Why don't zombies like hibiscus tea? A multi-subject approach to photosynthesis through the use of Grätzel cells

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ABSTRACT Traditionally, photosynthesis has been seen as the domain of biology, with some input from chemistry when dealing with chromatography, while, apart from a passing reference to the colour of leaves, physics has tended to steer clear of the process that provides the lifeblood of human existence. This article outlines how a recent technological advance can be used as a teaching resource in all three branches of science.

The development of new sources of electrical energy is always at the forefront of scientific research and the use of batteries and/or cells in school is often cited in published work to promote interest in science (see, for example, Lee, 2005 and Bullivant and Hare, 2006). Indeed, what follows in this article is not new (see, for example, Siemsen *et al*., 1998), but it provides an improved fabrication process that can be carried out more easily in schools, together with guidance on investigative work using the cells. Although the underpinning science may appear complex, the assembly and use of Grätzel cells is relatively simple; working units have been successfully constructed by mixed-ability groups of pupils in year 7 (age 11/12) and above.

Grätzel cells

The first published reference to Grätzel cells was in 1991 (O'Regan and Grätzel, 1991). These cells work by effectively mimicking photosynthesis but without the production of glucose. The cells transfer energy from incident light to electrical energy and require the use of an iodide electrolyte and a dye; as such, the cells may be referred to as dye-sensitive cells. A typical structure of a Grätzel cell is illustrated in Figure 1.

The negative side of the cell consists of a thin layer of titanium dioxide onto which dye molecules are adsorbed. The titanium dioxide particles are in turn attached to a commercially available conducting glass plate (rendered

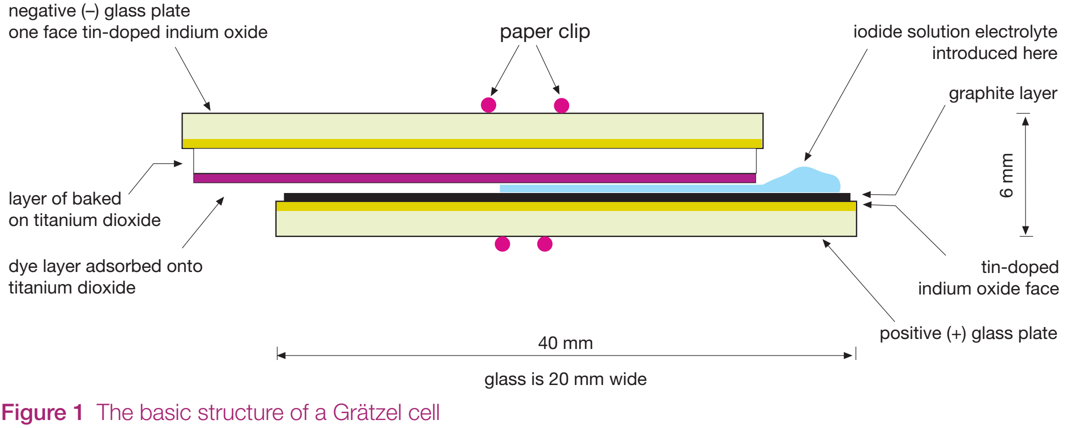


Figure 1 The basic structure of a Grätzel cell

conducting by a coating of tin-doped indium oxide, so thin that light can pass through it almost without loss). Incident light excites the electrons in the dye. These excited electrons become free electrons and pass into the conducting band of the titanium dioxide. The titanium dioxide layer thus develops a net negative charge and electrons flow, via the top conducting glass and a low-current device, such as a calculator, acting as an external load, to the iodide electrolyte via the lower conducting glass plate and graphite layer.

To complete the circuit, the dye ions (D^+) regain their lost electrons from the iodide electrolyte. Iodide ions (I^-) are oxidised (loss of electrons) to tri-iodide ions (I_3^-) as in the equation:

$$3I^- \rightarrow I_3^- + 2e^-$$

$$D^+ + e^- \rightarrow D$$

Electrons from the graphite layer reverse this reaction and reduce (gain of electrons) the tri-iodide ions back to iodide ions.

$$I_3^- + 2e^- \rightarrow 3I^-$$

The dye molecules (D) are now ready for the next excitation/oxidation/reduction cycle.

