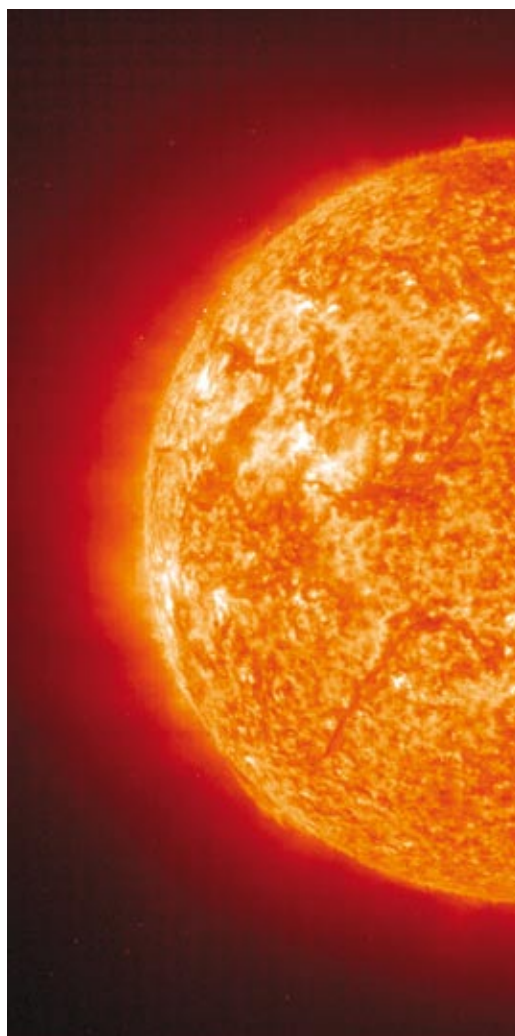


# Harnessing Light

Solar energy for a low  
carbon future



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## Solar energy for a low carbon future

*“Solar energy is the only energy source that is essentially pollution free and distributed across the planet.”*

Climate change, energy security, and a looming energy gap are all driving research and development into clean, renewable energy supplies. Scientists and engineers are looking at how to harness sunlight to help meet society’s demands to mitigate all of these potential problems.

An RSC policy seminar, chaired by **Professor Robin Perutz**, began by looking at how the field first developed and what challenges still need to be met. **Professor Anthony Harriman** of the University of Newcastle introduced the field of photochemistry and issues of funding and trained scientists. Exploitation of laboratory research was discussed by **Professor Sir Richard Friend** of Cambridge University, and new developments in solar cell technology were presented by **Professor Michael Grätzel**, from the Ecole Polytechnique Federale de Lausanne. Finally, how nature produces energy from sunlight and what mankind needs to do to emulate this, was discussed by **Professor Jim Barber** of Imperial College.

### Photochemistry: a beginning

One hundred years ago, the 20<sup>th</sup> century’s most famous scientist, Albert Einstein, worked out how light interacts with matter – the *photoelectric effect*. It was for this work he was awarded the Nobel Prize in Physics in 1921. Although there was some knowledge of photochemistry, it was down to Einstein that the close relationship between photochemistry and the photoelectric effect was determined.

Einstein’s work establishing the laws of photochemistry can be seen as the real starting point for understanding and exploiting solar energy. This is true regardless of whether this is taking place in manufactured solar cells, or in natural photosynthetic systems.

### Challenges for the future

There is a need to generate power effectively and efficiently from artificial solar cells, and also to use light to produce fuels, such as methane, methanol or hydrogen. Importantly, this needs to be done on a large scale.

After 100 years the question is now: can this be done? To an extent it can be, and scientists know a great deal about how photochemistry works. Crucially though, there is a need for further understanding of photochemistry and development of new technologies. Currently, about 3 giga Watts of energy is produced worldwide from solar cells, but there is a need to reduce their cost so that every household can have one on their roof. There is a surplus of solar energy falling on the planet, and mankind would only need to harness a small proportion of it to meet its needs.

