DYE-SENSITISED NANOCRYSTALLINE SOLAR CELLS

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The dominant photovoltaic device at the present time is the solid state junction, in which the materials and concepts of semiconductor technology are applied to the challenge of cost-effective solar energy conversion into electricity. An alternative approach is electrochemical, with semiconductor contacts to electrolytes sensitised to visible light by charge transfer dyes. The principle of operation of the sensitised photoelectrochemical device has close affinity to photography, and depends for its future development on materials science on the nanometric scale, and on molecular engineering to provide dyes with the energetics, chemical kinetics and absorption match to the solar spectrum, if it is to successfully enter the market in competition with the established products.

1. Sunshine, Photovoltaics and Photosynthesis

Any discussion of photovoltaic technology and its future utility as part of the overall energy market must begin with an objective assessment of the solar energy conversion problem and the adequacy of the solution proposed. Solar irradiation provides an annual energy input to our planet of 1.56 x 10^{18} kWh, in comparison with which our annual primary energy consumption is smaller by a factor of 10^4. However, this energy is distributed, non-uniformly, over the total surface of the earth, so obviously in practice it is not constantly available on a given area, and has a maximum power, at midday under a clear tropical sky, of only 1kW/m^2. A commercial photovoltaic system has a typical conversion efficiency of the order of 10 - 15%, so a panel giving 1 kW output under peak insolation (1 kW$_p$) has an area of at least 7m^2. Taking account of higher latitude, seasonal and weather considerations at a central European site, the typical annual electrical output of a photovoltaic system is about 800kWh per installed kW$_p$ of PV modules. There remains also the problem of load matching, given that power supplied by a PV system under our conditions is not coincident with maximum demand, and therefore conventional systems must remain available to maintain supply continuity, since an adequate technology for large-scale storage of electrical energy is not yet available. It follows that if PV is in the future to become a significant component of a European energy system, the solar energy panels must have a very large area, associated with low cost and extremely high reliability, as the economics of competition with other technologies demands a mimimum lifetime of several decades under outdoor conditions - extremes of temperature, wind, snow and hailstorms, as well as corrosion and even vandalism!

With typical commercial module conversion efficiency to electricity of 10%, 1 kWp of installed photovoltaic generation capacity represents a surface area of approx. 10 m^2. Practical achievement in German conditions is an annual electrical output under 1000 kWh/kWp.

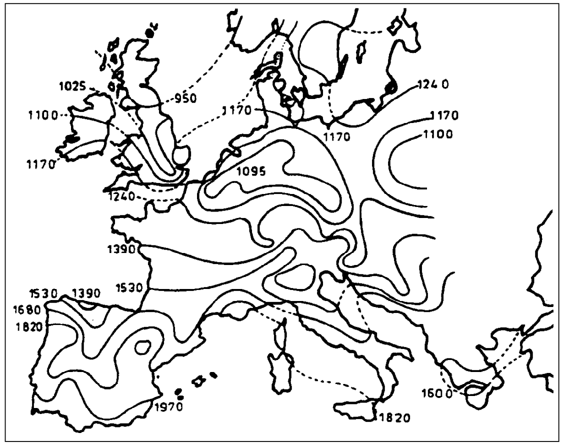


Fig. 1: Mean annual incident radiative solar energy in Europe, in kWh/m^2.

Photovoltaic technology is presently dominated by silicon solid state junction devices, where the materials and processing follow the practice of the semiconductor industry. They therefore involve costly and energy-intensive high temperature and high vacuum processing steps, with correspondingly long economic and energetic payback times. Even with government support and a highly motivated clientele, competitivity with conventional systems is far from being achieved. Alternative routes for conversion of sunlight to electricity are clearly required, both in their own right and as a stimulus to further progress in solid state PV. The original observation of a photoelectric effect, by Becquerel in 1839 was in fact with an electrochemical device (1). In this context, chemical systems, including the dye-sensitised photoelectrochemical cell, are emerging to challenge semiconductor physics for light-to-electricity energy conversion. At the same time, it is to be noted that our biosphere is effectively a solar energy conversion system of proven reliability over hundreds of millions of years. The natural organometallic dye in green plants, chlorophyll (Fig.2), absorbs sunlight and in the process of photosynthesis exploits it for the energy and materials needs of the biosphere; all animal existance in turn can be regarded as parasitical on plants. Even with a low energy conversion efficiency of about 1%, this process - and this molecule - have sustained biological life over geological time, due to the large surface area exposed by grasses and leaves. The dye-sensitised PV cell has emerged as a result of a biomimetic development strategy, inspired by this reality of nature. However in nature, once the functionality of the chlorophyll system was established as adequate to provide the energy to maintain a self-replicating organism, that molecule was retained despite the ongoing variation in plant structure, environment and genetics. There is a similar history over geological time for the haemoglobin molecule in animals, also a nitrogen-cage structure or porphyrin surrounding a metal, in this case iron. To emulate photosynthesis on the other hand there is no restriction of the metal or the surrounding organic complex, giving endless possibilities for molecular engineering of dyes.

