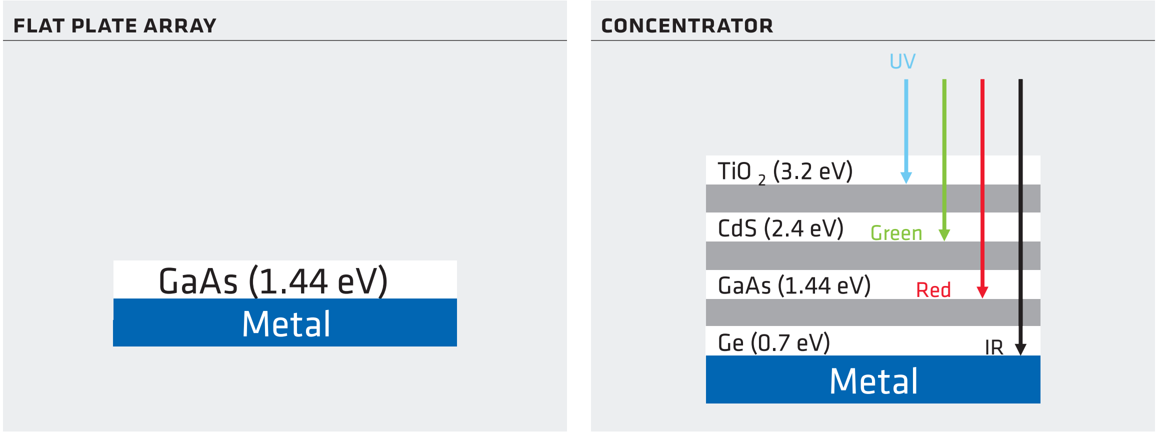
An example of this is systems designed to produce multiple excitons per photon. Really great new physics is being thought of here. But, at the same time, we need a strategy that would let us take these multiple excitons and collect them as a photo current. The phenomenon is called multiple exciton generation and not multiple photocurrent flow because there aren't clear strategies for how to wire even one of the nanoparticles to collect the multiple excitons, let alone wire an entire nanoparticle matrix that is generating multiple excitons and collect the photocurrent before electron-hole recombination occurs. As far as I can tell, no one has put forth a strategic vision for how to do this. This is another systems problem in need of serious effort.

Another approach to beat the SQL is, of course, multiple junction cells—i.e., multiple band gap layered materials (Figure 6), but they are very expensive. One reason that building multiple junction cells is expensive is that we need to get lattice-matched structures. If you epitaxially grow pure materials, you have to minimize the strain so you don't propagate defects at the layer boundaries. Otherwise, the layers you grow absorb light, but don't collect any carriers. But there's no fundamental reason that we should have to do it in such an expensive way.

Figure 6. Arrays of complementary band gap semiconductors.



Concentrator vs. Flat Plate Arrays
Why not stack several semiconductors to get better energy conversion? A large band gap semiconductor can get higher voltage out of the more energetic photons, then smaller band gap semiconductors underneath can extract additional energy from the remaining photons.

Polaroid film isn't like that. It's multiple layers of soft materials that absorb all the wavelengths of light and then undergo photochemistry. That's how they develop the charge transfer in the film. It's not clear that hard materials are the only way to get broad-spectrum light absorption and energy conversion. In my view, this should be a soft materials problem. We should have different production lines that make assemblies of structures in a soft material that absorbs blue light, another soft material that absorbs red, another one absorbs green light, and the way you build efficiency above the SQL is to laminate them together or you chemically assemble them together or chemically bond them together at the interfaces. This is a great problem that is not currently receiving a lot of attention.

Another approach to beating the SQL is "altering the Sun's spectrum," that is, up-conversion. In my view, the most promising potential for up-conversion isn't for solar electricity, but for solar fuels. The challenge of up-conversion for solar electricity is that the sun is not a coherent light source and if you're trying to simultaneously do an up-conversion, you need a flux of photons at a given wavelength sufficient to get a reasonable probability of up-conversion. While it is, in principle, a great physics experiment with a high intensity coherent laser in a laboratory, it is a challenge on the spectrum at one sun light intensity. While the physics is inherently interesting, the challenge for solar energy conversion is to have a clear strategy to obtain a real system from the incoherent light source at one sun, or possibly under some achievable level of concentration.

On the other hand, there are materials that do make fuel from sunlight, but they only absorb in the high-energy visible or the ultraviolet. So part of the problem is how do we make sufficiently stable materials that do this where the sun has a lot of photons? If you could up-convert the red photons, then we could use existing stable materials to help solve the problem. The difference between solar fuels and solar electricity, in this respect, is that if you want to make electricity you can trade current versus voltage. However, if the goal is to make fuel, you have to satisfy the system thermodynamics. For example, if hydrogen from water is the goal, if you don't get 1.23 volts at pH 7, you don't get hydrogen and oxygen, period. This fundamental constraint is an example of the different design requirements for fuel versus electricity.

...the challenge for solar energy conversion is to have a clear strategy to obtain a real system from the incoherent light source at one sun, or possibly under some achievable level of concentration.

