

# From ancient to future solar fuels

Plants like these sugar beet capture the energy of sunlight using photosynthesis. Scientists are trying to do the same to do the same with artificial photosynthetic systems.

## Key words

photosynthesis

catalyst

enzyme

solar energy

*With the world's population ever-expanding, energy demand is expected to double by 2050 and triple by 2100. In only 200 years, mankind has squandered what Nature has taken hundreds of millions of years to lay down as fossil fuels. The burning of these fossil fuels also releases carbon dioxide (CO<sub>2</sub>), increased levels of CO<sub>2</sub> in the atmosphere being a direct contributor to global warming. For the survival of our planet the question is, can we generate energy from a widely available, cheap, limitless source and can this be done without the release of additional CO<sub>2</sub> into the atmosphere? Rhiannon Evans is part of a research team trying to do just that.*

Fortunately, the answer is yes! The Sun is an inexhaustible source of energy, providing enough hourly to meet the current annual demand – if only we could harness it for use day and night. Developing clean, cheap, renewable, transportable and storable energy supplies to replace fossil fuels is one of the most important scientific and technological challenges of our age.

No man-made system developed thus far meets these criteria. Photovoltaic cells and wind farms for example convert sunlight and wind power into electricity only intermittently, when the sun shines or the wind blows. For a continuous energy supply we must be able to produce a storable fuel that can be transported for use where needed. Plants and algae do this already through the process of biological oxygen-making photosynthesis. In fact, fossil fuels are the stored energy from ancient photosynthesis – ancient solar fuels.

## Natural photosynthesis

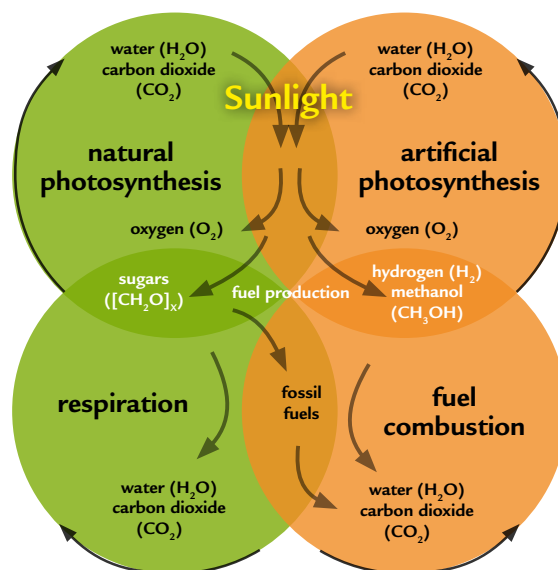
In photosynthesis, energy from the sun is stored in the substances which are produced. It does this by splitting water (H<sub>2</sub>O) into oxygen gas (O<sub>2</sub>), hydrogen ions (H<sup>+</sup>) and electrons (e<sup>-</sup>). The electrons are excited by the sunlight in a process we call 'charge separation', and they flow through the biological machinery in the cell by various electron transfer processes. The ultimate fate of these energised electrons is to combine with carbon dioxide (CO<sub>2</sub>), and H<sup>+</sup> to form organic molecules that

the photosynthetic organism, and we ourselves, can use as a fuel such as carbohydrates. These are polymers and can be represented as ([CH<sub>2</sub>O]<sub>x</sub>). During the process oxygen is released; we breathe the O<sub>2</sub> and use it in metabolic respiration allowing us to break down carbohydrates to provide energy. We also use the O<sub>2</sub> in combustion of fuels such as fossil fuels in internal combustion engines. Both respiration and combustion release the energy stored in the fossil fuel or the carbohydrate in an exothermic reaction, producing water and carbon dioxide, the reverse of photosynthesis, see Figure 1.

## Artificial photosynthesis

Ultimately, we would like to be able to exploit the chemical principles of natural photosynthesis such as light absorption, charge separation, electron transfer and fuel formation to develop efficient artificial solar fuel production. In order to develop these processes and tailor them to mankind's requirements, we must as scientists and engineers develop each fundamental component of the artificial photosynthesis (APS) system. The challenge is then to combine and refine the system.

The basic components of an APS system are summarised in Figure 2. We must have a light harvesting material capable of absorbing light and exciting electrons, a catalyst capable of efficiently replacing the electrons used in forming the fuel; an excellent source of those electrons is water. Water is



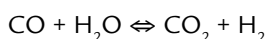
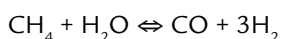
**Figure 1** The relationship between natural photosynthesis, respiration, and fuel combustion and the parallel principles of artificial photosynthesis

rather an inert substance however, and its stability means that it takes a lot of energy to split it apart. Lastly, we must have a fuel-forming catalyst, which will vary depending on the fuel we want to form.

