

WhitePaper

from the 7th Chemical Sciences and Society Summit (CS3)

Solar energy and photonics for a sustainable future



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About the Chemical Sciences and Society Summit (CS3)

The CS3 brings together leading researchers to discuss how the chemical sciences can help to tackle some of the most daunting challenges that our world faces. Previous summits have tackled topics as diverse as water resources, human health, and sustainability.

This White Paper, *Solar energy and photonics for a sustainable future*, summarizes the outcomes of the 7th CS3, held in Dalian, China, on 5–8 September 2017. More than 30 scientists from the five participating countries gathered to discuss four major themes in solar energy: photovoltaics; photonic materials; artificial photosynthesis and CO₂ reduction; and methods and standards. Their goals were to assess the current state of solar energy technologies, identify the most pressing research challenges in these areas, and make recommendations about how the field should progress.

The CS3 initiative is a collaboration between the Chinese Chemical Society (CCS), the German

Chemical Society (GDCh), the Chemical Society of Japan (CSJ), the Royal Society of Chemistry (RSC), and the American Chemical Society (ACS). The symposia are supported by the National Science Foundation of China (NSFC), the German Research Foundation (DFG), the Japan Science and Technology Agency (JST), the UK Engineering and Physical Sciences Research Council (EPSRC), and the US National Science Foundation (NSF). CS3 summits are held every two years, and rotate among participating nations.

This White Paper was written in consultation with the Chinese Chemical Society and CS3 participants.





Preface

As the most abundant energy source, solar energy is widely distributed, sustainable and most importantly, entirely free. It is globally recognized as the most ideal renewable energy source. Nowadays, under the pressure of air pollution and climate change, there is no doubt that the pace of adopting clean energy technologies will continue to accelerate, providing immense opportunities for research on solar energy utilization. Taking China as an example, attention to the construction of ecological civilization has never been paid as much as today. The Government has shown firm determinations to implement the strictest possible regulations for environmental protection and develop eco-friendly growth models and ways of life. According to the "Thirteenth Five-Year Plan for Solar Energy Industry", by the year of 2020, the total annual solar energy utilization in China is projected to reach to equivalence of 150 million tons of standard coal, reducing a total of 280 million tons of carbon dioxide emissions and 6.9 million tons of sulfur emissions. The Ministry of Science and Technology has established key projects in the field of photovoltaic technology, as well the National Natural Science Foundation of China has been providing continuous funding for fundamental research on solar fuels and advanced solar cells.

Higher efficiency, lower cost and better utilization of earth-abundant elements are the ultimate goals for scientists in solar energy. In the meanwhile, although the use of solar energy has so far mainly focused on photovoltaics and solar thermal utilization, however, new technologies such as artificial photosynthesis are in full swing and are expected to continue to bring exciting fruitions to the society.

CS3 was jointly initiated by the five chemical societies and funding agencies in 2009. Solar energy was the very first theme of the summit, and now we are revisiting it for the second time. Thanks to the innovation and diligence of scientists from all over the world, the past 8 years have witnessed remarkable progresses and transformative developments in this field.

The Sun is so generous, so how can we not appreciate and make the best use of it?

Vice President of Chinese Chemical Society

Vice President of National Natural Science Foundation of China



Executive summary

Solar energy can help to tackle climate change by drastically reducing carbon emissions and providing sustainable energy for the world. To radically increase our solar power capacity, we need a wide-ranging discovery programme to develop new light-harvesting materials, catalysts, and structures that help to manage light in solar energy devices. Computational screening, ultrafast analytical methods and other cutting-edge techniques will play a vital role in this effort.

Introduction

Climate change is one of the greatest challenges ever faced by humankind. The world's energy consumption continues to rise, and the majority of our energy sources — specifically coal, oil and gas — release the greenhouse gas carbon dioxide (CO₂). To tackle global warming, we need to cut CO₂ emissions by making a dramatic shift to renewable energy sources.

Solar energy can make a huge contribution to this effort. Photovoltaic (PV) modules already provide almost 2% of global electricity, and collectively offer more than 300 gigawatts (GW) of power capacity. But to decarbonize our energy systems, some projections suggest that PV capacity must grow rapidly in the coming decades, perhaps supplying 40% of our electricity by 2050. To meet that target, we urgently need new technologies to harvest and store solar energy more effectively.

Although PV electricity can be stockpiled in batteries, a promising alternative involves sequestering solar energy in chemical bonds, just as nature does during photosynthesis. For example, 'artificial photosynthesis' systems can harvest sunlight to drive the production of hydrogen, potentially useful as a transportation fuel. Hydrogen is also a valuable

reagent for making other chemicals — including liquid fuels and plastics — through reactions with CO₂, a strategy that could ultimately help to reduce the concentration of CO₂ in the atmosphere.

The chemical sciences play a crucial role in developing these technologies. Researchers are discovering materials, based on inexpensive and abundant elements, which can capture light or speed up photochemical reactions. They are also using a wide range of techniques to measure, understand and control how these processes work, in order to make them more reliable and efficient.

In September 2017, the 7th Chemical Science and Society (CS3) summit in Dalian, China, brought together leading researchers from around the world to discuss the current state of these solar energy technologies, and to identify the key research challenges they face. Their recommendations, documented in this White Paper, underline the significance, urgency and growing importance of this research.

It is clear that breaking out of the existing framework in the field of energy could bring potential clues to solving problems common to all humankind. Global-



scale approaches and initiatives can accelerate research drastically in this area.

Photovoltaics

Over 90% of the world's PV modules rely on the semiconductor material silicon to harvest sunlight, and in recent years their cost has plummeted, thanks to lower materials costs and economies of scale in factories. To spur the deployment of PV capacity, researchers need to develop solar cells that generate electricity more efficiently, and that cost even less money and energy to manufacture. It is equally important to reduce the overall system costs, since non-module costs dominate the cost of solar electricity, and this can be assisted by higher cell efficiency and variations in module product form.

There are various ways to lower the cost of silicon cells. Expensive components can be replaced with cheaper alternatives: swapping silver electrodes for earth-abundant metals such as copper or nickel, for example. Researchers are working on new methods to prepare thinner silicon films, which do not compromise the electronic quality of the material. To boost their efficiency, silicon cells can also be teamed with other PV cells that absorb a different part of the spectrum of light, forming so-called tandem or triple (multi-junction) cells.

Perovskite and wide-gap chalcopyrite cells are examples of promising tandem partners. Perovskite cells have made rapid efficiency gains over the past few years and should be relatively easy to manufacture, although there are concerns about their long-term stability and the lead content of the most promising perovskites. To make further improvements, researchers need a better understanding of fundamental processes inside the

cell, such as how light separates electrical charges, how those charges travel through the perovskite, and how the interfaces between different materials affect charge transport.

Organic PV (OPV) materials also show great promise. They are inexpensive, flexible, readily processed into large-area films, and cell efficiencies have improved steadily to more than 13%. Researchers are exploring a wide variety of ways to improve their performance further: OPVs are also being used with quantum dots, for example, and inverted bulk heterojunction OPVs containing polymers and small molecules may also become an important technology.

In all of these burgeoning PV materials, including chalcopyrites and kesterites, there is a need for more fundamental research. That is also true of novel and so far mostly unexplored multinary materials with optoelectronic properties equivalent to perovskites. Besides important research on these emerging materials, scientists should search for new wide-gap semiconductor materials that are needed for devices harnessing the full solar spectrum, by taking advantage of novel synthesis and computer-aided materials theory.

One of the principal arguments for developing alternatives to silicon PV cells is that their fabrication is very energy-intensive. In contrast, thin-film cells use less material, and are far less resource intensive. Yet the vast investment in silicon PV manufacturing makes it difficult for new technologies to compete in the market. Smart specialisation in currently niche markets may open doors for new technologies. For example, many of the technologies discussed in this report could be used in building-integrated photovoltaics (BIPVs), an application that is expected to gain a huge market in the long term.



Researchers developing new PV semiconductors typically spend a great deal of time making and testing the materials. Using computational models to predict the properties of those materials could accelerate this process considerably, by winnowing down the shortlist of materials to pursue in the lab. This computational approach must be underpinned by solid theoretical foundations, along with internationally-agreed standards that rate the effectiveness of solar energy materials. Indeed, this strategy — building robust datasets and reliable theories to enable computational screening — should be applied to all of the solar energy materials discussed at the CS3 summit. An extended ‘materials genome’ approach, based on a better understanding of fundamental cause-effect relations and an improved control of materials design and manufacturing across the different length scales, could become a key tool for further materials and device optimization.

Researchers also need to consider the sustainability of the elements in their cells, and the CO₂ emitted during the manufacture of a module. Rigorous life-cycle analyses can help to answer both of these questions. Ultimately, next-generation PV cells should rely on readily available elements, have a minimal environmental footprint, and boast a lifespan of 20 years or more. Crucially, they will only achieve commercial success if they offer high efficiencies that are comparable to current technologies.

Summary: New PV materials with abundant elements

New materials and fundamental understanding is still needed.