There is a massive challenge to get the technology right. Importantly, solar energy is the only energy source that is both essentially pollution free and distributed across the planet.

A huge effort is needed to solve those barriers to exploiting solar energy. It needs scientists, politicians, research fund providers, and many more, on board. It is not just a case of improving energy efficiency for current technologies, even though this is important, but there is a need for massive investment to take solar energy conversion forward.

# Harnessing Light

## Solar energy for a low carbon future

The effort required to attain the next generation of technologies has been compared to the Manhattan project. Although this is not entirely appropriate because solar energy conversion is a peaceful technology, it does indicate the scale of effort required.

### Photochemistry

Professor Anthony Harriman explained that it is important to contextualise solar energy conversion in regards to the fundamental field of photochemistry. Research has been going on for over 30 years concerned with trapping light in molecules in order to do something useful.

Photochemistry is using light, and not necessarily just the sun, to make a chemical reaction work. Over a number of years this has divided into two fields.

The first, the fundamental research, has focused on molecular species that are formed when a substance absorbs light. They are often very short-lived, and so there has been a need to measure them on increasingly short timescales.

The second, more applied area is often the reason why people are interested in photochemistry. It is concerned with how we can use light to carry out unusual chemical reactions, and even reactions that may not be possible using alternative techniques. Unusual species, or high energy states, can be created using light and they often have unique chemical properties. It is the understanding of how to produce these strange intermediates, and subsequently how to exploit them, that has been the driver for applied research.

These high energy intermediates can be dangerous. In a similar fashion to radiochemistry, there are examples in which photochemistry can lead to both good and bad consequences.

One example is sun exposure. It can lead to painful sunburn and can also lead to skin cancers. Conversely, though, the same

photochemistry can be applied to removing cancerous tumours.

### Science and nature

Scientists aspire to replicate many of the essential features of photosynthesis, the process by which plants use sunlight to produce oxygen and organic molecules.

The crude picture is that scientists would like to harness sunlight to obtain oxygen and hydrogen from water, a very difficult process to achieve, and to generate a fuel. In the past hydrogen would have been an acceptable fuel, but now attention has become focused, by warnings of climate change, on removal of carbon dioxide from the atmosphere to furnish a fuel.

Research aimed at producing artificial photosynthetic systems began in earnest in the 1970s, and carried on at a rapid rate for about 10 years. Since then, fundamental photochemistry research has died away. This is for several reasons, but primarily it is the lack of funding and the change in motivation. If the money and opportunities returned, then chemistry could be put back at the heart of developing artificial photosynthesis. Until that happens, the motivation will be driven elsewhere.

### How to collect light

Considering all known photochemical systems, it becomes possible to divide them quite clearly depending on the objective.

Firstly, it is necessary to collect sunlight. There is plenty of energy in sunlight, but it is dispersed and so it becomes essential to collect energy from a large enough area to be able to do useful chemistry. However, if the idea is to use sunlight to produce fuels then it must be done at a highly localised site otherwise more energy is expended concentrating it than is obtained from burning it.

In terms of the chemistry, light needs to be collected and then directed to sites

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# Harnessing Light

## Solar energy for a low carbon future

within the system in which high energy intermediates are formed. More specifically the light is used to drive what is called charge separation; one part of the system will become positively charged and another will become negatively charged. These charged species can then facilitate reactions to produce fuel.

In plants it is chlorophyll that absorbs light, and this is renewed naturally on a frequent basis, and the human body is capable of repairing itself when sunburnt.

Through the study of photosynthetic systems it has become apparent, however, that organic molecules exposed to sunlight for an extended amount of time will degrade.

This raises problems if artificial systems are constructed from expensive molecules. If they are fragile and degrade then it raises the question of how to repair them. Learning how to interrogate a complex system, find damaged components and then renew them is at least as challenging as it is to harness sunlight in the first instance.

