1st

European Union Science Olympiad

in Dublin, Ireland

TASK **A**

Task A

Photosynthesis

Introduction

Although the sun provides for an inexhaustible supply of clean energy in the form of light, using this energy requires the conversion of light into electrical, thermal or chemical energy. Solar cells allow for the conversion of light into electricity. In this experiment you will use and prepare solar cells and study the use of natural dyes in improving the efficiency of the cells.

Nature has, of course, used solar energy for millions of years. Plants harvest solar energy by conversion of light directly to chemical energy. This process is known as photosynthesis. In order to absorb light, plants use coloured compounds such as chlorophyll. The absorbed energy is used to synthesize carbohydrates from CO_2 and H_2O. Chlorophyll is found in the chloroplasts of plant cells. The chloroplasts use the light energy absorbed to reduce NADPH to $NADPH_2$.

This experimental problem consists of three tasks, all related to the study of photosynthesis.

- In task A.1, you will extract chlorophyll from spinach.
- In task A.2, you will build a chlorophyll-based solar cell and compare its working to that of a silicon photodiode.
- In task A.3, you will investigate a photoreduction reaction.

Material and equipment

For Task A.1

- Spinach leaves
- Sand
- Calcium carbonate
- Toluene
- Mortar and pestle
- Spatula
- Graduated cylinder
- Filtration apparatus
- Amber bottle
- UV-Visible spectrometer

For Task A.2

- Glass slide with a conducting coating and a thin layer of TiO_2 on one side
- Glass slide with a conducting coating
- Chlorophyll solution (from task A.1)
- Ethanol
- Electrolyte solution (0.5 *M* potassium iodide mixed with 0.05 *M* iodine)
- Silicium photo diode
- Multimeter
- Lamp

- Petri dish
- Binder clips
- Pencil
- Copper foil
- Crocodile clips

For Task A.3

- DPIP (2,6-dichlorophenol-indophenol) solution at pH 6.5
- Plastic cuvettes
- Phosphoric acid solution
- Unboiled chloroplast solution
- Boiled chloroplast solution
- Chlorophyllin solution
- Photolysis box
- Desk lamp
- Aluminium foil
- UV-Visible spectrometer

Task A.1: Chlorophyll extraction

Historically, extraction is one of the oldest of all chemical operations, and one which is used in everyday life. By simply making a cup of tea or coffee an extraction has been carried out. The addition of hot water to the tea leaves or the coffee beans extracts the various components responsible for the flavour, odour and colour. Extraction in the chemical sense means "pulling out" a compound from one phase to another, usually from a liquid or a solid to another liquid.

Green leaves contain many coloured compounds, in particular chlorophyll. Spinach, which is dark green, contains a high concentration of chlorophyll in its leaves. The chlorophyll in spinach leaves is easily extracted into non-polar solvents. In this experiment, spinach is first ground using a pestle and mortar, to aid in the extraction of the chlorophyll from the leaves. The solvent is then added to the ground spinach to extract the chlorophyll. The solid material remaining is then removed by filtration and the liquid filtrate retained for use in task A.2.
Procedure:

1. Add one spatula tip full of sand and one spatula tip full of calcium carbonate to the spinach sample provided (this helps the grinding process).
2. Grind the spinach sample provided for 5 minutes.
3. Working in a fumehood, measure out 50 cm^3 of toluene in the graduated cylinder provided and add it to the spinach. Grind for a further 5 minutes.
4. Let the mixture stand for 2 minutes
5. Set up the filtration apparatus provided. Place the filter paper into the funnel.
6. Filter the mixture through the filter paper.
7. Transfer the liquid filtrate to the amber bottle provided.
8. Record the UV-Visible spectrum of the sample and write down the wavelengths of the absorbance maxima on your answer sheet. Label your diagram "Graph 1".