1. Target higher efficiency

- Multi-junction devices — understanding, measuring

and controlling interfaces is key

- Light management — taking into account real properties of sunlight

2. Material development

- Generates fundamental understanding with wider scope
- Targeting application specific properties (BIPV etc)

3. New materials discovery

- Move away from empirical approaches
- Fusion of computational selection with experimentation including high throughput approaches
- Development of screening tools / methods and metrics (other than devices)

4. Sustainability

- Energy efficiency/energy balance
- Abundance
- Manufacturability
- Toxicity

Photonic materials

Another way to improve the efficiency of solar energy devices is simply to make better use of the light that falls on them. This ‘photonic’ approach has the potential to significantly improve PV cell efficiencies using low-cost technologies.

Changing the design of the solar cell, by strategically adding reflecting layers, for example, can increase efficiencies by a percentage point or more. Tiny structures such as towers, spheres or pyramid shapes on the surfaces of cells can scatter more light inside. Other structures, such as nanopillars and nanowires, can help the semiconductor to absorb light more efficiently.



Meanwhile, devices called luminescent solar concentrators can harness diffuse sunlight over a large area and funnel it down to a much smaller cell. This offers a very large light-collecting area for a relatively small cell size, potentially reducing the materials intensity of the cell itself. One of the more promising near-term applications for LSCs involves using them in BIPVs, either in windows or as decorative features.

Another approach aims to overcome an important limitation of semiconductors: they can only absorb part of the solar spectrum, so a lot of the sunlight that hits them is wasted. Materials known as upconverters can help to avoid this waste by combining two low-energy photons to make a high-energy photon, which can then be absorbed by the semiconductor.

In all these cases, researchers are trying to develop a deeper fundamental understanding of the energy-transfer processes involved in order to create photonic materials that are more efficient, long-lived and inexpensive. Data-driven discovery programmes are needed to accelerate the development of new photonic materials, and this work would be helped by well-maintained and accessible databases of materials properties, to enable computational screening of the composition, shape and structure of materials for optimum performance.

Manufacturers need cheap and scalable methods to make photonic structures for light capture and conversion. Various laboratory methods have been developed, but one of the more promising techniques is 3D printing. Chemists and materials scientists can help to develop the materials and technologies that could turn 3D printing into a practical manufacturing technology for photonic structures.

Research on photonic materials could offer significant

benefits to solar PV devices, but it may have an even greater impact on photochemical synthesis (see below).

Summary: Photonic materials and photon upconversion

1. Key metric: Radiative efficiency

- Need to measure luminescence, identify pathways for relaxation
- Opportunity for characterization of electronic relaxation and structural relaxation: vibronic relaxation (couple electronic relaxation measurements to ultrafast structural dynamics using coherent free-electron laser light sources)
- Need predictive theory for excited state lifetime and decay

2. Opportunity: Data-driven Discovery

- Large theoretical and experimental databases can be interrogated with machine learning
- Need databases of key materials properties (mobilities and excited state lifetimes)
- Data driven discovery can also be applied to photonic design and device design

3. Direction: Focus on schemes for 'Beyond-SQ Limit' Solar Energy

- Photonic design for light harvesting: reduce materials cost of absorbers by light trapping (plasmonics, dielectric light trapping)
- Upconversion, downconversion, downshifting: can be integrated with existing silicon solar PV; biggest need is new materials
- Multijunctions face a choice: join Si (Si-based tandem) or compete (requires new materials)
- IB band, MEG
- Hot carrier collection for PV and PEC: key issue is to collect carriers prior to relaxation



- Thermophotonics (LSCs, solar heat engines)

Artificial photosynthesis and CO₂ reduction

Generating electricity is not the only way to exploit solar energy. Sunlight can also be used to drive reactions that ultimately store energy within chemical bonds, so that energy from the Sun can be used after it sets. Researchers are developing devices such as photoelectrochemical cells (PECs) that can achieve this by splitting water to make hydrogen, for example.

Yet current systems are too expensive and inefficient for commercial deployment. They need new light-absorbing materials — and selective, effective electrocatalysts — that are cheap, safe, efficient, abundant, selective and robust. Researchers need to understand, at a molecular level, how the catalysts interact with their surrounding; and how charge and energy flow from a light-absorbing material to the catalyst. Research in these areas should help to integrate materials and catalysts with atomic precision.

Photoelectrochemical devices also need more efficient light-harvesting materials that can stand up to the rigors of the water-splitting reactions. In many of these challenges, researchers can take inspiration from natural photosynthesis itself, which uses a remarkable self-repairing catalyst made from abundant elements to oxidize water.

To minimize the impact of climate change, many researchers argue that we also need to develop technologies that remove CO₂ from the atmosphere on an industrial scale. But using photochemical processes to turn CO₂ into useful products poses a significant challenge, not least because it involves

breaking the strong carbon-oxygen bonds in CO₂ and form new carbon-carbon or carbon-hydrogen bonds. All of these processes are multi-electron reactions, and are energy demanding. For direct air conversion, it may also be necessary to develop materials to pre-concentrate the CO₂ to a local concentration for catalysis that is significantly higher than 400 ppm.

Some approaches use inorganic catalysts to speed up these reactions; others use materials such as carbon nitride or conjugated organic polymers; yet others unite semiconductors with enzymes, or even living organisms, to create hybrid catalysts.

Photoelectrochemical systems will have a better chance of widespread use if they are tailored to make, if needed, more complex higher-value molecules, as well as simple fuels. Indeed, researchers should consider the practicalities of these systems from an early stage, assessing whether they have the potential to be cost-effective and viable at large scales.

To make truly significant progress in this area — for example, by photochemically converting CO₂ to higher alkanes — there is a need for continued fundamental research that explores new concepts, unfettered initially by overly narrow technoeconomic analyses, since it is unlikely that small changes to existing systems will attain this goal.

Photocatalytic systems are at an early stage of development, so there is still a need for basic research on wide range of approaches. While it is too early for any detailed technoeconomic analysis to be useful in this area, an evaluation of the net energy costs of the conversion process will be useful in determining their viability.



Summary: Artificial photosynthesis and CO₂ reduction

1. Water oxidation, CO₂ reduction

- Target molecules, larger C-containing molecules
- H₂ and thermal catalysis
- CO₂ reduction and N₂ fixation

2. Light harvesting, charge separation

- band gaps, Fermi level and catalysts

3. Catalysis

- New catalyst concepts, inspired by natural photosynthesis

4. Integration of multifunctional materials and various components with atomic precision

- New aspects, including light manipulation and modeling

Methods and standards

Solar energy research is underpinned by the methods used to prepare and analyze materials. Analytical methods provide the data needed to develop new theories, and to identify the most promising materials by using data-driven approaches such as computational screening.

CS3 delegates discussed a range of analytical techniques that could help researchers in this area, particularly when studying processes that take place on incredibly short timescales and atomic spatial scales. Some of these techniques rely on large facilities such as free-electron lasers that produce very short, intense pulses of X-rays or ultraviolet light. All aspects of solar energy research can benefit from international and interdisciplinary collaboration on these techniques, by sharing expertise, facilities, and

best practice.

Researchers also need to agree on the best ways to measure the performance of solar energy materials, in order to make fair comparisons between devices. PV cells can be tested and certified at independent centres, but these services are not available for photoelectrochemical cells, the catalysts they depend upon, or upconversion/downconversion materials — nor have the most appropriate tests been developed. In order to drive research along the most promising paths, researchers need to agree on the best metrics that rate the performance of their devices.

One option worth considering is for journals to require researchers to provide standard performance measurements for their solar energy conversion systems, including solar cell efficiency and solar-to-fuel performance. To make this practicable, it would be necessary to establish validated test centres, as for photovoltaics, to verify these measurements independently, particularly when reported results break existing records or introduce a fundamentally new type of chemical reactivity.

Summary: Photofunctional materials and structures for light manipulation

1. Development of experimental techniques for a better understanding of fundamental photophysical and photochemical processes at interfaces to understand what determines efficiency in working devices

2. Develop theoretical and computational approaches to understand the complexity of photofunctional systems, from the molecular level of light-driven charge transfer processes between solid and electrolytes up to the device level



3. Development of cheap and scalable methods for the creation of 2D and 3D structures at the sub-micrometer length scale to improve the efficiency of light conversion systems

4. Explore opportunities to couple light energy into biological systems

5. Develop standards, best practices, and databases

Conclusions

CS3 delegates agreed that the path to a much greater deployment of solar energy technologies must include a wide-ranging materials discovery programme, often branded in the United States as a ‘materials genome’ approach. Researchers need to consider, where possible, potentially using computational selection to help guide their experiments. This will help to develop a genuine synergy between theory and experiment. High-throughput robotic discovery may also have an important role to play, particularly when coupled with computational selection (for example, a ‘funnel’ approach). Researchers should use a range of analytical methods to probe the mechanisms of solar energy processes, rather than focusing on performance metrics alone, thus building both large data sets and fundamental understanding to drive research forwards. Fundamental studies are more vital than ever, to advance knowledge and to develop more reliable predictive theories about key properties, such as charge transfer across the interfaces and the actual detailed mechanisms of photocatalytic solar fuel production.

This report is not about picking winners — solar energy clearly needs a broad base of scientific

research. Some systems have value because of their technological potential; others because of what we can learn about fundamental mechanisms. Nevertheless, researchers should keep an eye on the potential commercial viability of their devices, considering practicalities such as whether systems will be cost effective, scalable and sustainable.