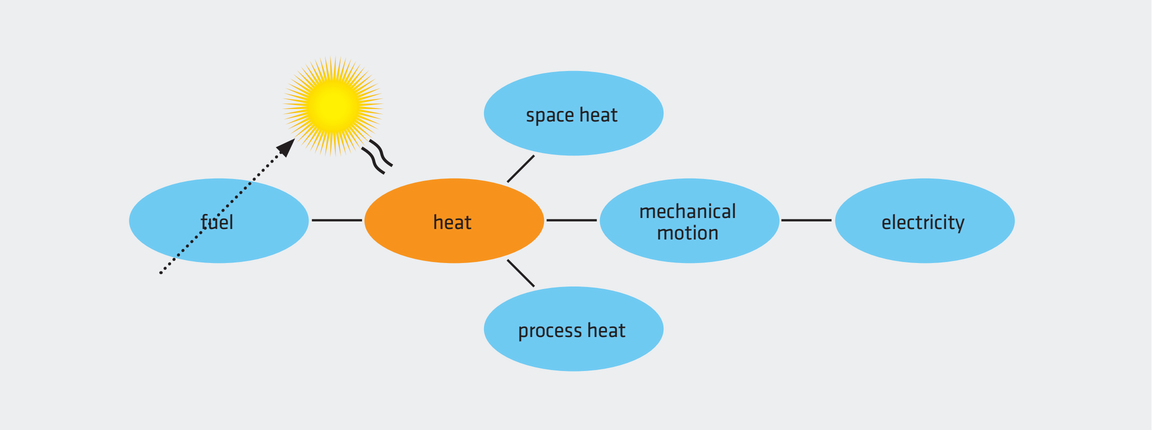
Dye-sensitization has already been discussed, but I would add that it is clear to say that even after 10,000 papers we just don't understand how these things work. The proof that we don't understand how these cells work is that we have been unable to change something to make it work better. The first dye-sensitized cell was reported at 7% efficiency. We are now on test cells at 11%, but most people get 8% in the lab most of the time. So it's pretty clear that there is a fundamental lack of understanding that is impeding their improvement. Therefore, we should be studying things to better understand how they work and then improve them. That's ultimately the proof of the pudding. For example, it's obvious that to move forward a workable replacement for iodide–triiodide is needed, and this may require a different material than TiO_2 with a different band gap. You have to do it in such a way that, if you change the band gap, electrons that get injected into the new material don't recombine with the redox mediator. Furthermore, we have no idea how to make fuel from these cells because the only redox couple that can now be oxidized efficiently is triiodide. Alas, the world doesn't need a whole lot of oxidized triiodide.

Dye-sensitization is a great idea and a terrific interdisciplinary training ground. This system is an entry point for lots of players because you don't need anything but blackberry juice, sunscreen and an oven. The accessibility of this system to the scientific community worldwide is a plus. Having a system to study that does not require growing junctions, doing solid-state doping or doing semiconductor processing makes dye-sensitization worth its weight in... ruthenium.

Solar Thermal

With solar thermal, heat is the entry point and designing systems for the conversion of photons to heat is fundamentally an easy thing to do (Figure 7).

Figure 7. Solar thermal conversion of heat.



Solar Thermal

– heat is the first link in our existing energy networks
– solar heat replaces combustion heat from fossil fuels
– solar steam turbines currently produce the lowest cost solar electricity
– challenges: new uses for solar heat and storing solar heat for later distribution

From the Report of the Basic Energy Sciences Workshop on Solar Energy Utilization

It's not as though we always have to make quantum based-photon conversion systems. What are the most cost effective ways to use heat to build a renewable energy system? Bear in mind that, if we make fuel from sunlight via heat, the 32% SQL is long gone. It's not relevant. Using a thermodynamic T∆S Carnot cycle approach the limiting efficiency is readily shown to be on the order of 60-70% not 32%. So, the fundamental physics of not being so tightly constrained and having to play these tricks with the photon conversion that you get by going to thermal solar conversion is appealing.

The down side is that machines for solar heat conversion (Figure 8) are expensive. If the goal is to build one of these dual access trackers to make the United States energy equivalent from now to 2050, we would have to build, deploy and install one every single second. On this basis, what is needed is robots. We need somebody to drop it from airplanes and have them open up like flower petals. This is not crazy, even on the nano scale. Flower petals do chemical/mechanical tracking of the sun, yet we don't have motors that do that. It would be a pretty neat thing if we had heat- or light-actuated chemical systems that could control our devices and track the sun. No one knows how to do that, but it is something worth a serious effort.

Figure 8. Concentrating, tracking solar thermal system.

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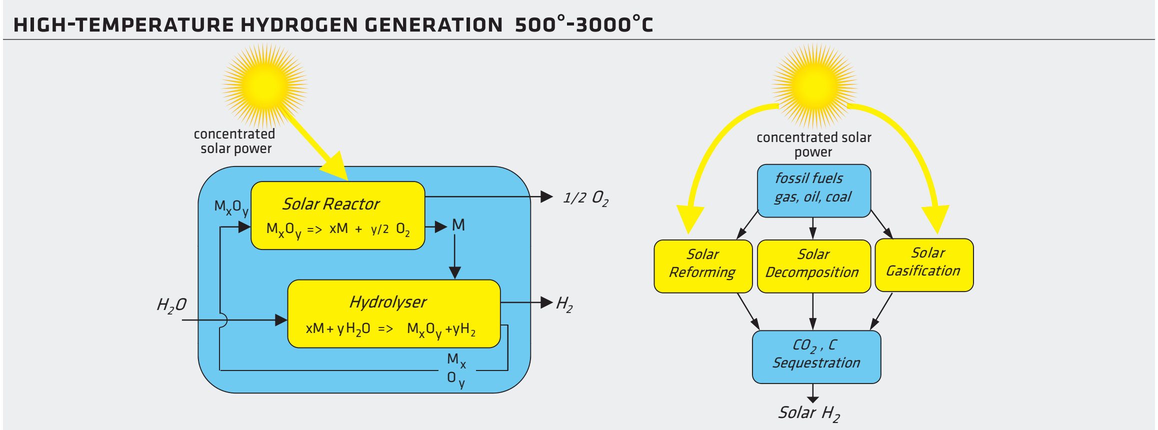
If focused sunlight is used, expensive catalysts are not needed. Many relevant chemical reactions are spontaneous at 1,000 degrees. For example, a zinc/zinc oxide cycle would work (Figure 9). Hot zinc reacts with steam to produce hydrogen and zinc oxide. At high temperature, zinc oxide spontaneously decomposes to zinc metal and oxygen, recycling the zinc. One of the most prominent of these schemes, proposed by Harold Agnew in 1973, involves the sulfur–iodine cycle, using heat from nuclear reactors to produce hydrogen, although to my knowledge this system has never been fully demonstrated.

