Institution: 010007857 Bangor University

Unit of Assessment: 08, Chemistry

Title of case study:
Dye-Sensitised Solar Cells

1. Summary of the impact (indicative maximum 100 words)

In 2012, it is estimated the $145bn was invested in solar photovoltaic technology. Dye-Sensitized Solar Cells (DSC) are expected to play an increasing role in renewable energy generation over the next decade and beyond, but several practical issues need to be overcome to facilitate large-scale economic production. Fundamental research at Bangor has laid the ground for collaborative work with industry which has overcome several of the key production constraints in their manufacture, increasing production speed and efficiency and substantially reducing costs. As a result, we have developed a Technology Roadmap with a major multinational partner (TATA) which has led to significant investment in plant and to the production of pilot products in the form of photovoltaic roofs, currently undergoing outdoor testing.

2. Underpinning research (indicative maximum 500 words)

Materials chemistry and renewable energy are important research themes within the School of Chemistry and this is exemplified by research on dye-sensitized solar cells (DSC) led by Dr. P.J. Holliman (appointed 1995).

Since 2002, Holliman's group has carried out research on functional coatings and photovoltaics focussing on three issue of major importance for the commercialisation of the cells:

- design and synthesis of low cost dye sensitizers and studies of their co-sensitization;[3.1-3.2]
- investigations of dye chemisorption for a fast sensitisation process;[3.1-3.3]
- research on low temperature processing of DSC.[3.4-3.5]

This research has led to long-term collaborations between Bangor Chemistry with Engineers at Swansea University (ultra-fast sintering, weathering) and TATA Steel (process engineering/scale-up). The research has been supported by a series of Welsh Government, EU, EPSRC and EPSRC/TSB industrially co-sponsored projects.

2.1. Dye sensitizers and co-sensitization of DSC.
The research was carried by 2 postdoctoral research assistants and 3 PhD students, under the direction of Holliman, in search of efficient, low cost sensitizers which work together to harvest more sunlight by DSC (2003–2013). This has produced 5 dye families, clay-stabilized pigments and the patented synthesis of infrared absorbing DSC dyes. We have also demonstrated that co-sensitizing dyes broadens spectral absorption and increases DSC efficiency by 30–40%, whilst reducing dye costs by more than 50%, compared to the widely used Ru-bipy dyes, by reducing raw material costs, and simplifying synthetic steps and purification.[3.1-3.2]

2.2 Ultra-fast process of dye sensitization and co-sensitization for DSC.
Conventional TiO_2 dyeing in DSC takes a long time, making it a critical issue for DSC manufacturing. Working with 2 PDRAs and 2 PhD students, Holliman has developed rapid dyeing methods leading to ultra-fast sensitization, ***reducing processing time from 18-24h to <5 mins.*** This work resulted in 3 patents from 2009–2012 (PCT/EP2010/051135, PCT/EP2011/059551 and PCT/GB2013/050171), with subsequent journal publication.[3.1-3.3]

This approach was further developed to demonstrate the world's first examples of ultra-fast co-sensitization of up to 4 dyes in less than 5min, eliminating oxidative degradation by air, reducing dye solution volume by ~100 times (significantly reducing costs of expensive dyes) and enhancing spectral response and device efficiency by controlling multiple dye loading (impossible using conventional dyeing).[3.1-3.3] This work was funded by Welsh Government Academia for Business (A4B) Proof of Concept funding supporting a PDRA in Bangor from 2010–2011, and from 2011, by EPSRC support for a PDRA in Bangor as part of a Swansea University-led innovation & knowledge centre SPECIFIC (Sustainable Product Engineering Centre for Innovation in Functional Industrial Coatings),[3.6b] as well as 2 PhD students.

2.3 Low-temperature processing of DSC.
Conventional DSC photo-anode manufacturing requires sintering of TiO_2 at >450°C. A consortium EPSRC project (2007–2010)[3.6a] comprising Bangor Chemistry (Holliman), TATA, Imperial College,London (Prof. J. Durrant – device characterisation), University of Bath (Prof. L. Peter – electrolyte development) and Swansea University (Prof. D. Worsley – lifetime testing) led to us producing the ***first examples of low temperature sintering of binder-containing TiO_2 colloids***. We demonstrated that the binder is essential for commercial manufacture, although previous approaches had simply left this out[3.4]. We developed combustion catalysts/promoters and chemical binders to reduce sintering to room temperature for longer sintering times leading to 3 patents, the most recent in 2012 [3.5].

Our work with support from the Welsh Energy Research Council (PDRAs 2006–2009), led to a patented ***room temperature platinisation*** procedure, to supplant a previous process carried out at 400°C.

Further Welsh Government A4B funding (PDRAs, 2010–2013), enabled us to scale-up the low temperature sintering and platinisation processes to A4 size. With EU (ERDF) support through the Low Carbon Research Institute, the Solar Photovoltaic Academic Research Consortium brought together researchers from Bangor (Holliman - sensitization and low temperature processing), Swansea (Dr. P. Igic - power electronics, Prof. D. Worsley – materials), Glyndwr (Prof. S. Irvine – thin film photovoltaics) and several companies to scale up photovoltaic manufacture leading to pilot line trials (2012) of the Bangor low temperature processes.