And one size does not fit all. Each country has its own unique set of natural resources, energy systems and economic circumstances. Using PV electricity to make hydrogen by electrolysis may make sense in one location; in other places, photoelectrochemical cells will be more viable. The key message is that the world needs a range of solar energy options, and funding should reflect that by supporting a variety of fundamental research and emerging technologies.

Multidisciplinary collaboration is increasingly important in solar energy research. Discoveries about PV semiconductors can often be applied to PECs, and vice versa; photonic strategies can help both. Consequently, the field needs to educate experienced researchers and bring in early-career researchers who are able to take a systems view of the field, offering a broader perspective on solar energy problems that draws on many areas, from physics, chemistry and biology to engineering and other areas. The trend towards training students in interdisciplinary centres gives cause for genuine optimism about the future of collaboration in this area.

Indeed, young scientists should flock to the field — after all, developing through robust fundamental research solar energy technologies to tackle climate change is one of the most important and inspiring challenges that chemistry has ever faced.



Chapter 1: Photovoltaics

The cost of photovoltaic electricity has fallen dramatically over the past decade, driving a rapid increase in the world's capacity to harvest solar power. This success story has relied on silicon solar cells, but the technology may face limitations that will hinder the massive capacity expansion needed to curb greenhouse gas emissions. Chemists, materials scientists and physicists have a vital role to play in improving the performance of silicon cells, and developing the next generation of photovoltaic materials.

Introduction

Solar power is booming. The manufacture of photovoltaic (PV) cells, which harvest light and convert its energy into electrical current, is now the world's largest optoelectronics industry. PV devices provide about 2% of global electricity, and offered more than 300 gigawatts (GW) of power capacity in 2017 (see Fig. 1.1), which corresponds to about 75 GW of conventional power stations running around the clock. PV manufacturing capacity has grown rapidly, especially in China, to around 70 GW per year.

This growth has been propelled by a range of factors. Economic incentives have helped to drive investment in renewable energy, for example, and a gradual increase in cell efficiency has improved the return on those investments. More than 90% of PV cells use the semiconductor material silicon, mostly in crystalline form, and today's commercial modules can convert about 20% of the light that falls on them into electricity (in the lab, silicon cell efficiencies can top 26%).

Arguably the most significant factor, though, has been the dramatic fall in the price of PV modules: typically, one watt-peak of solar power capacity now

costs less than US\$0.5. This is largely due to lower materials costs and economies of scale in Chinese manufacturing plants — indeed, CS3 delegates heard that a Chinese solar company recently released a 21.5% efficiency PV module at a cost of less than \$0.2 per watt-peak, comparable to coal power.

The blossoming of solar power is an astonishing and somewhat unexpected success story. A recent meta-analysis found that previous predictions from the International Energy Agency, the Intergovernmental Panel on Climate Change and other groups had consistently underestimated future PV growth.¹ It now seems possible that the world could get 40% of its electricity from PV by 2050, potentially making a huge contribution to reducing humans' CO₂ emissions.

Yet that target presents enormous challenges. It would demand an additional 1000 GW of PV capacity to be installed every year from about 2030. It also demands major innovations in electricity storage, such as using large batteries to smooth out the peaks and troughs of solar power — a technology reliant on chemistry and materials science, yet beyond the scope of this report as well as developments in power distribution systems and demand management. A potentially more efficient solution is to convert the



electricity into storable fuels, an approach that is discussed in Chapter 3.

Despite the remarkable rise of silicon PV cells, more developments in cell technology are likely to be needed in order to reach that 2050 target. Achieving higher module efficiencies and lower-cost production will require new materials, new module designs, and a better understanding of the fundamental processes involved in exploiting solar energy.

In the near term, one of the key challenges for chemists, materials scientists and physicists is to improve the performance of silicon cells as much as possible: even adding two percentage points to silicon PV efficiency could make a huge difference to the economics of solar PV. Meanwhile, finding ways to use less silicon, in cheaper forms, could improve the industry's sustainability while reducing module costs, leading to wider use of solar PV.

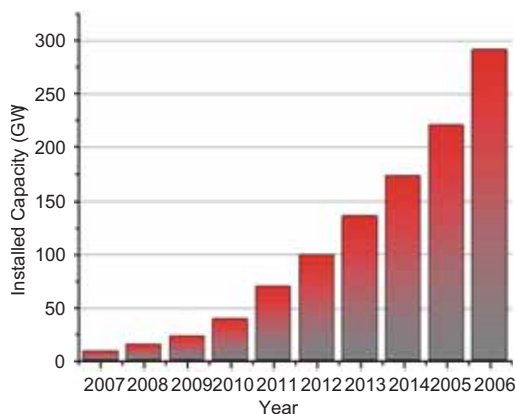


Figure 1.1: Global cumulative PV capacity
The International Renewable Energy Agency (IRENA), Renewable Energy Statistics 2017
<http://bit.ly/2rH2b2M>

The longer-term challenge is to identify silicon's extension and/or successor technologies. This next generation of PV cells must be more efficient, lower

cost, suitable for mass manufacture, and operate for decades — all with a minimal environmental footprint.

Improving silicon

Silicon itself makes up about 15% of the cost of a PV module. So using less silicon without hampering performance, or using a cheaper semiconductor altogether, offer routes to lower costs. Today's PV cells typically use a 120-150 micrometre-thick layer of crystalline silicon — any thinner, and the silicon tends to be fragile. Thus creative solutions are needed to realize high-quality crystalline silicon films on novel substrates, or to develop cost-effective methods for epitaxial growth and subsequent lift-off techniques.

A second strategy is to replace other expensive components within the module. Silver electrodes can account for up to 20% of a module's cost, so replacing silver with earth-abundant metals such as copper and nickel could reduce prices.

The cost-effectiveness of a solar PV module also depends on how much electricity it can deliver. Broadly, that process is well understood: when a photon of light of sufficient energy hits the semiconductor material in a PV cell, it excites a negatively-charged electron across the bandgap into the conduction band, and leaves behind a positively-charged 'hole' in the valence band. Electrons and holes then migrate to opposing electrodes, generating a current and a voltage.

The maximum theoretical efficiency of this process is known as the Shockley-Queisser (SQ) limit. It depends on a combination of factors, such as the cell's ability to absorb only certain wavelengths of light above the bandgap. Cells may be held back from the SQ limit by, for example, the loss of absorbed



energy when electrons and holes recombine (measured as the cell's 'external radiative efficiency'). If global PV capacity is to grow by an order of magnitude, researchers may need to push solar cells closer towards (and perhaps even past) the SQ limit.

One way to improve efficiencies relies on controlling light. Certain coatings can change the wavelength of some of the incoming light, for example, so that the semiconductor can absorb more of the photons that fall on it. Alternatively, materials that concentrate diffuse light onto a PV cell can improve module efficiency. These 'photonic' approaches are discussed in more detail in Chapter 2.

Another approach for boosting the efficiency of silicon PV cells is to add a second or third cell on top of it. In these multi-junction cells, the top cell absorbs one part of the light spectrum, and the unused light passes through it before being absorbed by the lower cell. Tandem cells and triple cells are already commercially available, but there is plenty of scope for improving their cost and performance.²

Many of the potential tandem or triple partners for silicon use alternative semiconductor materials. The semiconductor chalcopyrite CIGSSe (copper indium gallium sulfo-selenide) is already mass-produced in Japan and China, and its higher-bandgap cousin, based on the sulfide only, is a suitable tandem partner for silicon. Other potential tandem partners, such as those based on perovskites, have only been investigated in labs for a few years. Up till now, there has been a lack of effort to develop high-energy-bandgap absorbers.

Developing thinner films

Roughly 5% of installed PV capacity uses CdTe cells,

with typical efficiencies of about 22% in the lab and 16% in commercial modules. The semiconductor layer itself is cheaper than that of a typical silicon cell, because it employs a very thin film, rather than a relatively thick layer of silicon.

One measure of a PV cell's environmental footprint involves tallying all the material involved in the mining, extraction, processing and assembly that is involved in its manufacture — its 'materials intensity'. CdTe cells have a materials intensity of 74 tonnes per GW;³ by contrast, silicon cells consume about 1000 tonnes of materials per GW.⁴ This is a powerful illustration of why PV cells can and must improve on silicon.

Yet CdTe cells must also contend with a drawback: cadmium is toxic. In contrast, chalcopyrite (CIGSe or CIGSSe) modules are not hampered by concerns about toxicity, and more than 5 GW per year of production capacity is currently being installed in China.

One of the more recent arrivals to the family of thin-film cells utilizes a class of materials known as perovskites. Since 2009, the efficiency of perovskite cells has skyrocketed from about 4% to more than 22%.⁵ The cells can be created by cheap, low-temperature solution processing, and the structure of the perovskite compounds are relatively easy to fine-tune, enabling researchers to modify their optical and electronic properties.

But the best-performing cells in this class all rely on lead-based perovskites, raising health and environmental concerns. There are also lingering questions about the long-term stability of perovskites, which may hamper their commercial prospects. Nevertheless, there is much optimism that these



problems can be overcome, and companies are already developing production systems to make perovskite cells in tandem with silicon. Indeed, the tunability of perovskites may eventually enable perovskite-perovskite tandems, with each layer absorbing different wavelengths.

