Hydrogen: the fuel in water

In the search for cleaner and greener sources of energy there are many options on the table. Mathematics is helping to develop a method which harnesses the power of the Sun to unlock the energy of the hydrogen that lies hidden in water.

I t is the ultimate source of energy for the Earth. Trees and plants lock its rays into their leaves before passing that energy up the food chain. The coal, gas and oil we currently rely on to power our planet were formed when that organic material was trapped deep under the weight of the world's water. Without the Sun, life would be impossible.

However, the issues with using these so called "fossil fuels" are well publicised: their supply is dwindling and burning them pumps large amounts of carbon dioxide into the atmosphere. But it is not necessary to wait millions of years to harness the Sun's power in the form of these fossil fuels – the amount of sunlight falling on the Earth in just a single hour could provide the planet's entire annual energy needs at current consumption rates.

This is why solar panels have been lauded as a cleaner and renewable source of energy – the Sun has billions of years worth of shining yet to do. Solar panels have a flaw, though, when it comes to how they store energy. A small fraction of the incoming sunlight is converted into electricity and passed into a battery for safe-keeping. Except that it is not as secure as it could be: over time a battery leaks away the energy it stores. You never get as much out as the Sun puts in.

In the search for an alternative, mathematics is helping to find a more efficient way to harness the energy of the Sun, not involving solar panels but by using one of the most abundant substances on Earth: water. In this method, the energy from sunlight is used to split the water, chemically referred to as H_2O, into the hydrogen and oxygen it is comprised of. The hydrogen can then be used as a clean and green fuel; unlike fossil fuels, which give off harmful carbon dioxide, the only by-product of burning hydrogen is more water. Yet pure hydrogen doesn't occur naturally, it needs to be produced. However, only 4% of current hydrogen production is renewable or sustainable – the rest is still reliant on fossil fuels.

Unfortunately, sunlight doesn't have enough energy to split the water directly - it needs some help. This assistance comes in the form of a thin film of titanium dioxide – the same material used to paint the tramlines at Wimbledon tennis matches – which is applied to a sheet of steel, which in turn is in contact with the water. As the sunlight hits the titanium dioxide it creates charges which migrate to the surface and have the energy necessary to split the water. Sujata Kundu, at University College, London, is working to make this process more efficient. If she can

reduce the effort required get the charges to the surface, then lower energy light can be used. This means a higher proportion of the incoming sunlight is useful. There are two main ways this can be achieved.

> "The sunlight falling on the Earth in just a single hour could provide the planet's entire annual energy needs."

The first is to introduce tiny particles of other materials to the titanium dioxide. The process, called 'doping', adds in nanoparticles of gold and silver that measure around a billionth of a metre across. Kundu experimented with different ratios of the precious metals and then used mathematics to work out what effect they had. The energy required to create the charges needed to split the water is called the 'bandgap'. To work out this bandgap, the film is scanned using ultra-violet light and a graph is plotted of the intensity of light passing through the film. When the line on the graph suddenly drops, the light has been absorbed by the film, creating a charge.

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If too few dopants are added then the bandgap isn't reduced as much as it could be; too many and the film begins to take on different electrical and physical properties, adversely affecting its ability to help split the water.

The second way to increase efficiency is to find the optimum thickness of the titanium dioxide film. If the film is too thin then fewer charges are created and the rate of the reaction with water is lower. However, make the film too thick and the charge has too far to travel and is likely to recombine with the material before reaching the water.

