Dye-sensitised Solar Cells – Part 2

The first part of this subject described the Man Solar kit which can be used to produce dye-sensitised solar cells (DSSCs). These cells use a dye which directly converts the energy of sunlight into electrical energy using a process which, in some aspects, is similar to photosynthesis. Conventional solar cells are rather expensive owing to the cost of producing high grade silicon. In contrast, DSSCs use a nanocrystalline layer of titanium dioxide making them much cheaper to construct. This titanium dioxide layer acts both as a matrix for the photon-capturing dye molecules, and as a wide band-gap semiconductor.

This part describes some of the results obtained when various natural dyes were tested as photon-receptors, and the pH dependency. It also looks at the regeneration of the electrodes, and describes how to produce new titanium dioxide coated electrodes. Lastly there are suggestions of where this new technology could be incorporated within the 3-18 framework.

Testing sources of natural dyes

Several dyes have been prepared from plant material to compare their efficiencies. These include: fresh blueberries; hibiscus flowers (supplied in the kit); red cabbage; red onion skins; red capsicum (sweet pepper); and fresh spinach leaves. Beetroot has not been tested as it is reported that the dye will not absorb onto the titanium dioxide layer. The purple pigment in beetroot is a betalain, and not an anthocyanin, which may explain this observation.

In each case 10 g of chopped material was added to 50 ml of boiling water and left until cool. The cold dye solution was poured into a Petri dish and the titanium dioxide coated electrodes were left to soak in the dye for 10 minutes.

Dye source	Dye colour	Output current (mA)
Blueberries	purple	0.113
Hibiscus flowers	deep red	0.219
Red cabbage	deep purple	0.085
Red onion skins	deep red	0.050
Red capsicum*	pale orange	0.002
Spinach *	pale green	0.016

Table 1 *- Sources of natural dyes and their solar cell output currents.*

As the dye obtained from the Hibiscus 'flowers' produced the greatest current, it was therefore a more efficient solar cell than any of the other natural sources being tested. It is assumed that the dye probably contains a mixture of flavonoids.

These are based on glycosylated (i.e. sugar-linked) anthocyanidins (Figure 1) which have the following general structure:

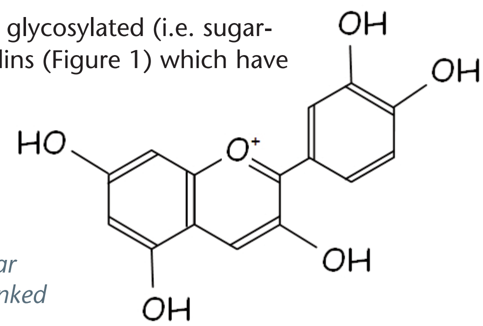

Figure 1 *- Molecular structure of sugar-linked anthocyanidin.*

The most important of these are: pelargonidin which gives the orange-red colour to geraniums, raspberries and strawberries; cyanidin which produces the magenta of ripe blackcurrants and red cabbage; delphinidin gives the blue colour to delphiniums and violas; and peonidin, which provides the purplish-red of peonies and cranberries. Flavanoids are also associated with antoxidant properties.

Possibly these compounds could be separated by chromatography to see which component in the mixture was the most effective in the solar process i.e the active ingredient.

It has been suggested that dye uptake by the titanium dioxide layer is improved by using a hot dye solution, but no evidence has been found to support this claim when red cabbage was used as the dye. Other dyes, of course, may behave differently and this might be worth investigating.

Testing the effect of pH

Most of the anthocyanins are pH sensitive. For example, the pigment that gives the intense blue colour to cornflowers in basic conditions is also responsible for the red colour of poppies in acidic conditions.

In schools, red cabbage is commonly used as a source of pH indicator dye. In conditions where the pH is below 3, this dye turns a pinkish red, whereas above pH 11 the dye turns a deep blue-green.

If a few drops of 0.1M hydrochloric acid or 0.1M sodium hydroxide are added to the surface of the titanium dioxide layer which has already been impregnated with the red cabbage dye, there is an immediate colour change.

When these electrodes were rinsed with distilled water and assembled as solar cells, it was found that the output current at pH 7 was higher than at pH 1 or pH 13 (Table 2).

pH of cabbage dye	Dye colour	Output current (mA)
1	dark pink	0.048
7	deep purple	0.083
13	dark green	0.015

Table 2 *- The effect of pH on thr output current of a red cabbage solar cell.*

* The dyes from red capsicum and spinach have also been extracted using ethanol. Although this results in a dye colour of much deeper intensity, there is no corresponding improvement in the output current from the consequent solar cells.