Figure 9. Solar thermochemical fuel production.



Scientific Challenges

High temperature reaction kinetics of
- metal oxide decomposition
- fossil fuel chemistry

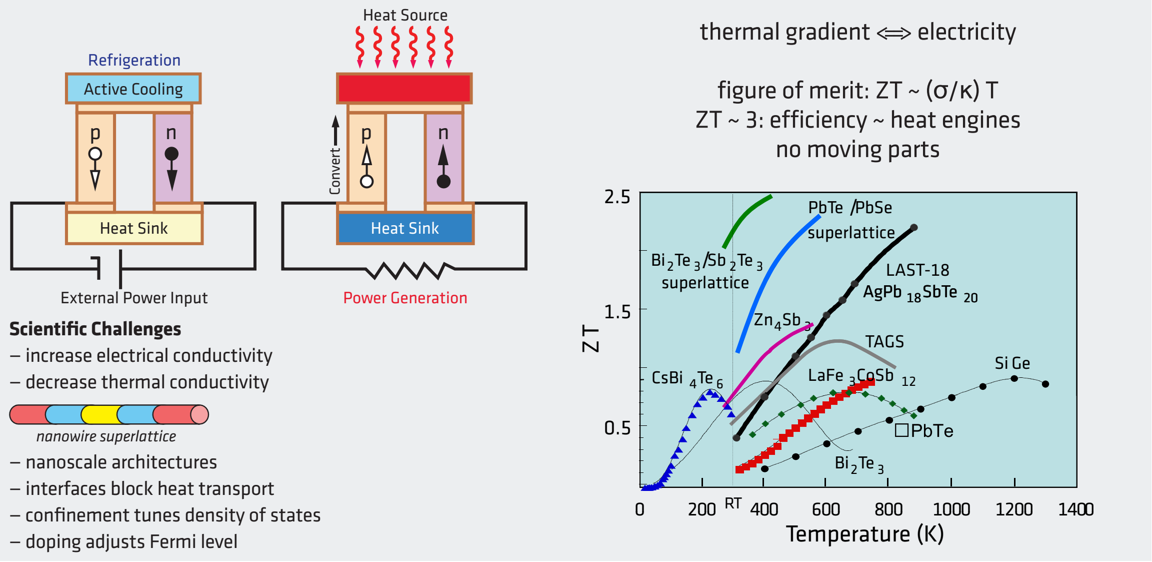
Robust chemical reactor designs and materials

A. Steinfeld, Solar Energy, 78,603 (2005) from the Report of the Basic Energy Sciences Workshop on Solar Energy Utilization

The challenge for solar thermal fuels is controlling the flow of heat and material. How do you get a bottle of light, a bottle that can take all this focused sunlight, get hot and not let the heat out, not let the light out, and get the chemical reactant flows in and the chemical product flows out? There are probably really clever chemical ways to think about doing this with selective membranes that would be optically transparent and that could be thermally insulated. Right now, this is entirely in the domain of mechanical engineering. There are people trying to build columns, cans and related reactor systems, but it's not clear how to solve the heat, light and materials flow problems simultaneously at acceptable cost. Presently, chemistry and materials science are not making advances in this area. However, if synthesis gas (i.e., "syngas," H_2 and CO) is the goal, Sandia has a demonstration system for the high temperature solar conversion of natural gas, methane or other hydrocarbons to syngas.

If the goal is to make electricity, rather than fuels, the optimal systems will operate with no moving parts. The figure of merit for these systems is to achieve a ZT product of three or greater (Figure 10). Conversion of heat to electricity has not escaped the thermoelectric community, who have been trying for some time to make materials with ZT of three or greater to replace mechanical and chemical refrigeration systems. Advances here could have a large impact in solar energy systems, as well. The principal challenge is to decouple the electron bath from the phonon bath, because it's the vibrations that quench the thermal electron excitation. Heavy elements, in particular bismuth, appear to have most the desirable quantum structure and have shown the greatest promise to date. People like Millie Dresselhaus lead in this area and, while no one has achieved a ZT of three yet, it's creeping up, and is now near 2.5 at room temperature. Really good thermoelectrics, especially those that could function at high temperature, could be a way to replace Sterling engines and would be very promising for solar thermal generation of electricity.

Figure 10. Thermoelectric conversion.



From the Report of the Basic Energy Sciences Workshop on Solar Energy Utilization

Solar Fuel

Solar fuel is a broad area extending from biofuels to inorganic solar fuel cells. A starting point for biofuel is the picture taken by Steve Long at Illinois (Figure 11). It's a great picture. When you actually ask farmers to grow the same crop over large areas, they don't get nearly as much as this test field. That's potentially bad, but there's an upside too. It means in principle that if you have rigorous control over farming and/or adaptive biology, you could optimize growth under the variable conditions of nutrient, sunlight, etc. and could make the average yield approach the peak yield.

