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Principles and Applications of Dye Sensitized Nanocrystalline Solar Cells (DSC)

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Abstract: At present dye-sensitised photosystems provide the only technically and economically credible alternative to the conventional and established solid state photovoltaic devices. Optical absorption by an electroactive dye and charge separation on the semiconductor take place on distinct sites within these photovoltaic cells, and in contrast to the solid state junction cell these are majority-carrier devices. In consequence the oppositely charged mobile carriers are restricted to separate phases and conventional recombination losses are therefore significantly inhibited. Also as a consequence, device photoconversion efficiency is maintained to low light levels. Various configurations of the dye-sensitised concept are under investigation, including electrochemical and heterojunction variants.

Keywords: Dye; Sensitization; Photoelectrochemistry; Titanium Dioxide.

Basic Concepts

While the concept has stimulated significant interest among electrochemists and photochemists, the operating principle of the dye-sensitized solar cell is less familiar to solid-state photovoltaic specialists. However, at the present state of its development and with growing awareness in the solar energy field in general, it was useful to review the basic concepts for that wider community on the occasion of PVSEC 14, Bangkok, January 2004. Solid state photovoltaic devices require a non-ohmic contact between two phases with different conduction mechanisms. A metal contact to a semiconductor can provide a Schottky barrier, while semiconductor layers with opposite carrier polarity in contact provide a p-n junction device. The excitation of the charge carrier pair follows on the absorption of a photon by the semiconductor, the energy of the photon being greater than the bandgap. Then the interfaces serve to separate the charge carriers, electrons and holes, so that a potential difference is developed and a current flows in an external circuit. In these devices, the materials are solids and the conduction is by electronic processes. These solid-state semiconductor based devices dominate photovoltaic science and technology. However, it should be remembered that the first observation of the photovoltaic effect by A.-E. Becquerel (1839) was in fact at a solid-liquid interface, with a photoelectrode contacting a liquid electrolyte in a photoelectrochemical cell (1). Nonetheless, intensive research over the past two decades has led to an inescapable conclusion: a relatively narrow bandgap, compatible with the photoconversion of visible light, is indicative of weaker chemical bonding in the semiconductor. It is therefore liable to photocorrosion which is incompatible with a stable extended lifetime as an energy conversion device. The resolution of this dilemma lies in the separation of light absorption and charge separation functions, by sub-bandgap sensitization of the semiconductor with an electroactive dye. A wide bandgap, intrinsically stable semiconductor, such as titanium dioxide with its bandgap of 3.1 eV, and which therefore normally exhibits a photovoltaic response only under ultraviolet irradiation, can then photorespond to visible light of wavelength 400 – 750 nm, or 1.6 – 3.0 eV photons. More recently other contacting phases as alternatives to electrolytes have come under investigation, particularly organic charge transport materials. Such devices however are more closely related to heterojunctions with sensitization than to purely electrochemical systems.

