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

Oliver Righton | Supervised by Dr Renald Schaub and Dr Iain Smellie

School of Chemistry | University of St Andrews

University of St Andrews

Solar power is one of the many technologies at our disposal when it comes to renewable energy, and transitioning to a future with a clean energy supply is equally reliant on academic research and commercial innovations. By designing experiments to illustrate the key concepts of photovoltaic cells, students can see for themselves where the latest developments are and how they can contribute to research.

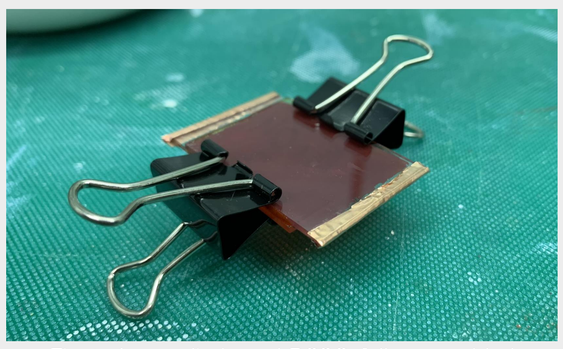

Fig 1: A santalin-based DSSC, fully assembled

Abstract

The undergraduate laboratory at St Andrews currently runs an experiment in which students assemble a dye-sensitised solar cell (DSSC) using anthocyanins on titanium dioxide. However, efficiencies remain low, at under 1% incident light conversion. This project investigated and tested new methods and compounds to improve this efficiency in ways that are feasible for the undergraduate students to understand and use in the solar cell.

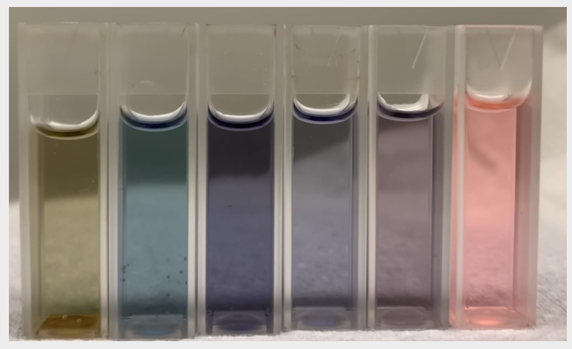

Fig 2: Purple yam syrup at pH 1 (left) to pH 14 (right)

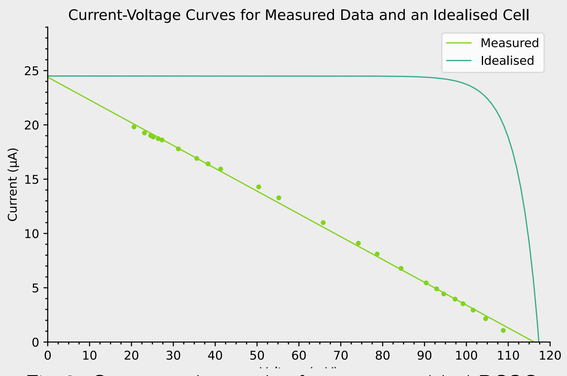

Fig 3: Current-voltage plot for an assembled DSSC compared to an ideal cell

To measure improvements to a DSSC, three values should be extracted from the experimental measurements using a current-voltage curve (Fig 3) and a power-voltage curve: open circuit voltage (V_{OC}) relates to the absorption energy of the dye, short circuit current (I_{SC}) the rate of successful light conversion, and Fill Factor (FF), the ratio of maximum power to I_{SC} and V_{OC}.

For this research, the DSSC has been split into two broad categories: dye and cell circuit. The dye refers to any light-absorbing components, while the cell circuit encompasses the transportation of electrons.

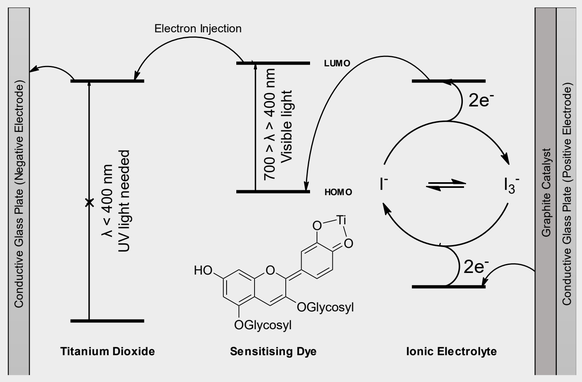

Fig 4: A schematic representation of a DSSC showing the energy levels of the electron as it travels

Modifications to Sensitising Dye

Investigation of Santalin A

Red sandalwood, *Pterocarpus santalinus,* contains a natural pigment called santalin (Fig 5a), as well as other dyes such as santarubin (Fig 5b). Powdered wood was washed with petroleum ether, acetone and dichloromethane to give dark red crystals.