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Similar results are obtained when undyed titanium dioxide electrodes are soaked in the cabbage dye at the three pH values, rather than changing the pH after the cabbage dye has been absorbed into the titanium dioxide layer.

It seems likely that not only is there a decrease in the efficiency of photon capture by the cabbage dye at extremes of pH, but also that the ability of the dye to adhere to the titanium dioxide layer is impaired.

Synthetic DSSC dyes

It is essential that the dyes used in commercial solar cells do not degrade even after years of exposure to the extremes of sunlight, and there is considerable research taking place to develop suitable synthetic dyes.

Most of the commercially, synthetic dyes which have been developed so far, contain transition metals and ligand complexes. A good example of this is Ruthenium 505 (Figure 2).

Chemical name: *cis*-bis(cyanido) bis(2,2-bipyridyl-4,4-dicarboxylato) ruthenium (II)

Its manufacturers claim that Ruthenium 505 efficiently sensitizes wide band-gap oxide semiconductors, like titanium dioxide, up to a wavelength of 650 nm. As it has excellent stability properties, Ruthenium 505 is suitable for photochemical experiments and solar cell arrays.

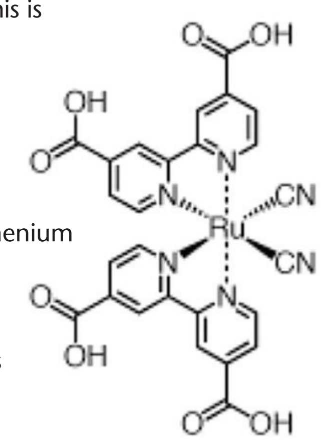

Figure 2 *- Ruthenium 505*

Regenerating the electrodes

The graphite coated electrodes can be reused, without any loss of efficiency, merely by rinsing off the old electrolyte and leaving them to dry. Once dried, a fresh layer of graphite can be applied if it is deemed to be necessary.

Regeneration of the titanium dioxide coated electrodes does not appear to be quite as simple. The dye can easily be removed from the titanium dioxide layer by soaking in cold water, or by pouring boiling water over the electrode (Table 3).

Method used to wash TiO_2 electrode	Output current after washing (mA)
Unwashed (control)	0.196
Overnight in water at room temperature	0.006
30 minutes in water at room temperature	0.007
2 minutes in boiling water	0.007

Table 3 *- The effect of washing procedures on the removal of Hibiscus 'flower' dye, using the residual output current as an indicator of effectiveness.*

However, the electrodes show a reduced ability to reabsorb the Hibiscus dye, as shown by the data obtained when a solar cell was repeatedly reassembled with the titanium dioxide electrode being washed in boiling water, dried, and re-dyed, between each cycle (Table 4).

Age of TiO_2 electrode (cycle)	Output current (mA)	Re-use Efficiency (%)
1st	0.223	100
2nd	0.121	54
3rd	0.082	37
4th	0.046	21

Table 4 *- The ageing effect on the titanium dioxide electrode in a Hibiscus 'flower' solar cell.*

Making new titanium dioxide coated electrodes

The titanium dioxide suspension is prepared by the incremental addition of 10 ml of very dilute ethanoic acid to 5 g nanocrystalline titanium dioxide powder (e.g. Aeroxide TiO_2 P25) while it is being ground with a mortar and pestle for 10 minutes. It should be noted that ordinary titanium dioxide will not adhere to the glass when sintered. Finally, adding one drop of dishwashing detergent and mixing again should produce a smooth paste.

Prior to coating the glass electrodes with titanium dioxide, they are attached on three sides to a white tile using adhesive tape, making sure that the conductive side is uppermost. A 3 mm wide strip holds the electrode on both sides and a 5 mm wide strip holds the top end.

One drop of the titanium dioxide slurry from a Pasteur pipette is then added at the top end of the electrode, and gently drawn down the glass surface using a glass rod which is resting on the two side strips of adhesive tape (Figure 3). This should produce a uniform thin layer.