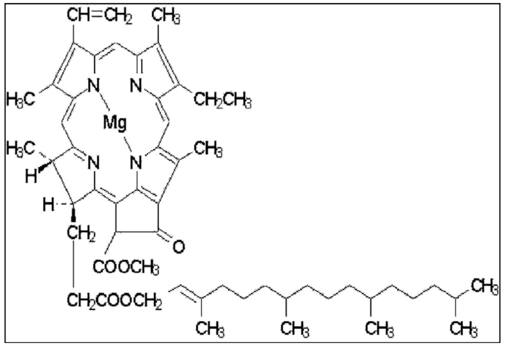
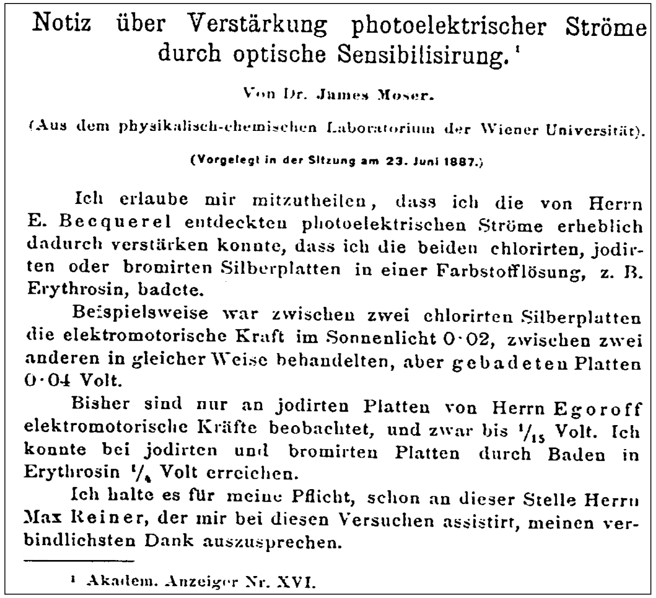


Fig. 2: Molecular structure of chlorophyll, the key to natural photosynthesis.

2. Sensitisation of Semiconductors

It could be asked why the use of a dye is necessary in chemical or electrochemical photoconversion devices. In the solid state cell, the semiconductor is at the same time the optical absorber of photons whose energy exceeds the band gap, and the site of charge separation to provide a photovoltage across a junction, p-n within the material or Schottky at a metal-semiconductor interface. On energy considerations, a semiconductor-electrolyte contact in a photochemical system is identical to the Schottky case, the redox potential of the electrolyte being the equivalent of the metal Fermi level. However, semiconductors with band gaps appropriate for the absorption and conversion of sunlight are liable to photocorrosion in contact with electrolytes; since positively charged holes arrive at the interface the species with which they are most likely to react oxidatively may be the semiconductor itself, unless the kinetics of the redox reaction are sufficiently fast to provide some degree of protection. Semiconductors with wide band gaps, and therefore stable under illumination in contact with electrolytes, are poorly matched to the solar spectrum; titanium dioxide, one of the better candidates, has a band gap of 3.1 eV., and therefore an optical absorption edge already in the ultraviolet. Association of the semiconductor with a separate optical absorber such as a suitable dye could then provide a photoeffect with visible light.

This particular problem was already well known in the physics of photography, contemporary in its origins, in the work of Daguerre (1837) and Fox-Talbot (1831) with the photoelectric observations of Becquerel. Silver halides were established as the standard photosensitive materials, but the formulation of photographic emulsions remained an art rather than a science for a further century, until the theory of the process was presented by Gurney and Mott in 1938 (2). However the limitations of early emulsions were gradually overcome, notable the inability to present realistically on a grey scale scenes observed in colour, given their insensitivity to mid-spectral and red light. It is now known that this is due to the wide bandgaps of the silver halide semiconductor grains, over 2.7 eV. Extension of the spectral response proceeded empirically, with the observation that the origin of the gelatin in the emulsion had a distinct effect. Only in this century was it recognised that organosulfur compounds in calf-skin gelatin were responsible, by producing a sulfide layer of wider sensitivity on each halide grain (3). A more systematic approach was followed by Vogel, as professor of photochemistry, spectroscopy and photography at the Königliche Technische Hochschule in Berlin towards the end of the 19th. Century. From 1873 onwards he researched the association of dyes with the silver halide grains, finding a photoresponse controllably extended into the red and even the infrared, making possible the panchromatic black-and- white (or more accurately, grey-scale) film and ultimately, with spectrally selective dyes, the modern colour film (4).



Notiz über Verstärkung photoelektrischer Ströme durch optische Sensibilisirung.[1]

Von Dr. James Moser.

(Aus dem physikalisch-chemischen Laboratorium der Wiener Universität).

(Vorgelegt in der Sitzung am 23. Juni 1887.)

Ich erlaube mir mitzutheilen, dass ich die von Herrn E. **Becquerel** entdeckten photoelektrischen Ströme erheblich dadurch verstärken konnte, dass ich die beiden chlorirten, jodirten oder bromirten Silberplatten in einer Farbstofflösung, z. B. Erythrosin, badete.

Beispielsweise war zwischen zwei chlorirten Silberplatten die elektromotorische Kraft im Sonnenlicht 0·02, zwischen zwei anderen in gleicher Weise behandelten, aber gebadeten Platten 0·04 Volt.

Bisher sind nur an jodirten Platten von Herrn **Egoroff** elektromotorische Kräfte beobachtet, und zwar bis $^1/_{15}$ Volt. Ich konnte bei jodirten und bromirten Platten durch Baden in Erythrosin $^1/_4$ Volt erreichen.

Ich halte es für meine Pflicht, schon an dieser Stelle Herrn Max **Reiner**, der mir bei diesen Versuchen assistirt, meinen verbindlichsten Dank auszusprechen.

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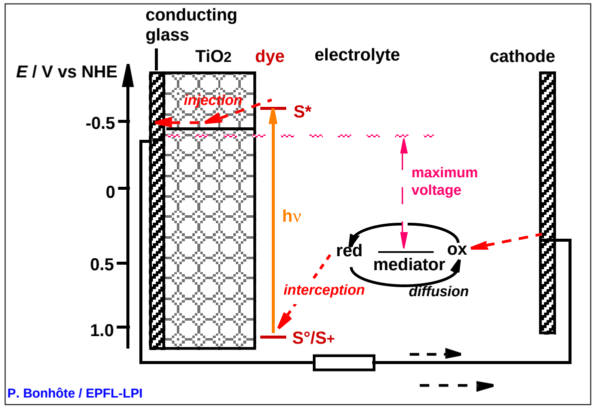
[1] Akadem. Anzeiger Nr. XVI.

