Highly Efficient Nanocrystalline Photovoltaic Devices

CHARGE TRANSFER SENSITISERS BASED ON RUTHENIUM AND OSMIUM ACHIEVE OUTSTANDING PERFORMANCE

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A new molecular photovoltaic system for solar light harvesting and conversion to electricity has been developed. It is based on the spectral sensitisation of a nanocrystalline semiconductor film by transition metal complexes. The film consists of nanometre-sized colloidal titanium dioxide particles sintered together to allow for charge carrier transport. Ruthenium and osmium based sensitisers have so far achieved the best performance both from the efficiency as well as the stability point of view. Carboxylated polypyridyl complexes of these two metals give extraordinary efficiencies for the conversion of incident photons into electric current, exceeding 90 per cent within the wavelength range of their absorption band. The outstanding performance of cis-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) is unmatched by any other known sensitiser. The present paper discusses the underlying physical principles of these astonishing findings. Exploiting this discovery, we have developed a low-cost photovoltaic cell whose overall light to electric energy conversion yield is 10 per cent under direct (AM1.5) solar irradiation. For the first time a device based on a simple molecular light absorber is attaining a conversion efficiency commensurate with that of silicon based photovoltaic cells, but at a much lower cost.

In a conventional *p-n* junction photovoltaic cell made, for example, from silicon, the semiconductor assumes two roles at the same time: it harvests the incident sunlight and conducts the charge carriers produced under light excitation. In order to function with a good efficiency the photons have to be absorbed close to the *p-n* interface. Electron-hole pairs produced away from the junction must diffuse to the *p-n* contact where the local electrostatic field separates the charges. In order to avoid charge carrier recombination during the diffusion the concentration of defects in the solid must be small. This imposes severe requirements on the purity of the semiconductor material, rendering solid state devices of the conventional type very expensive. Molecular photovoltaic systems separate the functions of light absorption and carrier transport. Light harvesting is carried out by a sensitiser which initiates electron transfer events leading to charge separate. This renders unnecessary the use of expensive solid state components in the system. While being simple from the conceptual point of view, the practical implementation of such devices must overcome formidable obstacles if the goals are to develop molecular systems which convert sunlight to electricity at an efficiency comparable to that of silicon cells, and meet the stability criteria for practical applications.

Our success in bringing this project close to commercial maturity owes much to the recent progress in molecular engineering of stable and efficient charge transfer sensitisers based on the

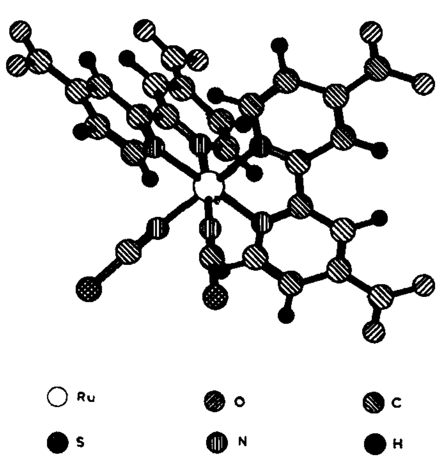

Fig. 1 Structure of *cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium(II), (I), which shows outstanding properties as a charge transfer sensitiser for nanocrystalline titanium dioxide films

platinum metals of ruthenium and osmium. The approach that we have taken will now be outlined in more detail.

Light Harvesting by Platinum Metal Complexes

The fundamental processes involved in photovoltaic conversion are:

- the absorption of sunlight
- the generation of electrical charges by light and
- the collection of charge carriers to produce electricity.