Most of the progress in perovskites, and other thin film materials like chalcopyrites, has been based on empirical work. CS3 attendees agreed that more fundamental research is needed to understand exactly how the perovskite cell works in order to boost performance further. In addition, an improved understanding on the precise control of relevant manufacturing processes is still missing, as it is for many other novel thin-film absorber materials. All this research should run in parallel with efforts to improve device integration and develop technologies that will aid mass production.

Another promising, but less studied, class of cells uses materials called kesterites, with efficiencies that have risen from less than 1% in 1997 to 13.8% in 2016.⁶ In addition, there are very many multinary elemental combinations that form semiconductors with the right absorption properties (bandgaps). However, the increasing complexity and missing knowledge in controlling their physical properties have so far hindered a systematic evaluation of their PV promise. Addressing fundamental questions about these materials, such as the relation between their structure, defects and performance, is necessary to boost efficiencies in the near future.

It will be hard for alternative PV materials to compete directly against commercial silicon modules. Industry has invested around \$800 billion in silicon manufacturing infrastructure, and that is not about to be usurped. But tandem cells offer next-generation

semiconductors an opportunity to piggyback on silicon's success, and establish a commercial foothold that will enable further cost savings as manufacturing processes mature. To improve the performance of these thin-film multi-junction devices, though, the cells will need better interfaces between the materials, with controlled adjustments. That must be supported by basic research to understand, measure and control these interfaces.

Going organic

Another promising form of PV cell relies on carbon-based (organic) molecules such as polymers. Organic PV (OPV) materials have several advantages: they are cheap, flexible, straightforward to make from readily-available materials, and easy to process into large-area films. The molecules' structures can be easily tweaked to adjust their properties, and this has delivered steady improvements in cell efficiency, to over 13%.⁷

OPVs come in an array of colours, and can be used as a tinted coating for glass that also generates electricity. This offers the cells access to a niche market that silicon cannot fill. These include some aspects of building-integrated photovoltaics (BIPVs), a market that is forecast to grow rapidly. However, the performance of OPVs can decline by 20% over their lifetime, caused by poor long-term stability to oxygen, ultraviolet light, moisture or temperature — all problems that currently prevent their use in BIPVs, but that basic research can help to solve. (BIPVs need not be transparent: CIGS modules, for example, are homogeneously black or coloured, and are very appealing to architects.)

A further application for organic and inorganic molecular systems are their integration with inorganic



absorber materials in hybrid systems, as already shown to be valuable for contact formation in many perovskite cells. Researchers are exploring a wide variety of ways to improve the performance of OPVs. They are also being used with quantum dots, for example, and inverted bulk heterojunction OPVs containing polymers and small molecules may also become an important technology.

Mass manufacture is currently a challenge for OPVs, as for any other new PV material. Processes used to make high-quality films in the lab need to be translated to higher volume fabrication processes for commercial production, and this can reduce their efficiency. So researchers are investigating alternative manufacturing processes that could be used commercially, along with PV polymers that are better suited to mass manufacture. Small molecules and quantum dot materials also provide opportunities for low-cost photovoltaics.

Fundamental research questions lie at the heart of these stability, efficiency and processing issues. Understanding exactly how these problems arise is the first step to solving them. That includes figuring out how the molecular structure of the polymer affects charge separation, how the distribution of charge within the polymer affects the movement of the excited electrons and holes, and even how the orientation of polymer molecules in the film can be altered to improve performance (see Chapter 4).

Conclusions

To judge the true potential of new PV materials and devices, researchers must be able to compare results between different systems. Consequently, reports of spectacular cell efficiencies must be backed up by independent confirmation at national

laboratories such as the US National Renewable Energy Laboratory (NREL). In addition, some journals have a checklist of performance metrics that must be reported for PV cells, and this is a useful protocol that should be adopted more widely to ensure that results can be assessed fairly.

Efficiency is a critical way to judge the success of a PV cell, of course, but there are other factors to consider. If the semiconductor is particularly cheap and easy to process, or more reliable over a longer time span, it could be preferable to slightly more efficient devices. Researchers also need to consider the sustainability of the elements in their cells, including the abundance of the elements, how they are mined and purified, their toxicity, and the energy used in manufacturing a PV module.

It is also vital to consider the balance between the CO₂ savings of deploying a particular PV technology, and the emissions caused by manufacturing the cell. Different PV materials will pay back this 'carbon debt' in varying amounts of time. The field is moving so quickly that it would be helpful to have more up-to-date life-cycle analyses of the various competing technologies to understand their overall impact on the environment.

Research into new semiconductor materials often relies on time-consuming empirical research — essentially, building each new cell in the lab and then testing it. Materials discovery could be speeded up by using computer modelling to predict the behaviour of new materials, calculating properties such as band gap, optical absorption, or defect tolerance. This sort of computational selection could help to direct which materials are pursued in the lab, especially if researchers also develop new high-throughput experimental screening methods.



Computational models must be underpinned by improved theories about the mechanisms involved in light harvesting and charge separation, particularly in materials such as perovskites and polymers. These theories could also be highly relevant to research on batteries or photoelectrochemical cells (see Chapter 3).

Even if alternative PV materials cannot beat commercial silicon cells today, they are still worth pursuing. Perovskite cells, for example, would not have experienced such a stellar rise if they had not built on two decades of work on dye-sensitized and organic solar cells.

The commercial success of silicon PV modules offers the first glimpse of a revolution in energy supply that could take place over the coming decades. But that will only happen if researchers develop alternative PV materials alongside silicon, while gaining a deeper understanding of their operation.

Recommendations

1. Improve the efficiency of silicon-based cells (including multi-junctions).

Researchers need to understand, measure and

control the interfaces between materials in multi-junction devices; and develop materials and structures that can maximize light harvesting and energy capture.

2. Develop existing alternatives.

Further efforts to understand the fundamental sources of energy loss within cells will lead to higher efficiencies. Exploiting niche markets that could become transformative in the long term, such as building-integrated photovoltaics, will help production methods to mature, potentially lowering costs.

3. Discover new PV materials.

Researchers must move away from trial-and-error research. Computational modelling of materials' properties, high-throughput screening, along with new analytical methods and metrics, will all help to accelerate materials discovery programmes.

4. Consider sustainability at all stages.

Even at the basic research level, researchers need to think about the abundance, toxicity, materials intensity, energy investment and potential manufacturability of new PV materials.



Chapter 2: Photonic materials

The efficiency of photovoltaic cells and other solar energy devices could be significantly improved by manipulating the light that falls on them. Various materials can be used to funnel more sunlight into cells, for example, or alter the spectrum of the light to improve energy conversion. Data-driven discovery programmes will help to develop cheap and efficient photonic materials for these tasks.

Introduction

Much of the research effort to improve photovoltaic (PV) devices has focused on semiconductor materials that capture light to generate an electrical current. Increasingly, though, there is a growing focus on manipulating light itself, as it falls on the PV cell and travels through it.⁸

This ‘photonic’ approach has the potential to significantly improve PV cell efficiencies using low-cost technologies, and in some cases may push cells past the Shockley-Queisser (SQ) efficiency limit (see Chapter 1). It should also benefit other solar energy technologies, such as photoelectrochemical cells (PECs — see Chapter 3).

In some cases, redesigning the internal structure of a PV cell can make better use of the light within its semiconductor layer. Miniature structures on the surfaces of the cell can help to channel more light into its active layer. And luminescent materials can concentrate the Sun’s rays to increase the cell’s power output, and also alter the wavelength of incoming light so that the semiconductor is able to absorb more photons.

Although researchers have seen promising results in all of these areas, the main challenge for the future is

to develop new photonic materials that are efficient, long-lived and inexpensive.

Redesigning the cell

One of the most important ways to move PV cells towards their SQ limit is to improve their external radiative efficiency. After incoming photons generate electrons and holes within a semiconductor material, those charge carriers often recombine before they can reach the cell’s electrodes. Recombination may release a photon that can generate more electron-hole pairs elsewhere in the semiconductor, a process called photon recycling; or it may lead to non-radiative processes, which often simply heat the semiconductor material. The external radiative efficiency of a cell essentially measures how often recombination leads to beneficial photon recycling.⁹

Meanwhile, a new design of silicon PV cell has become increasingly popular in recent years (see Fig. 2.1). This so-called Passivated Emitter Rear Cell (PERC) includes a ‘passivation’ layer at the bottom of the cell, and a smaller contact area between the rear metallic coating and the silicon wafer. Along with other tweaks to the cell’s architecture, this helps it to absorb more incoming light; reflects light back into the semiconductor material that would otherwise escape; and reduces energy-wasting recombination

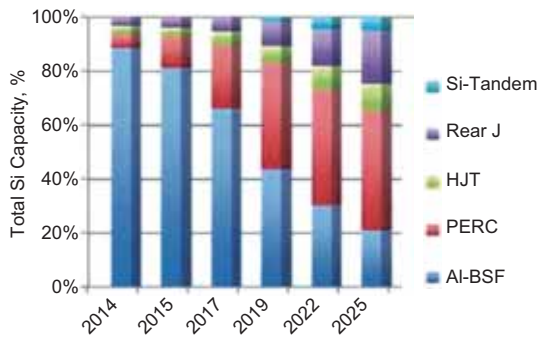


Figure 2.1: Passivated Emitter Rear Cells (PERCs) are becoming increasingly popular International Technology Roadmap for Photovoltaic (ITRPV) 2016 Results <http://bit.ly/2DJCmVp>

pathways. This design typically adds one percentage point to the efficiency of a cell, and more than half of all PV cells manufactured in 2020 are expected to be PERC cells.