Fig. 3: The first report in the scientific literature of the optical sensitisation of a semiconductor, silver chloride, the obvious choice because of its use in photography (Moser, Vienna, 1887).

Possibly influenced by these developments, and using the same silver halide semiconductors, the first sensitisation of a photoelectric effect was also reported over a century ago, in the text reproduced above (5). For the physics community it is instructive to note that Moser, writing 20 years before the Einstein theory of the photoelectric effect, correctly referred to sensitisation of the electrical current, which we now know to be proportional to the radiative intensity or flux of photons, but he reported his result in volts, although the photopotential is primarily a function of the semiconductor band-gap and is linked only indirectly with the intensity through carrier loss processes.



P. Bonhôte / EPFL-LPI

Fig. 5: Schematic of operation of the dye-sensitised electrochemical photovoltaic cell. The nanoporous sensitised semiconductor photoanode receives electrons from the photoexcited dye which is thereby oxidised. The charge-neutral state is restored by reaction with the redox electrolytewhich in turn is regenerated by reduction at the metallic cathode by the electrons circulated through the external circuit.

This historic parallel maintained between sensitisation in photography and in photoelectrochemistry still seems to come as a surprise (6). That the same dyes were particularly effective for both processes was recognised amongst others by Namba and Hishiki (7) at the 1964 International Conference on Photosensitisation in Solids in Chicago, which was a seminal event in the history of dyes in photochemistry It was also important for the presentation of a theoretical understanding of sensitisation, since it was still disputed whether the mechanism was an electron transfer or an energy-coupling process. The presently accepted model was determined shortly after in the work of Gerischer and Tributsch (8,9) on ZnO, which left little further doubt about the mechanism, and the significance for photoelectrochemistry of the dye-sensitisation phenomenon. It is now evident that the process involved the excitation of the dye from its charge-neutral ground state to an excited state by the absorption of the energy of a photon. One of the permitted relaxation processes is the injection of an electron into the valence band of the semiconductor, leaving the dye molecule positively charged. In the photographic process the injected electron reduces a silver ion, and thereby established the latent

image. In a photoelectrochemical cell, the injected electrons form a current in an external circuit, reaching a cathode in contact with the redox electrolyte. The uncharged ground state of the dye is in turn restored by electron transfer from the redox system, completing the circuit and providing a regenerative cycle functionally comparable with other photovoltaic devices, as presented in fig. 5.

The dye has clearly a charge transfer function, but it is not itself an electrical conductor. Therefore only molecules in intimate contact with the substrate can engage in the electron injection process. However, a monomolecular layer is not sufficient effectively to absorb the incident light for photovoltaic conversion of energy. This requirement of sufficient optical density of the absorbing structure leads to the use of nanocrystalline materials for the titanium dioxide semiconductor; by provision of an extended surface area, sufficient dye, chemisorbed as a monomolecular layer, can be retained on a given area of electrode to provide absorption to opacity of the incident light. The semiconductor structure, typically 10__ thick and with a porosity of 50%, therefore has a surface available for dye chemisorption enhanced by a factor of several hundred in comparison with the projected electrode surface area, due to that nanoscale crystallinity. From the micrograph, fig. 6, the grain size in a photoelectrode is under 10 nanometers; smaller grain size is evidently associated with enhanced surface area.

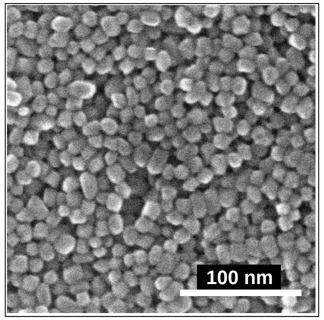


Fig. 6: SEM image of the surface of a mesoporous film prepared from a hydrothermally processed TiO_2 colloid.

It followed then to recognise that the major loss mechanism associated with polycrystalline or rough semiconductors in photovoltaics, the recombination of the photoexcited electrons with the mobile positive holes in the crystalline lattice or at surface or grain boundaries, is not applicable to the dye-sensitised electrochemical device (10). In amorphous silicon solar cells the suppression of recombination is carried out by reacting unsaturated bonds with hydrogen or fluorine. In the dye-sensitisation case, in contrast, no specific action is necessary, as the electron injected from the photoexcited dye finds itself in the semiconductor lattice, separated spatially and by a potential barrier from the oxidised dye species (Fig. 5) within picoseconds of the optical excitation event. The carrier loss mechanisms are comparatively slow (11), and although conventionally referred to as recombination, by analogy with the solid-state process, the loss of a photoexcited electron from the semiconductor should be regarded as a recapture by an oxidised dye species, or a redox capture when the electron reacts directly with an ion in the electrolyte. Either occurs on a millisecond timescale. This extreme ratio of the kinetics of the photovoltaic process to those of loss mechanisms is essential if the required cell lifetime is to be maintained. In the case of the photovoltaic device, at least 10^8 cycles through the regenerative process of photoexcitation of the sensitising dye, electron injection and neutralisation of the charged state by the redox electrolyte are required in a typical 20 years of outdoor operation, in contrast with the single cycle of the photographic process. This vividly illustrates the constraints for development of practical photovoltaic dyes.