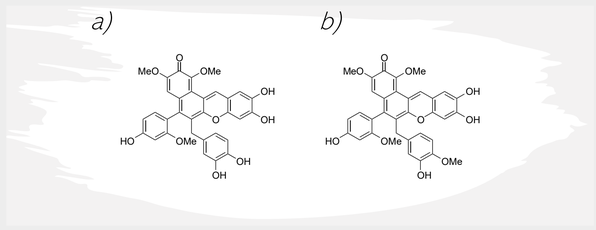

Fig 5a) Santalin A and 5b) Santarubin

Once isolated, the santalin A was used to assemble DSSCs that reached a maximum of 0.064 $mAcm^{-2}$ and 259.4 mV, with FF consistently at 20-25%.

An unreported property was solvatochromism with santalin. In acetone, it turns an orange-yellow, while in *d*-chloroform, a lime-yellow, and deep red in dimethyl sulfoxide. The mechanisms behind this effect are poorly understood but can be correlated with solvent polarity and excited state stability.

The effect of metal complexation with anthocyanins in these cells has been investigated, but not santalin. Adding manganese and copper salts to santalin solution shows that a colour change does take place, but a quantitative testing of its effect on the cell efficiency has not been conducted here.

Pomegranate Seeds

Ghann *et al.* reported pomegranate seeds to contain TiO_2-sensitising anthocyanins. Seeds were crushed and filtered to remove solid mass, then used to assemble DSSC. Cells achieved an average of 0.044 $mAcm^{-2}$,328.0 mV and FF < 25%, lower than expected. It is believed the TiO_2/anthocyanin films were too thin to absorb all the incident light.

Purple Yam Extract

The purple yam is an anthocyanin-rich plant found in Eastern Asia. The anthocyanins can be found in syrups, commonly marketed as ube.

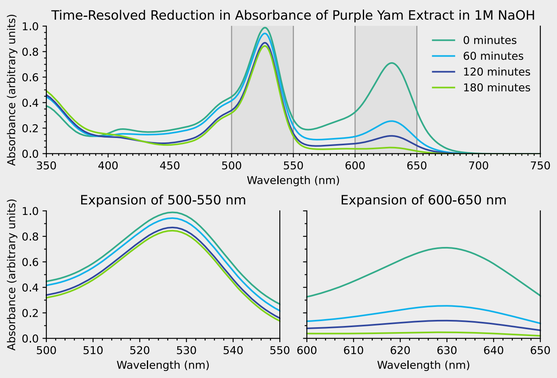

Fig 6: Kinetic UV-Vis spectra of ube syrup in NaOH, with expansions on the 500-550 and 600-650 nm regions

After 180 minutes of exposure to 1M NaOH, an irreversible colour change from purple to pink was observed. Breakdown under basic conditions is expected as anthocyanins can ring-open at high pH. Multiple sharp peaks could indicate additives, as anthocyanins typically show only one broad peak.

Modifications to Cell Circuit

Zinc Oxide Doping

TiO_2 has a low hole mobility of 0.1 $cm^2V^{-1}s^{-1}$. As a result, the mean drift velocity of the electrons is slow and increases the chances of voltage losses through recombination. Doping the structure of TiO_2 with ZnO (hole mobility 166 $cm^2V^{-1}s^{-1}$) reduces the recombination rate to increase open-circuit voltage.

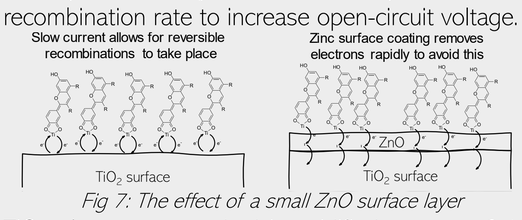

Fig 7: The effect of a small ZnO surface layer

TiO_2 plates were soaked in acidified aqueous 0.1M $ZnSO_4$ and sintered. Cells with Zn clusters generated photocurrents a factor of 7x lower than expected. Side products from decomposition or surface area reductions could be limiting the photoconversion.