Texture the surface

Researchers and PV manufacturers are able to texture the surfaces of their cells with tiny structures

to capture more light. Small towers, spheres or pyramid shapes can act as anti-reflective coatings that scatter more light into the cell, for example, which improves the device's efficiency (see Fig. 2.2). Other structures, such as nanopillars and nanowires, can absorb incoming light and generate an electric field that increases photon absorption within the semiconductor.

But one of the key challenges in this area is to understand which materials and shapes offer the best performance, and how best to arrange them on the surfaces of the cell. Building on that knowledge, researchers also need to develop technologies for cheap, large-scale production of these nanostructures. Various laboratory methods have been developed: colloidal particles on the surface of the cell can act as a template, for example, while plastic molds and 3D printing are also used to produce nanostructures.

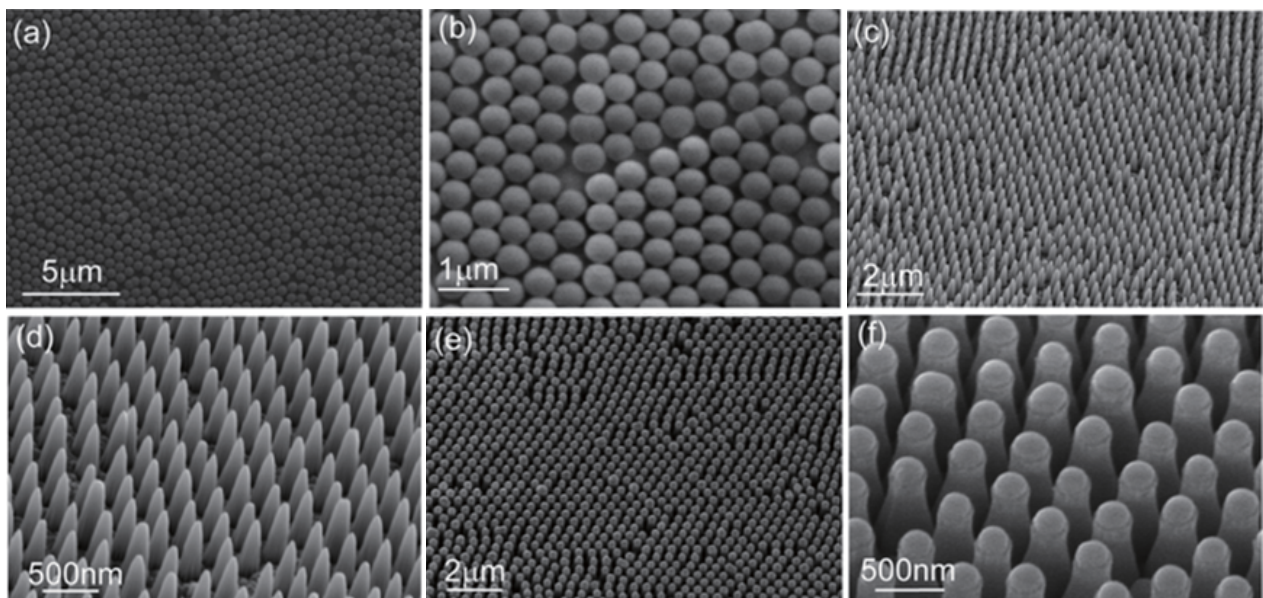


Figure 2.2: Surface structures can help to draw more light into PV cells J. Zhu et al, Nano. Lett., 2009, 9, 279. Reprinted with permission from (Optical Absorption Enhancement in Amorphous Silicon Nanowire and Nanocone Arrays, J. Zhu et al, Nano. Lett., 2009, 9, 279.). Copyright (2009) American Chemical Society.



3D printing, which is now widely used in manufacturing, builds complex shapes using a computer-controlled dispenser that deposits chemicals at precise points in space. Another process called interference lithography can offer similar results by using laser light to etch patterns into small structures. These processes enable gratings or holes to be patterned into tiny pyramids or cones, which could make them more effective at scattering light into the cell.

Although 3D printing is unlikely to be commercially viable as a way to create these structures on a large scale within the next 5 years, the technology is progressing very quickly. Chemists and materials scientists can accelerate that progress by developing materials that are suitable for printing, and studying how their shape and structure affects light absorption. Researchers also need to develop a fundamental understanding of the processes involved in energy losses at the interface between the photonic structure and the semiconductor. Based on this knowledge, it is already possible to computationally screen the shapes of photonic structures, as well as the materials themselves, to optimize their performance, and this is a key area for future advances.

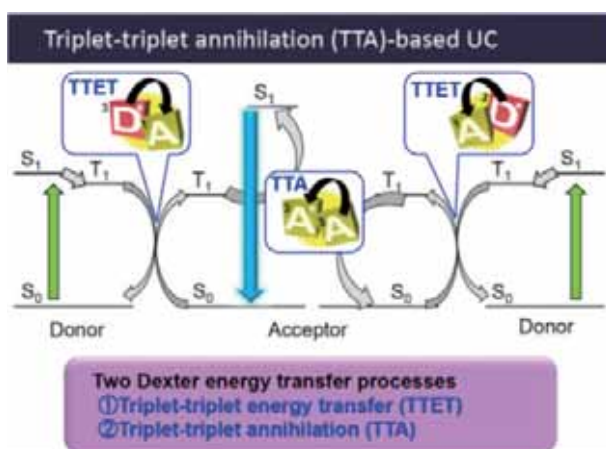


Figure 2.3: The mechanism of photon upconversion
N. Yanai

Catching the light

Larger solar panels can produce more electricity because their surface area catches more light — but they also use more materials, which makes them more expensive and resource-intensive. One way to circumvent this problem is to use a luminescent solar concentrator (LSC), a large panel that gathers light and funnels it into a much smaller solar cell.

Plastic LSC panels contain chemical compounds called luminophores, which absorb incoming light and then re-emit it. This re-emitted light travels along the LSC towards a solar cell that is typically mounted along the edge of the panel. This offers a very large light-collecting area for a relatively small cell size, potentially reducing the materials intensity of the cell itself (see Chapter 1). LSCs can also exploit diffuse light, such as indoor lighting or the weaker sunshine of overcast northern skies. Crucially, the LSC should use cheaper elements than a PV cell, and be easier to manufacture.

The LSC concept has been around for a long time, but these devices need to concentrate light more efficiently in order to be commercially viable. To achieve that, researchers are already developing materials, and new LSC designs, that are able to internally reflect re-emitted light at more oblique angles, to improve energy transport to the PV cell.¹¹

Chemists are also developing a wide range of luminophores that can absorb and emit light more efficiently and with low reabsorption losses. These include quantum dots that emit across a broad spectral range, as well as dye molecules.¹² Luminophores must be non-toxic, and remain stable over the lifetime of the plastic panel, potentially 20



years or more. Since the plastic panel itself may degrade over that length of time, more durable polymers would also help to commercialize LSCs.

One of the more promising near-term applications for LSCs involves using them as building-integrated panels, either in windows or as decorative features. Windows are often tinted by adding a plastic layer between two sheets of glass, and if that could be replaced by a LSC that channels light to a PV cell at the edge of the window, it could provide useful power. CS3 delegates heard that glassmakers are increasingly interested in this approach, and the efficiency of the system does not have to be particularly high for the window to eventually ‘pay for itself’ with the electricity it generates, as long as it does not adversely affect the optical properties of the window.

Change the spectrum

Semiconductors can only absorb light within a certain range of wavelengths — the range depends on the material — and this wastes the energy carried by light of other wavelengths. But some materials can take two low-energy photons that are not absorbed by a PV semiconductor, and convert them into a single higher-energy photon that can be absorbed. This process, called upconversion, allows a PV cell to exploit a broader swath of the spectrum of light. Upconversion of infra-red to visible light is particularly important, because it could open up access to a large chunk of the spectrum that is generally not used by PV cells.

Upconversion can theoretically increase the SQ limit of a silicon cell from about 34% to 44%. Today’s upconversion technology could be improved by developing better upconverter materials. More

efforts are required to improve the efficiency of (near) infrared-to-visible as well as visible-to-UV upconversion, which is more directly relevant to PV and photocatalysis.

Some upconverters are based on nanocrystals containing lanthanide elements, such as erbium and ytterbium. Ytterbium absorbs infrared light, and then transfers the energy to erbium, which emits green and red light. But these systems generally need to be illuminated with bright light to upconvert efficiently, and it can be difficult to fine-tune the materials’ composition so that they emit a particular wavelength of light.

Certain organic molecules can also act as upconverters. Light is absorbed by ‘sensitizer’ molecules, which ultimately transition into a longer-lived form known as a triplet state. This energy then transfers to ‘emitter’ molecules, which can come together to release their energy as a single photon in a process called triplet-triplet annihilation (see Fig. 2.3). Researchers working on these upconverters aim to develop materials that absorb as much light as possible, upconvert it with no energy loss, and then emit as much energy as possible at a shorter wavelength. Promising strategies include extending the lifetime of excited triplet states, speeding up energy migration, and avoiding processes that deactivate the triplets. Another hot topic in this area is ‘singlet fission’, in which a singlet excited state generates two triplet states.

