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**P3-5:** Fabrication and characterisation of a dye sensitised nanocrystalline solar cell

3rd Year Physical Laboratory - Department of Chemistry

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## **1 LEARNING AIMS**

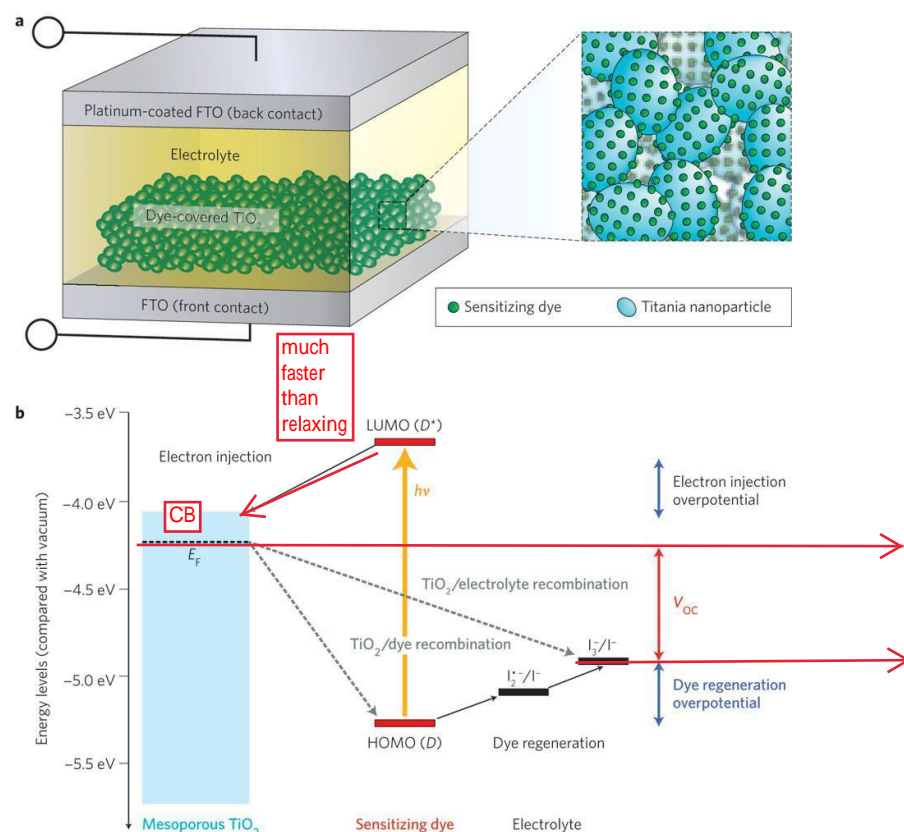
In this experiment you will gain experience in the fabrication and characterisation of photo-electrochemical solar cells.

You will develop skills in:

- Fabricating dye-sensitised photo-electrochemical cells.
- Electrical and spectroscopic characterisation of photovoltaic cells. The principles of dye sensitisation.