In any case, the components of the synthetic system must be selected to satisfy the high stability requirements needed for practical applications. A photovoltaic system must remain serviceable for 20 years without significant loss of performance. One of the most remarkable achievements of research in inorganic chemistry during the last two decades has been the development of a great variety of platinum metal complexes (1) mainly of the elements rhodium, osmium and ruthenium, and also rhenium, many of which are very stable and display good absorption in visible light. Our work has focused on the molecular engineering of suitable ruthenium and osmium compounds which exhibit the most promising properties so far. Thus we have developed bis(bipyridyl)Ru(II) complexes which have the general formula *cis*-X_2bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II), where X = Cl^-, Br^-, I^-, CN^-, and SCN^-. We have performed a systematic study of their luminescence, visible light absorption, electrochemical and photoredox behaviour (2). Among these compounds, *cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II), (I), displays outstanding performance as a solar light absorber and charge-transfer sensitiser, unmatched by any other dyestuff known so far. Its broad range of visible light absorption and relatively long-lived excited state render it an attractive sensitiser for homogeneous and heterogeneous redox reactions. The structural features of this complex are shown in Figure 1, and salient photophysical features of the *cis*-X_2bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II)-type charge transfer sensitisers have also been documented (2).

For light harvesting by sensitisers attached as a monolayer on a flat surface, there is the notorious problem of insufficient light absorption. On a smooth surface the monolayer absorbs less than 1 per cent of the incident light in the wavelength range of maximum absorption. One could naturally think, then, of depositing several molecular layers of sensitiser on the semiconductor in order to increase the light absorption. This would however be a mistaken tactic, since the outer dye layers would act only as a light filter, with no contribution to electrical current generation. The application of only a monomolecular film of sensitiser is therefore unavoidable.

We found a solution to the problem of light absorption through such extremely thin molecular layers by the use of nanocrystalline systems. It is possible, using the sol-gel method, to produce transparent films consisting of colloidal titanium dioxide particles with diameters of 10 to 30 nm. Electronic contact between the particles is produced by a brief sintering at about 500°C. A nanoporous structure with a very high internal surface area is thereby formed. For example, the effective surface of a 8 μm thick layer of such a colloidal structure is about 720 times greater than that of a smooth film. On the geometric projection of such a surface a sensitiser concentration of $\Gamma = 1.2 \times 10^{-7}$ moles/cm^2 is reached when nanocrystalline films are used. The optical density:

$$\mathrm{OD}(\lambda) = \Gamma \times \varepsilon(\lambda) \qquad \text{[i]}$$

calculated for this coating level is 1.68 using $\varepsilon = 1.4 \times 10^7$ cm^2/mole for the extinction coefficient, which is the value obtained for complex (I) at 536 nm. The light harvesting efficiency of the device, LHE(λ), is then given by:

$$\mathrm{LHE}(\lambda) = 1 - 10^{-\mathrm{OD}} \qquad \text{[ii]}$$

With an optical density of 1.68, 98 per cent of the light is absorbed by the film at the wavelength of the absorption maximum of the sensitiser. When derivatised with *cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxlate) ruthenium(II) the light harvesting capacity of such films becomes superior to that of amorphous silicon. Nature, in fact, uses a similar means of absorption enhancement by stacking the chlorophyll containing thylakoid membranes of the chloroplasts to form the grana structures.

Light Induced Charge Separation

The role of the ruthenium complex is the same as that of chlorophyll in the green leaf; it must absorb the incident sunlight and exploit the light energy to induce a vectorial electron transfer reaction. In place of the biological lipid membrane a titanium dioxide film is employed. Apart from acting as a support for the sensitiser, it also functions as the electron acceptor and electronic conductor. The electrons injected by the sensitiser travel across the nanocrystalline film to the conducting glass support serving as current collector. The driving force necessary for the rapid vectorial charge displacement is small, corresponding to about 0.1 eV, which is required to drive the electron injection process.

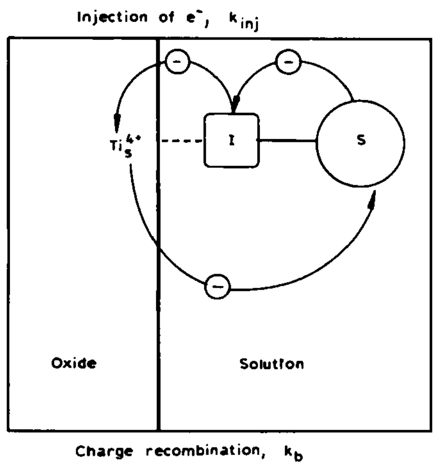

Fig. 2 Photoinduced charge separation on the surface of titanium dioxide, k_{inj} and k_b represent the rate constants for electron injection and recombination, respectively. S is the sensitiser and I is an interlocking group