An interesting challenge in biofuels, from a chemist's viewpoint, is that lignocellulose, which makes up a significant fraction of the dry weight of the plant, is recalcitrant. We have no clue how to break it down under mild conditions. It must be boiled in sulfuric acid or given cellulase enzymes and we don't know what to do with the lignins. Nature has made these units refractory by design, to protect the plant, but there's no law of chemical biology that says that you couldn't put a designer weak link, such as a click chemistry reaction site, into lignocellulose in a genetically modified plant, so that the link will still survive under agricultural conditions but unzip the lignocellulose readily when fed the right chemical activator during processing.

Figure 11. Leveraging photosynthesis for efficient energy production.

SWITCHGRASS

HYDROGENASE $2H^+ + 2e^- \Leftrightarrow H_2$

– photosynthesis converts ~ 100 TW of sunlight to sugars: nature's fuel

– low efficiency (< 1%) requires too much land area

Modify the biochemistry of plants and bacteria:

– improve efficiency by a factor of 5-10

– produce a convenient fuel methanol, ethanol, H_2, CH_4

Scientific Challenges

– understand and modify genetically controlled biochemistry that limits growth

– elucidate plant cell wall structure and its efficient conversion to ethanol or other fuels

– capture high efficiency early steps of photosynthesis to produce fuels like ethanol and H_2

– modify bacteria to more efficiently produce fuels

– improved catalysts for biofuels production

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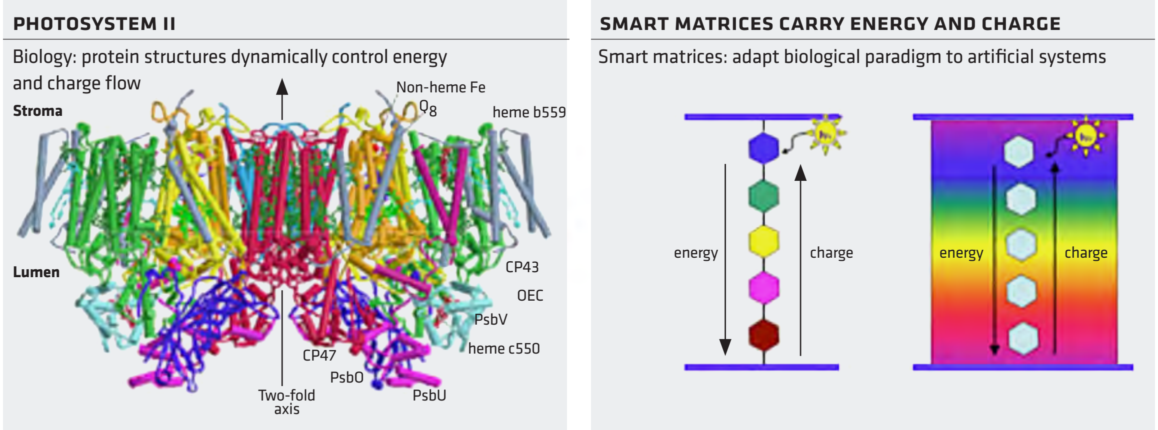
As far as I can tell, nobody's working on that. Everybody is working on more robust and efficient conversion processes through genetic engineering. While that's important, we've been doing that in one form or another, via plant breeding, for hundreds of years. But, as chemists and molecular biologists, we should be able to put our own bonds in there and make them susceptible to the reactions we select. Otherwise, what you've got to do is boil this lignocellulose in sulfuric acid. It takes a lot of energy to do this. This is, in part, why the energy in and energy out advantages of corn ethanol are so equivocal. A lot of the energy in processing the lignocellulose is used just for its decomposition. Furthermore, cellulases are pretty slow and are intolerant of alcohol, so you need a two-step process. Having to ferment the plant material to produce alcohol separately from having the cellulases do the digestion greatly complicates and reduces the cost effectiveness of bio-refineries.

While a single step process for lignocellulose breakdown and fermentation would be a great advance, one should also consider how to get a product other than ethanol, which kills the bugs that make it, at 15% ethanol, and thereby requires distillation to separate ethanol from the bulk water. For example, butanol would be much better, because it's immiscible with water and can be skimmed. Designing the system for one-step processing from degradation to fermentation to pure fuel under mild conditions, and without the need for distillation, would greatly advance biofuels technology. This is within the capability of modern chemistry and molecular biology.

We all know how photosynthesis works. I don't think I need to go into that. Except, even today, it's still true that if you know a biological structure, which we now pretty much know for photosynthesis, that doesn't mean you can take the active site out and make it work outside the living system (Figure 12).

Figure 12. Photosynthetic structure and smart matrices.



PHOTOSYSTEM II

Biology: protein structures dynamically control energy and charge flow

SMART MATRICES CARRY ENERGY AND CHARGE

Smart matrices: adapt biological paradigm to artificial systems

Scientific Challenges

Engineer tailored active environments with bio-inspired components
Novel experiments to characterize the coupling among matrix, charge, and energy
Multi-scale theory of charge and energy transfer by molecular assemblies
Design electronic and structural pathways for efficient formation of solar fuels

