Development of Photovoltaic Cells as Educational Material on Sustainability and Green Energy

Oliver Righton

or37@st-andrews.ac.uk

Supervised by Dr Renald Schaub and Dr Iain Smellie

School of Chemistry | University of St Andrews

Abstract

Solar power is one of the many promising technologies at our disposal when it comes to renewable energy, and transitioning to a future with a clean energy supply is reliant on academic breakthroughs[1]. By designing experiments to illustrate the key concepts in a photovoltaic cell that also serve as data collection, students can contribute to ongoing research and explore the key concepts of photovoltaics. The physical chemistry laboratory in the University of St Andrews currently runs an experiment for students to assemble a dye-sensitised solar cell (DSSC), but incident light conversion remains low at under 1%. This project investigated and tested several new methods and compounds to improve this efficiency, and from these, the use of a red sandalwood pigment and surface modification with acetic acid are recommended to be integrated into this laboratory experiment.

Background

Silicon solar cells work in a cycle initiated by a particle of light (a photon) striking the cell surface. To reach the next step of the cycle, the energy carried by the photon must match exactly the energy gap in the semiconductor material (bandgap) to promote an electron from the lower level to the upper level. When an electron is promoted, a positive hole is left where it started and both the electron and hole are known intuitively as an electron-hole pair. The electron then moves to the edge of the cell and into the wires of the circuit. The electron drops in energy as it releases it to the circuit, which can be used in a local or national grid to power devices like our computers or mobile phones. Once the electron has completed a full circuit, it recombines with the hole and can be promoted up again to repeat this cycle, generating solar power for as long as the cell is under illumination[2].

In 1991, Brian O'Regan and Michael Grätzel came up a novel design for photovoltaic cells[3]. Dye-Sensitised Solar Cells (DSSCs) work on the same basic cycle but introduce some more steps. Instead of striking a silicon surface, photons instead strike a dye molecule attached to the surface of nanocrystalline titanium dioxide (TiO_2). The electron-hole pair is generated on the dye and the electron flows into the titanium dioxide and around the circuit as before. When it reaches the counter-electrode on the other side of the cell, it reacts with an ionic electrolyte solution containing iodide (I^-) ions to form triiodide (I_3^-). The triiodide ions move to dye molecules, are reduced back to iodide, and the electron-hole pair recombine to restart the cycle.

Titanium dioxide is used in these cells because it has incredible abundance in our lives. Many UV-blocking lotions, toothpastes or paints use nanocrystalline TiO_2 for its brilliant white colour[4]. However, it lacks a bandgap matching the visible region of the electromagnetic spectrum ($400 \text{ nm} < \lambda < 700 \text{ nm}$), so a dye is needed to sensitise it and enable significant photon absorption. To be suitable for sensitising, the dye must meet three main criteria[5]:

1) Absorbance in the visible region of the electromagnetic spectrum

2) Presence of polar groups to facilitate adsorption (chemical adhesion) to the TiO_2 surface

3) An unoccupied molecular orbital at a similar energy level to the conductance band of TiO_2

Absorbance of light in the visible region is easily tested by eye or can be quantitatively measured using UV-Vis spectrophotometry. The presence of polar groups can be tested by immersing a plate of TiO_2 into a solution of the dye and then observing whether a colour change occurs on the plate surface. Molecular orbital energies are more difficult to verify directly but assembling a functional cell using a given dye implies that the overlap is sufficient for successful operation.

In a DSSC, this dye molecule can be one of various groups of molecules. The highest efficiency dyes use a ruthenium metal centre with bipyridyl and thiocyanate ligands, but the cost of ruthenium is somewhat prohibitive to low-cost solar energy. Another group, called anthocyanins, are a class of natural dye found in red and purple fruits and flowers that can sensitise TiO_2 in a DSSC.

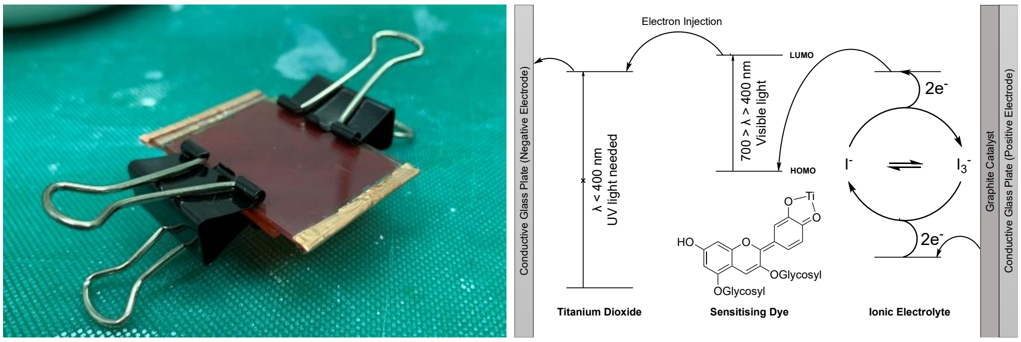

Figure 1: An assembled DSSC using santalin (left) and a schematic diagram of a DSSC (right)