3. Semiconductor Film Processing

As already mentioned, titanium dioxide is one of the better candidates for use as a sensitisable semiconductor. Work in Lausanne began with an investigation of TiO_2 as substrate for a chemisorbed sensitizing dye, first on particles (12) in the 1980's, then on photoelectrodes (13). The material has many advantages for sensitized photochemistry and photoelectrochemistry: it is a low cost, widely available, non-toxic material, and as such is even used in health care products. The original semiconductor film used for our early photosensitization experiments (14), a fractal derived by hydrolysis of an organo-titanium compound, has since been replaced with a nanostructure deposited from colloidal suspension. This evidently provides a much more reproducible and controlled porous high surface area nanotexture. Further, since it is compatible with screen printing technology for deposition on a conducting transparent substrate, it anticipates future production requirements. Hydrothermal techniques are employed for the synthesis of the nanoparticulate anatase TiO_2 powder used in colloidal from as the screen printing ink for dye solar cell fabrication, a technology which is continuously evolving to yield film microstructures which increase the photovoltaic performance of such devices through better optical management. Other oxide semiconductors which have been studied in the context of dye sensitized photovoltaics include ZnO, SnO_2, Nb_2O_5, and $SrTiO_3$ (15-19).

The microstructure of the semiconductor is of course a compromise, to achieve an optimal optical absorption and photovoltaic performance. Nanosize grains give the greatest surface area, but pores must be sufficiently large that the mobility of the charge carriers in the electrolyte, the redox ions, is not unduly inhibited. Also some degree of optical scattering by larger particles in the semiconducture film is also desirable, particularly for devices which function under indirect illumination such as vertical building facades. Processing parameters

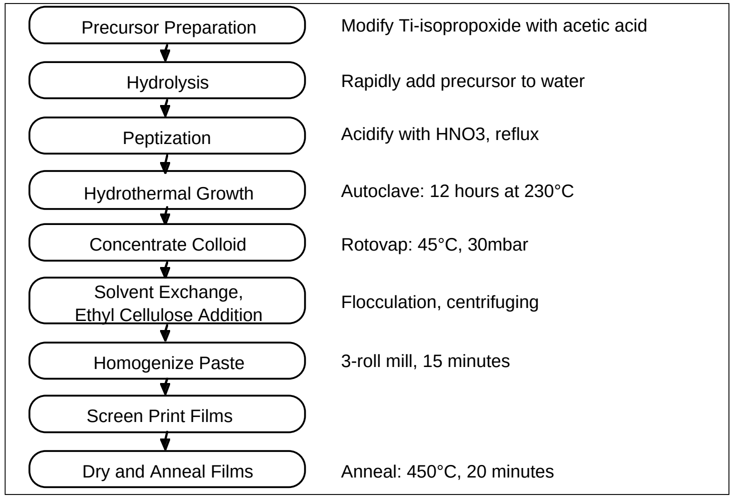


Table 1: Flow diagram for the preparation of TiO_2 colloids and mesoporous films.

such as precursor chemistry, hydrothermal growth temperature for the titania powder, and sintering conditions are varied in the optimisation precedure. A flowsheet for hydrothermal processing is presented in Table 1 as an example of the required development work, and in fig.7 the control of grain size which results from it, as determined by a nitrogen adsorption method.

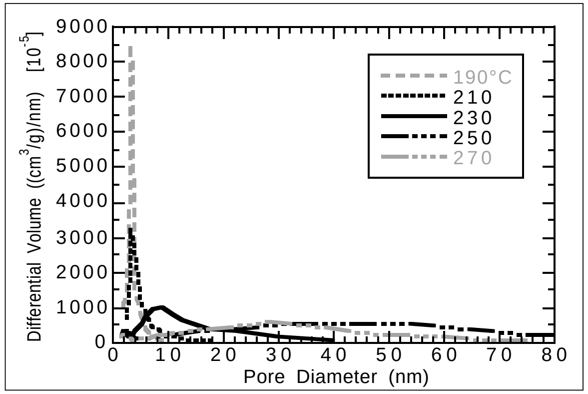


Fig. 7: Influence of hydrothermal growth temperature of TiO_2 colloids on the pore size distribution. Curves obtained from N_2 desorption data using the BJH model.