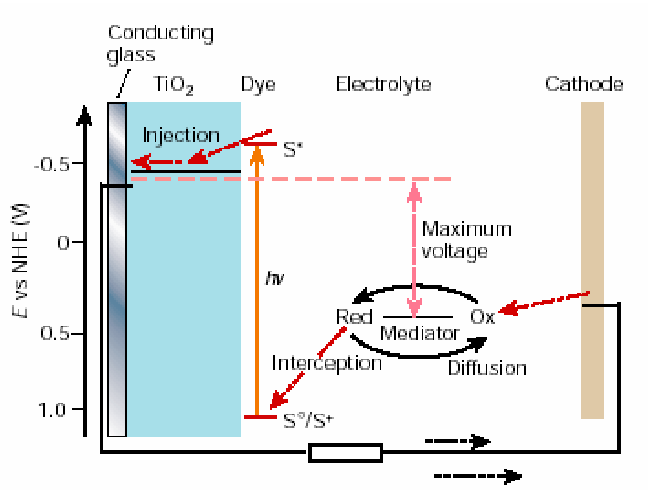
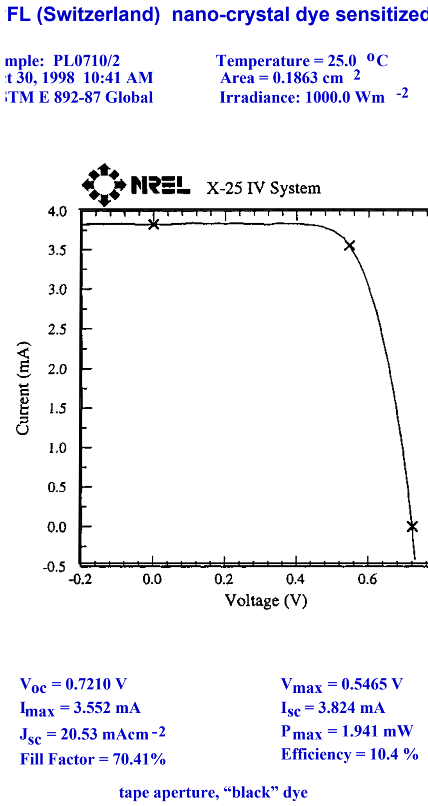


Figure 1. Schematic of operation of the dye-sensitized electrochemical photovoltaic cell. The photoanode, made of a mesoporous dye-sensitized semiconductor, receives electrons from the photo-excited dye which is thereby oxidized, and which in turn oxidizes the mediator, a redox species dissolved in the electrolyte. The mediator is regenerated by reduction at the cathode by the electrons circulated through the external circuit.

Photoelectrochemical Cell Components

The sensitization principle has been known in photoelectrochemistry for over a century (2), and has been applied in photography to secure wide-spectrum response, at first in panchromatic black-and-white emulsions, and more recently with spectrally selective dyes in colour photography (3). The work of Gerischer and Tributsch (4,5) on ZnO, definitively established the mechanism of dye sensitization and indicated its significance for photoelectrochemistry by finally rendering compatible effective wideband visible spectral absorption with the stability of an semiconductor substrate, otherwise sensitive only to ultraviolet. It is now evident that the process involves the excitation of the dye from its charge-neutral ground state to an excited state by the absorption of the energy of a photon, followed by relaxation through electron loss to the semiconductor substrate. The dye is left as a surface-adsorbed cation. This process is presented schematically in Figure 1, where it is associated with neutralisation of the dye cation by reaction with a redox species in the contacting electrolyte, which in turn recovers an electron from a counterelectrode, thereby constituting a closed regenerative cycle for the conversion of incident light into an electric current. The standard redox system is the iodide/tri-iodide couple, I^-/I_3^-. This regenerative photoelectrochemical device is evidently functionally equivalent to a conventional solid-state photovoltaic cell. However, as only a monomolecular adsorbed film of the sensitizing dye can transfer charge to the substrate, the original sensitized devices had low optical absorption, and therefore low photovoltaic efficiency. It remained therefore to associate the dye with a nanostructured semiconductor, so that the active interface area for light absorption and charge transfer greatly exceeded the projected geometrical area of the surface and gave the required opacity and light absorption, to provide a device capable of challenging the efficiency of its solid-state counterpart. Since the first presentation of this device (6), further development work has enabled these dye-sensitized cells to reach a white-light conversion efficiency exceeding 10% (Fig.2). That such a performance is attainable with a nanostructured semiconductor is due to the ultra-fast kinetics of electron injection from the excited dye into the solid. That separation of charge carriers, associated with the majority carrier nature of the device where the electrons enter an n-type material, strongly inhibits charge carrier recombination losses. Electrons can be lost only through recapture by the dye cation or by the redox electrolyte after crossing a phase boundary – an inherently slow process.



FL (Switzerland) nano-crystal dye sensitized cell

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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

Figure 2. Certified i/V characteristic under simulated sunlight, of a dye-sensitized photo-electrochemical cell, showing a conversion efficiency > 10%. The functional equivalence to a conventional solid-state cell is evident.