## 2 INTRODUCTION

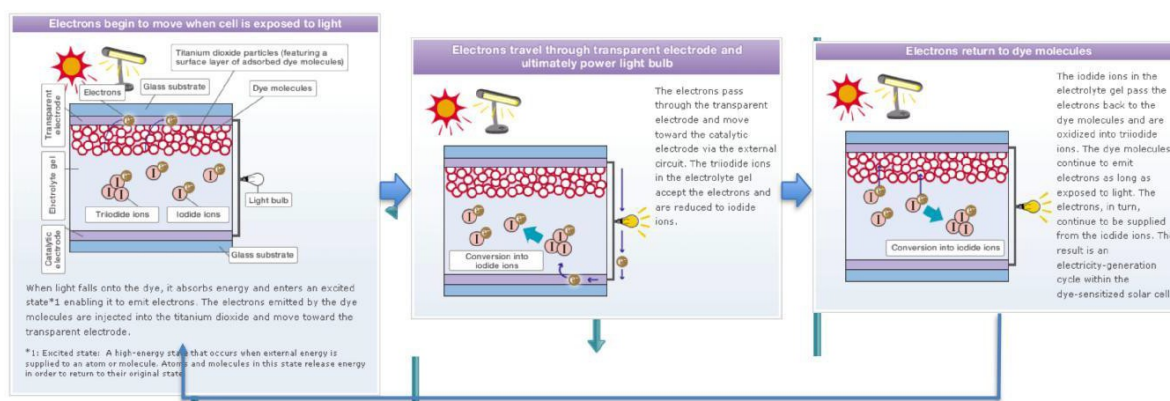
Dye-sensitised solar cells (DSSCs) are a promising technology for low cost photovoltaic power generation. First reported by Grätzel and O'Regan in 1991, they have subsequently attracted widespread commercial interest due to their potential for low cost solar power generation. The structure of a typical DSSC is shown in panel (a) of Fig. 2.1. A glass substrate is first coated with a transparent conductor such as fluorine-doped tin oxide, which acts as the cathode in the final device. The FTO is then coated with a layer of highly porous nanostructured titanium dioxide (titania) semiconductor, which has an extremely high surface area by virtue of its nanoporosity. The substrate is next immersed in a solution of an appropriate dye molecule, which attaches as a monolayer to the nanostructured titania. A second glass substrate with a platinum-coated FTO electrode (which acts as the anode) is then placed on top of the dye sensitised titania. The voids in the centre of the device are then filled by capillary action with an iodine / iodide based liquid electrolyte.



**Fig. 2.1** Dye-sensitised solar cell (DSC) device schematic and operation. a, Liquid-based DSCs are comprised of a transparent conducting oxide (such as fluorine-doped tin oxide, FTO) on glass, a nanoparticle photo-anode (such as titania) covered in a monolayer of sensitising dye, a hole-conducting electrolyte and a platinum-coated, FTO-coated glass back-contact. b, Energy level and device operation of DSCs; the sensitising dye absorbs a photon (energy  $h\nu$ ), the electron is injected into the conduction band of the metal oxide (titania) and travels to the front electrode (not shown). The oxidised dye is reduced by the electrolyte, which is regenerated at the counter-electrode (not shown) to complete the circuit. VOC is determined by the Fermi level ( $E_F$ ) of titania and the redox potential ( $I_3^-/I^-$ ) of the electrolyte. (Taken from: Hardin et al. 10.1038/nphoton.2012.22).

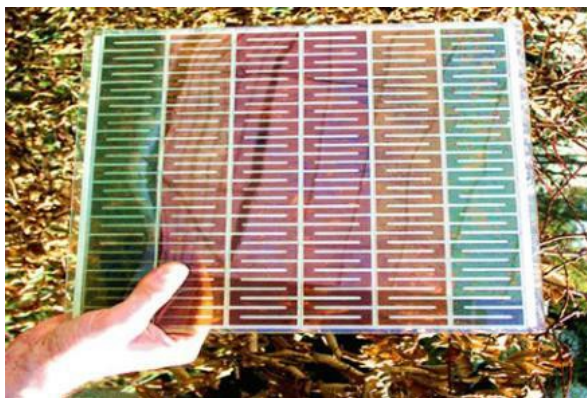
The origin of the current generation is explained in panel (b) of [Fig. 2.1](#), and [Fig. 2.2](#). When a dye molecule absorbs a photon, an electron is promoted to an unoccupied molecular orbital and then undergoes **ultrafast charge injection** into the continuum of conduction band states in the titania. The electron subsequently passes through the titania to the transparent FTO cathode, and from there is extracted into the external circuit.