The efficiency of light induced charge separation at the oxide semiconductor surface is expressed by the quantum yield of charge injection (ϕ_{inj}). This represents the fraction of the absorbed photons converted into conduction band electrons. Charge injection from the electronically excited sensitiser into the semiconductor is in competition with other radiative or radiationless deactivation channels. Taking the sum of the rate constants of these non-productive channels together as k_{eff} results in:

$$(\phi_{inj}) = k_{inj}/(k_{eff} + k_{inj}) \qquad \text{[iii]}$$

One should remain aware that the deactivation of the electronically excited state of the sensitiser is generally very rapid. Typical k_{eff} values lie in the range from 10^6 to 10^9 /s. To achieve a good quantum yield the rate constant for charge injection, k_{inj}, should be at least 100 times higher than k_{eff}. This means that injection rates which exceed 10^{11}/s must be attained. In actual fact, in recent years sensitisers have been developed that satisfy these requirements. These dyes should incorporate functional groups ("interlocking groups") as, for example, carboxylates or other chelating groups, which besides bonding to the surface of the titanium dioxide, also effect, as is illustrated in Figure 2, an enhanced electronic coupling of the sensitiser with the

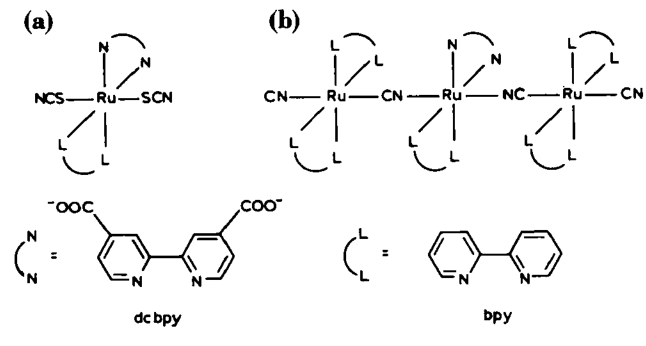

Fig. 3 Ruthenium-based charge transfer sensitiser complexes used to convert light to electricity with nanocrystalline titanium dioxide films: (a) mononuclear $Ru(dcbpy)_2(SCN)_2$; (b) polynuclear $\{[Ru(bpy)_2(CN)]_2Ru(dcbpy)_2P(CN)_2\}$. Photosensitisers should be able to tune spectral, redox and photophysical properties, (requiring light harvesting and efficient charge injection) and they have surface chelation needs

conduction band of the titanium dioxide semiconductor.

Very promising results have so far been obtained with ruthenium complexes where at least one of the ligands was 4,4′-dicarboxy-2,2′-bipyridyl. Examples are shown in Figure 3. The carboxylates serve to attach the ruthenium complex to the surface of the oxide and to establish good electronic coupling between the π^* orbital of the electronically excited complex and the 3*d* wavefunction manifold of the titanium dioxide film, see Figure 4. The substitution of the bipyridyl with the carboxylate groups also lowers the energy of the π^* orbital of the ligand. Since the electronic transition is of MLCT (metal to ligand charge transfer) character, this serves to channel the excitation energy into the correct ligand, that is the one from which electron injection into the semiconductor takes place. With molecules like these, the charge injection is in the picosecond or even femtosecond time domain (4).

As the last step in the conversion of light into electrical current, a complete charge separation must be achieved. On thermodynamic grounds, the preferred process for the electron injected into the conduction band of the oxide film is recapture by the sensitiser cation. This reaction is obviously undesirable, since instead of generating electrical current it merely generates heat. An important kinetic parameter for the characterisation of the recombination rate is the rate constant, k_b. It is of great interest to develop sensitiser systems for which the value of k_{inj} is high and that of k_b low. Fortunately, for the transition metal complexes we use, the ratio of the injection rate to the recapture rate k_{inj}/k_b is greater than 10^3, and in some cases it exceeds even one million. The reason for this behaviour is that the molecular orbitals involved in the back reaction overlap less favourably with the wavefunction of the conduction band electron than those involved in the forward process. For example, for *cis*-dithiocyanatobis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) bound to the nanocrystalline oxide film, the injecting orbital is the π^* wavefunction of the carboxylated bipyridyl ligand, since the excited state of this sensitiser has a metal to ligand charge transfer character. The carboxylate groups interact directly with the surface titanium(IV) ions resulting in good electronic coupling between the π^* wavefunction and the 3*d* orbital manifold of the conduction band of the titanium dioxide. As a result, electron injection from the excited sensitiser into the semiconductor membrane is an extremely rapid process occurring in less than a picosecond, see Figure 4.