Now answer question 1 on the answer sheet

Task A.2: Nanocrystalline solar cell

Solar cells are devices capable of converting the light they absorb to an electric current. Semiconductor junctions form the basis of nearly all commercial solar cells. Photons absorbed by the semiconductor junction excite electrons into the conduction band and create holes in the valence band. The electron and hole are then swept apart at the junction and create a photovoltage. To achieve this, the energy of the photon must be greater than the so-called band gap of the semiconductor, i.e. it must give an electron enough energy to jump from the valence band to the conduction band.

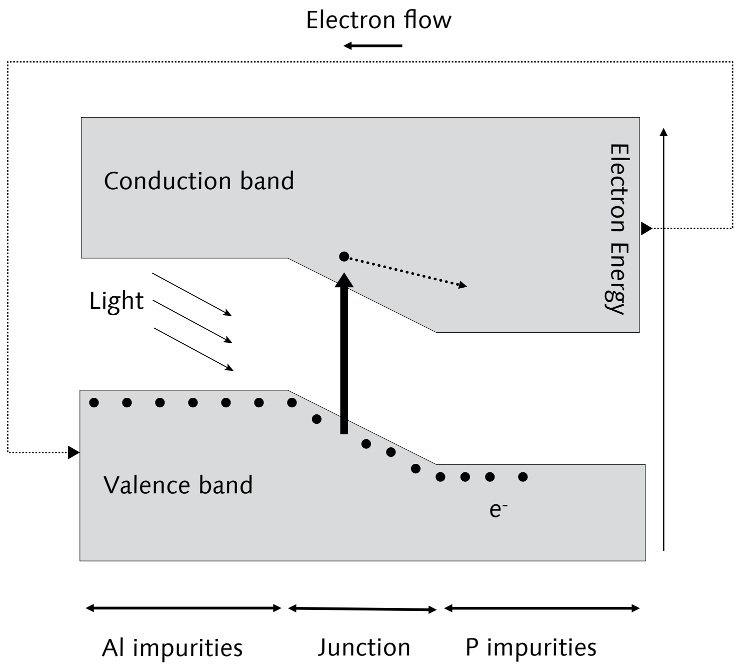

Figure 1: A p-n junction solar cell: a silicon photodiode.

The purpose of this task is to build and quantify the output of a different type of solar cell called a Graetzel cell. In this particular type of Graetzel cell the charge separation takes place at a TiO_2/chlorophyll/electrolyte interface instead of a semiconductor junction.

The cell operates as follows. A layer of dye molecules (in this experiment the green dye chlorophyll) is deposited on a TiO_2 substrate. When the chlorophyll is excited by visible light, it will transfer electrons to the TiO_2 conduction band. In this process chlorophyll is oxidized (it loses an electron). The chlorophyll+ ion will not be able to absorb another photon of light and transfer another electron to the TiO_2 until it is reduced. The electrons used to reduce the chlorophyll+ ion come from the electrolyte (where 3 I^- ions in the electrolyte give up two electrons to become I_3^-). At the other end of the cell the I_3^- picks up an electron to form 3 I^-, again completing the circuit. A photovoltage and a photocurrent are thus generated.

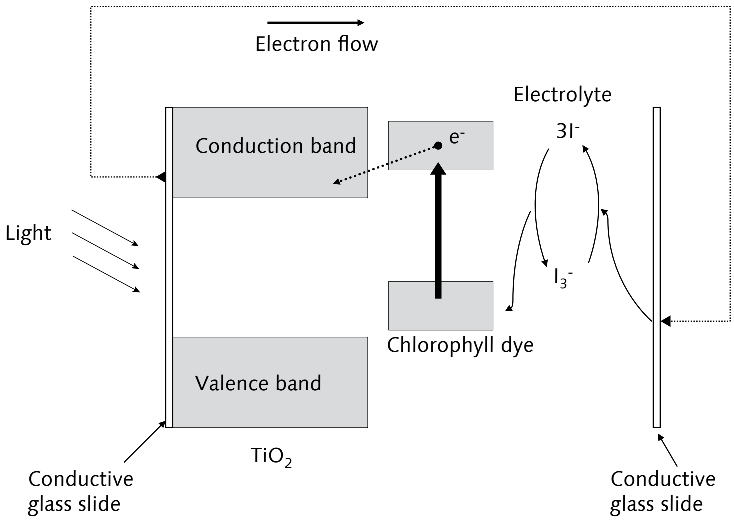

Figure 2: Dye-sensitized solar cell.