Constructing a Grätzel cell

There are three steps in constructing a Grätzel cell:

1. preparation of graphite and titanium dioxide plates;
2. adsorption of dye onto titanium dioxide;
3. assembly of the Grätzel cell.

These steps are described below.

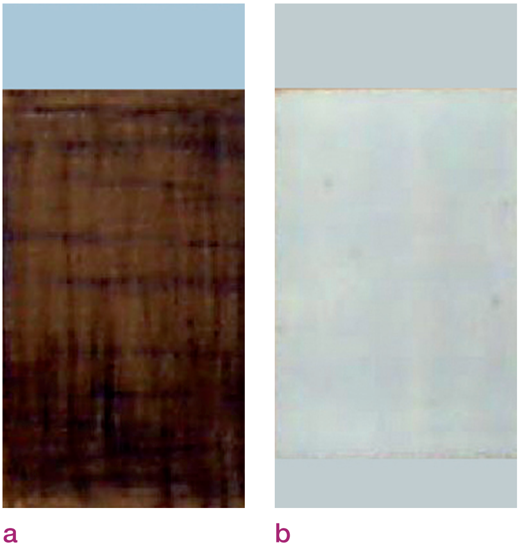
1. Preparation of graphite and titanium dioxide plates

Both titanium dioxide and graphite plates are prepared from commercially obtained transparent glass plates that have been treated on one side with a transparent thin layer of conducting substrate (tin-doped indium oxide). Both plates are prepared onto the conducting sides. (Currently, six pairs of pre-coated plates are available for the sum of 15 euros – see *Sources*.)

The graphite plate is prepared by colouring in the plate with graphite using a pencil (Figure 2a). The titanium dioxide plate can be re-coated with a thin layer of titanium dioxide paste, which is then sintered (baked) over a blue Bunsen flame for around 3 minutes (Figure 2b). In order to avoid cracking the glass plates, it is best to raise their temperature gently by holding them in tongs and slowly introducing them to the Bunsen flame. If available, an oven (set at 500 °C), such as those commonly used for ceramics work in a school art department, would give a more controllable source of heat. Removing the plates from the oven and cooling them rapidly in air tends to produce some discolouration of the titanium dioxide layer; this can be avoided by turning the oven off and allowing the plates to cool more slowly. Although this sintering process is relatively straightforward, it can be time-consuming and we would recommend that this be carried out in advance by either the teacher or laboratory technician.

2. Adsorption of dye onto titanium dioxide

For those wishing to make explicit links to photosynthesis, chlorophyll extracted from green plants or purchased as a water-soluble reagent from a chemical supplier such as Philip Harris (see *Sources*) would work. However, hibiscus tea is found to work exceptionally well. 1 g of hibiscus tea leaves is added to 50 cm^3 of water in a 100 cm^3 beaker and allowed to boil for 2 minutes. The titanium dioxide plate is then immersed in the hibiscus tea solution for 5 minutes to allow the dye to adsorb onto the titanium dioxide layer. The excess dye is then washed off using water and the plate (Figure 3) is left to dry in air, or the process can be speeded up by use of an oven or hairdryer.



a b

Figure 2 Prepared graphite (a) and titanium dioxide (b) plates

Other vegetable dyes can be used for adsorbing onto the titanium dioxide plate in a similar manner. These include: blackcurrants, black tea, cranberries, onion skin, raspberries, Ribena, strawberries and even turmeric powder. Suggested quantities to use are listed in Table 1.

3. Assembly of the Grätzel cell

In our trials, we used a commercially available (from Man Solar – see *Sources*) iodide electrolyte. However, should the reader wish to make up his/her own version, an effective (although not cost-effective) electrolyte solution can be made from 0.1 mol dm^{-3} lithium iodide and 0.05 mol dm^{-3} iodine in a solvent of 80% ethylene carbonate and 20% propylene carbonate.

To assemble the Grätzel cell, the dyed titanium dioxide plate is placed on top of the graphite plate. It is important that the plates are placed slightly offset to allow for electrical contact. To keep the plates in position, a paperclip is used to firmly clamp the two plates together. Finally, a drop of iodide electrolyte (from a small dropping pipette) is placed on the exposed part of the lower plate, next to the edge of the upper plate, and left for 2 minutes to allow the electrolyte to flow through the whole of the cell. The Grätzel cell is complete and ready for generating electricity (see Figure 4).