Importantly, the charge-transfer step from the dye to the oxide typically occurs on a very short timescale (**100 fs**), meaning the photo-excited electron is removed from the dye molecule long before it has a chance to relax radiatively to the ground-state. The dye cation that is left behind after the electron transfer process is **re-reduced** by an iodide electrolyte as shown in [Fig. 2.2](#). In this step, the "missing" electron is **restored** by taking an electron from a dissolved iodide ion  $I^-$ , which is thereby discharged to the neutral state. It is energetically favourable for **two neutral iodine atoms in solution to associate with one iodide ion to form a singly charged tri-iodide ion  $I_3^-$** . The tri-iodide ion is attracted to the negatively charged anode where it re-ceivees two electrons, and is converted into three separate  $I^-$  iodide ions, which are then free to supply their excess electron to other dye cations, allowing the whole process to repeat. **The electrons "consumed" at the anode are replaced by "pulling" excess electrons from the counter electrode via the external circuit.** As the electrons flow through the external circuit they are able to do useful work.



**Fig. 2.2** Operating principle of a DSSC.

DSSCs based on this design can achieve solar to electric power output efficiencies of **7–10%**, and remain stable over **10 years** based on the results of accelerated lifetime trials (although great care must be taken to seal the cells properly). Moreover, in contrast to conventional solar cells, these devices are fabricated from relatively low cost materials by simple production processes. DSSCs are currently being developed for a range of niche markets, e.g. transparent photovoltaic windows (see [Fig. 2.3](#)), which can't be fabricated using conventional silicon based technology.



**Fig. 2.3** Photograph of a DSSC module.

The detailed operating mechanisms of DSSCs involve the interactions of nanometer sized semiconductor particles, molecular dyes and a liquid electrolyte. At present these interactions are incompletely understood, but in some respects the operating mechanisms have closer parallels with plant photosynthesis than conventional solid state photovoltaic devices. The purpose of this practical is to introduce you to the fabrication and characterisation of DSSCs. Further information can be found in [References](#). Reference [1](#) is essential reading for this practical ([Link to Paper](#)).

### 3 EXPERIMENTAL

#### 3.1 Materials

You will require the following materials:

1. Five pieces of 2.5 x 1 cm FTO conducting glass onto each of which has been deposited 1 cm<sup>2</sup> of 8 micron thick nanocrystalline TiO<sub>2</sub>.
2. Two pieces of 2.5 x 1 cm FTO conducting glass coated with platinum for counter electrodes.
3. 1.5 mL of the following sensitizer dye: 10<sup>-3</sup> M cis-Bis(isothiocyanate)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II) in a 1:1 tertiary butyl alcohol : acetonitrile solvent system. Note that the dye is often referred to as "[Z907](#)" in the dye sensitised literature.
4. One alternative natural dye of your choosing.
5. Solaronix Mosalyte TDE 250 electrolyte solution in dropper bottle (0.6 M potassium iodide and 0.1 M iodine in anhydrous 3-methoxy-propionitrile).

**Caution: Take care not to touch the face of the electrodes. The glass plates should be held with tweezers or by the edges of the glass at all times.**

### 3.2 Experimental procedures

#### 3.2.1 Staining the titanium dioxide with the dye

Consult Ref 1 for possible sensitising dyes, staining procedures etc. You will be provided with the Z907 sensitizer dye. In addition, you will need to identify an additional natural dye for experimentation. Prior to sensitisation, the films should be heated in an oven to 450 °C for ten minutes to remove organics / adsorbed water. The films should then be allowed to cool to ~80°C before covering them with the sensitising solution.



**Fig. 3.1** Furnace used for heating films before sensitising.

Photo

Photo again

The films should be left in the sensitising solution until strongly pigmented — typically hours to overnight depending upon the dye. Following sensitisation the films should be rinsed briefly in ethanol to remove unbound dye.

The absorption spectrum of each film should be measured before and after sensitisation. When measuring the spectrum, ensure the entire light beam of the spectrometer passes through the film. If the light beam is too big, reduce the size of the beam with black tape and redo the spectrometer background calibration. A strongly sensitised film should exhibit a peak optical density of at least one, and preferably greater than two (otherwise a significant fraction of the incident light will be wasted).

Spectrum





**Fig. 3.2** UV/Vis spectrometer for film absorption spectrum measurements.

You will have only enough Z907 solution to sensitise two films. Your remaining films should be sensitised with alternative pigments. You are encouraged to use alternative sensitising solutions, which you should obtain for yourselves (see Ref 1 for ideas).