Experimental procedure

You are asked to make a solar cell with the chlorophyll that you have extracted from spinach. You will compare the voltage readings of both the conventional silicon photodiode and the Graetzel cell when illuminated with a lamp.

For the Graetzel cell you will need to prepare two glass slides, which will form the front and back of the solar cell. The two slides are already partially prepared. Both slides have a conducting coating on one of their sides for electrical measurements. The slide that looks white has a thin layer of TiO_2 on top of the conducting coating (slide 1), the other slide has only the conducting coating (slide 2). There are still a number of things you must do:

Procedure to make the Graetzel cell:

1. Soak the TiO_2 coated slide (slide 1) in a petridish containing chlorophyll solution. The slide should be left in the solution (with the TiO_2 coated side facing upwards) for one hour.
2. Clean the conductive glass slide (without the TiO_2, slide 2) with ethanol.
3. Test which side of this glass slide is conductive (slide 2) and complete question 2 on the answer sheet.
4. Coat this slide (slide 2, which is the counter electrode) with carbon using the "2B" pencil supplied. The carbon catalyses the reaction which reduces the electrolyte thus completing the circuit.
5. The chlorophyll-dyed TiO_2 slide (coated slide 1), which is the electrode, should be left to dry for 5 minutes, washed in ethanol and gently blotted dry.
6. Place the electrode (coated slide 1) flat on the bench, with the coated side upwards. Check that it is completely dry.
7. Gently turn the counter electrode onto the electrode and offset the two plates so that all of the TiO_2 is covered by the counter electrode and an undyed strip of slide (where there is no TiO_2) is left exposed at either end of the cell. See Figure 3 below.
8. Clamp one of the other two edges of the cell with one of the binder clips provided.
9. Place a few drops of the supplied electrolyte solution (0.5 M potassium iodide mixed with 0.05 M iodine) at the opposite edge of the plates.
10. Allow the electrolyte to be drawn along the cell by capillary action.
11. Remove the excess electrolyte from the exposed areas of the glass by wiping with ethanol, using tissue (or cotton swabs). It is very important that all of the electrolyte is removed from the two exposed parts of the cell or your readings will be seriously affected. Attach the second clamp.
12. Place copper foil tape on the exposed edges of the slides. Attach crocodile clips to the copper foil to make the contacts. Ensure that this does not short-circuit the cell.

Figure 3: The Graetzel cell.

The task:

- Demonstrate the operation of the Graetzel cell by measuring the optical response of the cell. *Do not bring the light source closer than 5 cm to the cells*. **Your lab supervisor must observe this and sign off on the answer sheet.**
- Measure the open circuit voltage for both the chlorophyll-dyed cell and the silicon photodiode for various levels of light intensity.
- Note: if the open circuit voltage you measure is less than 10 mV, you may need to add another drop of electrolyte, and repeat from step 11.

Now answer questions 2–8 on the answer sheet.

Task A.3: Photochemical reduction of indophenol

In this experiment, you will investigate photosynthesis. A blue dye (2,6-dichlorophenol-indophenol or DPIP, see Figure 4) will be used instead of NADPH.

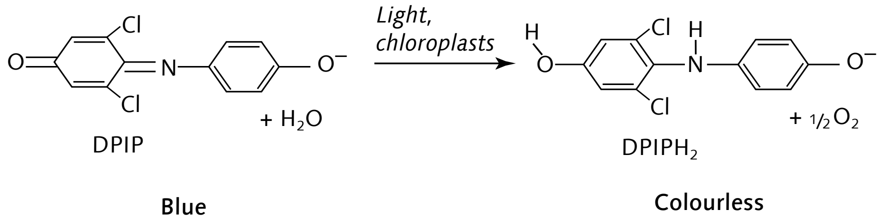

Figure 4: Photochemically driven reduction of DPIP.