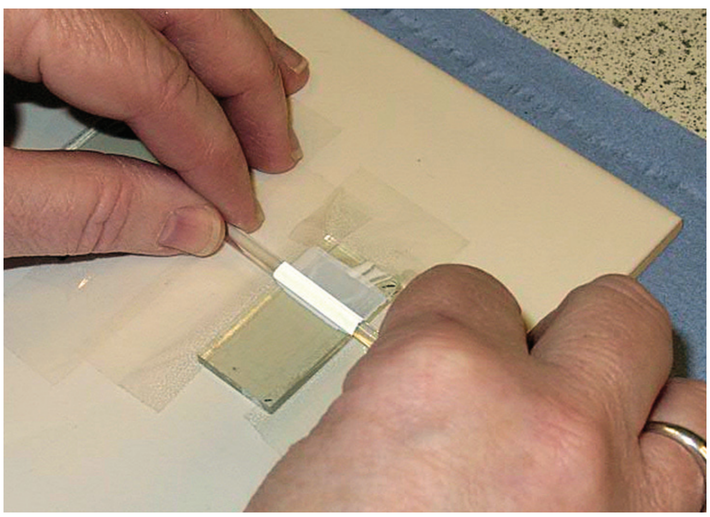

Figure 3 *- Applying the titanium dioxide layer to the glass electrode*

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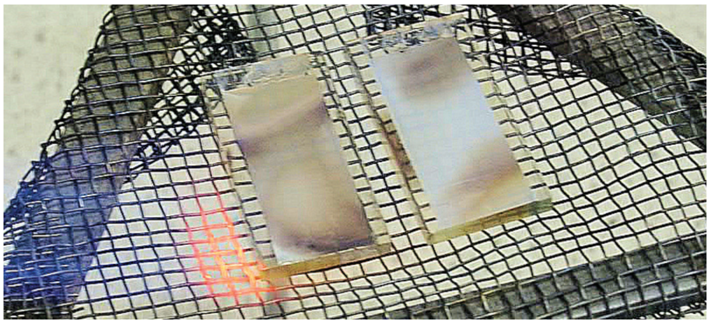

Figure 4 *- Sintering the titanium dioxide layer with the blue flame of a Bunsen burner.*

After the coating has dried (a hair-drier speeds up this process), the adhesive tape is removed and the electrode is placed on a wire gauze for sintering. As a blue Bunsen flame is passed slowly over the titanium dioxide surface, it turns dark brown and then goes white. This process only takes about 3 minutes (Figure 4).

After sintering, the coated electrode must be allowed to slowly cool to room temperature, otherwise the glass is liable to crack or shatter.

Sources of material

Most of the items in the Man Solar 2000 kit will already be in schools or can be purchased locally. However it might be considered prudent to purchase a kit which is proven to work, before attempting to substitute in alternative materials which may, or may not, work equally well.

Hibiscus 'flowers', Hibiscus tea or 'Flor de Jamaica' can be purchased in many health food stores. Alternatively dried Hibiscus flowers can be purchased on the internet for about £2 per 100 g (e.g. www.Mexgrocer.co.uk) or by post from:
MexGrocer, 1 Tennyson Rd, Stockport, SK5 6JJ.
Tel : 0800 849 9042 (Information Line Only)

The tri-iodide electrolyte can be prepared by dissolving 0.127 g iodine (I_2) in 10 ml of ethane 1,2-diol (ethylene glycol – Harmful vapour) and then adding 0.83 g potassium iodide. The solution should be thoroughly stirred and stored in a dark container.

Electrically conductive glass is produced in Britain as Pilkingtons K Glass ™ (4 mm). A single sheet of glass (30 cm x 30 cm) could be cut by a glazier to produce over 100 electrodes (2 cm x 4 cm). To minimise the risk of fingers being cut by sharp glass, the sides of each glass electrode should be passed through a hot Bunsen burner flame.

Pilkingtons K Glass™ appears to be the same as Pilkingtons TEC Glass™ (Transparent Electrically Conductive Glass) which is produced by Pilkingtons in the United States.

Nanocrystalline titanium dioxide powder (e.g. Aeroxide TiO_2 P25) is available from various chemical suppliers.

Man Solar also sell the following single materials but there is a minimum order charge:
Article 001: One set contains 6 titanium dioxide coated conductive glass electrodes and 6 conductive glass electrodes.
Article 002: One set contains 12 conductive glass electrodes. These are ready to be sintered with titanium dioxide or coated with graphite.
Article 004/005: Titanium dioxide solution to be deposited and sintered onto article 002
Article 013: Dried Hibiscus flowers

MAN SOLAR B.V., Westerduinweg 3,
1755 LE Petten, The Netherlands
E-mail: mansolar@ecn.nl. Internet: http://www.mansolar.com

Linking to Curriculum for Excellence – Experiences and Outcomes

There are a number of ways in which dye-sensitised solar cell technology could be incorporated into science learning and teaching, and some of the opportunities are illustrated below. It could also provide the focus for inter-disciplinary links with a cross curricular theme, as well as encouraging the principles and practice of "A Curriculum for Excellence". Shorthand links to the www.science3-18.org website are also shown [].