In total, 9 patents have been filed (7 through Bangor University and 2 through TATA) on metal surface treatments for inherent lubricity, development of DSC sensitizers, ultra-fast and precision controlled multiple dye sensitisation for DSC and rapid low temperature processing.

3. References to the research (Bangor authors in Boldface)

3.1 **P. J. Holliman, M. Mohsen, A. Connell, M. L. Davies, K. Al-Salihi,** M. B. Pitak, G. J. Tizzard, S. J. Coles, R.W. Harrington, W. Clegg, C. Serpa, O. H. Fontes, C. Charbonneau, M. J. Carnie, Ultra-fast Co-Sensitization and Tri-Sensitization of Dye-Sensitized Solar Cells with N719, SQ1 and Triarylamine Dyes, *J. Mater. Chem.*, **2012**, 22, 13318–13327. DOI: 10.1039/c2jm31314f [Citations: 8]. (Submitted to REF2014, ID 0810).

3.2 **P. J. Holliman, M. L. Davies, A. Connell, B. V. Velasco** and T. M. Watson, Ultra-fast dye sensitisation and co-sensitisation for dye sensitized solar cells. *Chem. Commun.*, **2010**, *46*, 7256–7258. DOI: 10.1039/c0cc02619k [Citations: 22]. (Submitted to REF2014, ID 0809).

3.3 T. Watson, **P. Holliman,** D. Worsley, Rapid, continuous in situ monitoring of dye sensitisation in dye-sensitized solar cells. *J. Mater. Chem.*, **2011**, *21*, 4321–4325. DOI: 10.1039/c0jm03607b [Citations: 11]. (Submitted to REF2014, ID 0811).

3.4 **P. J. Holliman, M. L. Davies, A. Connell,** M. J. Carnie and T. M. Watson, Rapid, Low Temperature Processing of Dye Sensitized Solar Cells. Peer reviewed chapter in *Functional Materials for Energy Applications*, Eds. J. A. Kilner, S. J. Skinner, S. J. C. Irvine, P. P. Edwards **2012**, Woodhead Publishers, Cambridge, pp. 42–66. ISBN-13: 978-0-87509-059-1. (http://www.woodheadpublishing.com/en/book.aspx?bookID=2340)

3.5 **P. J. Holliman**, D. Al-Husenawi, **A. Connell** and **E. Jones**. Low temperature sintering of dye sensitized solar cells using peroxides. PCT/GB 2013/050308. Filed 10th February **2012**.

3.6 EPSRC research Grants:
(a) “Metal Substrate Mounted Flexible Dye Sensitized Semiconductor Solar Cells”, EP/E03585X/1, **2007–2010**. Total £282,362;
(b) “Sustainable Product Engineering Centre for Innovative Functional Industrial Coatings – SPECIFIC”, EP/I019278/1, **2011–2016**. Total to Bangor: £465,673.

4. Details of the impact (indicative maximum 750 words)

Research at Bangor on ultra-fast DSC co-sensitization has directly influenced the commercial sector. Since 2006, Holliman's group has focused on large scale, low cost PV working with TATA, Dyesol and G24i on roll-to-roll PV manufacturing with the aim of becoming market competitive (cost, efficiency and lifetime) *versus* the market-leading crystalline silicon. Line trials have been carried out with TATA and Dyesol (Shotton) using their £1.5M roll-to-roll pilot line.[5.1-5.4] Holliman's group are scaling ultra-fast DSC sensitization, increasing DSC efficiencies (by 30–40%) by improving spectral response using four dyes in minutes. This avoids longer processing and large dye baths containing 100's g of expensive dye (*ca.* £500/g). Following the launch of the SPECIFIC IKC (2011) Bangor has linked with Swansea partners to develop building-integrated modules (roof mounted, windows etc.).[5.4-5.6] This is important because roll-to-roll lines run at the speed of the slowest process, so doubling dyeing time halves productivity making ultra-fast sensitization essential for roll-to-roll DSC manufacture.

Since 2008, in addition to the six industry-facing PDRAs at Bangor, three new jobs were created at the joint TATA/Dyesol PV Accelerator in Shotton, employing ex-Bangor researchers Rugen-Hankey, Vaca Velasco and Ketipearachchi. Holliman is Bangor PI on an Industry/Welsh Government/TSB/EPSRC funded Innovation Knowledge Centre opened at Swansea University in 2011 (SPECIFIC).[5.5-5.6] SPECIFIC works at Technology Readiness Levels (TRL) 3–7 on "Buildings as Power Stations" to functionalise the building envelope. Hence, SPECIFIC is an exploitation vehicle between invention (TRL1–3) and commercialisation (TRL 6–9). Scaling and line trials of Bangor-generated IP (working with TATA, Dyesol, G24i and/or SPECIFIC) have taken the sintering and dyeing inventions from TRL1–3 to TRL 4–5 using large substrates (A4 size) which are larger than that required for fully scaling this technology into modules (see Technology Roadmap below).