By contrast, the back reaction of the electrons with the oxidised ruthenium complex involves a *d*-orbital, localised on the ruthenium metal, having only a small electronic overlap with the titanium dioxide conduction band. The spatial contraction of the wavefunction upon oxidation of the ruthenium(II) to the ruthenium(III) state further reduces this electronic coupling. This, together with the fact that the driving force for the back electron transfer is large enough to place it in the inverted Marcus domain explains the relatively slow backward electron transfer which, typically, is in the microsecond time domain.

Thus, in analogy to natural photosynthesis, light-induced charge separation is achieved on kinetic grounds, the forward electron transfer being orders of magnitude faster than the back reaction. As a consequence, the presence of a local electrostatic field is not required to achieve good efficiencies for the process. This distinguishes the nanocrystalline devices from conventional photovoltaic cells (5–9), in that the successful operation of the latter is contingent upon the presence of a potential gradient within the *p/n* junction.

Photovoltaic Performance of Ruthenium Based Sensitisers

In our nanocrystalline cell, the electrons injected into the semiconductor from the excited transition metal complex are collected as an electrical current and result in photovoltaic conversion of light energy. The incident monochromatic photon to current conversion efficiency is given by the equation:

$$\eta_i(\lambda) = \mathrm{LHE}(\lambda) \times \phi_{inj} \times \eta_e \qquad [iv]$$

where $\eta_i(\lambda)$ expresses the ratio of the measured electrical current to the incident photon flux for a given wavelength, while η_e is the charge collection efficiency. Using ruthenium or osmium complexes of the type shown in Figure 3, in conjunction with nanocrystalline titanium dioxide films, solar cells are now available for which all three factors in Equation [iv] are close to unity (2, 10–14). Thereupon, within the wavelength range of the absorption band of the sensitisers a quantitative conversion of incident photons to electrons is obtained.

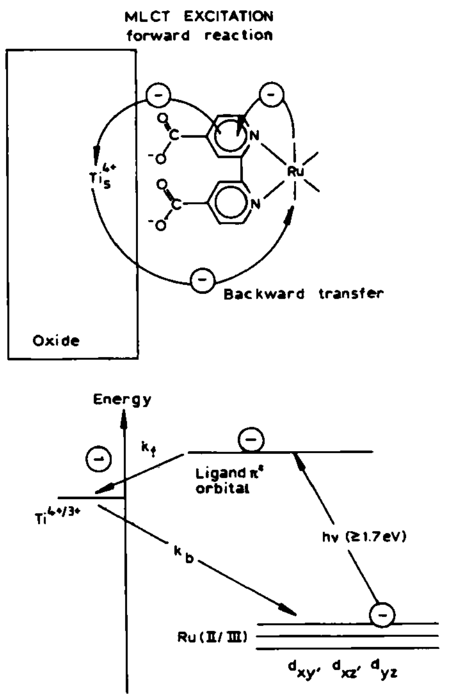

Fig. 4 The photoinduced heterogeneous electron transfer cycle with the molecular orbital diagram for Ru complexes anchored to the titanium dioxide surface by a carboxylated bipyridyl ligand. The visible light absorption of these types of complexes is a metal-to-ligand charge transfer transition. The carboxylate groups are directly co-ordinated to the surface Ti ions, producing intimate electronic contact between sensitiser and semiconductor. There is spatial contraction of the *d* orbitals upon oxidation from Ru(II) to Ru(III)

