Sarah Mackintosh

**Key words**
photosynthesis
chloroplast
photocatalyst
reduction

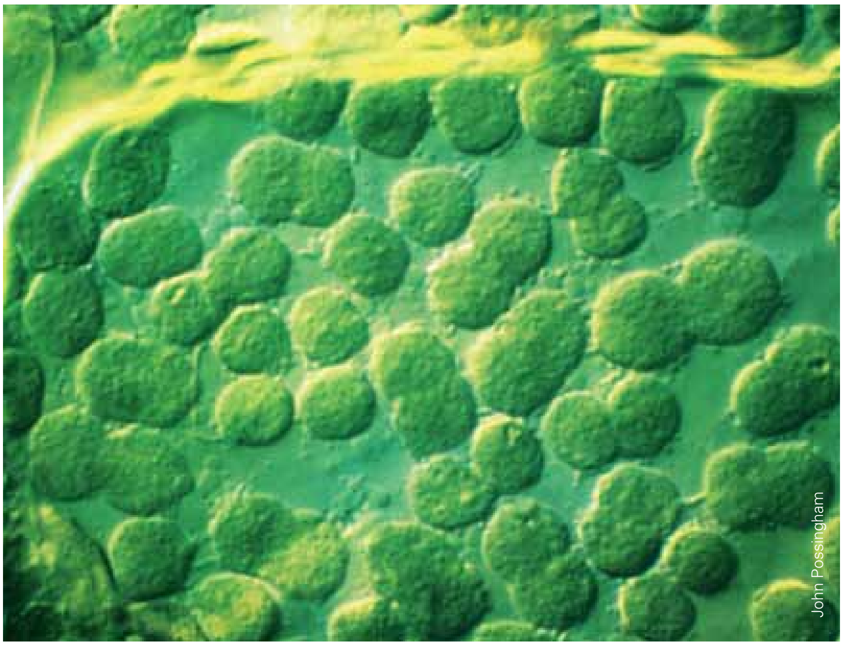
# Artificial photosynthesis

*Trees and plants use sunlight to convert $CO_2$ and $H_2O$ into sugars and $O_2$.*

*We are using up fossil fuels and emitting carbon dioxide into the atmosphere – these two problems combined are likely to cause increasing tension worldwide in the coming decades. Here,* ***Sarah Mackintosh*** *describes one promising solution to both issues.*

After a cold winter, global warming may seem irrelevant, but there is no doubt that the climate is changing. This is primarily to do with the amount of carbon dioxide ($CO_2$) that we are emitting into the atmosphere causing an imbalance in the carbon cycle. The $CO_2$ level in the atmosphere has risen from a pre-industrial level of 270 ppm (parts per million) to the current level of 379 ppm.

At the same time, our fossil fuel supply is beginning to run short; this may be a good thing for our atmosphere, but it is bad for us. There are many solutions to these problems including using alternative sources of fuel or storing the $CO_2$ underground. However, as yet we have not found a renewable source to provide enough energy for the world and we have not been able to store 100% of $CO_2$. It looks as though we will be reliant on fossil fuel for some time to come and we will still need to try to deal with the amount of $CO_2$ emitted. One promising option to these problems is to 'recycle' the $CO_2$, by breaking the $CO_2$ molecule up into different fuels such as methane ($CH_4$) or methanol ($CH_3OH$).




*Chloroplasts in the leaf of a green plant absorb light and use it to turn carbon dioxide into more complex and useful molecules. Some of these chloroplasts are dividing.*

## Photosynthesis

The idea of recycling $CO_2$ comes from nature. During the day, plants absorb $CO_2$ and produce $O_2$ through the process called photosynthesis. Plants utilise sunlight and a natural catalyst called chlorophyll to produce sugars and $O_2$ by oxidising $H_2O$ and reducing $CO_2$. The reactions are:

$$6CO_2 + H_2O \text{ (+ light energy)} \longrightarrow C_6H_{12}O_6 + 6O_2$$

*carbon dioxide + water (+ light energy) ⟶ glucose + oxygen*

**Reducing $CO_2$ means removing the oxygen from it.**

Energy conversion efficiency is ratio of the useful energy output to the energy input. The higher the efficiency, the more energy is converted into a useful form.

However, the energy conversion efficiency of natural photosynthesis is relatively low. The efficiency limit of energy conversion is about 6%, but is usually as little as 0.8%. Scientists are looking into the use of artificial catalysts which are activated with sunlight (photocatalysts) to try to increase this level of efficiency.

## Sounds good so why aren't we doing it?

$CO_2$ is a relatively inert and stable compound, and therefore it's very challenging to try to break up or reduce it. Semiconductors are the most suitable photocatalysts for $CO_2$ reduction because they are best able to reduce $CO_2$ into fuels such as methane or methanol. The equation below shows the reduction of $CO_2$ into methanol and oxygen. Unfortunately the reaction is not favourable, so even by utilising the catalyst the fuel yield is very low.