Examples of curriculum materials

If natural light is not available or is not sufficiently strong, the light from an overhead projector or desk lamp will power the cells. Using dye from hibiscus tea, between three and five cells connected in series will generate a total voltage of 1.2 V, sufficient to power a small electronic calculator. Some commercially available kits include low-powered fans and melody modules.

This work was piloted with a group of 40 trainee teachers, a mixed group of biology,

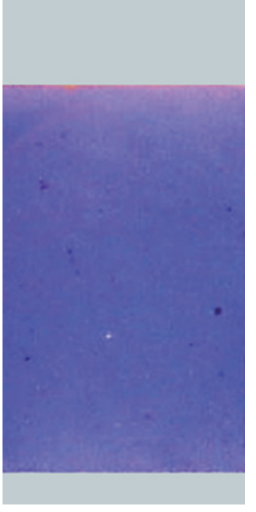


Figure 3 Prepared titanium dioxide plate dyed with hibiscus tea

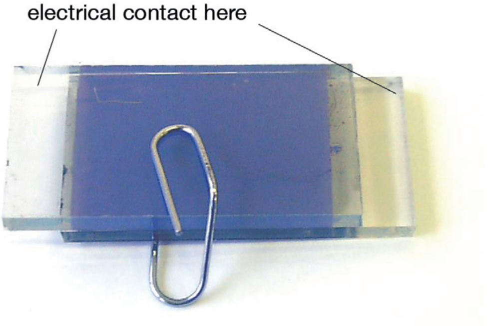


Figure 4 Prepared Grätzel cell, ready for generating electricity

Table 1 Suggested quantities for various vegetable dyes

Vegetable material	Suggested quantities to use
blackcurrants	crush 5 blackcurrants and simmer in 10 cm^3 water
black tea	simmer a tea bag in 50 cm^3 water
cranberries	crush 4 cranberries and simmer in 10 cm^3 water
onion skin	simmer 5 pieces of skin in 50 cm^3 water
raspberries	crush 2–4 raspberries and simmer in 10 cm^3 water
Ribena	simmer 10% solution for 2 minutes
strawberries	crush 2–4 strawberries and simmer in 10 cm^3 water
turmeric powder	simmer 0.3 g in 50 cm^3 water

BOX 1 Zombie attack

You are walking through a graveyard on your way back from a friend's house just as the Sun is about to rise. You hear something rustling in a bush. You begin to walk faster. Your heart is pounding. Just as you get close to the gates to leave the graveyard you feel cold breath on the back of your neck. You gasp as you fall to the ground.

A few moments later you wake up and feel a stabbing pain in your leg. You look down and see a bloody wound. You notice something familiar about the marks on your leg. You have seen them before in a research paper your uncle wrote. You put all the links together and realise you have been bitten by a ZOMBIE!

You remember your uncle investigated suspicious attacks in the village a few months ago but kept everything top secret in his lab. You hobble your way towards your uncle's lab and break in through the window. You manage to find the files about the zombie attacks in a cabinet. You realise you have one hour to take the antidote or you will become a zombie. The antidote is in a locked cabinet with an electronic keycode pad ... but there is no power.

Your task

Construct a Grätzel cell, which can be used to generate a voltage using sunlight, from the equipment found in the lab kitchen. Each group will investigate the effects of a different dye on the voltage produced. We will share all our results at the end of the lesson to decide which dye would be best to use to power the electronic keycode pad and get to the antidote in time!

Items available in the lab kitchen

- conductive glass from LCD screen on microwave*
- titanium dioxide (TiO_2) from the chemical cupboard
- iodide solution from chemical cupboard
- pencil
- paperclips
- wires
- voltmeter
- Ribena
- tea bags
- cranberries
- keycode pad (calculator used in class to represent this)

*[NB While we are not advocating that pupils dismantle a microwave oven to source conducting glass plates, this is an example of a commercial application of conducting glass. If a teacher were to resort to such a source, it would be essential that any mains lead were removed and all precautions taken to avoid pupils cutting themselves on sharp/broken glass.]