Finding this ideal thickness is achieved by trial and error, but mathematics is required in order to accurately produce films in a variety of thicknesses. The titanium dioxide film is attached to the steel by dip-coating. In this process the steel is placed into a solution of titanium dioxide and slowly withdrawn leaving the coating attached. The rate at which you withdraw the steel dictates how thick your film is. Using a mathematical equation to describe the relationship between the speed of withdrawal and film
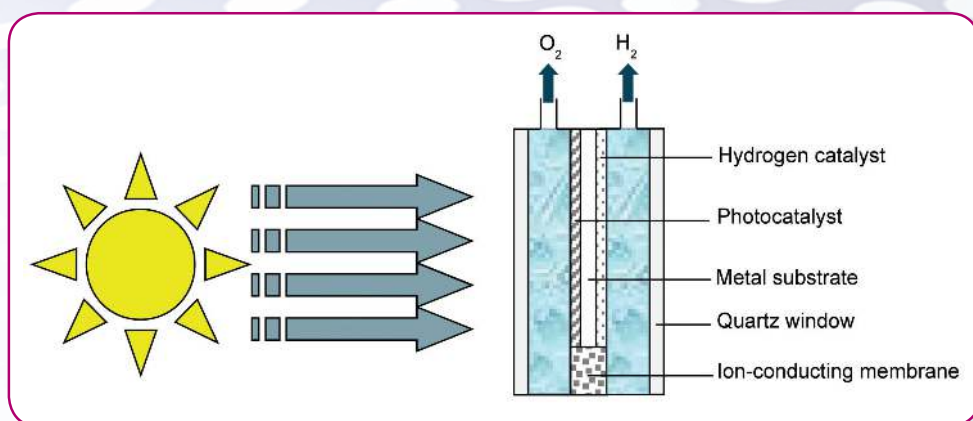
thickness, Kundu found the ideal thickness to be 120 nanometres – about a thousandth of the width of a human hair. The thickness can then be double checked by using mathematics to analyse the patterns created by the waves of light adding together as they pass through the film, much like ripples on a pond.

In the future, further optimisation of the efficiency of the device and the ability to maintain that efficiency as the technology is scaled up, is what's need for deployment on an industrial level. In that battle to wean

ourselves off of fossil fuels, and onto more a sustainable way to power our energy needs, mathematics is on the front line.

TECHNICAL SUPPLEMENT

Photocatalyst

The titanium dioxide acts a semiconductor photocatalyst. When the light hits it, charged species are produced that act as a catalyst for splitting the water. The charges can move through it because it can conduct electricity, more so than an insulator but less than a full conductor.

Bandgaps

The bandgap is the energy required to promote an electron from the valence band to the conduction band within the semiconductor. A typical bandgap for titanium dioxide is 3.2 electron-volts. Using the fact that the energy of light is inversely proportional to its wavelength, only light with wavelength of less than 380 nanometres is capable of supplying this energy and liberating the electrons that can then split the water. Sunlight with a wavelength of less than 380nm sits in the ultra-violet part of the spectrum. If you can reduce the bandgap through doping then you start to utilise the visible part of the spectrum too, increasing the rate of the reaction with water.

Dopants

To check the effect the dopants have on the films, a UV spectrum of each is taken. When the spectrum exhibits a strong absorption line, the light has been absorbed and an electron promoted. By manipulating the data points around this area, a Tauc plot – pioneered by Czech-born physicist Jan Tauc - is created from which the bandgap can be extrapolated.

Film thickness

The speed at which you withdraw the steel from the titanium dioxide solution was found empirically to have a relationship which is very close to linear. The approximate equation, which holds only around the approximate thicknesses required, is $y = mx + c$, where y = thickness in nanometres, x is the rate of withdrawal in centimetres per minute, m is 0.5 nanometres per centimetre-minute and c is 50 nanometres. A slower withdrawal than the thinnest films achieved gives striated films as the stutter of the motor pulling substrate out of the solution becomes more pronounced.

The thickness is then tested by shining light through it, before using an equation containing the subsequent interference maxima and minima and parameters describing the substrate and film material.

References

Kundu, S., Kafizas, A., Hyett, G., Mills, A., Darr, J.A., Parkin, I.P. (2011) An investigation into the effect of thickness of titanium dioxide and gold–silver nanoparticle titanium dioxide composite thin-films on photocatalytic activity and photo-induced oxygen production in a sacrificial system. *Journal of Materials Chemistry,* 21, 6854. DOI: 10.1039/c0jm03492d

Ni, M., Leung, M.H.K., Leung, D.Y.C., Sumathy, K. (2007). A review and recent developments in photocatalytic water-splitting using TiO2 for hydrogen production. *Renewable and Sustainable Energy Reviews,* 11, 401-425.