Another example of an impact of Bangor's research is WG-supported STRIP initiative (Steel Training Research and Innovation Partnership) to deliver high quality University research to industry to improve industry competitiveness.[5.8]

Holliman has undertaken two funded secondments (Oct–Dec 2011 and July 2012–Jan 2013) to work with senior TATA and SPECIFIC management and economists (Mr. Kevin Bygate and Mr. Kian Woodward, TATA and Prof. Dave Worsley, SPECIFIC) on a PV Technology Roadmap (TRM).[5.1] These were based at TATA (Shotton) and SPECIFIC (Swansea) and involved visits to TATA sites in the UK and India and SPECIFIC partners (*e.g.* NSG). The roadmap is a strategy for PV commercialisation which compares PV technologies in terms of feasibility, manufacturing, processing and lifetime issues as well as current/predicted markets and product form. It has been developed through SPECIFIC and its industrial partners (e.g. TATA, NSG, BASF who have staff seconded into the centre) and the recently Welsh Government-funded Ser Cymru Solar project (£6M, 2013–2018) working between Swansea, Imperial College and Bangor.

Thus, the research carried out at the School of Chemistry in Bangor has been contributing to the evolving global PV sector through the development of scaled PV manufacturing by accelerating dye sensitization by *ca.* 2000 times (24h becoming 1 min) and reducing processing temperatures (from 450-550°C to room temperature). We have scaled these inventions to A4 size and carried out feasibility and lifetime testing with G24i, Dyesol and TATA and line trials with Tata/Dyesol proving low temperature processes can also take place much faster (30 min becoming 4 min). These process are now being utilised by our industrial partners.[5.1]

Holliman has established a strong partnership with TATA Steel (scaling, route to market) and Prof Worsley (SPECIFIC- rapid processing, lifetime testing) working on PV commercialisation particularly that based on the results of his research on DSC. Holliman has developed a Technology Roadmap for PV[5.1] which sets the strategy/targets to develop scaled building integrated PV (BIPV) to replace bolt-on crystalline silicon modules. TATA have already produced BIPV roofs based on this strategy which are undergoing outdoor testing.[5.8]

Associated with this research, using EPSRC support (Holliman, 2008-2010), the bilingual English-

Welsh language schools lecture Chemistry Show-Sioe Cemeg was presented to over 2000 children annually by Dr Robyn Wheldon-Williams.[5.9] In 2013, Dr Matthew Davies (SPECIFIC PDRA in Dr Holliman's group) led a 15 strong team to South Africa showing how to make dye-sensitized solar cells from natural dyes to over 1300 school children over a 2-week visit.[5.9]

5. Sources to corroborate the impact (indicative maximum of 10 references)

5.1 **PV pilot line trials and collaborative work on PV Technology Roadmap** with TATA and SPECIFIC can be verified by letter on file from Director of Business Development, TATA Colors and CEO SPECIFIC, Baglan.

5.2 **PV pilot line trials, scale-up and collaborative work** with Dyesol can be verified by letter on file from Technical Manager, Dyesol, St Asaph.

5.3 **Collaborative work with TATA STRIP** on novel surface lubricity treatment can be verified by letter on file from Senior Technologist, Product Technology, TATA Steel STRIP, Port Talbot. See also: http://www.welshcountry.co.uk/index.php/news-from-around-wales/232-south-east-wales/5570-forward-looking-partnership-supports-steel-industrys

5.4 **DSC technology on prototype steel roofing material** (18.09.2012): http://www.dyesol.com/posts/cat/corporate-news/post/watch-video-dyesols-dye-solar-cell-dsc-technology-on-tata-steels-roofing-material/

5.5 **Dr Holliman interview** "SPECIFIC: An opportunity to make a real product": http://www.youtube.com/watch?v=4SjSz43i5G8

5.6 **For Bangor partnership with SPECIFIC see:**
http://www.dailypost.co.uk/business/business-news/20m-scheme-turn-wales-buildings-2649375
http://www.walesonline.co.uk/news/local-news/20m-scheme-turn-wales-buildings-2022427
http://www.plusplasticelectronics.com/buildingsinfrastructure/work-on-coatings-for-low-carbon-buildings-gets-underway-41833.aspx
http://www.tatasteeleurope.com/en/news/news/2010/2010_specific

5.7 http://www.building4change.com/page.jsp?id=723

5.8 **BIPV Development Project** (17.06.2011): http://www.slideshare.net/PVaccel/bipv-development-projectppt-8335044

5.9 **Schools outreach work** in the UK is evidenced by final reports, evaluation forms and pictures sent to EPSRC as funding body (reports for 2009 and 2010 are on file as examples). Web reports of the schools work in South Africa (2013) are also held on file.