The key quantities to measure from a solar cell are also important to define. The short-circuit current (I_{SC}) is measured with no external resistance on the cell and represents the maximum rate of flow of electrons around the circuit. The open circuit voltage (V_{OC}) is measured while the cell is under theoretically infinite resistance and measures the maximum charge separation in the cell. The maximum power (P_{max}) is calculated by systematically varying the series resistance and plotting a current-voltage (IV) curve. The Fill Factor (FF) of the cell is expressed as a percentage and represents the ratio of P_{max} to $I_{SC} \cdot V_{OC}$. FF has a maximum of 100%, while I_{SC} and V_{OC} have no upper bounds and increases to either are considered an upgrade.

Project Aims

The CH3721 Physical Chemistry Laboratory course at the University of St Andrews already includes preparation and testing of dye-sensitised solar cells. Previous work by Fraser Mealyou has yielded significant improvement to the consistency of assembly[5]. This project aimed to use these modifications to quantitatively test a series of modifications to the cell that are viable to scale up for student experience. These changes will be verified and tested further by a future research project.

Experimental

UV-Vis spectra were recorded on a Shimadzu UV1900 spectrophotometer with a six-cell attachment for parallel spectra. A 100 W LED lamp was used to illuminate the assembled cells, with a quoted manufacturer efficiency of 23%. In all of the cell assemblies for this project, the below procedure was used. Modifications to this method will be noted where appropriate.

P25 TiO_2 nanoparticles (Degussa) were mixed with 1% aqueous acetic acid to form a smooth paste. Conductive glass plates (indium tin oxide, 70 Ω/□) were placed into a stainless-steel cast and the doctor blade method was used to create a thin film. Carbon counter electrodes were produced by pencil on glass surface. Plates were annealed at 450 °C for 30 minutes (thin films) or 5 minutes (counter electrodes). Films were then immersed in dye solution and left for 30 minutes. The plates were rinsed with solvent (ethanol for anthocyanins, acetone for santalin) and dried with nitrogen. Two drops of I_2/KI solution in ethanediol were placed onto the TiO_2 and the plates clamped together. Half an hour was allowed for the solution to fully soak into the nanostructure. Cells were immediately tested under LED illumination.

Discussion

Novel Dye Analysis

A simple method to improve the efficiency of the cell is to use a different anthocyanin. The pigments in the vicinity of the laboratory include blackberries and wildflowers that can be extracted simply. However, this method of discovery neglects dyes available in other areas of the world, which could outperform those previously tested.

Red Sandalwood

Previous work by Tennakone *et al.* reports the characteristic red dye from sandalwood to perform at high efficiency and stability in a DSSC device[6]. Red sandalwood powder was immersed in petroleum ether for 24 hours, followed by dichloromethane for a further 24 hours, then finally washed with acetone to give an orange solution, which was dried to give dark red-black crystals of santalin A.

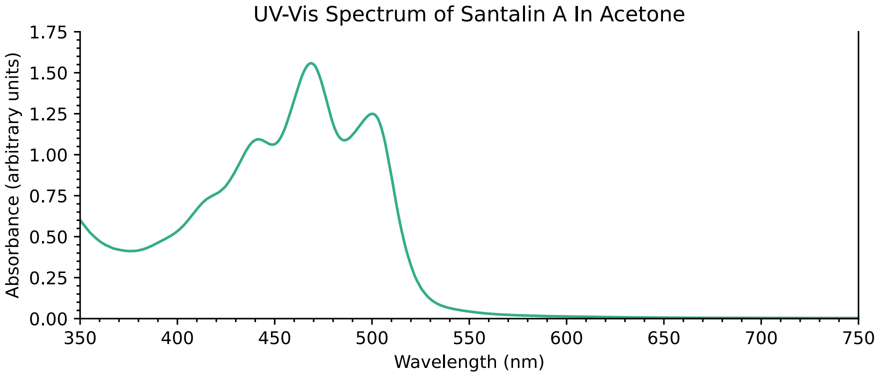

Figure 2: UV-Vis spectrum of santalin in acetone, peak maxima at (441, 1.094), (469, 1.558) and (500, 1.250)

In the DSSC device, santalin adsorbed quickly to give a pink/orange plate and achieved an average P_{max} of 765 nW. The cause of this low P_{max} could be due to two factors: the efficacy of santalin dye or the resistance of the copper-aldehyde tape used to establish electrical contact. The cell is highly sensitive to changes in series resistance and so if the tape is not sufficiently conductive, use of silver colloid paint will be necessary to ensure clip contact while also providing low series resistance.