A graph which presents the monochromatic current output as a function of the wavelength of the incident light is known as a "photocurrent action spectrum", and Figure 5 shows such action spectra for three ruthenium complexes, illustrating the very high efficiency of current generation, exceeding 75 per cent obtained with these complexes. When corrected for the inevitable reflection and absorption losses in the conducting glass serving to support the nanocrystalline film, yields of practically 100 per cent are obtained. Historically, RuL_3 (L = 2,2′-bipyridyl-4,4′-dicarboxylate) was the first efficient and stable charge transfer sensitiser to be used in conjunction with high surface area titanium dioxide films (10). In a long term experiment carried out during 1988 it sustained 9 months of intense illumination without loss of performance. However, the visible light absorption of this sensitiser is insufficient for solar light conversion. A large improvement

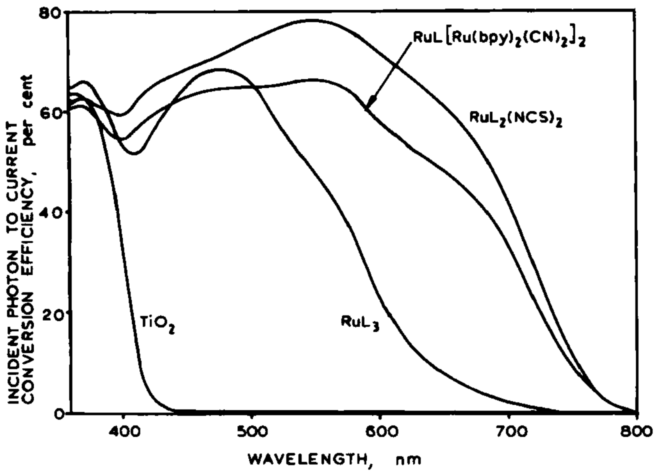

Fig. 5 A photocurrent action spectrum obtained from three different ruthenium based sensitisers attached to the nanocrystalline titanium dioxide film. The blank spectrum obtained with the bare titanium dioxide surface is shown for comparison. The incident photon to current conversion efficiency is plotted as a function of the wavelength of the exciting light

in the harvesting of light is achieved with the trinuclear complex of ruthenium (11, 16, 17) whose two peripheral ruthenium moieties were designed to serve as antennas (16). However, the most successful charge transfer sensitiser investigated so far is without doubt *cis*-dithiocyanatobis(2,2′-bipyridyl-4,4′-dicarboxylate)-ruthenium(II). This achieves close to quantitative photon to electron conversion over the whole visible range (2). Even at 700 nm the current generation is still 40 to 50 per cent efficient.

The photovoltage of our cell represents the difference between the Fermi level of titanium dioxide under illumination and the redox potential of the electrolyte, see Figure 6. Using the triiodide/iodide redox couple in *N*-methyloxazolidinone solution, under full sunlight an open-circuit cell voltage of 0.7 to 0.9 V can be measured. Under a 1000-fold lower intensity the cell voltage is about 200 mV

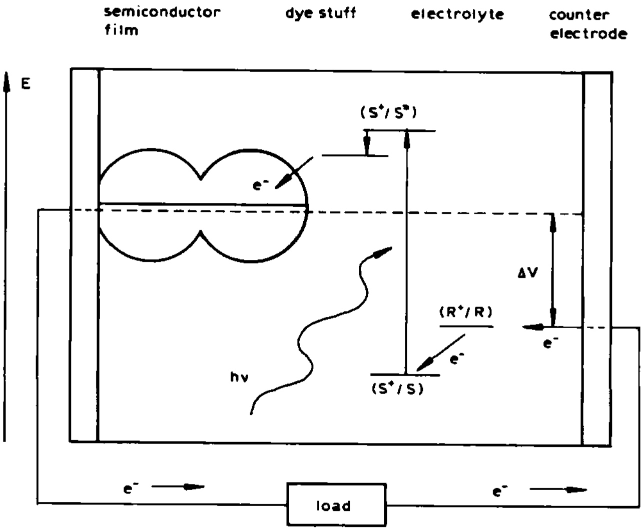

Fig. 6 Representation of the principle of the new photovoltaic cell showing the electron energy level in the different phases. The cell voltage observed under illumination corresponds to the difference in the quasi-Fermi level of the titanium dioxide under illumination and the electrochemical potential of the electrolyte. The latter is equal to the Nernst potential of the redox couple (R/R⁻) used to mediate charge transfer between the electrodes

smaller, a relative change of cell voltage of only 20 to 30 per cent. For the conventional silicon cell the cell voltage decreases by a factor of 3 for a comparable change of light intensity, showing that the photovoltage of our cells is significantly less sensitive to variations in light intensity than are conventional photovoltaic devices. This is an important advantage for the application of the nanocrystalline cell in consumer electronic devices. At this stage industrial companies are already involved in production of such cells which will reach the market quite soon.