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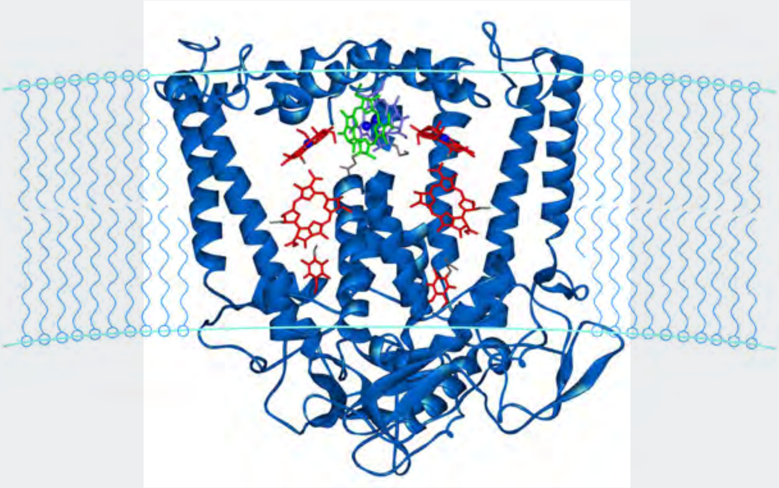
In fact, I think there are few examples in the chemical community—except possibly cytochrome P450 or cytochrome hemes—of somebody being able, once they knew the structure of an enzymatic active site, to take that structure, make it themselves, and get it to function.

Nonetheless, knowing that something can be done is important, even if one does not emulate the structural detail of nature. So it's good to know that birds fly, and use that to have humans figure out how birds do it, but airplanes don't have to have feathers. Design principles are often more important than mechanistic details.

Nature has some bad news too that is not often appreciated. Let's look at the structure of *rhodobacter sphaeroides,* for which the German group won the Nobel Prize in the '90s. The structure shown is a later one from Doug Reese's group at Caltech (Figure 13). The important point here is that nature does have to obey the same laws of physics as we do in solar cells.

Figure 13. Bacterial photosynthetic reaction center.

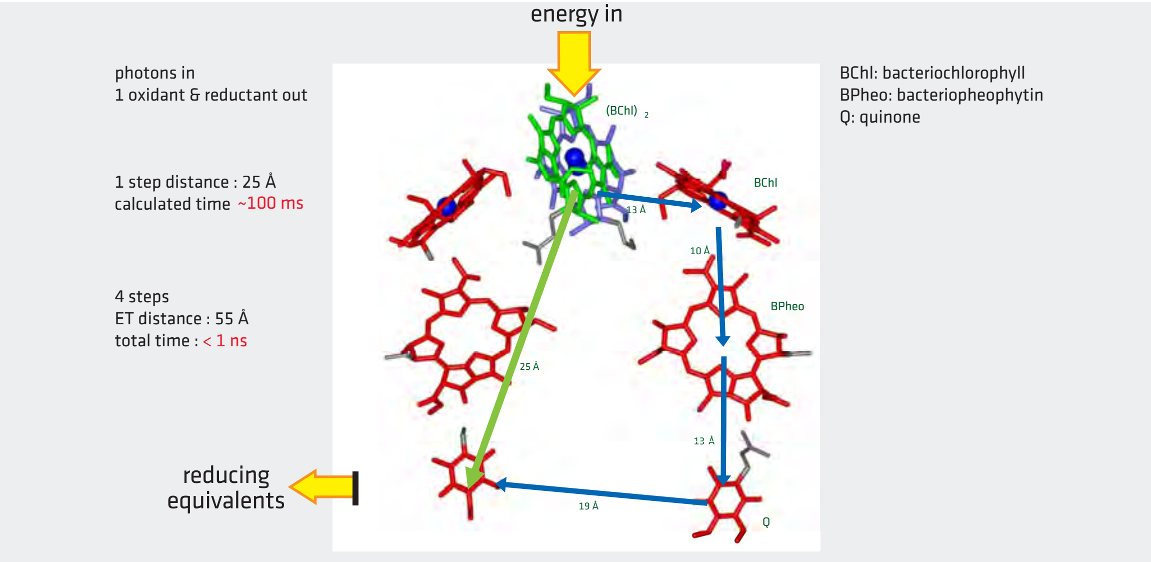
rhodobacter sphaeroides



Stowell, M.H.B.; Rees, D.C.; et. al. Science 1997, 276, 882.

So, there's C2 symmetry around this axis that generates the special pair in the photosystem, and the question is, with C2 symmetry, how does the excited electron know to go left or right? If it went equally left and right, it would short-circuit itself. There needs to be asymmetry somewhere, to direct the electrons in the same direction most of the time. Well, there isn't any asymmetry at the level of secondary structure; however, there is an asymmetry right at the top, in the protein itself (Figure 14). There's an amino acid or two that have a different electric dipole on one side than the other, placed strategically to make sure that excited electrons move, nine times out of ten or more, one way rather than the other way. That's really important, because it shows you that you need to have asymmetry in the system. This is a system-level design feature to control charge recombination to keep in mind as we build solar devices.