Device Optimization

It is evident that to achieve this level of photovoltaic performance and maintain it over an adequate in-service life requires optimization of each component in the system and attention to their synergies. Of particular importance is the choice of a suitable electroactive dye; in this aspect the development was inspired by the natural prototypes, the porphyrins and the chlorophyll molecule with its magnesium ion within a nitrogen "cage" in particular (7). As the basis for photosynthesis in plants, chlorophyll requires a photoexcited state attainable by the absorption of photons widely across the visible spectrum, exactly as does a photosensitizing dye. The energy level of the excited state, or LUMO - lowest unoccupied molecular orbital - must lie higher than the conduction band edge of the semiconductor, so that an electron can be injected during the relaxation process. For optimum absorption of white light, therefore, the HOMO – highest occupied molecular level – should be about 1.5 eV lower. In terms of photoexcitation, the HOMO-LUMO gap is completely analogous to the bandgap in the energetics of a semiconductor.

An appropriate molecular structure for the sensitization of a titanium dioxide semiconductor had been identified already (8) by Clark and Suttin, using a ruthenium tris-bipyridyl complex. By substitution of carboxylic groups on the pyridyl rings, chemisorption of the molecule to a titanium dioxide surface can by enhanced, producing a stable photoanode. However with this sensitizer, the HOMO-LUMO gap is about

2.0 eV, and as a result the photovoltaic response is limited above wavelengths of 600 nm., as shown in Figure 3 (curve RuL_3; L = dicarboxylbipyridyl, or dcbpy). With detailed molecular engineering, the electronic structure of the molecule was modified to raise the HOMO level and thereby extend the response towards the red end of the spectrum. Figure 3 presents this progress, first using cyanide (CN) and later thiocyanide (SCN) substituents. Ultimately a "black dye", absorbing across the whole visible spectrum and providing a panchromatic response, was evolved by associating the ruthenium "core" with a terpyridyl complex, and three spectrum-modifying thiocyanide groups.

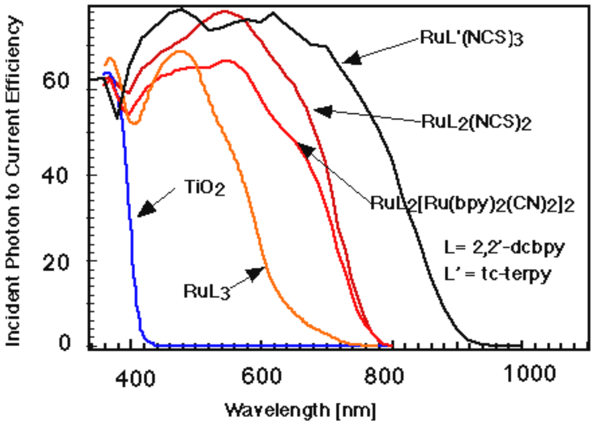

Figure 3. The photocurrent action spectrum of a cell containing various sensitizers, where the incident photon to current conversion efficiency is plotted as a function of wavelength.

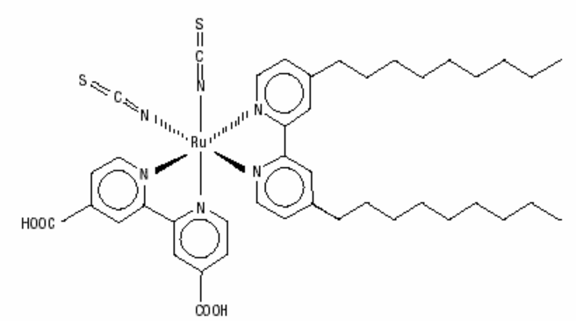

Figure 4. Structure of the Z-907 amphiphilic dye (*cis*-Ru(H2dcbpy)(dnbpy)(NCS)2, where the ligand H2dcbpy is 4,4•-dicarboxylic acid-2, 2•-bipyridine and dnbpy is 4,4•-dinonyl-2,2•-bipyridine) (10).