Testing the solubility of santalin revealed it behaves solvatochromically, a phenomenon where the colour of its solution is changed by the polarity of the solvent. Santalin does not dissolve in non-polar solvents, but produces a solution of orange in acetone, yellow-green in *d*-chloroform, and deep red in dimethyl sulfoxide. To my knowledge, this property has not been reported previously and presents a potential new research opportunity.

Pomegranate Seeds

Pomegranate is a well-established anthocyanin source for the DSSC, seeing use by Ghann et al. to achieve efficiencies up to 2%. The dye is extracted by crushing the seeds in a pestle and mortar, then filtering away the solid. Cells produced in the laboratory achieved 16 µW at 0.215 mA, which is within the expected ranges of a cell produced by the university students, but lower than Ghann et al. reported. The films being made by the cast were relatively thin, which means that the light may not have been fully absorbed by the anthocyanin. Though there was not time to investigate further, the cast has been modified for the coming year by doubling film thickness. Data collected from the CH3721 laboratory course will verify whether this has improved the conversion efficiency.

Purple Yam

The purple yam is a rich source of anthocyanins found in tropical Asia and South America[7]. These anthocyanins can be extracted with ease and are found in the commercial supplement ube syrup, having previously been used to achieve efficiencies of up to 2.05%[8]. In this project, an extracted solution was bought commercially, avoiding those containing additives for colour.

The effect of pH on natural dyes is an important property to investigate when looking at how they could perform. The syrup was qualitatively tested by immersing it in solutions of varying pH using solutions of HCl, AcOH, distilled water, $NaHCO_3$, NH_3 and NaOH. The immediate colour change is shown below (Fig. 1a) and overnight colour change shown in Fig. 1b.

Figure 3: Purple yam extract immediately upon addition (left) and after 24 hours (right)

The overnight change to pink in NaOH was unexpected and was investigated further. The purple colour did not return on addition of acid, remaining pink. UV-Vis analysis shows two distinct peaks, indicative of two different absorption bands. This is unusual for anthocyanins, which usually have a single broad absorption. Thin layer chromatography of the solution on silica resolved separate compounds responsible for these peaks. The peaks seen at λ_{max} = 525 and 625 nm line up with extracts of phycoerythrin and phycocyanin from spirulina cyanobacteria, which suggests the colour of the extract used in this project may be enhanced with additives despite our efforts to avoid them.

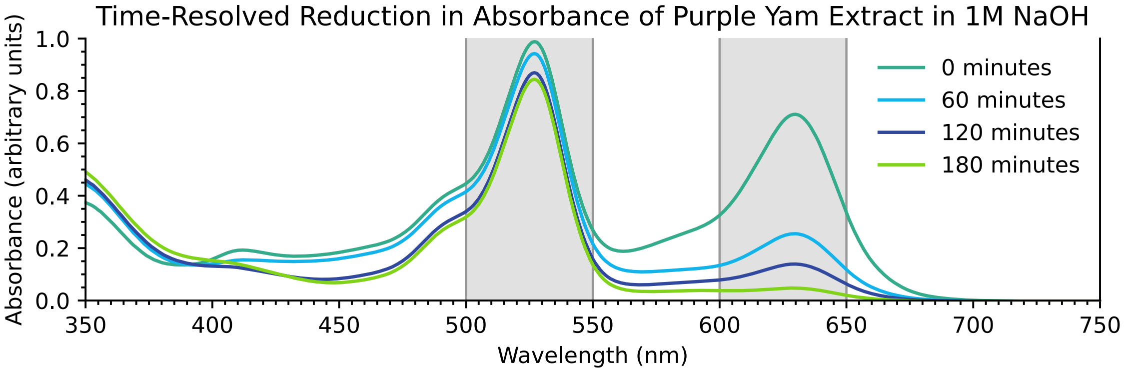

Figure 4: Kinetic UV-Vis spectra of commercial purple yam extract in 1 moldm^{-3} sodium hydroxide

Time-resolved UV-Vis spectroscopy was run for a sample of extract in 1M NaOH. Absorbance at 625 nm was found to decompose rapidly and irreversibly, while the peak at 525 nm was minimally affected and is responsible for the pink colour after several hours. The purple yam extract was trialled as a sensitiser, but unfortunately did not adsorb onto TiO_2. It could be that the anthocyanins present do not have polar groups to bind but given the evidence for multiple unknown coloured compounds also present, it may be that the concentration of anthocyanins in the commercial product was too low to successfully sensitise the plate.