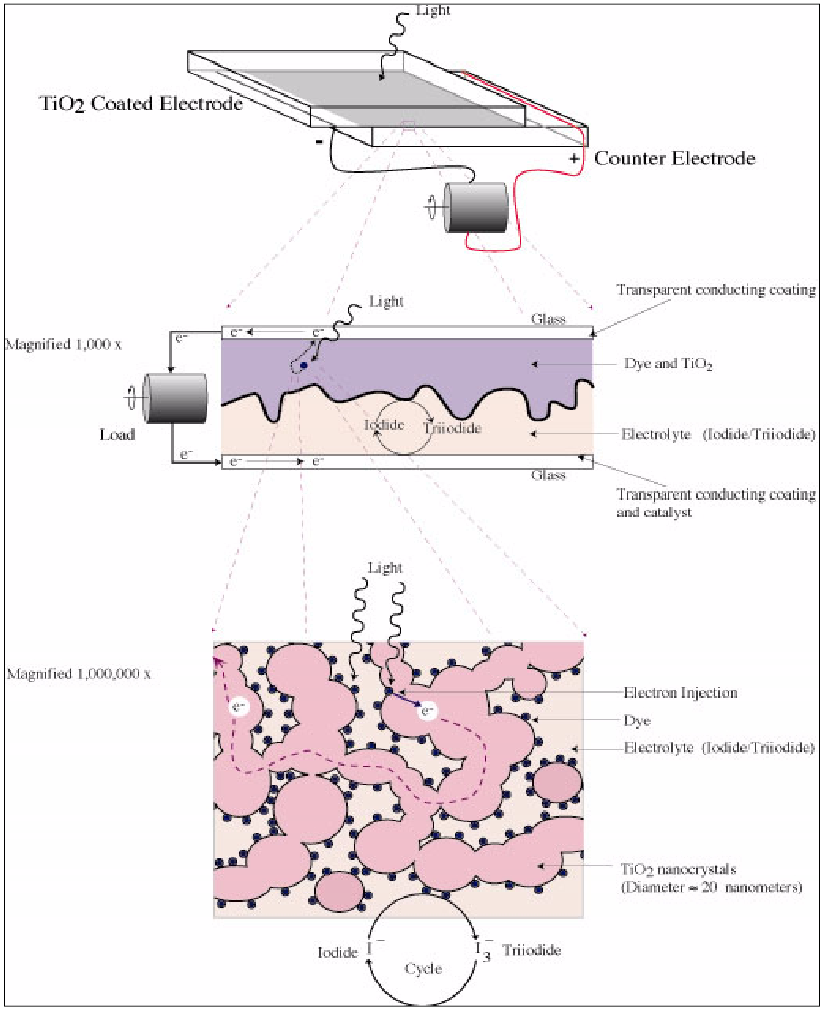


Fig.8: Structure of dye-sensitised photoelectrochemical cell on different scales. (Top): a complete cell (centimetric scale). (Centre):electrodes and electrolyte, micron scale. (Bottom): nanocrystalline semiconductor interconnected porous layer, with adsorbed monolayer of dye and entrained electrolyte (nano scale).

For the photoanode, the screen printed pattern using the hydrothermally grown powder in an ink is sintered to the conducting glass substrate, and the dye monomolecular layer applied. The cathode or counter-electrode is usually a similar glass, treated to electrocatalyse the redox reaction, for example with highly dispersed platinum. The cell is completed with an edge seal to contain the electrolyte, usually a liquid although gel or solid variants are also possible. Cell structure on successively smaller scales is shown in fig. 8, ultimately reaching the molecular dimensions of the dye itself.

4. Dye Development

The constraints determining the dye selection have already been indicated, and the production of a suitable formulation is a demanding exercise in synthetic chemistry. Firstly and evidently there is the matter of an optical absorption spectrum closely matched to the application of the photovoltaic device, whether it be to the solar spectrum for energy conversion or to artificial light sources for indoor use. With a high optical absorption coefficient across the visible spectrum, the excitation process should be rapid but subsequent relaxation slow, as already explained. For attachment to the semiconductor surface the molecule should adsorb strongly, by preference through a specific chemical bond, to the substrate, but avoid aggregation so that a monolayer coverage forms spontaneously on contact between the semiconductor and the dye in solution. To facilitate this chemisorption, carboyxlate or phosphonate groups, which bind strongly to titanium sites in the oxide, are integrated into the dye molecule. The dye structures selected for intensive development arose originally from biomimetic considerations, given the role of photosynthesis in the natural world. However, whereas plant photosynthetic processes rely on chlorophyll, a magnesium organometallic molecule, the synthetic chemist can select from the whole range of complex-forming metals to design an appropriate metal-ligand charge transfer structure. When develoment of the photovoltaic device started, ruthenium pyridyl complexes were already attracting considerable interest as photochemical reagents (20), so they have since been the principal focus of dye sensitiser development.

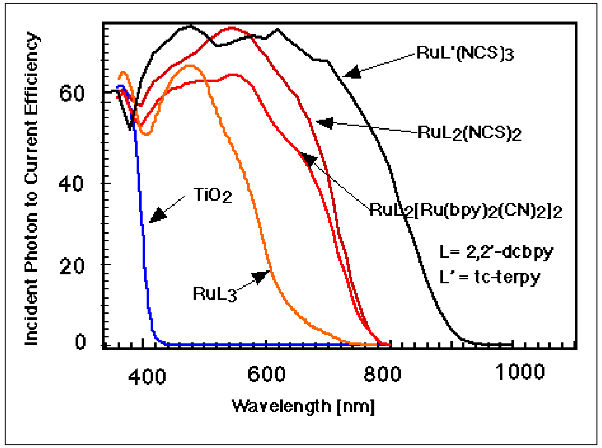


Fig.9: The photocurrent action spectrum of a cell containing various sensitizers, where the incident photon to current conversion efficiency is plotted as a function of wavelength.

The first priority for any PV cell is of course efficient conversion of incident radiation, requiring the spectral match of the optically absorbant component to the incident light, and in this regard the early dyes were inadequate. Development of dye molecules for extension of sensitivity, ultimately into the infra-red, is dramatically illustrated in fig. 9. The progress in extension of the absorption spectrum of ruthenium complexes from the early tris-bipyridyl ("RuL_3") molecule, absorbent only in the blue region and therefore appearing red, to the present-day wide-spectrum material ("$RuL' (NCS)_3$"), panchromatic, absorbing right across the visible range and therefore presenting itself as a "black" dye, has been a key step in cell development. The strategy has been to retain ruthenium as the metallic component, with structural modification of the ligands to tune the energetics of the molecule. The LUMO level (lowest unoccupied molecular orbital) to which the photoexcited electron in promoted must remain above the conduction band edge of the semiconductor substrate if electron injection is to occur. Extension of the spectral sensitivity is then accomplished by raising the HOMO (highest occupied molecular orbital) of the molecule, as in fig. 10. This molecular engineering process is of particular interest to physicists, as there is a close analogy to band gap modification in compound semiconductors.

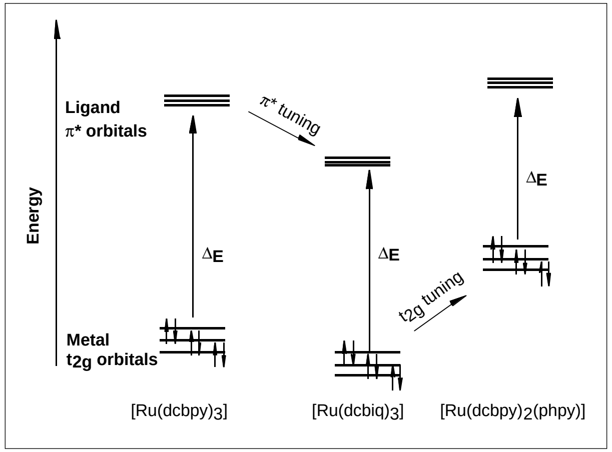


Fig.10: Tuning of HOMO (t_{2g}) and LUMO (_*) orbital energy in various ruthenium polypyridyl complexes.