Once sensitised, the films should be stored either in the sensitising solution or (for the Z907 dye) under a drop of propylene carbonate and a cover slide in a sample tube.

Photo for record.

### 3.2.2 The counter electrode

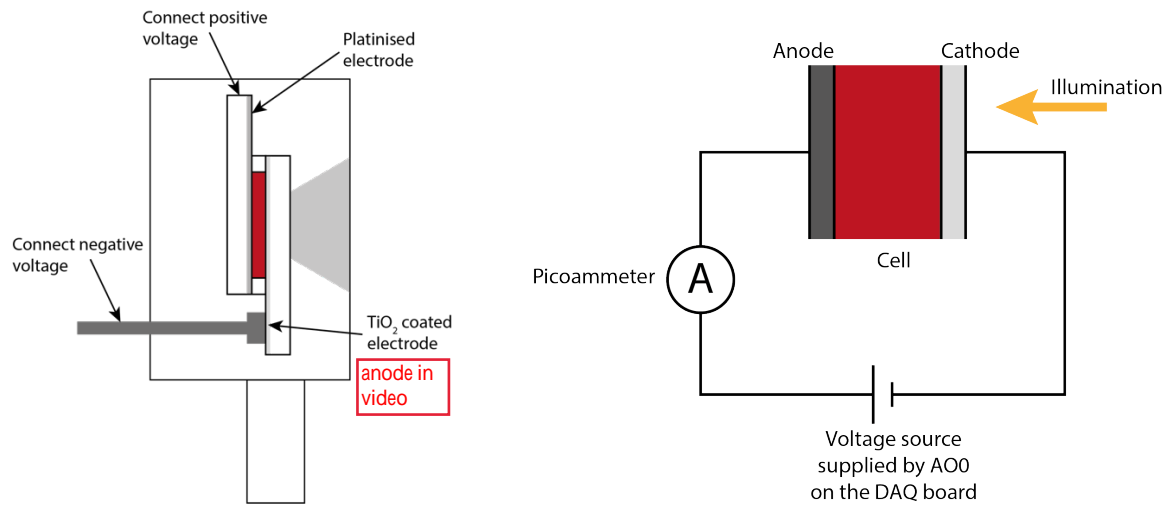
In this experiment you will be provided with pre-prepared platinum coated conducting glass films. Please do take time to check which side is conductive with a multimeter. The thin platinum layer serves as a catalyst for the tri-iodide to iodide regeneration reaction.