Circuit Modifications

The sensitising dye is not the only variable in the DSSC. Alterations to the electrolyte or adding surface modifications to the TiO_2 alter the internal or surface chemistry, which presents a range of options to test in the procedure to reduce the series resistance of the cell or reduce side reactions taking place.

Solid-State Electrolyte Systems

The iodide/triiodide solution is suitable for the DSSC, but has several issues: iodine is highly corrosive, the solvent is toxic, and the electrolyte evaporates over the course of several days. Wide bandgap semiconductors such as cuprous iodide (CuI) or cuprous thiocyanate (CuSCN) have the potential to replace the solution-based electrolyte and solve these problems[9]. Their synthesis brings additional educational content of solid-state materials and efficiency improvements, though a reliable method for the teaching laboratory has yet to be produced.

The main challenge that solid-state electrolytes bring is the difficulty in completely filling the nanopores of the TiO_2. Electrochemical methods use a solution of semiconductor with an applied current to grow the semiconductor inside the pores but are limited by the ion mobility in solution as well as availability of equipment[10]. Evaporative deposition also uses a solution of semiconductor and a heated substrate. The solvent rapidly boils off to leave solid material behind in the pores, though formation of bubbles limits the reliability of fully filling the pores. The main issue that both methods have to face is short-circuiting if the semiconductor contacts both electrodes, as well as the poor solubility of CuI and CuSCN in common solvents without toxic complexing agents such as thiourea.

Evaporative methods were successful in producing a visible thin film on a cell, but no photocurrents were generated under illumination, which is suspected to be a result of short-circuiting. Despite this, further attempts to produce a solid-state film are recommended.

Acid Modification of Titanium Dioxide Surface

Improvement of I_{SC} by up to 210% has been reported by Liu and Wang[11] using acid etching of the nanostructure after the adsorption of dye molecules. The increase comes from formation of hydroxyl groups, which beneficially alter the surface chemistry of the TiO_2 for lower electrical resistance[11].

Three cells were assembled in the standard method. Prior to assembly, the dye-soaked plates were placed into acetic acid in toluene (1% v/v) for 24 hours to undergo etching. After this time, the plates were washed with acetone and assembled as normal. Early conclusions from this testing suggests up to a 208% increase in short-circuit current but further testing would be needed to confirm this. Within the CH3721 lab course, this could be implemented with overnight etching rather than the full 24 hours.

Pyridine Derivatives

Side reactions are a common source of current loss and avoiding these would lead to an increase in the total current. In the DSSC, voltage losses in unwanted electrochemical processes within the electrolyte can decrease FF when the flowing electron moves directly into the solution rather than around the circuit. To solve this, a layer of tert-butylpyridine can be deposited onto the nanostructure[12]. It allows facile electron flow into the structure to restore functionality to the dye but reduces the tendency for electrons to participate in side-reactions, reducing shunt resistance and therefore increasing FF. The cells tested with this compound in the electrolyte yielded a 6.55% increase in I_{SC}, but experienced a significant drop in V_{OC}, with no change to FF.

Zinc Doping

Titanium dioxide has a bandgap aligned for electron injection from anthocyanins and ruthenium dyes but electron mobility is low[13], which leads to recombination of electron-hole pairs . Zinc oxide is a metal oxide semiconductor with similar properties to TiO_2, but its electron mobility is significantly higher[14]. Surface coating with zinc oxide reduces the recombination rate, which has been found here to increase V_{OC} at the significant expense of I_{SC}.

A set of cells were made up with the standard procedure with the only change being that the titanium dioxide films were soaked in acidified zinc sulfate hexahydrate (0.1 M) immediately after deposition. The plates were then sintered and assembled as normal. No significant photocurrent was recorded from any of these cells. This could be due to impurities in the sulfate salt or side products from the thermal decomposition reaction, so the use of zinc nitrate or acetate could be investigated as alternatives for surface coatings.