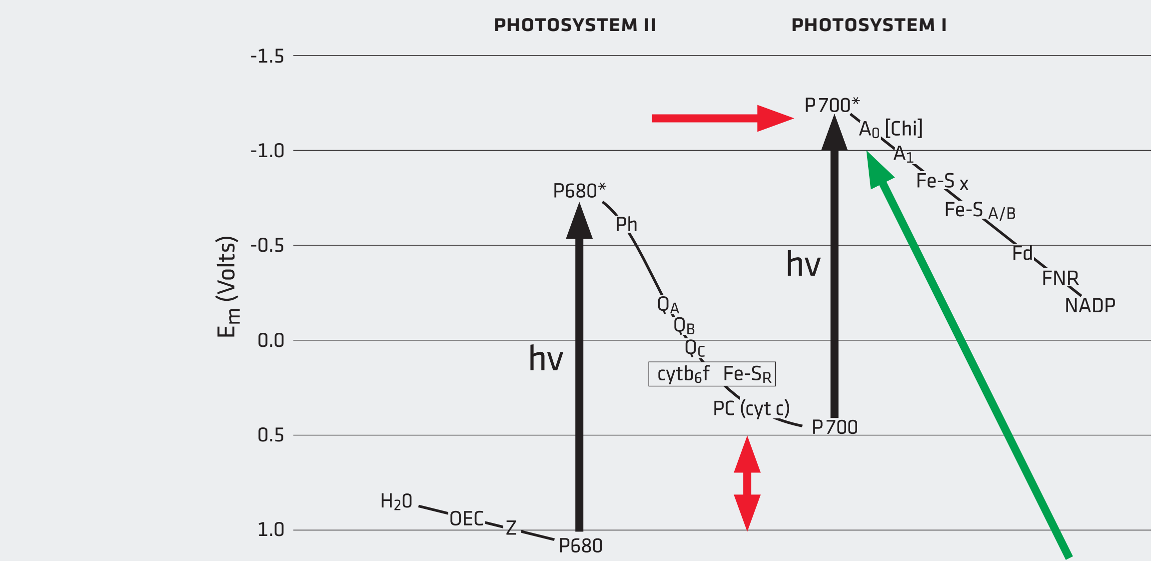
Figure 14. Asymmetry leading to directional electron flow.



Boxer, S.G. Annu. Rev. Biophys. Biophys. Chem. 1990, 19, 267.

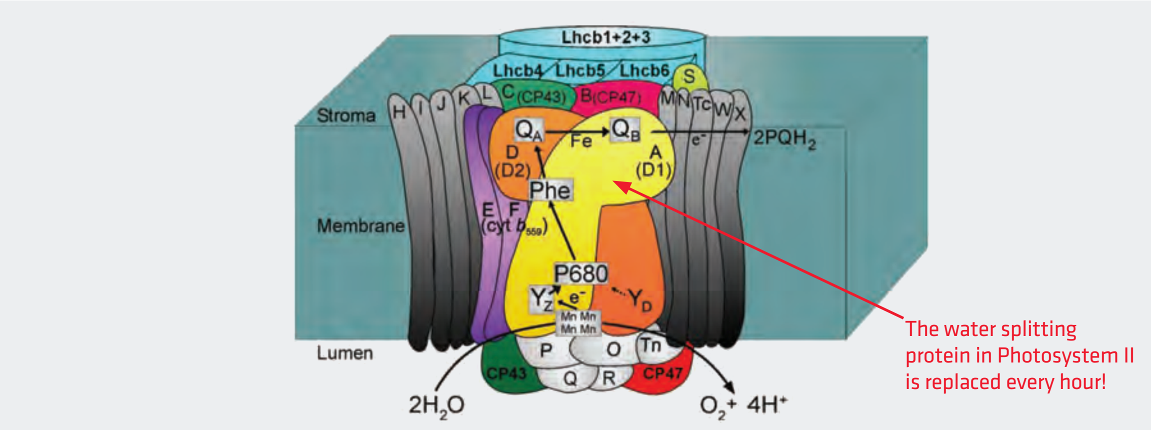
Nature teaches us another lesson: it is not perfect. Let's look at the energetics of photosynthesis (Figure 15) and grade it as a machine designed by a student who comes in and says, "I built a machine that converts light into fuel." We know the energetics of this process and that you give up a lot of energy just to move that excited electron off the special pair through the photosystem to get to the quinone. In fact this is a 1.7ev excitation and you're only left with 0.7ev by the time you're through the quinone. That's the reason nature has two photosystems to get the chemical potential to split water, because it has to string together two 0.7ev's to get the needed 1.4V and only then can it produce NADH, ATP, or make its version of hydrogen and then make oxygen. If it doesn't have that 1.4V it can't do it.

Figure 15. Energetics of photosystem I and II, "double photosystem".



Nature has another problem. It has a molecular shuttle between photosystem one and two. Most people don't realize that photosynthesis, actually double photosystem photosynthesis as we know it, saturates at a tenth light intensity of the sun. It does not produce any more charge separation above this level because nature optimized itself in the canopy. Moreover, the D1 protein (Figure 16), suffers radical damage and needs to be rebuilt every 30 minutes, and it would suffer even more radical damage if it didn't saturate the system at a tenth light intensity of the sun. The reason for that is that there's a molecular diffusion time to shuttle the quinone between one system and the other, and if you calculate the physical diffusion time needed to move a molecule of quinone between the two requisite photosystem sites, it matches a saturation flux of photosynthesis at a tenth the solar intensity. So nature has a bottleneck. It just can't move electrons faster between one system and the other if it relies on a molecule to carry the electron. So it's possible to think about de-bottlenecking photosynthesis, by replacing the molecular shuttle with a wire. Moreover, one could argue that if you had pigments in there that weren't those greasy, organic "chicken fat" pigments but something else that shuttled electrons more quickly, you wouldn't have to sacrifice 0.7ev just to separate the charge over that distance. I think it's not impossible to think about black plants instead of green plants and plants that don't saturate at a tenth light intensity of the sun. We just have to understand what the physical bottlenecks really are and then work on them.

Figure 16. Defect tolerance and self-repair.



The water splitting protein in Photosystem II is replaced every hour!