### 3.2.3 Assembly of the device

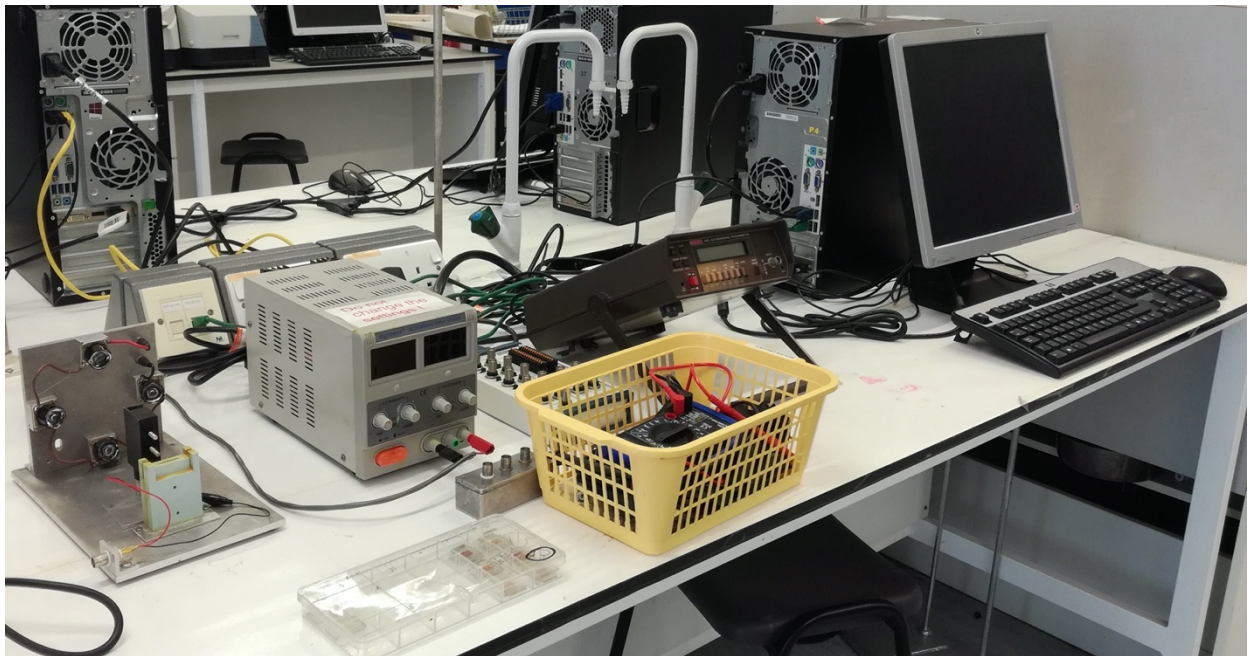
Photo for setting up

The rinsed working and counter electrodes are placed in the sample holder as shown in Fig. 3.1 (left). One or two drops of the iodide/iodine electrolyte solution can then be placed at the top edge of the cell where the plates face each other. The liquid is drawn into the space between the electrodes by capillary action and can be seen to "wet" the stained TiO<sub>2</sub> film. The device is now complete and ready to test (see below).

Care should be taken to avoid electrical shorts between the exposed regions of the TiO<sub>2</sub> working electrode and the counter electrode. Use the diamond scribe to electrically isolate areas on the glass which may give unwanted short circuits. Furthermore, considerable care must be taken not to scratch the two electrodes, especially the TiO<sub>2</sub> film. If the electrolyte dries out during an experiment, more can be added.



**Fig. 3.3** (left) schematic showing connections to sample holder; (right) circuit diagram showing setup for cell measurement.



**Fig. 3.4** Equipment used for solar cell electrical testing.

### 3.2.4 Electrical testing

Electrical connections are made to the cell in accordance with Fig. 3.1 (right). A three-way connector box is used to connect the cell in series with a Keithley 485 pico-ammeter and a voltage source that is derived from a data acquisition (DAQ) card. (To connect to the DAQ card, use the AO0 analogue output on the BNC-2110 connector box). The entire setup is controlled using a simple LabVIEW program.



## 3.2.5 Using lab view software to collect current-voltage curves:

- 1) Double click on the icon on the desktop "Solar Cells Software 2020.vi"
- 2) Wait for LabView to open then click the run button (right pointing arrow in the top bar).
- 3) Insert appropriate parameters for your voltage – current measurement and click "Run".
- 4) Wait for your measurements to finish and click "Save data" to export your data as a csv file.