If you consider the solar flux across the UK there is enough sunlight available in the North of Scotland to run solar cells efficiently. In Cornwall, it may become necessary to attenuate the light so as to avoid damage to the molecules in the solar cells.

### The beginnings of artificial photosynthesis

Initially it was thought that photosynthesis in plants was occurring through a random distribution of chlorophyll in leaves, and that this should be relatively easy to replicate in the laboratory. However, an increased understanding of photosynthesis shows us that this is not the case.

Nature has learnt to position molecules precisely, with angles, orientations and distances carefully determined. Scientists may be able to reproduce parts of this system, and to understand the different reactions occurring, but to build and manipulate artificial systems

on this scale is currently beyond them. Considering molecules on this scale of complexity illustrates the need for repair mechanisms. It would take a huge effort to reproduce the photosynthetic centres artificially, and so if components get damaged there needs to be a way to remove and replace them instead of beginning again from scratch.

Scientists can duplicate many of the essential features of photosynthesis, from collecting light to carrying out reactions, but so far coupling them all together into one system has proved elusive.

### Photovoltaic cells

An alternative method to harness energy from sunlight is to exploit minerals and inorganic materials. Currently, this is the way that the field is developing, and arguably this is the less intellectually challenging in the first instance. It is looking at the problem in a more applied manner.

Rods, porous tubes and other structures can be produced from inorganic materials and minerals. Catalysts can then be embedded in these structures and light used to produce the intermediates that will generate the desired reactions. This is the direction that the field of photochemistry is taking at the moment. The same principles are being exploited, but with different materials.

### The many uses of photochemistry

Photochemistry has brought more, and can bring many more, beneficial applications than just energy generation. Importantly, they all rely upon the same basic principles: the interaction of light with matter to create unusual chemical species. Applications are highly diverse, and range from advanced molecular computers to medical diagnostics.

Photochemistry can provide answers to many of the challenges facing society, especially in pollution control and environmental clean-up.

Systems based upon the use of titanium dioxide can already be found commercially,

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# Harnessing Light

## Solar energy for a low carbon future

and can be used for large scale clean-up of buildings. Large scale ultraviolet systems can also be used to purify water supplies. This could be done in remote and developing countries with current technology and to massive benefit. The cleaning of stagnant water with dye molecules could also be achieved, leading to temporary eradication of mosquitoes, and hence malaria.

Photodynamic therapy (PDT) works along the same principles. A molecular compound is injected into a tumour, and then a laser is used to excite it and generate chemical species that will burn out the tumour. This can be done selectively, so that damage to neighbouring tissues is minimised. A recent system based on gadolinium was used to both image the tumour and then to remove it.

Another application is in the development of fluorescent sensors. Species can be developed that will detect chemicals or antibodies, which is particularly relevant for the detection of diseases. Literally any substance or species can be detected in an automated way and photochemical processes used to count and separate them. Fluorescence facilities can be found in all forensic laboratories and dyes are also used as security markers in bank notes.

The development of new pigments and dyes is essential to achieving artificial photosynthesis, but will have many spin-offs in diverse areas.

The majority of scientists working in photochemistry now work in the fields of molecular electronics and molecular photonics, and these fields could be competing with that of artificial photosynthesis by taking away the intellectual challenge. For example, it could be argued that the same circuitry used in artificial photosynthesis can be used to duplicate everything needed to make a computer work.

In summary, a great deal of the basic research that could have gone into solving the energy crisis has gone into other areas. Whilst there have been some spectacular discoveries, is the development of a new

computer more important than solving the energy crisis? Many scientists with the right expertise are now coming to the ends of their research active careers. There is a risk that their knowledge and skills could be lost. The problems of energy generation from sunlight can be solved, but for many reasons time is now running out.