A trimer structure, consisting of three ruthenium bis-biphridyl entities, cyanide bridged, and chemisorbed through carboxylate groups to the titania surface, gave the first significant extension of absorption spectrum, on the principle that an antenna structure with consequent charge transfer could be appropriate. However monomer structures are inherently simpler, and modification of pyridyl complexes by nucleophilic groups provided a more promising route. By

thiocyanate substitution, this gave rise to the dye $RuL_2(NCS)_2$, (L=bipyridyl), for several years our standard chromophore and the basis for most of the system development work. Under the product name N3 it is now probably the best-understood photosensitisation molecule, particularly for its charge exchange kinetics (11). In the ground state the metal ion is in oxidation state (II), but on excitation it loses a further electron to the organic ligand structure, a metal-to-ligand charge transfer. Loss of the electron through the bridging carboxylate to the semiconductor substrate occours within picoseconds, faster than other relaxation processes and explaining the high quantum efficiency of the sensitised system.

Isomerism of the dye molecule can permit the identification of structures with variant optical properties. For example the standard N3 is a cis-isomer (both NCS thiocyanate groups on the same side of the molecule); the corresponding trans-isomer has an extended sensitivity into the infra-red, but over time it tends to revert to the cis-structure. A trans-type configuration can be stabilised by replacing the L_2, bis-bi-pyridyl ligand system by a single tetrapyridyl coordination (21).

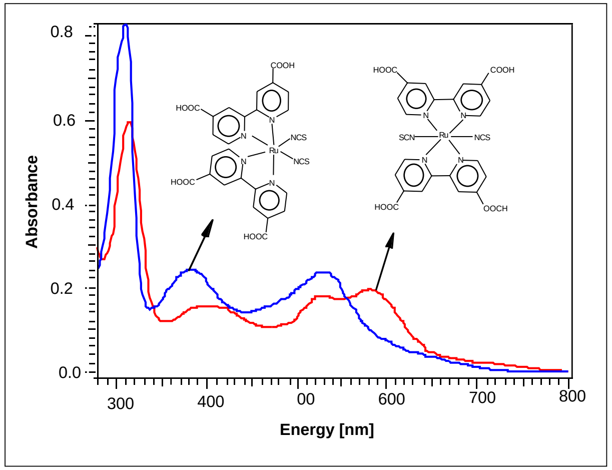
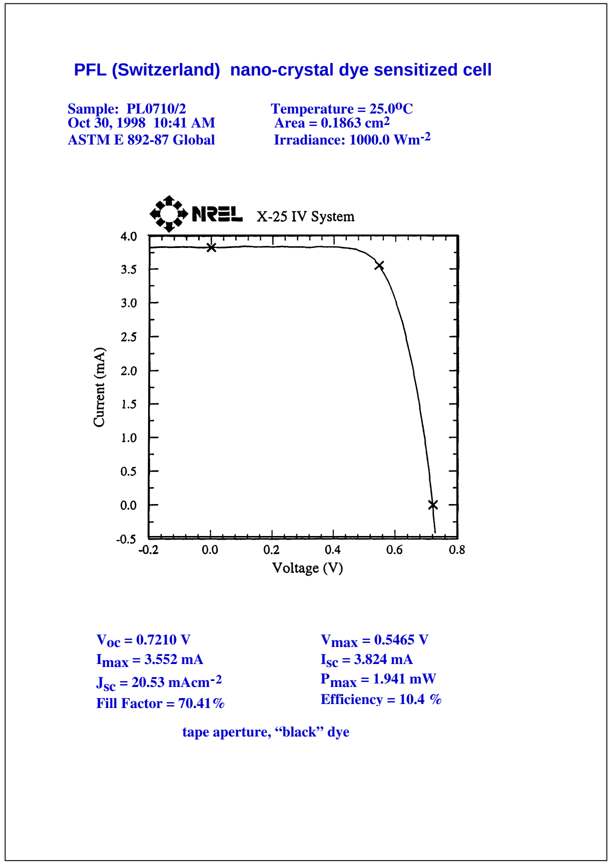


Fig.11: UV-visible absorption spectra of *cis*- and *trans*-bis(2,2'-bipyridine-4,4'-dicarboxylic acid) ruthenium (II) $(NCS)_2$, or N3-type, complexes.

Addition of a third thiocyanate group, with the necessary reduction of pyridyl complexation from bis-bi- to ter-pyridyl, gives the structure of the state-of the art black dye, "$RuL' (NCS)_3$", whose spectral sensitivity extends throughout the visible and into the infra-red, approaching the ideal absorption edge position (1.4 eV) for optimal solar energy conversion. It can be expected that this type of molecular engineering will make available suitable dye formulations for a variety of applications, such as infra-red sensitive dyes with lower visible absorptivity, useful for "transparent" cells, or dyes with selective absorption, the resulting color presentation being determined for example by architectural preference for building-integrated PV.



PFL (Switzerland) nano-crystal dye sensitized cell

Sample: PL0710/2
Oct 30, 1998 10:41 AM
ASTM E 892-87 Global

Temperature = 25.0°C
Area = 0.1863 cm^2
Irradiance: 1000.0 Wm^{-2}

V_{oc} = 0.7210 V
I_{max} = 3.552 mA
J_{sc} = 20.53 $mAcm^{-2}$
Fill Factor = 70.41%

V_{max} = 0.5465 V
I_{sc} = 3.824 mA
P_{max} = 1.941 mW
Efficiency = 10.4 %

tape aperture, “black” dye

Fig. 12: Certified performance characteristics of a "black dye" [RuL'(NCS) $_3$] cell.