We can produce molecular hydrogen ( $H_2$ ) through solar-driven processes:

- Hydrogen is an excellent energy carrier – its combustion in oxygen releases a huge amount of energy ( $286 \text{ kJ mol}^{-1}$ ) with only water as the by-product.
- The chemical bond of molecular hydrogen is very strong and so a catalyst is required to reduce the energy required to break this bond, otherwise the reaction is too slow.

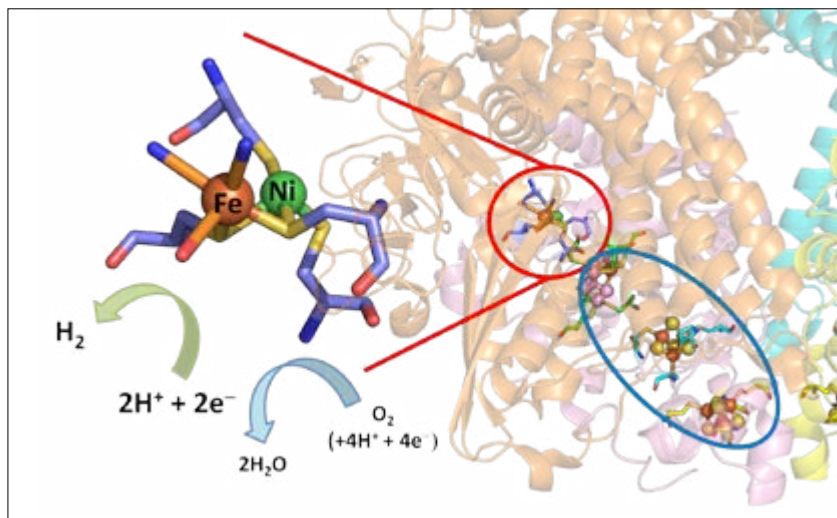
Unlike fossil fuels, hydrogen is not a primary fuel that we can mine at source, it must be made. If hydrogen is to be used as a clean fuel, the methods of its production must be clean and the way in which we utilise hydrogen as a fuel, releasing the energy stored in its chemical bond must also be renewable and sustainable. Currently, industrially produced hydrogen is not a clean source of hydrogen – the majority is produced using the fossil fuel methane ( $CH_4$ ) in a process known as steam reforming, with an additional  $H_2$  molecule being recovered in the subsequent water-gas-shift reaction:



These processes are not a viable option for a clean future fuel as the hydrogen is derived from limited fossil fuel reserves and produces  $CO_2$ . Electrolysis

of water is another way to produce hydrogen. The best catalyst for both hydrogen production and oxidation however is the expensive and rare noble metal platinum. Relying on platinum makes the processes expensive and not a long-term option.

Nature has already overcome this problem – microorganisms have utilised metals that are more readily available to them and contain hydrogen catalysts that make use of common metals such as iron (Fe) and nickel (Ni). These biological catalysts – enzymes known as hydrogenases (Figure 3) – are able to interconvert protons and electrons into hydrogen at rates that rival platinum. Hydrogen is used as a fuel by some microorganisms.

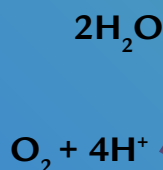


**Figure 3** Hydrogenase enzymes can make hydrogen using common and cheap metals at their active sites

## Artificial photosynthesis

### Water oxidation catalyst

Breaks down (oxidises) water ( $H_2O$ ) into oxygen ( $O_2$ ), protons ( $H^+$ ) and electrons ( $e^-$ ). These low energy  $e^-$  fill the 'hole' formed regenerating the light-harvesting materials.

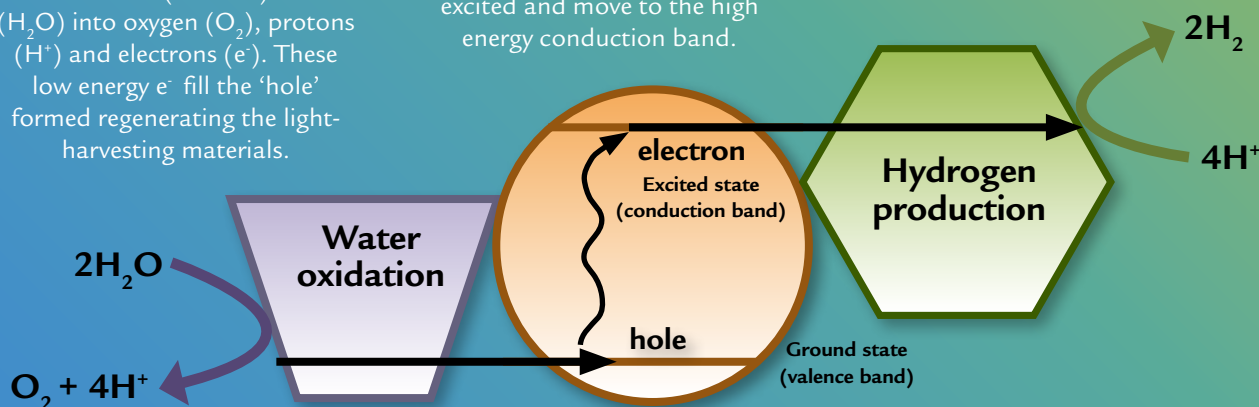


### Light-harvesting material

Light-harvesting materials (e.g. semiconductors) absorb solar energy. Electrons become excited and move to the high energy conduction band.