### Industrial exploitation

Professor Sir Richard Friend discussed the need to match good laboratory science with engineering at a large enough scale to make it work. The ability to transfer science to industry is crucial to achieving solar energy generation on a useful scale.

The current problem is that people will pay more money to have a nice laptop screen than they will to have the same area of photovoltaic cell. This is because electricity is cheap, and high value products are needed to justify large investments in laboratories. However, some good news is that much of the technology developed in displays is directly transferable to solar cells.

One of the icons of the 20<sup>th</sup> century was the silicon chip. Fantastic functionality can be achieved in a small area, which is useful for producing computers. However, they require expensive clean rooms and the price of silicon is rising. Silicon solar cells can produce energy from sunlight at reasonable efficiencies, but, even after considering the rising costs of fossil fuels, they do not seem commercially attractive. New technologies are required.

A much older technology is moveable type face, used to print books and newspapers for 500 years or so. Importantly, it allows cheap, variable printing day after day, whereas a \$2 billion silicon chip plant can only produce one type of product.

It is important that scientists do not see these worlds in isolation. What is needed is the functionality of the silicon chip with the low processing costs that make newspapers, books and plastics so cheap.

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# Harnessing Light

## Solar energy for a low carbon future

***“Technology only works if it can be exploited for the right price.”***

The aim should be to paint or print active molecules over large areas. To achieve this, molecules need to be able to carry out the same function as silicon, and photosynthesis is an indication that nature got there a long time ago.

The most important point is how to process the new technologies; technology only works if it can be exploited for the right price. The general rule for solar cells is that one third of the cost is the semiconductor, one third is the packaging, and the final third is getting it installed. All three factors need to be reduced. Making the semiconductors out of plastic instead of silicon could allow cheaper and more durable cells. This could affect the whole cost base.

### Organic electronics

Organic light emitting diodes (OLEDs) are of current interest to scientists as they may provide high performance, low cost lighting and display solutions. Interestingly, there are many parallels with photovoltaics; OLEDs can be viewed as the reverse process.

Polymeric semiconductors, components of OLEDs, are highly fluorescent materials.

They can be made to radiate intense light of a characteristic colour through excitation by either absorption of light or by passing an electric current through them. It is the latter excitation route that is used in OLED devices.

Very efficient OLEDs can be produced by painting layers of organic semiconductors onto a substrate. Even in simple structures it is possible to get fluorescence by exciting the molecules using an electric current. What has caught the imagination of industry is that organic molecules can be printed cheaply. Commercially available printers can cost less than £100 and produce photo-quality images. This resolution is good enough to produce displays, and much cheaper than the patterning used to produce silicon chips.

The concept is therefore to make ink functional; not just a blob of something on a piece of paper. Using polymeric semiconductors means that this is achievable.

### OLED displays

Functional display screens can be produced by printing red, green and blue spots of materials in the right position and then exciting electrically. It has required a huge research effort to achieve this, and after 15 years the displays now look very good.

Importantly, they also have good lifetimes. Blue is the most critical of the three pigments, and they can now run for 20 years before degrading to half of the initial brightness. Displays can now be produced up to 40 inches in size. A large challenge is the falling price of liquid crystal displays (LCDs), but OLEDs can give better images, use less power and are lighter in weight. This final factor will make them highly attractive to the portable electronics industry.

Typically, transistors are made from layers of silicon, a semiconductor, backed onto an insulator, such as silica. Charges, or electricity, can move through the device in a controlled manner.

But plastics can also be used as semiconductors. Printable, conducting polymers could be utilised for all parts of the transistor, furnishing an all plastic component that can be made using ink jet printing technology.

Since the first plastic transistors were produced, the technology has developed and they are now approaching the abilities of more established silicon devices. This means that they are good enough to turn into products. A new spin out company from Richard Friend's research group, called Plastic Logic, is based in Cambridge and working to develop displays based on this technology.