The interaction between the dye molecule and the adsorbant surface also influences the energetics of the dye and the kinetics of its chemical reactions. For example it is known that on adsorption of a carboxylated dye, a titania surface becomes positively charged, due to the deprotonation of the acid dye. The consequent interface potential gradient obviously enhances electron injection efficiency, leading to a higher photocurrent. However efficiency does not proportionately rise, since the positive shift of band edge is associated with a lower open-circuit voltage. Optimisation of the cell efficiency also requires a control of protonation of the

dye. With this in mind several salts of N3 with organic cations such as tetrabutylammonium and imidazolium have been investigated (21). These salts are also more soluble, facilitating purification by recrystalisation and thereafter adsorption to the semiconductor from the more concentrated solution. The thermal dehydration behaviour shows the association of only 1.5 molecules of water per Ru ion, for the optimum di-tetrabutylammonium salt, with a thermal stability thereafter to 190˚C; at that point the organic cation tends to dissociate. When adsorbed on the semiconductor the dye stability is further enhanced, decarboxylation requiring over 300˚C. This remarkable rise is attributed to the strength of the Ti ion to carboxylate bond between the semiconductor surface and the chemisorber molecule. This confirmation of the thermal stability of the surface-bonded dye therefore opens the prospect of a very wide temperature window for processing the sensitised semiconductor during any manufacturing routine, simplifying bonding and sealing processes by permitting thermal treatment and curing of sealants even after the dye has been admitted to the cell.

Modification of the surface of the semiconductor to optimise adsorption and charge transfer behaviour is a further option. Several years ago, deposition of an outer intrinsic titania (22) or a solid solution layer (23) on the semiconductor was investigated in order to control the interface properties after dye adsorption. Evidently a nanostructure emulating the oxide or insulator layer in MOS or MIS solid state Schottky devices has a similar effect in defining the bandedge characteristics in the photoelectrochemical case.

5. Solid State Heterojunctions

Given that a dye at the interface in a photoelectrochemical cell can sensitise the system to photons of lower energy that would not otherwise be absorbed by the semiconductor, the possibility presents itself that the same effect could be verifiable at a semiconductor interface to a different conducting phase. Here we are not considering the special cases of gel or polymer electrolytes (24), because in these charge transport is by the same mechanism as in a conventional liquid electrolyte. The sensitised solid state cell, while functionally similar, requires a contact between the n-type titania semiconductor substrate and a metal or p-type semiconductor. Since the sensitising dye provides charge separation but not charge transport, and is distributed at an interface in the form of an immobilised molecular species, it is evident that for charge transfer each molecule must be in intimate contact with both conducting phases. This applies in the first instance to the wide bandgap porous semiconductor substrate into which the photoexcited chemisorbed molecules inject electrons. It is also evident that in the photoelectrochemical format of the sensitised cell the liquid electrolyte penetrates into the porosity, thereby permitting the required intimate contact with the charged dye molecule necessary for charge neutralisation after the electron loss by exchange with the redox system in solution. It is not immediately evident that an interpenetrating network of two conducting solids can be established so easily that an immobilised molecule at their interface can exchange charge carriers with both. This is a

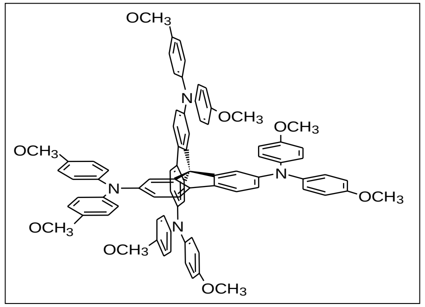


Fig. 13: structure of spirobifluorene hole-conducting p-type organic semiconductor. The flourene structures are perpendicular, conjoined through a carbon site common to both.

particular obstacle to the realisation of a sensitised nanostructured Schottky junction. However use of transparent organic semiconductors is a possibility, and initial results in our laboratory (25) and elsewhere (26) are promising. In both cases the hole conducting p-type materials are deposited by spin coating from the liquid phase in order to achieve the necessary intimate contact. In the latter case a mixture of polymers was used, which phase-separate spontaneously on removal of a solvent, whereas the Lausanne laboratory introduces a solution of the conducting compound into a previously-sensitised nanostructure. The charge transfer material currently used is a spirobifluorene, proprietary to Hoechst (27) as shown in Fig. 13. As a matter of technical precision, if this materials functions in the cell as a hole conductor, the device constitutes a sensitised nanostructured heterojunction.

6. Applications for Sensitised Photovoltaic Devices

Commercial success is not an immediate and necessary consequence of the development of a technically elegant system. Therefore the efficiency and stability of the dye solar cell must be associated with practical and economic advantages. On the technical side, the efficiency of conventional solid state junction cells falls off rapidly with increasing temperature and decreasing light intensity, whereas the sensitised system remains more constant under both operating parameter variables. The cell fabrication processes are intrinsically less demanding - no high vacuum or high temperature treatment steps, with therefore a low "grey" energy demand, whereas silicon devices require up to 5 gigaJoules per square meter of cell surface. The energy recovery time for the sensitised system should therefore be distinctly shorter. For architectural applications the possibility to select for cell color, even transparency, and texture gives additional freedom of action in building design, and with the incorporation of a light

diffusive function, by admixture of large grains in the semiconductor layer for example, the effect of variation of light incidence angle can be less marked. The cells may be bifacially sensitive, thereby capable of increased output when mounted over high albedo surfaces. Finally even on the parameter of energy conversion efficiency amorphous silicon is already successfully challenged, even though crystalline silicon cells may still retain a margin of advantage. To illustrate this competitivity, in fig. 14 the incident photon conversion efficiency spectrum of a state of the art dye photoelectrochemical cell is compared with those of new and of aged a-Si solid state devices under daylight conditions.