When DPIP is oxidised it is blue, but when it is reduced it becomes colourless. The use of DPIP in this experiment instead of NADPH allows you to monitor the process of photosynthesis (i.e. the absorption and conversion of light to chemical energy) by observing the change in colour of DPIP from blue to colourless. In this experiment you will test the ability of chloroplasts to carry out photosynthesis under different conditions and also examine the importance of biological structure as well as light absorbing properties in utilising light energy.

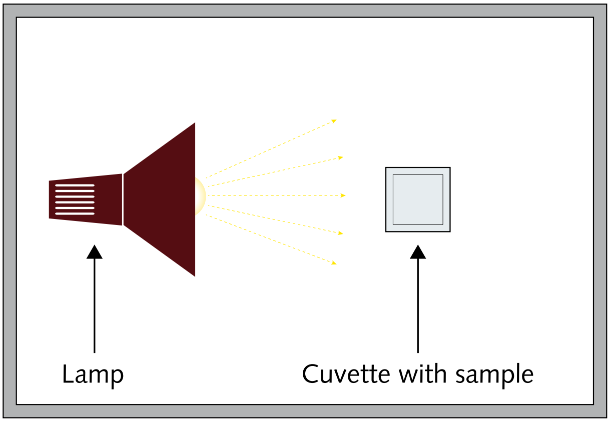

Figure 5: Schematic diagram of photolysis box.

Experimental Procedure

a) Chemical reduction of DPIP

1. Solution 1: Add 2.5 cm^3 of DPIP solution at pH 6.5 (supplied) to a clean plastic cuvette. Carefully add 0.5 cm^3 of the ascorbic acid solution. Observe the changes.
2. Solution 2: Add 2.5 cm^3 of DPIP solution at pH 6.5 (supplied) to another clean plastic cuvette. Carefully add 1.0 cm^3 of the phosphoric acid solution to bring the pH to 1.5. Observe the changes.

3. *Now answer question 9 on the answer sheet.*

b) Qualitative determination of photochemical reactivity

In duplicate prepare the following samples. One set of solutions, Set A, is kept in the dark all the time. The other set, Set B, will be exposed to light. However, **initially they should all be kept in the dark** by wrapping them in the aluminium foil provided.

Solution 1: 2 cm^3 DPIP/phosphate buffer solution at pH 6.5 with 1 cm^3 of unboiled chloroplast solution.

Solution 2: 2 cm^3 DPIP/phosphate buffer solution at pH 6.5 with 1 cm^3 of boiled chloroplast solution

Solution 3: 2 cm^3 DPIP/phosphate buffer solution at pH 6.5 with 1 cm^3 of chlorophyllin solution

4. Place one of each solution under the desk lamp provided and monitor changes visually after 15 minutes. Answer question 10 on the answer sheet.

c) Quantitative determination of photochemical reactivity

5. Use a solution that you have determined to undergo a photochemical reaction in part (b) and prepare three samples of that solution in the same manner. Label these D, E and F. Keep all solutions in the dark when not in use.
6. Record the UV-Vis spectrum of solution D immediately. Photolyse solution D in the photolysis box provided over 15 min (see Figure 5 and consult supervisor if unsure) recording the UV-Vis spectra every 5 minutes. Print and attach the spectra to your answer book. Label this spectrum "Graph 3".
7. To obtain useful kinetic data and hence determine the rate of the reaction, you will monitor the photolysis at an optimum wavelength. Select this wavelength and write it down under question 11 on your answer sheet.
8. Accurately, photolyse solution E in the photolysis box provided (see Figure 5), recording the absorption at the optimum wavelength chosen at regular intervals over 10 minutes under question 12 on your answer sheet. Repeat this for solution F (to check the reproducibility of the experiment).
9. Using the graph paper provided plot the absorbance versus time and determine the rate of change of absorbance with time (i.e. the rate of photochemical reduction of DPIP) for each of the solutions E and F examined under question 13 on your answer sheet. Label as 'Graph 4' and 'Graph 5' and attach to your answer book.