Crucial to this commercialisation process

# Harnessing Light

## Solar energy for a low carbon future



The use of solar cells for energy generation is growing by 40% per year, but it still remains a minor contributor overall. Sustainable growth of this sector is the goal, but it requires a decrease in the time taken for the energy used during manufacture to be paid back by energy generation through use.

has been the raising of over \$100 million of venture capital funds, which means the company can now go into full scale production. This is going ahead in Dresden, Germany, which was found to be a more attractive commercial environment to do this than the UK. The product will be an electronic, flexible book.

This reinforces the importance of turning science into engineering. Companies had to be created in the UK to facilitate this process as there is a lack of indigenous companies. The UK is a good place to do this, and the same challenges will apply to the energy sector.

### From plastics to photovoltaics

In photovoltaics, unlike OLEDs, it is essential to prevent fluorescence occurring after molecular excitation, in this case caused by absorption of sunlight. The aim is to maximise energy conversion. One way to do this is to

use a juxtaposition of different molecules or polymers, so that after absorption of light the two different chemical species will take on opposite charges. These charges can then be collected to give a working solar cell and thus produce an electric current. Nature is very smart and photosynthesis is very good at capturing light and also at funnelling charges to the reaction centre. The key is to absorb light close enough to the point at which charges are separated so that energy isn't wasted. There is a huge effort to have these charge separation sites, or heterojunctions as they are termed, distributed throughout the cells so that wherever light is absorbed then the charge separation can take place. The remaining difficulty is getting the charges to flow to the electrodes and generate electricity.

One way to do this is to mix two different polymers together to give very complex interpenetrated networks. This results in good quality solar cells.

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# Harnessing Light

## Solar energy for a low carbon future

The principle challenge is to understand what scale of effort is required to take interesting science from the laboratory through to engineering products.

Scientists need to have the ambition to create companies that can do this. When applications are apparent then it becomes much easier to attract and energise students to get involved in the research.

### The energy gap

Professor Michael Grätzel highlighted the potential energy gap situation facing society. By 2050 it is estimated that there will be an energy shortfall of 14 tera watts (TW) across the planet. There are many ways of harnessing renewable energy, but over 100000 TW of energy falls on the Earth as sunlight, suggesting that solar energy generation should be at the forefront. There are plenty of zero or low population regions on Earth that could be made available.

The main challenge is carrying out energy conversion at a reasonable cost. There is an encouraging 40% annual growth rate in the use of photovoltaics, but it still remains a very minor contributor overall.

By 2030 it is predicted that photovoltaics will be generating 200 GW peak. However, this is measuring energy generation at full sunshine; clearly the average is less than this. In Switzerland, for example, average energy generation by photovoltaics will be about a factor of 6 or 7 times smaller than peak generation.

Technology must be able to payback the energy used during manufacture in a short time for the industry to become sustainable. Even a payback time of 2 years is not sufficient to maintain a 20% growth rate. A sustainable industry would not require additional energy from other sources in order to maintain a sustained growth.

Programmes in Germany, Italy and Spain

have encouraged the growth of terrestrial photovoltaics. These do get criticised for being subsidised programmes, but ultimately the costs that electricity companies incur as a result of using renewables is paid for by their customers.

### The end of silicon?

A significant problem is the price of silicon. It used to be \$9 per kg, but is now at over \$150 and predicted to rise to \$200 in the future. This drives the cost of energy generated by silicon solar cells upwards, and is currently around \$6 per peak watt. The reason for it is that there simply isn't enough available silicon to meet our growing consumer electronics demand.

It is clear that a new approach is needed. Continuing with silicon technology will not bring the cost of solar generated electricity down below \$1 per peak watt, which it needs to be in order to be competitive. There is a need for a new, disruptive technology and, importantly, it must also have low cost processing.