### Hydrogen production catalyst

The most commonly used  $H_2$  production catalyst is platinum (Pt), but this is expensive and rare. Hydrogenase enzymes produce  $H_2$  at comparable rates to Pt and are precious metal free.



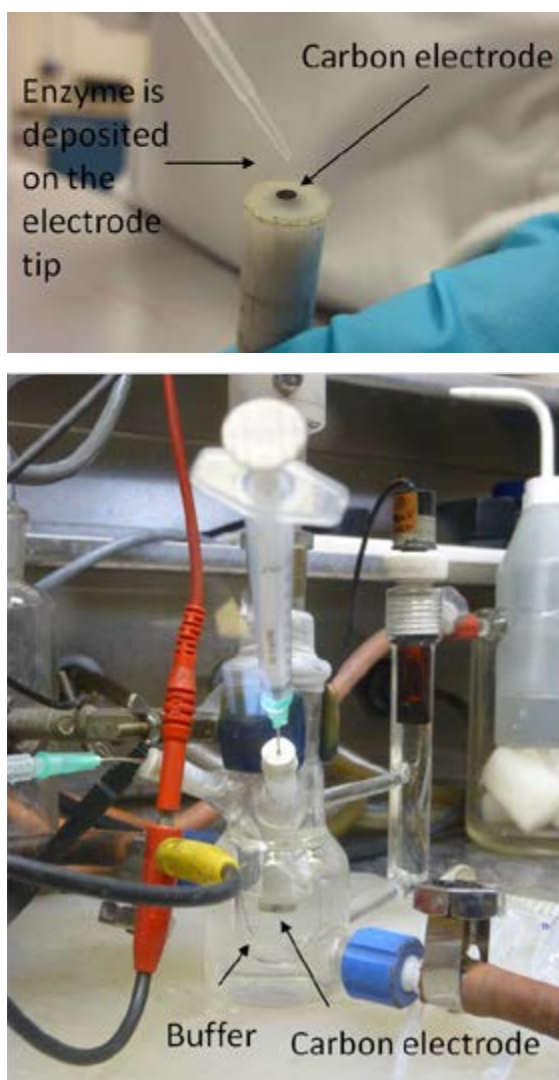
**Figure 2** The fundamental components of an artificial photosynthesis system

## The problem with oxygen

As is suggested in Figure 2, in an artificial photosynthesis system that uses water as its source of electrons and protons, oxygen is produced, just like in natural photosynthesis. Although they are amazing hydrogen catalysts, hydrogenases can be inhibited by oxygen.

Again, nature has a solution – oxygen-tolerant hydrogenases. Through the study of oxygen-tolerant hydrogenases, not only can we begin to understand the secrets behind their hydrogen catalysis capabilities, but also how they do this in the presence of oxygen. We have been able to show that these enzymes can use the electrons generated by the oxidation of hydrogen and store them in specialised clusters of iron and sulfur atoms (Figure 3 blue oval) ready to reduce the attacking oxygen to harmless water.

We study the enzymes using the technique ‘Protein Film Electrochemistry’ (PFE) where we adsorb the enzyme to a carbon electrode (Figure 4) and monitor the activity of the enzyme as an electrical current, with electrons flowing between the electrode and the enzyme via the iron-sulfur clusters.



**Figure 4** An example of the carbon electrode being coated with an enzyme film (top) and a typical Protein Film Electrochemistry set-up (bottom)

There are numerous examples of hydrogenase enzymes in biology. They can differ by the metal content at their active sites, by the rate at which they reduce hydrogen ions (make hydrogen) and oxidise hydrogen, and also by the conditions in which they do this most efficiently and without degradation. We can monitor and study all of these characteristics by PFE.

We have already shown that they can be capable of attachment to various light harvesting materials such as semiconductors (e.g. titanium dioxide,  $\text{TiO}_2$ ) for solar hydrogen production. However, for commercial and industrial hydrogen production, isolated hydrogenases would not be a viable option – they take time to purify from the microorganisms and don't always last very long and so they are not financially feasible.

Research is now focusing on unravelling what makes hydrogenases so brilliant at hydrogen catalysis and this will lead the way to the creation of man-made catalysts based on the specialised chemistry of hydrogenases, and will enable the use of common, cheap metals such as iron and nickel.



*The author at work: hydrogenase protein film electrochemistry is carried out in a glove box which is filled with an inert atmosphere of nitrogen so we can avoid exposure of the enzymes to oxygen and other inhibitors.*

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