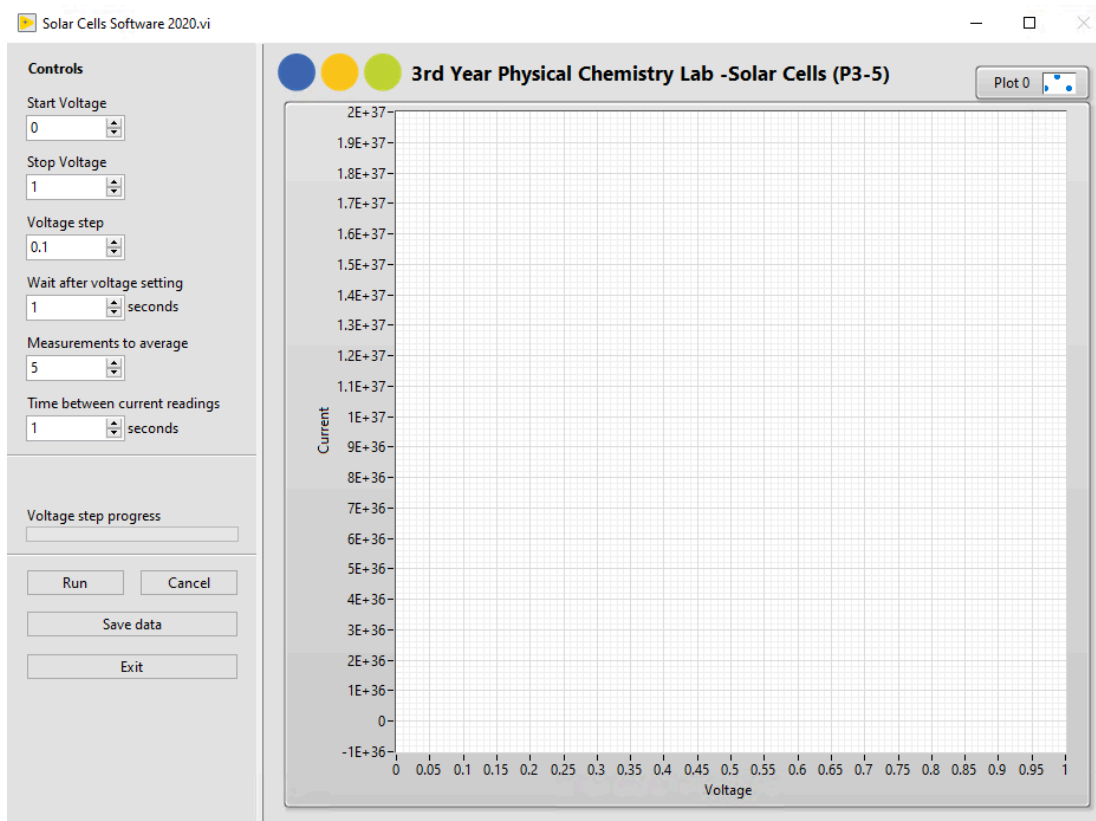


Fig. 3.5 LabView software for running voltage – current measurements

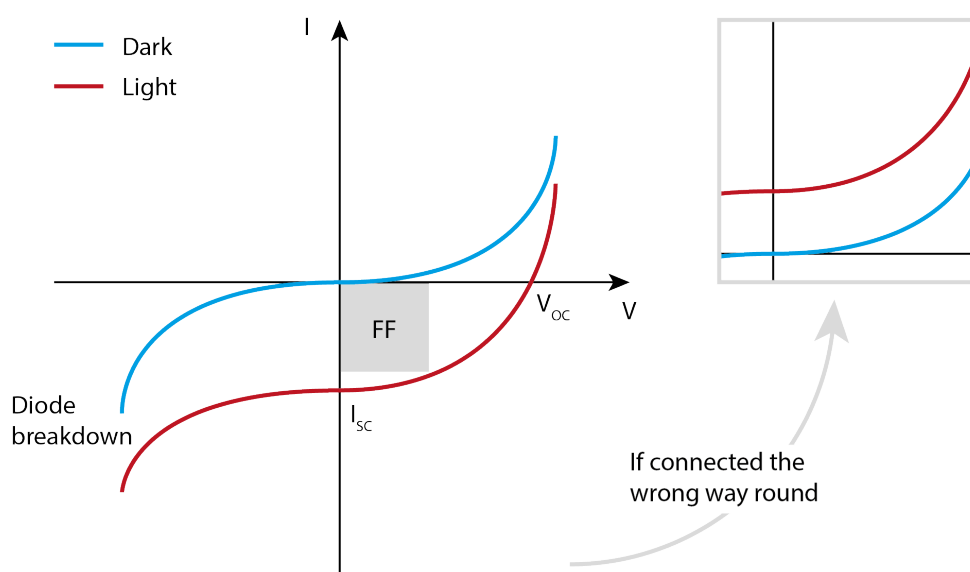


Fig. 3.6 Typical current-voltage plot for solar cell device

### 3.3 Experimental observations

Measure absorption spectra for your sensitising solutions before and after sensitising the films, and also measure the absorption spectrum of your sensitised films (see above). Is the absorbance of your film consistent with the loss of dye concentration in your solution?