Scientific Challenges

– Understand defect formation in photovoltaic materials and self-repair mechanisms in photosynthesis

– Achieve defect tolerance and active self-repair in solar energy conversion devices, enabling 20–30 year operation

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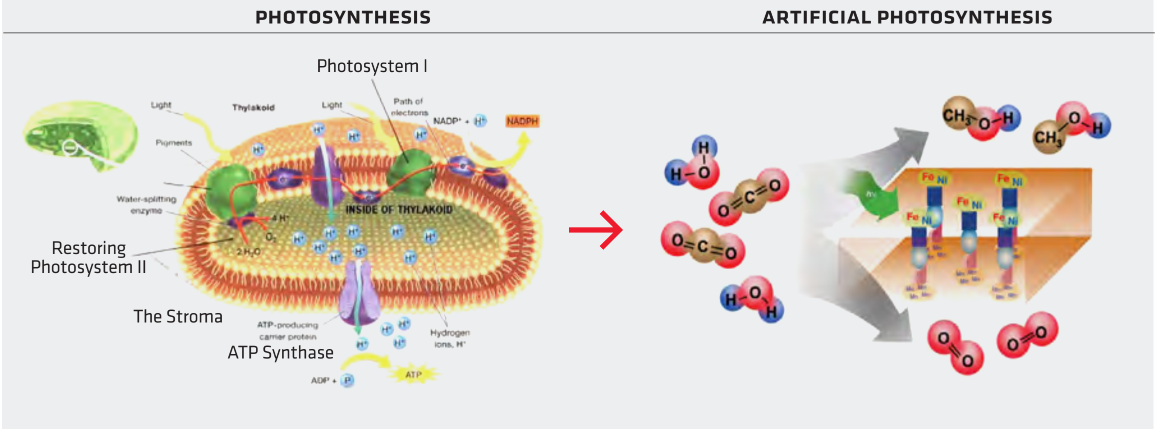
If you don't think nature can be modified to do it, why not try to do it ourselves? (Personally, I believe both approaches should be pursued simultaneously.) Why not take artificial parts and construct a double photosystem. We know from nature that this works. We know photoelectrochemistry works; the picture has been in freshmen chemistry textbooks for 15 years. With current semiconductor technology, we can convert sunlight into fuel more efficiently than the fastest growing plant. So we know this works and that we can beat what evolution did. To help us now, however, there are three requirements: it must be cheap, robust and efficient. At the present time, I can give you two at a time. You pick the two. I just can't give you the third. If you want it cheap and efficient, it's not robust. If you want it cheap and robust, it's not efficient. If you want it efficient and robust, it's not cheap. This is where the challenge—and the payoff—resides.

The reason for this dilemma is that the wide band gap materials that are stable, that do split water, don't absorb much sunlight. Materials that absorb a lot of sunlight can be efficient but they're not stable. It may be possible that there is one material that is oxidatively stable, reductively stable and absorbs a lot of visible light. Possibly, that's too much to ask, but we need to find out and this will require experimental examination of a large number of materials. In the last 30 years, theory has not been successful in telling us where to look. We have to conclude that we're not smart enough to know where to look, so we must just look everywhere.

One of the things our energy innovation hub is going to do is screen and catalogue a million different compounds a day. That's evaluating more photocatalysts in one day than have been collectively evaluated to this point in human history. With the system we are developing, you'll be able to sit and type into a computer on an Excel spreadsheet and order up any combination of elements sintered into oxides or sulfides or nitrates, whatever you want, and we're going to run them and determine their solar activity. The entire solar community will be invited to provide materials for testing. We're going to crowd-source the whole thing.

Nature has other systems-level lessons to teach us. In addition to stringing together two photosystems, it separates the products through a membrane that also passes protons (Figure 17).

Figure 17. Mission of the Joint Center for Artificial Photosynthesis.



Melvin Calvin, 1982: It is time to build an actual artificial photosynthetic system, to learn what works and what doesn't work, and thereby set the stage for making it work better

10-Year JCAP Goal, 2010: To demonstrate a manufacturably scalable solar fuel generator, using earth-abundant elements, that, with no wires, robustly produces fuel from the sun, 10 times more efficiently than (current) crops

For any system we build, we had better separate the products, because they have more energy than the reactants. If that's hydrogen and oxygen and in the presence of a good catalyst, you had better separate the products—not only because you might have an explosion but, on a cloudy day, if you don't separate products you'll just short circuit and recombine everything. The other thing that nature has done is to deal with the presence of oxygen. If you split water or work in air, you need to deal with oxygen. It is important to study hydrogenases, but in any practical water splitting system, the hydrogen-evolving catalyst will need to either be protected from oxygen by compartmentalization, or made robust to oxygen exposure, or the system won't really work. The same design principles apply for the water oxidation half reaction. In nature, it's not reductively stable. It's only oxidatively stable. That's fine because it never sees reductive equivalents. How do we do that in artificial systems? How do we build something that works in the air, that actually compartmentalizes the reduction and the oxidation so that they can be independently optimized and not degrade when one sees the other? I've got some ideas on how to do that utilizing permeable membranes, and that's also something we're going to try to do in the Hub.

When I first joined the DOE, the legendary Melvin Calvin was in my program and he made many of these points (Figure 17). Now it's 2010, and we haven't done it yet. That is, nobody has a real artificial photosynthesis system that they can hold in their hand and study. To realize Melvin Calvin's dream, we need to figure out what works and what doesn't work, so we can make it better. I am a believer in the importance of getting a complete system that works, even if at low efficiency, one that has oxygen and hydrogen bubbles and flows and plumbing, even if it doesn't work perfectly, (Figure 18, Figure 19). It's OK if it's not robust, efficient and cheap all at the same time, because if we have a complete working artificial system, we then have something to understand and optimize.

Figure 18. Artificial solar fuel system design.