Table of results

Type of dye	Voltage generated (volts)	Does calculator (keypad) turn on?
Ribena		
Tea bags		
Cranberries		

In our experience, we have found that as few as three hibiscus tea cells connected in series are sufficient to power a typical button-battery operated calculator.

chemistry and physics graduates, all following a one-year Postgraduate Certificate in Education course in secondary science. Working in mixed-subject groups, the students suggested and piloted a series of investigations, two of which are outlined in Boxes 1 and 2. Whilst both scenarios may appear rather contrived, the 'zombie attack' in particular is sufficiently macabre to have a certain 'gross appeal' to many teenagers.

Other approaches

As asserted in the early sections of this article, photosynthesis has traditionally been seen as the domain of biology. However, Grätzel cell technology can be adopted for use as a vehicle through which all branches of science in the secondary curriculum can be addressed. In particular, the action of light-sensitive-dye molecules, as part of an energy-transfer process, parallel the reaction in photosynthesis. Other approaches that have been suggested include:

- Investigating the effect of connecting Grätzel cells in series circuits.
- Investigating the effect of connecting Grätzel cells in parallel circuits.
- Investigating the effect of different organic dyes on the power output of a Grätzel cell.
- As a prompt for discussion on advantages and disadvantages of different renewable energy sources.
- For a comparison of conventional solar cells with Grätzel cells.
- Investigating the effect of using different-coloured lights on the current output of a Grätzel cell.
- Investigating the relationship between the distance between the source of light and the power output of a Grätzel cell.
- Use of the chemistry underpinning Grätzel cell technology as a practical application of oxidation/reduction and reversible reactions.
- Using dyes obtained from green plants, investigating the output of a Grätzel cell with light of different wavelengths.

BOX 2 Shipwreck

On a school trip around the Caribbean you become shipwrecked and stranded on a deserted island!

The supplies you have been able to salvage include a pack of Grätzel cell kits. You also have a mobile phone, which you can use to contact an oil tanker you can see on the horizon ... but the battery is damaged beyond repair.

To get the Grätzel cells to work you need to go out and find a suitable dye to act as the electron donor.

Things to consider:

- What colour dye will work best?
- What voltage/current do you need to power the mobile phone?
- How many Grätzel cells will you need to achieve this?
- How will you configure them?

Risk analysis

Risk	Dangers	Precautions
Iodide solution splashed into eye (low hazard)	Harmful	Wear eye protection
Sintering the titanium dioxide plates	Burns to fingers	Present pupils with pre-prepared plates
Removing LCD display on microwave	Cut fingers on broken/sharp glass. Electrocution	Do not allow pupils to dismantle microwave ovens Remove mains lead before dismantling
Simmering titanium dioxide plates in solution of vegetable dye	Burns from hot apparatus / spillage of boiling water	Standard laboratory precautions
Titanium dioxide (low hazard)		Standard laboratory precautions
Eating any of the vegetable samples	All natural products, regularly consumed by the public – negligible risk	Standard laboratory precautions

Sources

Individual components or complete Grätzel cell kits (from 49 Euros upwards) are available from Man Solar at: www.mansolar.com/
As detailed earlier, an alternative electrolyte could be made up from its constituents although the organic solvents required are not likely to be readily available in a secondary school chemical store and the small volumes required for the experiment may not make it a cost-effective option.

Conducting glass plates: For an alternative supplier of conducting glass which could be used for Grätzel cell work see: www.delta-technologies.com/
The LCD on a microwave oven is made of several layers, one of which is tin-doped indium oxide conducting glass (see *Howstuffworks* on: www.howstuffworks.com/lcd2.htm) and therefore non-functioning microwaves are a potential source of conducting glass electrodes. A cheaper, and more readily available, source would be the LCD from a calculator, although the non-display areas have been etched away which results in only a small area remaining. Larger surface areas of conducting glass can also be found in self-dipping rear view car mirrors and some high-tech conservatory windows.

Vegetable dyes: Water-soluble chlorophyll is available from suppliers, such as Philip Harris. At the time of writing, 10 g is available (reference number: C7A6 7003) at a cost of £15. Alternatively, a green vegetable, such as spinach, could be used in the same way as any of the other sources. Most supermarkets would carry a range of suitable vegetable materials for experimentation; hibiscus tea bags are less commonly stocked and we sourced these from health food stores (fresh hibiscus tea bags were found to be far more effective than older ones).

Further information on experiments and resources can be obtained from the Department of Chemistry, Loughborough University: www.lboro.ac.uk/departments/cm/business/Gratzel.html

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