The overall efficiency, η_{global}, of the photovoltaic cell can easily be calculated from the integral photocurrent density (i_{ph}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (ff) and the intensity of the incident light (I_s).

$$\eta_{global} = i_{ph} \times V_{oc} \times ff/I_s \qquad (v)$$

In Figure 7, the current-voltage characteristic of a nanocrystalline cell sensitised by (I) is shown. The photocurrent measured at 96.4 mW/cm² of simulated solar intensity was 18.3 mA/cm², the open circuit voltage was 0.72 V, and the fill factor was 0.73, yielding a value of 10 per cent for the overall efficiency of the cell.

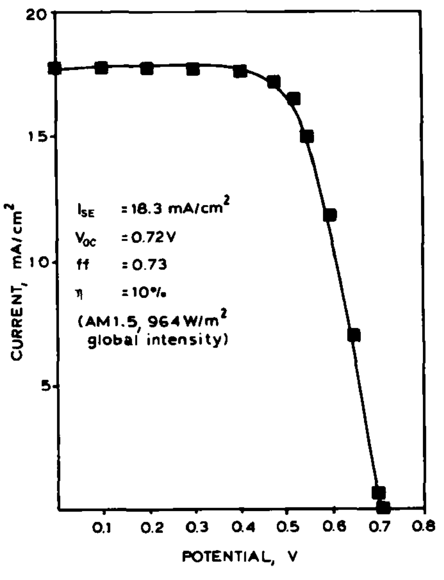

Fig. 7 Photocurrent voltage curve for a nanocrystalline photovoltaic cell which is based on the complex *cis*-Ru(2,2′-bipyridyl-4,4′-dicarboxylate)(SCN)$_2$ as sensitiser

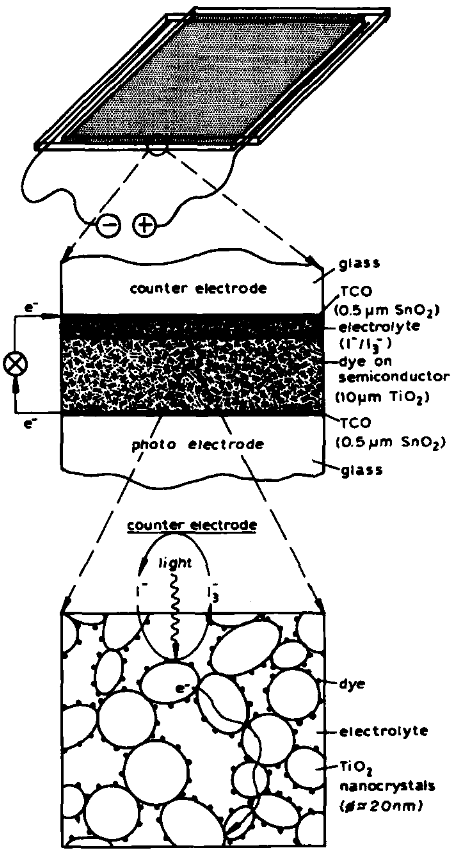

Fig. 8 Layout of a nanocrystalline solar cell. The transparent dye derivatised titanium dioxide film is sandwiched between two conducting glass electrodes. It harvests light from both front and back sides. TCO is a transparent conducting oxide coating layer which contains a highly active, stable platinum electrocatalyst