Cell Electrolyte

Solution-Based I_2/I_3^-	Solid-State CuI/CuSCN
- Corrosive I_2 attacks dye molecules in DSSC - Environmental issues with toxic organic solvent used - Lasts only several days before evaporation	- Inert semiconductor coexists with sensitiser - No chance of leaking with a solid substrate - Solid material can remain in cell for indefinite period

TiO_2 substrates were prepared and heated to 60 °C. CuI was sparingly dissolved in MeCN and dropped onto the plate until a white layer of CuI was built up until over the TiO_2. These cells did not produce any measurable photocurrent, potentially due to short-circuiting from CuI contacting both cell electrodes.

AcOH Surface Modification

Work by Liu and Wang reports modification of the titania surface by acetic acid to add OH groups, which beneficially alters the TiO_2 electrical surface chemistry. Plates are etched immediately after dye adsorption in a 1% v/v acetic acid in toluene solution overnight. Preliminary results from these cells indicated an increase in I_{SC} of 208.9% with Liu and Wang observing a 210% increase.

tBu-Py Surface Coating

Unwanted side reactions with the iodine/iodide electrolyte play a large part in reducing photocurrent. Tertbutylpyridine has been used previously by Kusama *et al.* in ruthenium dye-based cells to reduce these reactions and so improve cell efficiency.

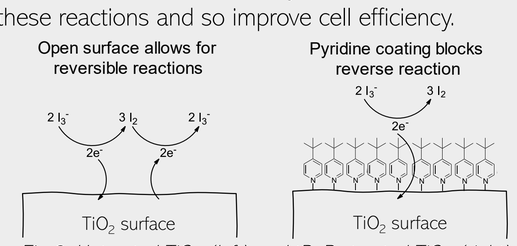

Fig 8: Untreated TiO_2 (left) and tBuPy-treated TiO_2 (right)

The mechanism behind its effect is unclear. The aromatic system is deficient in electron density, so movement of electrons into the ring is favoured. Titanium(IV) ions in the lattice are also deficient and so movement into the crystal is thermodynamically allowed. Steric hindrance from a ^{t}Bu group and an electron-rich electrolyte disfavour backwards movement in a diode-like fashion (Fig 8b). In anthocyanin-sensitised cells, there was a 6.55% increase in I_{SC} observed upon soaking with tBuPy.

Acknowledgements

Thanks must go to Lord Laidlaw and the Laidlaw Foundation for their support in bringing me this opportunity. Many thanks also to my supervisors, lab technicians, and my Laidlaw cohort.

LAIDLAW SCHOLARS

Conclusion

Several possible improvements to the DSSC have been quantitatively tested for their use. Of these, the use of santalin and surface modification with acetic acid have shown significant promise and are recommended to be used to increase the educational value of this experiment to students.

Solid-state semiconductors were not achieved, but further attempts to find a reliable synthesis is recommended. In-house extraction of purple yams to compare with commercial syrup is another opportunity for further work.

References

1. B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737–740.
2 H. Kusama, Y. Konishi, H. Sugihara and H. Arakawa, *Solar Energy Materials and Solar Cells*, 2003, **80**, 167–179.
3 Q. Liu and J. Wang, *Solar Energy*, 2019, **184**, 454–465.
4 W. Ghann, H. Kang, T. Sheikh, S. Yadav, T. Chavez-Gil, F. Nesbitt and J. Uddin, *Sci Rep*, 2017, **7**, 41470.
5 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.
6 P. Wang, L.-D. Wang, B. Li and Y. Qiu, *Chin. Phys. Lett.*, 2005, 22, 2708–2710.
7 T. Bak, M. K. Nowotny, L. R. Sheppard and J. Nowotny, *The Journal of Physical Chemistry C*, 2008, **112**, 12981–12987.
8 N. A. Jayah, H. Yahaya, M. R. Mahmood, T. Terasako, K. Yasui and A. M. Hashim, *Nanoscale Res Lett.*, 2015, **10**, 7.