One of the key challenges is to ensure that two energized emitters can actually meet. Some systems have relied on emitter molecules that diffuse through a polymer until they collide with each other, but this diffusion process tends to be slow, and many emitters lose their energy before they meet a



partner. A potential solution to this problem would be the control of energy diffusion by controlling the structural arrangement of the materials. For example, it is possible to use platinum complexes to capture activated emitters and hold them in position, until enough emitters accumulate around the particle to undergo triplet-triplet annihilation.¹³ An alternative approach does not require emitter molecules to move around at all — instead, energy passes along a relay of emitters until two neighbours are energized, and able to join forces to emit a photon.¹⁴

In principle, upconversion technologies might add at least one percentage point to the efficiency of silicon cells. They could have an even greater impact on photochemical synthesis, which uses light to drive chemical reactions that make fuels and other useful products (see Chapter 3). For example, it may be possible to upconvert visible light into ultraviolet light, which could provide a titanium dioxide photo-electrode with sufficiently energetic photons to oxidize water and produce hydrogen gas in a photoelectrochemical cell.

In other situations, the reverse process — downconversion of an ultraviolet photon into two visible-light photons — may also be useful for some forms of solar energy harvesting.

Recommendations

1. Manipulate light to boost the efficiency of PV cells and other solar devices.

Photonic materials can help PV cells to exceed their

theoretical efficiency limits. Researchers should develop the materials, screening techniques and theoretical understanding needed to commercialize photonic approaches.

2. Use a range of photonic tactics.

Develop materials that retain more light within the semiconductor layer and improve their external radiative efficiency. Channel more light into the cell, using surface nanostructures and luminescent solar concentrators. Upconvert or downconvert unused wavelengths of light to help semiconductors absorb more photons.

3. Discover new photonic materials.

Develop cheaper, more efficient photonic materials. Create large, well-maintained and accessible databases of materials' properties to drive discovery programmes, with the help of machine learning and high-throughput screening. Screen materials for key properties such as luminescence. Improve theoretical understanding of photonic processes such as upconversion/downconversion.

4. Find cheap and scalable methods to make photonic structures.

Researchers should develop the materials and methods needed to mass-produce photonic nanostructures, including techniques such as 3D printing, in order to commercialize light-management strategies.



Chapter 3: Artificial photosynthesis and CO₂ reduction

Sunlight can be used to drive chemical reactions, such as splitting water to make hydrogen gas. This could offer a much more efficient way to store solar energy than feeding batteries with photovoltaic electricity. To make these ‘artificial photosynthesis’ systems commercially viable, though, researchers must develop new light-absorbing materials and catalysts, and understand precisely how they work.

Introduction

Despite the huge improvements in photovoltaic cells over the past few decades (see Chapter 1), storing the electricity they produce remains a major challenge. Even state-of-the-art batteries are an inefficient, expensive and resource-intensive way to stockpile energy — although the costs of lithium ion batteries, for example, are falling sharply. On average, a battery weighing one kilogram can store up to 0.5 megajoules (MJ) of energy. That stands in stark contrast to compressed hydrogen, which can store up to 140 MJ per kg. Hydrogen is also versatile: it can be used as a fuel, or reacted with other compounds to make methane, ammonia, liquid fuels and a host of other essential chemicals.

Storing energy in chemical bonds is hardly a new idea — after all, that is how nature hoards solar energy during photosynthesis, when plants use sunlight to react carbon dioxide with water to make carbohydrates and oxygen. On a sunny day, one mature tree can process 10,000 litres of CO₂, producing 12 kg of carbohydrates and enough oxygen to meet the needs of five humans. Globally, about 150 billion tonnes of carbon is captured by photosynthesis every year, according to estimates presented by CS3 delegate Wolfgang Lubitz. It is the primary source of

our food — without photosynthesis, humans could not exist on Earth.

Photosynthesis is already used to store energy in liquid transportation fuels. The ethanol that powers cars in Brazil, for example, is produced by fermenting sugars from sugar cane. But storing solar energy in this way uses vast areas of land, competes with food crops for resources, and is most effective in tropical climates.

It is possible to store the Sun’s energy in hydrogen by using photovoltaic cells to generate electricity, which can then split water by electrolysis. But this two-step process may introduce inefficiencies, and electrolyzers are relatively expensive. So researchers are developing artificial photosynthesis systems that mimic aspects of the natural process, while potentially being much more efficient.

Artificial photosynthesis harvests sunlight to separate electrical charges in a material, and then uses those charges to drive catalytic processes that store energy in chemical compounds. Some systems simply split water to produce hydrogen and oxygen, while others go on to react that hydrogen with CO₂ to produce more complex compounds. The challenge for chemistry is to develop light-absorbing materials that can drive these processes, and catalysts that make



them proceed at a practically useful rate.

Splitting water

One of the most promising approaches to artificial photosynthesis is the photoelectrochemical cell (PEC). The cell contains two electrodes, immersed in water that contains electrolytes, and separated by a semi-permeable membrane (see Fig. 3.1). One — sometimes both — of these electrodes is made from a semiconductor material that harvests light to separate electrons and holes, just like a photovoltaic device (see Chapter 1).

The holes drive an oxygen evolution reaction (OER) at the cell's anode, which splits water into oxygen gas (O_2) and protons (H^+). Meanwhile, electrons drive a hydrogen evolution reaction (HER) at the cell's cathode, with protons and electrons combining

to make hydrogen gas (H_2). Both electrodes have catalysts on their surfaces to accelerate these reactions, and these materials are typically formed into a thin layer that allows light through to the semiconductor beneath. The catalysts need to be cheap, safe, efficient, abundant, selective and robust.

The semiconductor in the HER electrode is often silicon, although cadmium selenide and copper oxides are also used. Texturing the surface of the semiconductor can help to increase the surface area for the HER catalyst and capture more light, improving the overall efficiency of the system.¹⁵ Meanwhile, the OER electrode may use light-absorbing materials such as titanium dioxide, iron oxide, bismuth vanadate,¹⁶ or tantalum nitride,¹⁷ amongst others. In both cases, a range of HER and OER catalysts are being investigated, often using materials based on cobalt, molybdenum, and nickel.¹⁸

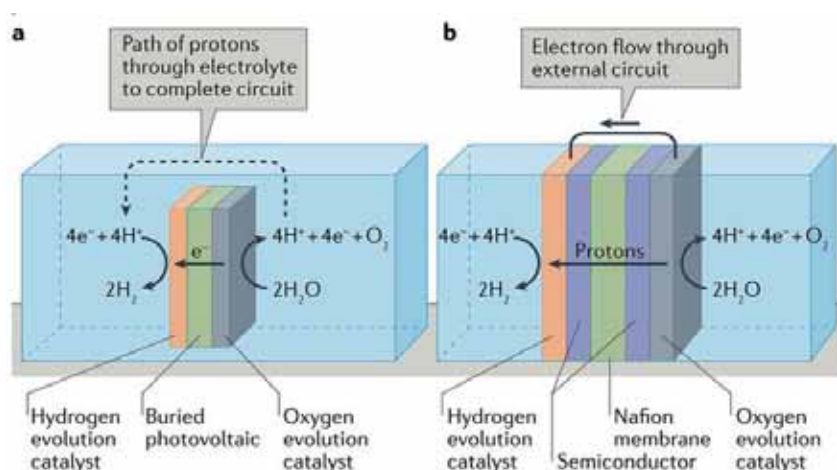


Figure 3.1: Artificial photosynthesis systems can be 'wireless', composed of from a sandwich of materials (left), or 'wired' to create a photoelectrochemical cell (right).

I. Roger et al, Nat. Rev. Chem. 2017, 1, 0003.

Reprinted by permission from [Springer Nature]: [Springer Nature] [Nature Reviews Chemistry] [Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting, I. Roger et al, Nat. Rev. Chem. 2017, 1, 0003], Copyright (2017).

In theory, the minimum voltage needed to split water under standard conditions at room temperature and one atmosphere of pressure is 1.23V (per electron). But an additional voltage, known as the

overpotential, is needed to make the reaction run at a practically useful rate. Semiconductors that are able to supply this additional voltage tend to absorb shorter wavelength light, which limits the range of the



solar spectrum they can absorb and reduces their efficiency. This trade off is one of the key challenges for PECs, and there are several potential solutions.

One approach is to use more efficient catalysts. By speeding up the reaction, they reduce the overpotential that is needed to drive the water-splitting processes at an acceptable rate. For example, a tantalum oxynitride photoanode can perform photoelectrochemical water splitting under visible light. It relies on cobalt oxide nanoparticles to scavenge photogenerated holes and suppress deactivation on the surface of the tantalum oxynitride. Connected to a platinum counter-electrode, the photoanode can generate dioxygen with a relatively low applied voltage.¹⁹

The best PECs using photoanodes and/or photocathodes have a solar-to-hydrogen conversion efficiency of about 2.5%.^{16, 17} Meanwhile, using high-performance triple-junction solar cells to generate electricity, and then feeding that power into a water electrolysis system, can achieve a solar-to-hydrogen conversion efficiency of more than 20%.²⁰

However, higher efficiencies are expected for better-adjusted multi-absorber structures. Energy can often be lost as charge travels between the materials, and solving that problem will require a basic understanding of the transport processes going on at the interfaces.