### New solar cell technology

Dye sensitised solar cells (DSCs) represent a new strategy for photovoltaics. They differ from silicon solar cells as they use relatively inexpensive inorganic dye molecules as light harvesters, and the charges are carried away in, for example, inorganic nanoparticles such as titanium dioxide or by conducting polymers.

These dye molecules can undergo hundreds of millions of turnovers, *i.e.* light absorption and charge transfer, with only minimal damage. Laboratory simulations have demonstrated that they could conceivably run for over 30 years.

Another key issue is the structure of the cell itself. Flat devices have very poor performance, but nanocrystalline structures can give high currents and high conversion efficiencies, currently confirmed up to 11%. In these structures the charges generated by

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# Harnessing Light

## Solar energy for a low carbon future

light absorption are rapidly diffused across the inorganic polycrystalline network to the electrical contacts, and thus current is generated.

Where could this end? It is possible to envisage a situation in which electric-powered cars parked in a garage are charged from the energy generated by photovoltaic cells on a house roof or incorporated into windows.

Of utmost importance is the need to motivate young people and get them interested from a young age. These advances cannot occur unless bottom up enthusiasm is achieved.

### The start of photosynthesis

Almost all the energy mankind uses comes in one way or another from photosynthesis, says Professor Jim Barber. Worldwide, 86% of our energy comes from fossil fuels and 11% from biomass.

Photosynthesis began in earnest on this planet about 2.5 billion years ago. This led directly to an explosion in biological activity, allowing organisms to prosper and diversify on an enormous scale. It involves splitting water into hydrogen and oxygen, and it is the latter, released directly into the air, that accounts for the change from an oxygen-poor to oxygen-rich atmosphere.

Around this time the ozone layer also formed, and the combination of these two events allowed biological life to explore new environments, particularly the terrestrial one.

It is from this point onwards that the massive amount of photosynthetic activity occurring ultimately resulted in the formation of fossil fuels. Worryingly, the quantities of fossil fuels mankind uses in one year took over 1 million years to form by the process of photosynthesis.

The photosynthetic process in living organisms can be broken down into basic reactions: the splitting of water to yield oxygen and hydrogen, followed by the use of hydrogen to reduce carbon dioxide to form organic matter.

Photosynthesis occurs in plant leaves, in small structures termed chloroplasts. These chloroplasts have high surface area membranes, in which the water splitting reaction occurs, and an internal aqueous compartment in which the fuel production step occurs.

### The perfect cycle

Within the chloroplast membranes are two enzymes which carry out the photoconversion. They are termed photosystem 1 (PS1) and photosystem 2 (PS2). It is actually PS2 which carries out the splitting of water, and PS1 provides additional energy. Both rely on the absorption of sunlight.

The hydrogen from the water splitting reaction is used immediately in the 'dark reaction', which does not require light, to reduce carbon dioxide and produce organic molecules.

Biology has a perfect solution to the energy problem. Sunlight is used to drive a cycle in which splitting water leads to the production of organic molecules, which in turn form fossil fuels. These organic molecules store hydrogen which originated from water. What drives a 747 as it flies across the Atlantic? Essentially, the water splitting reaction of photosynthesis!

### Organic molecules as fuel

The burning of organic molecules results in the recombination of hydrogen with oxygen to form water and release energy. This could be exploited either by combustion of the organic matter as we currently do, or by respiration as humans do when food is oxidised in the body.

About 100000 TW of energy falls on the Earth each year from the sun, and about 200 TW, or 0.2%, of it is fixed by plant life. This is mankind's primary source of fuel, and in an attempt to alleviate fossil fuel usage and carbon dioxide emissions, biomass is being increasingly used.

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# Harnessing Light

## Solar energy for a low carbon future

***“Countries that have large land masses may be able to grow significant amounts of biomass energy usage without competing with food production.”***



Sugar cane can fix sunlight with an efficiency of 2%, ten times the planetary average for wild plants. In Brazil it is fermented to produce ethanol, and over 50% of cars run on ethanol-based fuels.