The Sciences, Materials, Properties and uses of substances,
SCN 4-16a Researching novel materials
I have carried out research into novel materials and can begin to

Hazards and control measures

Chemicals & procedures	Main Hazard	Control Measures
Iodine/tri-iodide electrolyte incl. ethane-1,2-diol	Harmful	Wear nitrile gloves and indirect vent goggles.
Glass electrodes (assembling solar cell)	May have sharp edges and may break if pressed too hard.	Hold glass electrodes carefully and add bulldog clips gently.
Glass electrodes (sintering of titanium dioxide)	May shatter if heated and cooled too rapidly.	Heat on a wire gauze and leave to slowly cool.
Boiling water for dye-bath	Scalding	Don't touch or move beaker containing the boiling hot dye-bath.

Table 5 *- Hazards and control measures.*

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explain the scientific basis of their properties and discuss the possible impacts they may have on society. [http://tinyurl.com/SCN-4-16a]

Activities which could link to this outcome:

i. Build a DSSC.
ii. Compare 3 or 4 different plant dyes, including beetroot to show that not all coloured dyes work.
iii. Add solar cells together in series and use a multimeter to find out the voltage required to operate a pocket calculator or melody module.
iv. Research the use of cheap DSSCs in developing countries where there is no National Grid.

The Sciences, Planet Earth Energy sources/sustainability,
SCN 2-04b Exploring non-renewable energy sources
Through exploring non-renewable energy sources, I can describe how they are used in Scotland today and express an informed view on the implications for their future use.
[http://tinyurl.com/SCN-2-04b]

The Sciences, Planet Earth, Energy sources/sustainability,
SCN 3-04b Issues with renewable energy
[http://tinyurl.com/SCN-3-04b]
By investigating renewable energy sources and taking part in practical activities to harness them, I can discuss their benefits and potential problems.

Technologies, Tech. developments in society, TCH 2-02b Renewable & sustainable energy
[http://tinyurl.com/TCH-2-02b]
I can investigate the use and development of renewable and sustainable energy to gain an awareness of their growing importance in Scotland or beyond.

Activities which could link to this outcome:

i. Build a DSSC.
ii. Compare 3 or 4 different plant dyes, including beetroot to show that not all coloured dyes work.
iii. Back the solar cell with reflective foil to see if the output current is increased.
iv. Plot the relationship between output current and light intensity (by measuring the distance from a light source or using a light meter).

The Sciences, Topical science, **SCN 4-20a** Current and future developments
I have researched new developments in science and can explain how their current or future applications might impact on modern life.
[http://tinyurl.com/SCN-4-20a]

Activities which could link to this outcome:

i. Build a DSSC
ii. Compare the output currents of a DSSC and a silicon solar cell at different light intensities.
iii. Research future applications – providing energy in developing countries when there is no opportunity to recharge them through a national grid. (e.g. LED lighting, radios, refrigerators, water purification, mobile phone rechargers).

The Sciences Planet Earth Energy sources/sustainability
SCN 4-04a Risks and benefits of energy
By contributing to an investigation on different ways of meeting society's energy needs, I can express an informed view on the risks and benefits of different energy sources, including those produced from plants.
[http://tinyurl.com/SCN-4-04a]

Activities which could link to this outcome:

i. Build a DSSC
ii. Compare the DSSC to another renewable source of energy in terms of cost, energy output, reliability and level of technology required to build it.
iii. Discuss attitudes towards "green energy" sources such as solar cells, wind turbines and bio-fuels.

The Sciences, Forces, electricity & waves, Electricity,
SCN 4-09a Current, voltage and resistance
Through investigation, I understand the relationship between current, voltage and resistance. I can apply this knowledge to solve practical problems. [http://tinyurl.com/SCN-4-09a]

Activities which could link to the first part of the outcome:

i. Build a DSSC
ii. Add a variable resistance across the DSSC and plotting the relationship between voltage and current.
iii. Plot the relationship between power and voltage, to find the maximum power point.
iv. Use these graphs to examples of appliances which would / would not operate using a DSSC.

Open-ended Investigation Projects

As pupils will be unfamiliar with dye-sensitised solar cells they have tremendous potential as the basis of open-ended investigations.

Possible starter questions might include:

i. Which flower petals produce the most effective dye for a DSSC?
ii. Is there a significant degradation of the dye over a period of time, as shown by a decrease in the output current? (The student would need to ensure that it is not just the electrolyte drying up)
iii. Is dye degradation accelerated by increasing the intensity of light?
iv. Does the ionic environment (concentration and type of ions) affect the photon-trapping efficiency of the dye?
v. Can the mixture of anthocyanidins in a plant extract dye be separated (e.g. by chromatography) to see which is the most effective component?