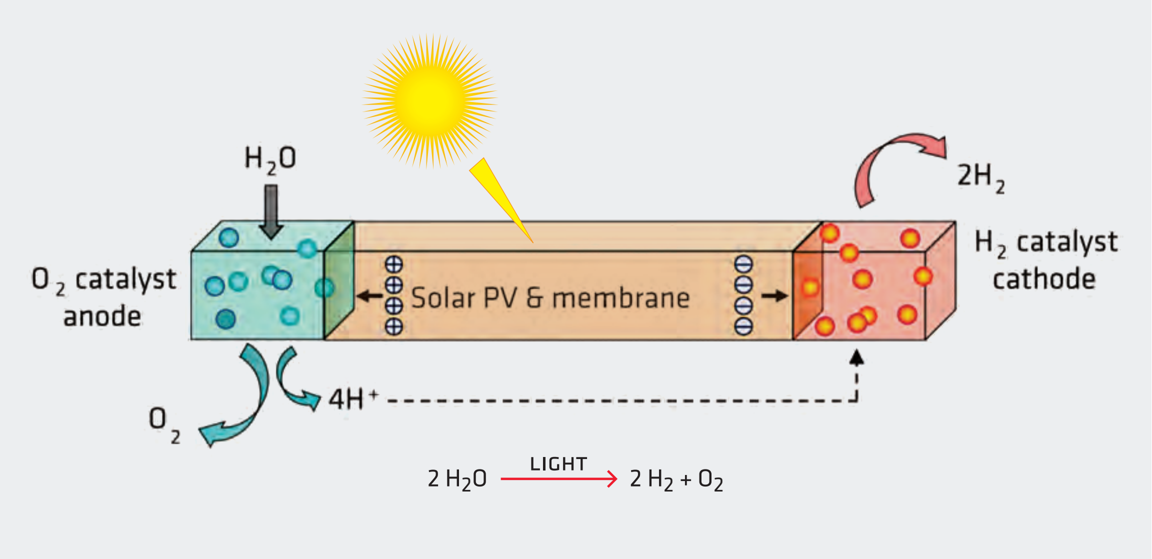


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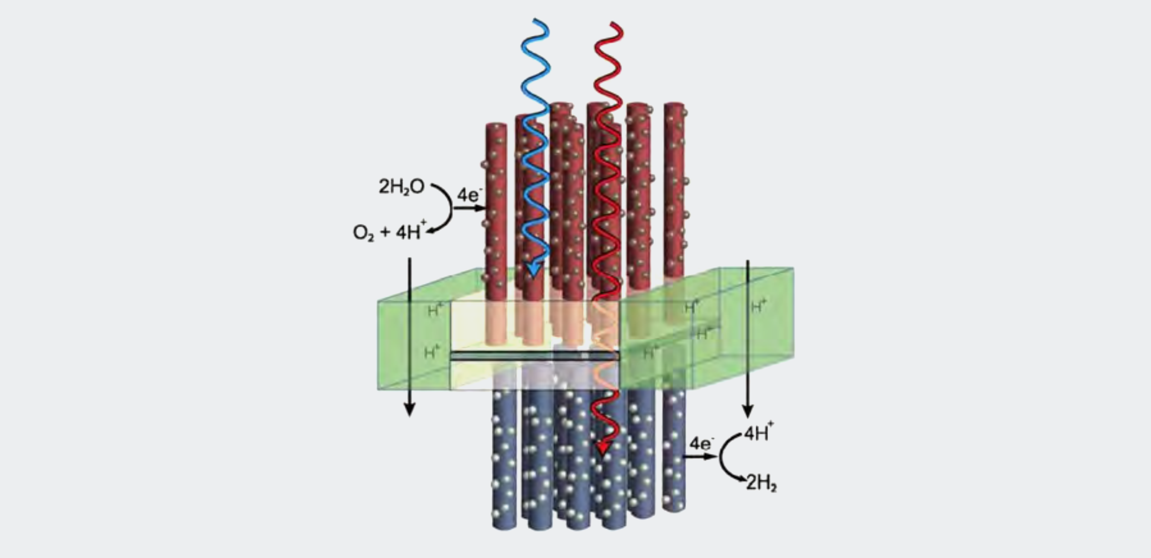
Figure 19. Constructing pieces of a synthetic solar hydrogen fuel generator.



Summary

In summary, I have tried to take a broad view of various approaches to solar energy conversion, outlining what is possible in principle and identifying some of the particularly important problems and bottlenecks. I have also tried to describe how important it is not only to look to nature for design principles, but not to be confined or limited by the boundary conditions imposed on nature. I sincerely hope these discussions can form the basis for continued dialog on working practical solar energy conversion systems and the rapid evolution and progress to artificial systems that can be put into service and further improved.

About Nathan S. Lewis

Nathan S. Lewis is the George L. Argyros Professor of Chemistry at the California Institute of Technology and has served as the Principal Investigator of the Beckman Institute Molecular Materials Resource Center at Caltech since 1992. As one of the foremost solar energy researchers in the world, he specializes in functionalization of silicon and other semiconductor surfaces, as well as chemical sensing using chemiresistive sensor arrays.

Dr. Lewis earned B.S. and M.S. degrees at Caltech and a Ph.D. from the Massachusetts Institute of Technology. In July 2010, Dr. Lewis was named as director of the Joint Center for Artificial Photosynthesis, a U.S. Department of Energy Innovation Hub, and tasked with developing revolutionary methods to generate fuels directly from sunlight. He has been appointed chair of the Editorial Board for Energy & Environmental Science and chair of Research Corporation for Science Advancement's Scialog Review Panel.

Design: Godat Design

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