Crops such as sugar cane can grow very quickly and can fix sunlight with an efficiency of 2%, ten times higher than the planetary average for wild plants. Theoretically, this efficiency could be raised to 5%.

In Brazil this is being done. Originally the drive to increase sugar cane growth was to produce sugar, but increasingly it is being fermented to make ethanol. Over 50% of vehicles in Brazil run on ethanol-based fuels. As the price of fossil fuels has risen, this route has become even more economical.

Brazil, however, has a large landmass and a tropical climate, both suitable for growing large quantities of biomass.

In the USA there has been intense effort to look at the potential of biomass as a fuel source. A recent report from the Department of Energy (DoE) estimated that up to 30% of the USA's energy needs could be met by biomass against current levels of 3%. Currently there are about 6 million cars on

the road in the USA which could run on ethanol based fuel (termed E85), but only about 2% of them do because it is either unavailable or uneconomical.

Countries that have large land masses may be able to grow significant amounts of biomass for energy usage without competing with food production. In the UK, however, the supply of energy from biomass currently stands at around 1.5%, most of which stems from refuse. It is estimated that this could realistically only rise to about 5%.

### Photosynthetic organisms

It is possible to trick some photosynthetic organisms into generating hydrogen directly. Several types of algae, such as green algae, can be encouraged to produce hydrogen, which simply bubbles off. The chemical process is carried out by a class of enzymes called hydrogenases. These enzymes are, however, sensitive to oxygen and so a two-step process is needed. The first step

# Harnessing Light

## Solar energy for a low carbon future

releases oxygen and builds up biomass, and the second burns the biomass to produce hydrogen.

There is a great deal of interest in this process. In the USA the DoE is funding research, and in Europe progress is also being made. In the UK, however, not much research is being carried out in this area.

### Research needs

A huge research effort is needed that brings together chemists, biologists, physicists and engineers to tackle this issue.

In 2005 a meeting was held in Washington DC which subsequently led to the US administration providing an additional \$100 million for solar research, with more money promised for the future.

### The artificial leaf

An artificial leaf would split water to produce oxygen and hydrogen, and then use that hydrogen either directly as a fuel or to reduce carbon dioxide to produce organic fuels.

Of course, the structures of the enzymes in the photosynthetic systems are very complex. PS2, for example, is comprised of 19 different subunits, and only right at the centre of its structure is buried a collection of four manganese ions and one calcium ion that act as the catalytic site for splitting water. If scientists are to emulate this, it is worth knowing that the challenge is not to split water, but rather to form the oxygen-oxygen bond. Nature does this on a huge scale, and we now have a good idea of how this is achieved.

Research groups are now trying to create artificial leaves by using ruthenium and manganese complexes to try and mimic natural processes. These don't necessarily require the presence of large proteins or chlorophyll. If these could be built, then it would be possible to generate oxygen and hydrogen from water.

Mimicking the dark reaction is also highly desirable. If this can be achieved then the artificial leaf can become a reality. In natural systems the reduction of carbon dioxide takes place by an elaborate series of reactions collectively called the Calvin cycle. There is a desire to do this artificially, but the chemistry is very difficult. Nature has solved this problem and although it is very complicated, this means that scientists will eventually be able to do this as well.

In the UK there is no real equivalent to this. However, European scientists have produced a report, funded by the European Science Foundation, to bring together scientists from different disciplines to discuss how to move forward with developing new technologies and concepts for solar energy capture.

If the production of fuel from the splitting of water is achieved, then yet another of Jules Verne's predictions will come true:

*"I believe that water will one day be used as a fuel because the hydrogen and oxygen which constitute it used separately or together will furnish an inexhaustible source of heat or light. I therefore believe that when coal deposits are oxidised we will heat ourselves by means of water. Water is the fuel of the future."*

Jules Verne, *L'île Mystérieuse*  
(The Mysterious Island), 1874

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