(Take care to use appropriate controls to account for light scattering by the  $\text{TiO}_2$  films). The effective surface area of each  $\text{TiO}_2$  film is  $\sim 500 \text{ cm}^2$ . Estimate the percentage mono-layer coverage you have achieved (see also Ref 2). Has the dye adsorption reached saturation?

cal

Photoelectrical characterisation:

You will be provided with a reference cell that uses metal iodide / iodine as the electrolyte and cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-di-carboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II) as the sensitizer dye. This dye is often referred to as Z907 in the solar cell scientific community.

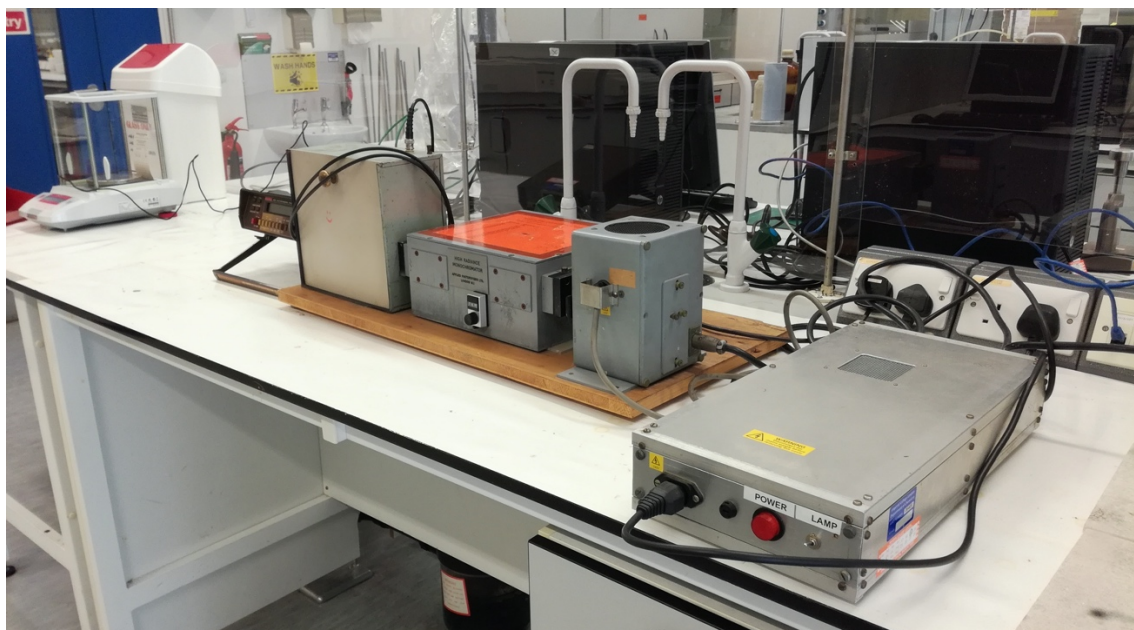
Ensure the reference cell is evenly illuminated and centred in the middle of the light beam.

Vary the voltage applied across the reference cell from 0 to 0.7 V, connecting the  $\text{TiO}_2$  electrode as the negative electrode. Measure the current flowing through the cell both in the dark and under illumination using 1/10th full sun intensity ( $\sim 10 \text{ mWcm}^2$ ). Determine the cell open circuit voltage ( $V_{\text{OC}}$  = voltage at which current under illumination goes to zero), the short circuit current ( $I_{\text{SC}}$  = current under illumination at zero volts), the optimum power output of your cell (maximum value of IV), the power conversion efficiency (optimum power output / light power incident) and the fill factor ( $\text{FF} = \text{optimum power output} / I_{\text{SC}} V_{\text{OC}}$ ) of the cell as a function of illumination intensity. Once you have gained familiarity with the measurement using the reference cell, repeat these measurements with your own devices. How do your devices compare with the reference device? How does their efficiency change with time?

det. and cal.