This equation shows the reduction of a single molecule of $CO_2$. If you are not happy with the fraction 3/2, try multiplying each term by 2.

$$CO_2 + 2H_2O \xrightarrow{\text{light}} CH_3OH + \tfrac{3}{2}O_2$$

*carbon dioxide + water* $\xrightarrow{\text{light}}$ *methanol + oxygen*

If the fuel yield can be improved, the photocatalyst can be utilised in direct sunlight, thus keeping energy costs low. There are a number of different types of photocatalyst and whilst they are all activated by light, some are activated by the UV spectrum of light and some are activated by visible light.

Titanium dioxide-based photocatalysts have been used in much of the research for $CO_2$ reduction because they are widely available, low in cost, very chemically stable, have high photo-catalytic activity and are resistant to corrosion. A great deal of the research carried out in photocatalysis has been completed in Japan, Taiwan and here at Nottingham University.

## Testing the reactions in a laboratory

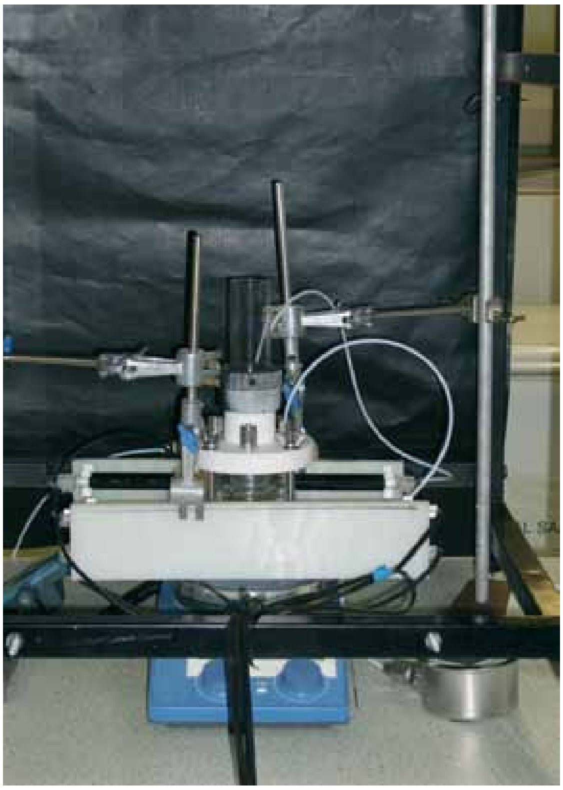
In order to test and improve $CO_2$ reduction, experimental work is carried out in a laboratory. Small reactors are used to contain the photocatalyst and the $CO_2$. Artificial light sources are used in the laboratory so that the energy source, whether it is UV light or visible light, can be isolated, thus reducing the number of variables in an experiment. The fuel produced in the experiment is collected and analysed in a gas chromatograph.

## Current research

The activity of the photocatalyst can be enhanced by metal 'doping', which means that a metal is added to the surface of the catalyst to change its properties very slightly. A great deal of research has been carried out at Nottingham University to test different metals and different amounts of metal to enhance the process. These metals include copper, palladium and rhodium which have all been doped onto titanium dioxide. However yields are still low and although titanium dioxide is a good photocatalyst, it is activated by the UV spectrum of sunlight. Unfortunately, sunlight only contains approximately 3% UV light so now the research carried out is more focused towards catalysts which are driven by visible light in order to maximise the use of solar energy.

The type of reactor and the type of support used for the catalyst to carry out the photoreduction is also of vital importance in this process. Maximizing the surface of the catalyst for the $CO_2$ to react on is imperative to increase the fuel yield. Two-phase and three phase reactors are mainly used in $CO_2$ photo-reduction, including slurry, optical fibre and monolith reactors.

Much of the research which has been previously carried out at Nottingham has used a 'slurry reactor'. In this reactor, the catalyst is suspended in water in a glass reactor which is then pressurised with pure $CO_2$. However this reactor has limitations because the catalyst cannot be recycled and the light is not distributed evenly throughout the system.