Concerning the electrolyte, a compromise has in the past been required between viscosity, which simplifies the cell sealing process, and ionic mobility, since the redox cations must diffuse to the counter-electrode for the reduction reaction which maintains the regenerative characteristics of the cell. One consequence of low ionic mobility is a limitation of the cell efficiency under high intensity illumination, such as AM1.5 daylight, indicated by a reduced fill factor. The characteristics of the electrolyte must also accommodate the wide range of temperatures to which the cell is exposed in normal outdoor service. Cell stability requires an insensitivity to impurities such as traces of water in the organic solvent supporting the redox electrolyte. Recent developments therefore have included a gelation additive to the electrolyte, associated with a modified dye structure to optimise the cell characteristics in regard to stability and thermal tolerance (10). As an example of dye molecular engineering, the molecule (laboratory code Z-907) shown in Fig. 4 has of course the two bipyridyl ligands bonded to ruthenium to establish photosensitivity; two thiocyanide ligands to modify the spectral response; two carboxyl groups to chemisorb to the semiconductor oxide surface; and finally two hydrocarbon chains to present a hydrophobic surface to the electrolyte, thereby rejecting contaminant water. The consequence of this structure is the self-assembly of a monomolecular dye layer of specific orientation to provide the required physical properties, uniformly chemisorbed on the nanostructured semiconductor surface.

A similar development process and attention to detail was required for the semi-conductor substrate. On the transparent support – glass or polymer – a layer of transparent conducting oxide (TCO) such as indium-doped tin oxide provides the contact to the active semiconductor. In the earliest prototypes of the cell this was a fractured and fractal layer deposited by a sol-gel process. In current practice a hydrothermal process can be applied (9) for grain ripening of nanocrystalline particles in the anatase structure, as shown in Figure 5.

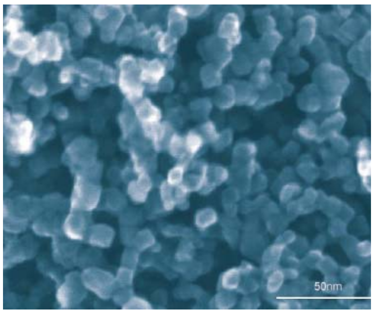

Figure 5. Scanning electron micrograph of the surface of a mesoporous anatase film prepared from a hydrothermally processed TiO_2 colloid. The exposed surface planes have mainly {101} orientation.

Sensitized Heterojunctions

The success of gelled electrolytes is an encouragement to proceed further in the search for alternative contacting charge-transport phases to substitute the electrolyte in a sensitized photovoltaic system. One such alternative is to be found in the organic conductors, now the object of considerable research effort. With liquid or gel electrolytes, of course, the formation of a junction intimate on the molecular scale between the sensitized surface and the contacting conductor is spontaneous. Formation of a similar contact between two interpenetrating solid phases presents obvious difficulties. There is an advantage if the contacting material is a p-type semiconductor; in attempts to fabricate sensitized Schottky junctions there is the possibility of an ohmic contact with the TCO layer, short-circuiting the cell. The first devices of this type used inorganic *p*-type semiconductors, for example CuI (12) or CuSCN (13), as hole conductors replacing the redox electrolyte. Conversion efficiencies only of the order of 1% have been reached with such cells. The lack of photostability of the Cu(I) compounds and the difficulty of realizing a good contact between the two interpenetrating nanostructured inorganic materials presented considerable practical challenges.

Organic charge-transport materials have advantages in this respect. An amorphous organic p-type material, or hole conductor with positive charge mobility characteristics, can be introduced into the nanostructured TiO2 film by a simple spin-coating process and readily adapts its form to the highly irregular oxide surface. Cells based on a spirobisfluorene-connected arylamine compound filling the pores of a dye-sensitized nanocrystalline TiO_2 film have reached a conversion efficiency of 2.56% at full sunlight (14). The high open-circuit voltage of these devices, exceeding 900 mV, is particularly noteworthy and promises further substantial improvements in performance. In general, dye-sensitized heterojunction cells offer great flexibility because the light absorber and charge-transport material can be selected independently to obtain optimal solar spectral absorption and high photovoltage. The great advantage of such a configuration is that the charge carriers are generated by the dye precisely at the site of the junction where the electric field is greatest, enhancing charge separation.