Conclusion

A multitude of methods have been trialled in this research, with some more successful than others. Most methods improved the I_{SC} value of the cell at some cost to V_{OC}, with the exception of ZnO doping, which reduced I_{SC} significantly but increased V_{OC}. Despite literature reporting an increase in FF for cells treated with acetic acid or tertbutylpyridine, no improvement was observed and FF remained below 25%. The two novel cell modifications recommended for use are the surface modification by acid and use of santalin A. For further investigation, the use of ZnO doping and purple yams present potential opportunities not explored here.

Santalin presents an intriguing opportunity to use a non-anthocyanin dye to sensitise the TiO_2 as it exists in a single molecular form, unlike anthocyanins. This brings the potential for precise characterisation of the pigment and chemical modifications to be made to alter its absorption. Preliminary results from metal complexation also indicated a shift in colour and so the effect of transition metal ions on cell performance could be investigated in a similar way to anthocyanins.

The modification of surface chemistry provides a large boost to I_{SC} and therefore efficiency if V_{OC} can be maintained. The results should be verified on several cells and confirmed before use, but the addition of this step into the procedure is viable in the context of the CH3721 course and brings educational content on how modifying surface chemistry on the microscale has impacts on macroscale devices.

Zinc acetate and zinc nitrate are both alternative zinc salts that could be used to produce the ZnO surface layer. The improvement to V_{OC} demonstrated here could be a useful modification if the decrease in I_{SC} could be avoided using these salts.

Purple yams can be sourced locally within the UK and around St Andrews. Extraction of anthocyanins and examination using UV-Vis spectrophotometry should be used to compare to the prepared yam syrup investigated in this report. The extract used here is suspected to contain coloured additives rather than anthocyanins, and future work extracting pigment from purple yam solids could confirm differences between commercial and in-house extracts.

Acknowledgements

I would like to thank Lord Laidlaw and the Laidlaw Foundation for their support in making this project possible, as well as Dr Iain Smellie and Dr Renald Schaub for their guidance throughout. For the materials and facilities, many thanks go to the laboratory technicians Mr Patterson, Mr Stewart and Ms Keiller. My thanks to Camille Ryder for provision of yam syrup and to both her and Callum Murison for their ceaseless optimism and encouragement.

Finally, to the Laidlaw team at the University of St Andrews and the cohort who worked alongside me. This work would not have been possible without you.

References

1 Q. Schiermeier, J. Tollefson, T. Scully, A. Witze and O. Morton, *Nature*, 2008, **454**, 816–823.

2 S. R. Wenham and M. A. Green, *Progress in Photovoltaics: Research and Applications*, 1996, **4**, 3–33.

3 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737–740.

4 M. Skocaj, M. Filipic, J. Petkovic and S. Novak, *Radiol Oncol*, , DOI:10.2478/v10019-011-0037-0.

5 F. Mealyou, Master's Thesis, University of St Andrews, 2023.

6 K. Tennakone, G. R. R. A. Kumara, I. R. M. Kottegoda, V. P. S. Perera and P. S. R. S. Weerasundara, *J Photochem Photobiol A Chem*, 1998, **117**, 137–142.

7 A. Crowther, L. Lucas, R. Helm, M. Horton, C. Shipton, H. T. Wright, S. Walshaw, M. Pawlowicz, C. Radimilahy, K. Douka, L. Picornell-Gelabert, D. Q. Fuller and N. L. Boivin, *Proceedings of the National Academy of Sciences*, 2016, **113**, 6635–6640.

8 K. Wattananate, C. Thanachayanont and N. Tonanon, *Solar Energy*, 2014, **107**, 38–43.

9 P. M. Sirimanne, M. K. I. Senevirathna, E. V. A. Premalal, P. K. D. D. P. Pitigala, V. Sivakumar and K. Tennakone, *J Photochem Photobiol A Chem*, 2006, **177**, 324–327.

10 J. Wu, Z. Lan, J. Lin, M. Huang, Y. Huang, L. Fan, G. Luo, Y. Lin, Y. Xie and Y. Wei, *Chem Soc Rev*, 2017, **46**, 5975–6023.

11 Q. Liu and J. Wang, *Solar Energy*, 2019, **184**, 454–465.

12 H. Kusama, Y. Konishi, H. Sugihara and H. Arakawa, *Solar Energy Materials and Solar Cells*, 2003, **80**, 167–179.

13 T. Bak, M. K. Nowotny, L. R. Sheppard and J. Nowotny, *The Journal of Physical Chemistry C*, 2008, **112**, 12981–12987.

14 N. A. Jayah, H. Yahaya, M. R. Mahmood, T. Terasako, K. Yasui and A. M. Hashim, *Nanoscale Res Lett*, 2015, **10**, 7.