*The reactor at Nottingham is surrounded with UV lights. Once the experiment is running all other light is shut out using the black curtains to minimise the variables in the experiment.*

### Look here!

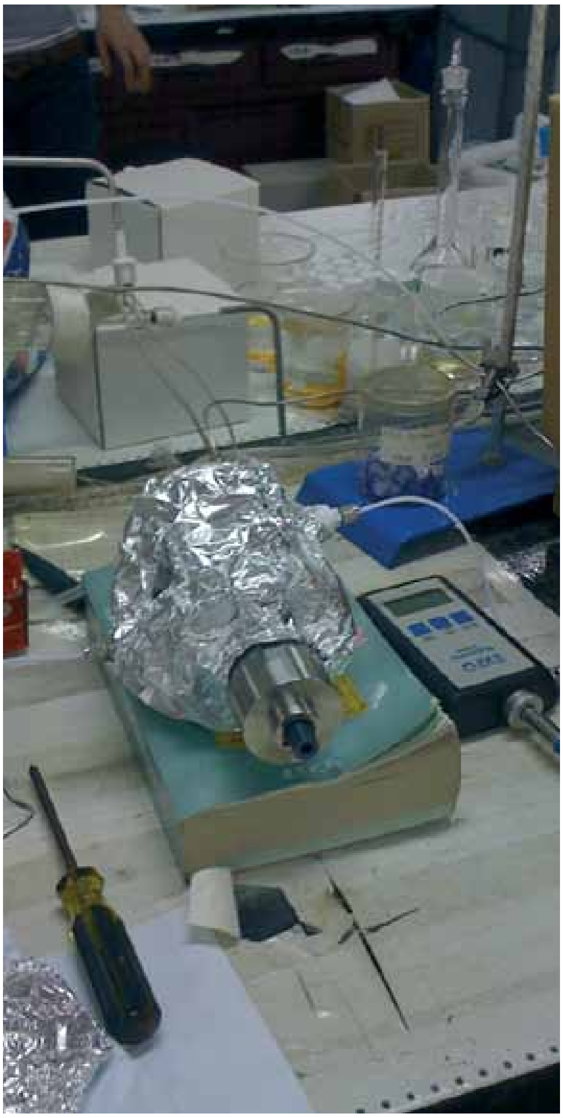
You can read Sarah Mackintosh's earlier article on carbon capture here: *http://www.sep.org.uk/catalyst/articles/catalyst_20_4_451.pdf*

Find out more about the work of the National Centre for Carbon Capture and Storage at *www.ncccs.org.uk*

An optical fibre reactor incorporates optical fibres for providing light transmission and for the solid support of the photocatalyst. The optical fibres can deliver light uniformly to the photocatalyst surface and consequently increase the efficiency of conversion. However, their configuration does not effectively utilize the entire reactor volume and the catalyst-coated surface area is relatively low since the optical fibre is usually thin.

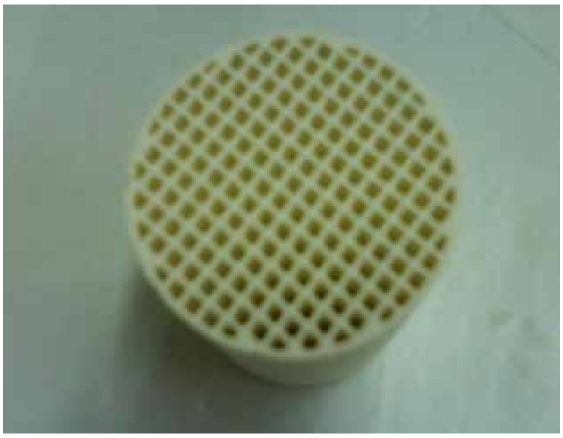
## A trip to Taiwan

I recently went to the National Taiwan University to learn about a different reactor with which they have a lot of experience. It is called a monolith reactor. The photocatalyst is coated onto a monolith which is a tube with a honeycomb shape inside.



*The monolith reactor is set up differently to the reactor at Nottingham but it can still be used with either UV light or visible light.*

This reactor takes advantage of the fact that the monolith has a high surface to volume ratio. However, the efficiency of the monolith is hindered since limited light can penetrate through the cells of the honeycomb substrate so we push optical fibres through the monolith to carry the light to the catalyst.



*The honeycomb monolith in which the reactants meet the catalyst.*

As you can see, there are good points and bad points surrounding all of the different technologies currently in experiment. There is still much work to be done before $CO_2$ recycling becomes commercially viable but, once it is, the process will be a low energy option to combat climate change and provide us with fuel.

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The National Centre for Carbon Capture and Storage

### Did you know?

- A semiconductor is a material that conducts electricity but which has a higher resistance than a good conductor such as a metal.
- Photocatalysts are used in many different applications including splitting water to obtain hydrogen, water treatment and in the decomposition of crude oil.
- Titanium dioxide is used in self-cleaning glass and in the disinfection of water.
- Gas chromatography works by using a flow-through narrow tube known as the *column*, through which different chemical constituents of a sample pass in a gas stream at different rates depending on their various chemical and physical properties and their interaction with a specific column filling. As the chemicals exit the end of the column, they are detected and identified electronically. This is a more complex version of paper chromatography, used to separate coloured inks and pigments.