Applications

It is very satisfactory to note that the dye-sensitized device is now emerging from the research laboratory and that pilot production and field evaluation can be reported. Figure 6a shows an installation on the roof of the CSIRO (Commonwealth Scientific and Industrial Research Organisation) building, Australia (Courtesy of Sustainable Technologies International Ltd.). At the same time, cells on flexible substrates appropriate for application in consumer goods and under low-level illumination are emerging from industrial development laboratories are realizing the "artificial leaf" in practice, Figure 6b (Hitachi-Maxell, Japan).

(a) (b)

Figure 6. (a) large-area DSC installation, CSIRO Australia.
(b) artificial leaf, Hitachi-Maxell, Japan.

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References

[1] Becquerel (Edmond), A. E. (1839) Memoire sur les effets électriques produits sous l'influence des rayons solaires, *C.R.Acad.Sci.,* Paris, **9**, 561 – 567.

[2] Moser, J. (1887) Notiz über Verstärkung photo-elektrischer Ströme durch optischer Sensibilierung, *Monatsh.Chem.,* **8**, pp.373.

[3] West W. (1974) First hundred years of spectral sensitisation, *Photogr.Sci.Eng.*, **18**, 35 - 48.

[4] Gerischer, H. and Tributsch, H. (1968) Electrochemische Untersuchungen zur spectraleu sensibilisierung von ZnO-Einkristallen, Ber. Bunsenges, *Phys. Chem.,* **72**, 437 - 445.

[5] Tributsch, H. (1968) Ph.D. thesis, Techn. Hochschule München, Germany.

[6] O'Regan, B. & Grätzel, M. (1991) A low-cost, high efficiency solar cell based on dye-sensitized colloidal TiO_2films, *Nature*, **353,**737–740.

[7] Grätzel, M. (1999) The artificial leaf - bio-mimetic photocatalysis, *Cattech,* **3,** 3–17.

[8] Clark, W. D. K. and Suttin, N. (1977) Spectral sensitisation of n-type titanium dioxide by polypyridine-ruthenium complexes, *J. Amer. Chem. Soc*, **99** 4676 – 4682.

[9] Brooks, K. G., Burnside, S. D., Shklover, V., Comte, P., Arendse, F., McEvoy, A. J., and Grätzel, M. (1999) Mesoporous nanocrystalline thin films for electrochemical applications, *Proc. Am. Ceram. Soc., Indianapolis*, U.S.A. April 1999 / Electrochem. Mater. Devices 115 – 122.

[11] Wang, P., Zakeeruddin, S. M., Moser, J. E., Nazeeruddin, M. K., Sekiguchi, T. and Grätzel, M. (2003) A stable quasi-solid-state solar cell with an amphiphilic ruthenium sensitizer and polymer get electrolyte, *Nature Mater.,* **2**, 402-407.

[12] Tennakone, K., Kumara, G. R. R. A., Kumara-singhe, A. R., Wijayantha, K. G. U. and Sirimanne, P. M. (1995) A dye-sensitized nano-porous solid-state photovoltaic cell, *Semicond. Sci. Technol.*, **10**, 1689–1693.

[13] O'Regan, B. and Schwarz, D. T. Large enhancement in photocurrent efficiency caused by UV illumination of dye sensitized heterojunctions. *Chem. Mater.,* **10,** 1501–1509.

[14] Krüger, J. Bach, U. and Grätzel, M. (2001) High efficiency solid-state photovoltaic device due to inhibition of interface charge recombination. *Appl. Phys. Lett.*, **79**, 2085–2087.