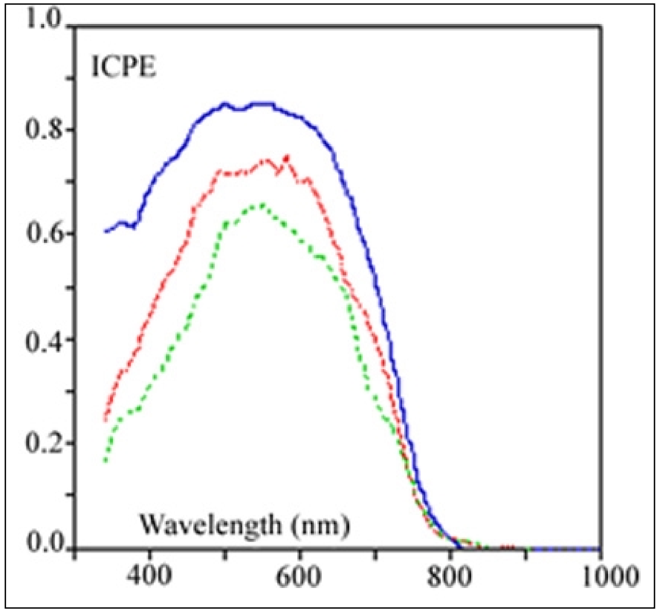


Fig. 14: Spectral response, given as incident photon conversion efficiency against wavelength, of a dye-sensitised cell (——) in comparison with a new (-------) or used (······, 800 W/m^2) amorphous silicon cell.

A second area of competitivity is for indoor devices, under artificial light. In the dye-sensitised cell one of the parameters most difficult to optimise is the fill factor, related as it is to ion diffusivity in the electrolyte and therefore to its viscosity. The lower intensity under artificial light indoors is advantageous for the sensitised device, as its conversion efficiency is maintained or even raised, whereas that of conventional junctions falls aff as the open-circuit voltage decreased in those circumstances. Behavior under indoor conditions, including under a variety of artificial light sources, is compared with that of a-Si cells in fig.15.

7. Conclusion

Whereas the total solar energy input to earth is extremely high, at a given site the energy density is low and intermittent, a fact which constrains its integration into the energy economy, particularly in the absence of a high-volume energy storage technology. To compensate for these difficulties and to compete technically and economically with more conventional processes, solar photovoltaic systems must be of large area, low cost, and very high long-term reliability. It is not therefore a simple technology to implement. Stimulation of imaginative energy conversion procedures for electricity production from sunlight is therefore highly desirable, and the emergence of the dye-sensitised photoelectrochemical solar cell is therefore not only of interest in its own right, but is also just that type of stimulus required, both to motivate advances in solid state devices, and also as a verification that alternative procedures are possible.

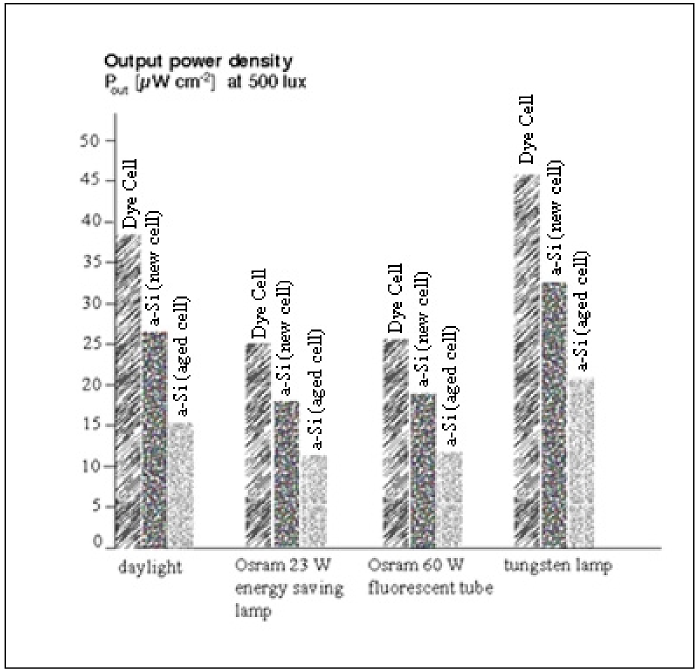


Fig. 15: Comparison of power outputs of a dye-sensitised nanocrystalline photoelectrochemical cell and of a-Si devices, new and aged, under typical indoor illumination from natural or artificial sources.

The use of dye-sensitised semiconductors has a long development history, in parallel for image and information storage through photography and now as an energy conversion technology through applied photochemistry to rival the established solid state devices. The photoelectrochemical system, and the related dye-sensitised heterojunction. In some aspects the various solar energy conversion devices may be regarded as having complementary advantages, so that market possibilities specific to the sensitised systems can be expected to emerge. After a decade of gestation, therefore, the sensitised cell is now approaching technical maturity, so commitment to production is now more a question of commercial judgement, not technical limitation.

8. Acknowledgements

It is evident that the development of a new technical concept is a team effort, here involving specialisations from ceramic thin film processing to organometallic synthesis. Many of the collaborators in this effort are cited in the references below. Their efforts are appreciated. Research and development are impossible without resources and institutional support.The Swiss Federal Office of Energy funded the initial work on this concept; thereafter several industries have shown their confidence in its potential by licensing the relevant patents. International interest is reflected by the engagement of the European Office of Aerospace Research and Development, Air Force Office of Scientific Research, and Materials and Manufacturing Directorate, United States Air Force Research Laboratory, and of the European Union within Framework Programme 5 in association with other research institutes and industry.

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