Tiny variations in the structure of photoactive materials can have a big impact on their ability to separate electrons and holes. Seeding materials such as titanium dioxide with dopants can help, as can optimizing the shape and crystal structure of catalyst particles.²¹ But researchers still need better

methods to measure, understand and control charge separation processes in order to improve molecular catalysts, materials, and assemblies thereof (see Chapter 4).

Photocatalysis

Many researchers developing photocatalysts are looking to nature for inspiration.²² Plants contain a protein called photosystem II, which uses the energy from light to convert water into dioxygen and protons. The protons are then used in a variety of other chemical processes in the cell, including one that ultimately turns CO₂ into carbohydrates. At the heart of photosystem II is a catalytic structure containing four manganese ions that bind and cleave two molecules of water, as well as a calcium ion to help guide the water into place.²³

Photosystem II offers many important lessons for chemists trying to replicate photosynthesis. Manganese and calcium are cheap, abundant elements. The catalyst avoids high-energy intermediates, and big energy jumps, as it breaks water apart. It binds water molecules in a way that produces oxygen more efficiently. Its catalytic structure is embedded in a protein that manages the flow of inputs and outputs, and protects the catalyst from degradation. The catalytic structure also self-assembles, and self-heals when it breaks down. That is an impressive resumé for any catalyst, and chemists must learn all they can about every step in photosystem II's catalytic cycle if they are to replicate it successfully in an artificial system.

Researchers are also investigating catalytic organic materials such as polymers.²⁴ One advantage of using an organic catalyst is that researchers can



easily tweak its structure to modify its properties, for example. Whereas organic catalysts are generally tailored to perform either the HER or OER, very recently Chinese researchers reported that a polymer called PTEB could catalyze both HER and OER.²⁵ However, there are significant challenges in understanding the catalytic reaction mechanism in these systems, as well as improving their long-term stability under operating conditions.

Artificial photosynthesis systems can have a 'wireless' configuration, combining HER catalyst, photovoltaic materials and OER catalyst into a single sandwich (see Fig. 3.1). These can be used as a photocatalytic sheet,²⁶ often described as an 'artificial leaf', or free-floating particles.²⁷

One way to harvest a wide range of visible light involves using two different photocatalysts connected by a 'shuttle redox couple' — a chemical reaction that can transfer electrons from one photocatalyst to the other. For example, an iodate-iodide redox couple can be used with niobate and tungsten trioxide photocatalysts to generate hydrogen and oxygen gases under visible light.²⁸

A major challenge for PEC water splitting is to efficiently separate charge within semiconductor-based photocatalysts. That could be achieved in certain crystals, such as bismuth vanadate, if the oxidation and reduction reactions involved in water splitting occur on different facets of the crystal. BY selectively depositing different cocatalysts on each face of the crystal, photogenerated electrons and holes can be separated to different faces of the material.²⁹

The efficiencies of these systems are gradually improving, but the cost of the materials involved may

remain a barrier to commercialization.

The carbon challenge

To minimize the impact of climate change, it is not enough to merely curb our greenhouse gas emissions: many researchers argue that we need to develop chemical technologies that remove CO₂ from the atmosphere on an industrial scale. In general, that involves 'reducing' CO₂ molecules, by substituting their oxygen atoms for hydrogen or carbon atoms, for example. These chemical reactions can produce fuels or other useful chemicals. For example, ruthenium-based catalysts can turn CO₂ into syngas, a mixture of carbon monoxide and hydrogen that is used in major industrial processes to make ammonia, fuels and other products.³⁰

Using materials that combine different catalytic properties can also help. A highly stable zinc oxide–zirconium oxide catalyst can convert hydrogen and CO₂ into methanol, for example, because each metal plays a different catalytic role in the whole reaction sequence.³¹

It should be noted that because CO₂ is very stable, converting CO₂ into fuels costs energy and cannot contribute usefully to carbon emissions mitigation when fuel synthesis costs more than the energy that is finally supplied by burning the fuel.

One of the remarkable aspects of natural photosynthesis is that it draws CO₂ directly from the air, even though the concentration of the gas in the atmosphere is 400 parts per million. The prospects of developing a synthetic catalyst that can process CO₂ directly from air are still remote, not least because many of these catalysts cannot



operate in the presence of oxygen. But roughly 10% of anthropogenic CO₂ emissions come from heavy industries such as steel or cement works, where the CO₂ output is much more concentrated, and thus a more promising feedstock for catalytic systems. Indeed, porous materials called covalent organic frameworks can already help to concentrate CO₂ for catalytic reduction.³²

Another interesting option is to create artificial photosynthesis systems by uniting semiconductors with enzymes or even living organisms. Semiconductors are good at capturing light and separating charge, while the enzymes in biological systems are highly selective and efficient catalysts. Combining the two into a semiconductor-enzyme or semiconductor-organism hybrid could, in principle, offer the best of both worlds.

For example, a light-absorbing ruthenium complex can deliver electrons to a hydrogenase enzyme, which unites the electrons with protons to produce hydrogen gas.³³ More recently, researchers have used nanocrystals of semiconductors to drive enzymes such as hydrogenases and nitrogenases.³⁴ This general approach could be applied to a wide range of chemical reactions, potentially opening up solar-powered routes to high-value chemicals.

Outside of their native cellular environments, however, enzymes are often fragile. Moreover, extraction of pure enzymes may not be scalable or economical. So semiconductor-organism hybrids have recently been explored as an alternative approach. For example, the bacterium *Methanosarcina barkeri* has been teamed with platinum or nickel sulfide, which are biocompatible hydrogen evolution reaction (HER) electrocatalysts. Together, they can convert CO₂

into methane; and by introducing indium phosphide photocathodes and titanium dioxide photoanodes, the system can be fully solar-powered.³⁵

Conclusions

PEC systems that split water to produce solar hydrogen have made good progress over the past decade. Researchers must now make these systems more durable, using cheaper and more abundant materials, and more suitable for scale up. PECs also need to be more efficient, and this could be achieved not only by developing new materials — following similar strategies as for advanced PV systems — but also by understanding how energy losses can occur at the interfaces between those materials (see Chapter 1). Photonic techniques, such as upconversion, could also play a key role here (see Chapter 2), as could a combination of computational and high-throughput screening techniques. This work must be underpinned by basic research to understand the mechanisms of light harvesting, charge separation, charge transfer, and catalytic processes in molecules and materials. Natural photosynthesis should continue to serve as a source of inspiration for new catalyst concepts.

At translational stages researchers must also consider the practicalities of these systems from an early stage, assessing whether they have the potential to be viable in terms of energy investment as well as cost, and whether they are achievable at large scales. Technoeconomic and energy cost analyses can help to assess the costs and benefits of various solar technologies, to understand how photoelectrochemical approaches compare with, for example, photovoltaics.

Chemically reducing CO₂ remains a huge challenge,



but it is a key frontier for science because it has the potential to be such a transformative technology, allowing this greenhouse gas to be removed from the atmosphere. Chemical systems that reduce CO₂ will have a greater commercial viability if they produce higher-value molecules. The energy costs of CO₂ reduction may, however, limit their potential to contribute to CO₂ emissions mitigation at scale when compared with alternative mitigation routes. Similarly, finding ways to use the oxygen produced from water-splitting, as well as hydrogen, could add value to the process and effectively lower the cost of the hydrogen it produces.

It is also important to bear in mind that 'one size does not fit all'. Countries have significantly different natural resources and energy systems, and there is certainly not a single, global solution to harvesting solar power. Research funding should reflect that by supporting a broad range of fundamental research and emerging technologies.

Recommendations

1. Develop new photoelectrochemical materials.

Researchers should continue to seek light-absorbing molecules, assemblies and materials and catalysts

for water-splitting and CO₂ reduction that are cheap, safe, efficient, abundant, selective and robust.

2. Study these materials at the molecular level

Understand their chemical, structural, and electronic properties; probe water oxidation and CO₂ reduction mechanisms in more detail using all the advanced experimental tools available, from synchrotrons to ultrafast lasers, to materials analysis with atomic precision. A directed effort to achieve synergy between theory and experiment is essential here.

3. Improve the integration of photoactive and catalytic components.

Understand and control the interfaces between these materials to minimize the loss of voltage and current in integrated systems. Develop cheap and commercially viable deposition techniques to control the structures of materials and interfaces with atomic precision.

4. Compare the costs and benefits of photoelectrochemical systems.

Life-cycle analyses and analysis of energy balance and potential scale will help to identify most promising technologies to pursue, especially when coupling different components to existing devices such as photovoltaic cells. For systems that convert CO₂ into other products, focus on making more complex, higher-value molecules as well as C1 products.



Chapter 4: Methods and standards

Analytical techniques provide the vital data needed for solar energy research to make progress. Researchers can use these data to accelerate research, by exploiting approaches such as the computational screening of materials. They must also collaborate to agree on common standards for measuring the performance of solar energy devices, so that the most promising avenues of research are easier to identify.