Photocurrent action spectrum: Monitor the short circuit current of the reference cell as a function of illumination wavelength, using the tungsten lamp / monochromator setup. Using the table of light intensity output for each wavelength (attached to the roof of the monochromator), determine the incident photons to current efficiency (IPCE = electrons out / photons incident). Now repeat this measurement with your own devices. (Note: this measurement is only practical with reasonably efficient cells due to the lower illumination intensity so calculate from your white light data what current you expect to obtain and decide whether the pico-ammeter provided will be able to measure this). How do your devices compare with the reference device?

compare with the ref., effect of the time



**Fig. 3.7** Lamp / monochromator system for measuring IPCE.

unsensitised film

Experimental notes: Is the dye really needed — compare the results obtained above with unsensitised films. Note the stability of the current outputs. If the output is unstable, what is this due to? Is the instability induced by light? If so, you could reduce the illumination intensity. Can the output be restored by the addition of more electrolyte?

#### 4 DISCUSSION

Consider the absorption spectra, current-voltage curves and photocurrent spectra obtained using the different dyes:

- Is the dye absorption spectrum changed by adsorption to the  $\text{TiO}_2$ ? If yes, why might this be?
- Do your absorption spectra match the photocurrent action spectra? Would you expect them to?

Current-voltage curves of ideal photovoltaic cells obey the diode equation:

$$I = I_{pc} + I_0 \left[ \exp \left( \frac{eV}{nk_B T} \right) - 1 \right] \quad (4.1)$$

where  $I$  and  $V$  are the cell current and voltage respectively,  $I_{pc}$  is the light-generated current (assumed to be independent of  $V$ ),  $I_0$  is a constant that gives the magnitude of the dark current, and  $n$  is the ideality factor. Ideally, the parameter  $n$  should be unity; in practice, for reasons that are not fully understood,  $n$  is typically two or more for dye sensitised cells. The background to the diode equation can be found in many textbooks, e.g. 'The Physics of

Semiconductor Devices' by D. A. Fraser (537.311.33 FRA in the library). How well do your current-voltage curves fit this equation in the dark and in the light?

A typical problem for cells is the occurrence of low resistance "shorts" between the two electrodes. In the most extreme case, this results in the current being proportional to voltage:  $V = IR_s$ , where  $R_s$  is the resistance of the short. Do the shapes of your current-voltage curves suggest this is a significant problem in your devices?

What is limiting the power output of your cells: low optical absorption or electrical losses within the cell? What are the relative magnitudes of the currents obtained with and without illumination and are dark currents a significant loss mechanism? How do your results differ with different dyes? Why? How stable were your cells? What was the cause of instability?

Two final teasers:

1. In this experiment, we employ a simple two-electrode electrochemical cell, with no reference electrode. Therefore how are the absolute chemical potentials / Fermi levels in the cell controlled? In other words, when you apply a voltage across the cell, is the working electrode becoming more negative or the counter more positive on an absolute electrochemical scale?
2. The photocurrent results from electrons flowing through the  $\text{TiO}_2$  and holes through the electrolyte. The  $\text{TiO}_2$  and the electrolyte have a very high contact area. Why don't the electrons and holes simply recombine, which would result in no current output (there is no 'correct' answer to this, as scientists working in this area cannot agree. You should just try to come up with a plausible, and justified, suggestion).

## 5 REFERENCES

1. G. P. Smestad and M. Grätzel, J. Chem. Educ. 1998, 75, 752-756 ([Link to Paper](#)).
2. B. O'Regan and M. Grätzel, Nature, 1991, 353, 737-740 ([Link to Paper](#)).
3. General introductions: M. Grätzel, Curr. Opin. in Colloid Interface Sci., 1999, 4, 314-321 ([Link to Paper](#)); M. Grätzel, Nature, 2001, 414, 338-344 ([Link to Paper](#)).
4. A more in-depth review: A. Hagfeldt and M. Grätzel, Acc. Chem. Res., 2000, 33, 269-277 ([Link to Paper](#)).