Introduction

Delegates at the CS3 summit were clear that new materials, along with better theories to explain and predict their behaviours, are absolutely critical to achieving a major increase in the use of solar energy technologies.

These two factors — experiment and theory — are intimately connected, driving each other forwards in a virtuous circle. Experimental results help to shape new theories, and these theories offer guidance and fresh challenges for experimentalists. However, this synergy depends on another crucial component: experimental techniques. Preparative techniques enable researchers to make new materials and modify their properties, while analytical techniques allow scientists to measure those properties. Innovations in both help research to leap forwards.

Solar energy research demands a diverse array of analytical methods, capable of taking measurements at many different timescales and spatial scales. The data provided by these techniques can help to uncover the basic mechanisms that determine the performance of solar energy devices. They can also help to make theories more predictive, enabling researchers to develop materials in a more strategic way. For example, solar energy

research could proceed much more quickly by exploiting computational screening — running ‘virtual experiments’ on novel materials to find promising candidates before actually synthesizing them in the laboratory. Meanwhile, novel preparative methods can help researchers to fine-tune the properties of these materials, or develop solar energy devices that are more amenable to mass manufacture.

Analytical and preparative techniques are often applicable across a wide range of scientific fields, and interdisciplinary collaboration can provide an important way to improve and then apply these techniques to new problems. Researchers also need to share expertise and best-practice in these methods, along with common standards so that experimental results can be compared.

Measuring up

The fundamental processes of solar energy devices, such as light absorption, charge separation and charge transfer, depend on many different properties of the materials involved, and different techniques are used to measure each one.

Experimentalists can use time-resolved microwave conductivity to measure the mobility of charge carriers, for example, and to assess how that



is affected by the orientation of molecules in a material.³⁶ This can help researchers to design new materials with better charge mobilities for photovoltaic applications, and study how charges move at the interfaces between materials.

In artificial photosynthesis systems, researchers need to be able to track how tiny variations in the structure or composition of a catalyst affect its performance. Take titanium dioxide, which is a widely used photocatalyst that absorbs ultraviolet light (see Chapter 3). Seeding crystals of the material with other elements — a process called doping — can shift the spectrum of light that it absorbs. But to control this effect, researchers need to work out which dopants to use, where to place them in the crystal, and in what concentration and chemical state. Techniques such as electron microscopy can help to answer these questions with atomic precision. Meanwhile, spatially-resolved surface photovoltage spectroscopy can reveal how electrons and holes separate to different parts of a photocatalyst.³⁷

Photochemical processes often happen at ultrafast timescales, taking just nanoseconds (10^{-9} s, or billionths of a second) or even femtoseconds (10^{-15} s, or billionths of one billionth of a second). Working at these timescales, sensitive instruments can freeze-frame the action to capture the vibrations of a molecule, or the trajectory of an electron. Take X-ray crystallography, for example, which has been used for a century to determine the structure of crystals, revealing precisely where its atoms sit in space. More recently, time-resolved X-ray crystallography has been able to produce a series of snapshots showing how a molecule's structure changes after it absorbs a photon, revealing how a catalyst's structure affects its behaviour in a photocatalytic reaction.³⁸

Electron diffraction offers another way to determine how structures change when they absorb light. Recently, researchers used a powerful 'electron camera' at the SLAC National Accelerator Laboratory in California to show that when light hits a perovskite material (see Chapter 1), it deforms the lattice of lead and iodine atoms in the crystal, potentially helping electrical charges to move through the material.³⁹ This could explain why certain perovskite cells are so efficient, and point scientists in the right direction to improve that performance.

Another technique, electronic spectroscopy, can reveal how the structure of a molecule, such as a protein, changes as it absorbs light,⁴⁰ and it has been used to study how the structure of molecules involved in natural photosynthesis affects their function.

Advanced surface science techniques allowing in-situ or even in operando experimental studies of intermediates and their electronic properties at solid/electrolyte interfaces are under development at many synchrotron sources. These techniques, together with theoretical electronic structure calculations, will allow researchers to identify which electronic structures and electronic states are essential for efficient electron transfer processes.⁴¹

Finally, two-dimensional optical spectroscopy can measure how the electronic as well as the vibrational states of a molecule change as it absorbs a photon. The technique first excites the molecule with one laser pulse, known as the 'pump'; and then follows it an instant later with another pulse, known as the 'probe', to measure how the molecule has changed. Recent advances include ultrafast multipulse experiments that allow researchers to follow energy propagation along the molecules in real time.⁴²



Researchers have used these types of multipulse techniques to study, for example, how solar energy is converted to electricity in PV devices that include a light-absorbing dye molecule,⁴³ and the technique can be applied to a wide range of other systems.

This brief survey offers a mere glimpse of the techniques that can be used to build up large datasets of materials' properties. These datasets can help to hone theories and improve computational screening, which promises to be an extremely powerful way to accelerate materials discovery programmes. It may also be possible to use machine learning to tease out predictive patterns in these data sets.

Computational screening relies on models that can accurately predict properties such as band gap, optical absorption, defect tolerance, charge mobility and more, based on the composition of a material. Unfortunately, there are still many instances where these models fail. For example, some of the processes that influence charge transfer across material interfaces are still shrouded in mystery, and fundamental studies are needed to understand this so that researchers can reduce energy losses in devices.

Nevertheless, computational screening is already being used to study classes of materials with relatively well-understood behaviours. For example, researchers have applied computational screening to predict which composition of lead bismuth sulfide has the optimum light-absorption and mobility properties for PV cells.⁴⁴ Meanwhile, a recent computational screen of more than 11,000 possible perovskites identified a group of materials that avoided using toxic lead compounds, while retaining good performance.⁴⁵ There are very many more multinary elemental

combinations that form semiconductors with the right absorption properties (bandgaps). However, the increasing complexity and lack of knowledge in controlling their physical properties have so far hindered a comprehensive evaluation of their PV potential, following a systematic materials genome project of advanced solar converter systems.

This sort of computational design is much harder for polymer-based materials, however, because the mechanisms of charge separation and transport in these systems are not fully understood. In situations like this, where researchers cannot make reliable predictions about a material's properties, they can speed up materials discovery using an approach called combinatorial chemistry. This method is already widely-used in drug development, and uses robots to analyze large libraries of different materials in high-throughput screening tests. Such high-throughput screening methods could also be applied to the photonic materials discussed in Chapter 3.

Conclusions

Many of the analytical techniques outlined in this chapter are routinely used in university laboratories and research institutions. But some depend on large facilities such as free-electron lasers or synchrotrons that can produce incredibly brief, high-energy laser pulses. These include the Dalian Coherent Light Source in China, the European XFEL in Germany, the UK's Diamond Light Source, the SLAC National Accelerator Laboratory in the United States, and SACLA in Japan. Indeed, SACLA recently helped to reveal how the catalytic complex at the heart of photosystem II (see Chapter 3) forms the double bond between two oxygen atoms.⁴⁶ This underlines the importance of such national facilities and international



cooperation in solar energy research.

As they explore how best to apply all these methods, solar energy researchers should collaborate widely to share their expertise. Techniques that prove successful in one area — PV cells, for example — could prove invaluable in studying some puzzling aspect of artificial photosynthesis, for example. Indeed, progress in solar energy research may depend on developments in completely different fields, such as electronic engineering. Programmes that bring together expertise from a very wide range of disciplines to address problems in solar energy research can help to push the field forwards, particularly in overcoming obstacles to commercialization. CS3 delegates noted successful examples such as the Joint Center for Artificial Photosynthesis in the US, the Korean Center for Artificial Photosynthesis, and the Solar Energy Action Program of the Chinese Academy of Sciences.

Researchers must also collaborate to determine the best ways to assess the performance of their solar energy devices. The community of photovoltaic researchers has benefitted enormously from laboratories that will conduct independent tests of a photovoltaic cell's efficiency, such as the service provided by the US National Renewable Energy Laboratory. This has helped to identify the most promising PV systems to pursue.

For the photoelectrochemical cells that have been developed so far, research groups often measure the performance of their systems in different ways, making it difficult to make fair comparisons. In such cases, it would be useful for researchers to agree on reference standards that researchers can compare their own systems against; and for journals to ensure

that researchers report their results in that context. In addition, renowned laboratories or research centres in this field could be authorized to verify these measurements independently, particularly when reported results break existing records.

Recommendations

1. Develop and apply analytical techniques across all relevant time-, energy-, and spatial-scales to study solar energy processes.

Use these techniques to probe fundamental photophysical and photochemical processes in molecules, materials, and at interfaces, the whole way through to understanding what determines efficiency in working devices.

2. Develop and apply theoretical and computational approaches to understand solar energy processes.

Tackle the problem at every scale, from the molecular level of light-driven charge transfer processes up to the device level. Continue integration of experiment and theory.

3. Develop cheap and scalable methods to create new photofunctional materials.

Control the composition and structure of materials at many scales, from atomistic to macroscopic; use high-throughput systems to make and screen novel materials for key properties.

4. Develop standards, databases and share best practice.

Agree on key metrics and reference standards to measuring the performance of photofunctional materials; foster multidisciplinary and international collaborations to make best use of analytical and preparative techniques.



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