Practical Development of Nanocrystalline Solar Cells

Meanwhile, the development and testing of the first cell module for practical applications has begun. The layout of the module is presented in Figure 8. The cell consists of two glass plates which are coated with a transparent conducting oxide (TCO) layer. The nanocrystalline titanium dioxide film deposited on one plate functions as a light trap. Visible light is absorbed by a monomolecular layer of the ruthenium complex which functions as the charge transfer sensitiser. On illumination, this injects an electron into the titanium dioxide conduction band. The electrons pass over the collector electrode into the external current where they perform work. They are then returned to the cell via the counter electrode. The sensitiser film is separated from the counter electrode by the electrolyte. In the electrolyte there is a redox couple, for example triiodide/iodide, whose role is to transport electrons from the counter electrode to the sensitiser layer, which has been left positively charged as a result of the electron injection. The counter electrode is made of glass covered with a transparent conducting oxide (TCO) layer that serves as a current collector. A small amount of platinum (5–10 μg/cm^2) is deposited onto the TCO to catalyse the cathodic reduction of triiodide to iodide.

By developing a new mode of platinum deposition we have engineered an extremely active electrocatalyst, which attains exchange current densities of more than 0.1 A/cm^2 at a platinum loading below 0.1 g/m^2. Furthermore this electrocatalyst is very stable and does not show long term anodic corrosion, as was seen to be the case for platinum deposits produced by conventional sputtering or galvanic methods. These favourable characteristics have allowed overvoltage losses to be minimised, thus increasing the efficiency and stability of cell operation (18).

Upon long term illumination, complex (I) sustained more than 5×10^7 redox cycles without noticeable loss of performance, which corresponds to about 10 years of continuous operation in natural sunlight. By contrast, practically all organic sensitisers tested so far have undergone photo-bleaching after less than 10^4 redox cycles. This clearly outlines the exceptionally stable operation of the newly developed ruthenium charge transfer sensitisers, which is of great advantage for the practical application of these devices. It may be argued that the presence of ruthenium renders the price of the sensitiser too high for commercial exploitation, or that there is an insufficient supply of ruthenium. However, the required amount of ruthenium is only 10^{-3} moles/m^2 of cell module surface, and corresponds to an investment of around U.S.\$ 0.07/m^2 for the noble metal. One ton of ruthenium alone incorporated into the charge transfer sensitiser (I) could provide 1 gigawatt of electrical power under full sunlight. This is more than twice the total photovoltaic capacity presently installed worldwide.

Apart from its efficiency and stability any future photovoltaic technology will be valued according to its environmental and human compatibility. There is great concern about the adverse environmental effects and acute toxicity of CdTe or $CuInSe_2$ which are being considered for practical development as thin solar cells. Such concerns are unjustified for our nanocrystalline device. Titanium dioxide is a harmless environmentally friendly material, remarkable for its very high stability; it occurs in nature as ilmenite, and is used in quantity as a white pigment and as an additive in toothpaste. Similarly ruthenium has been used without adverse health effects as an additive for bone implants.

Commercial applications will begin in the near future. Contracts for the industrialisation of these cells have been signed with the Wissenschaftspark Gelsenkirchen for modules of 100 peak watts output and higher, which it is hoped will lead to applications in the utility market. Meanwhile for consumer applications co-operation has been established with Leclanché and Glass Trösch, and the first product – a self powered bathroom scale will be marketed during the present year. In full production, a cost estimate commissioned from the Research Triangle Institute (North Carolina, U.S.A.) predicts a module cost of U.S. \$0.60, per peak watt rating.

Quite aside from its intrinsic merits as a photovoltaic device, the sensitised nanocrystalline photovoltaic device will undoubtedly promote the acceptance of alternative energy technologies, not least by setting new standards of convenience and economy for the photovoltaic industry as a whole.

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Ruthenium Clusters Breathing Carbon Monoxide

It has been noticed that catalysts constructed by building metal microframeworks on support surfaces have a different chemistry to conventionally supported catalysts. In conventional cluster catalysis the supported clusters decompose into fragments, or aggregate together into larger clusters, and while the states of such catalysts are known before and after the reaction, not much is known about them during catalysis. Additionally little is known about catalysts whose activity originates from promoters inside a metal framework, or their effects.

Therefore work has been undertaken by researchers in Japan to discover what happens in metal microframeworks during catalytic reactions involving supported ruthenium and rhodium clusters ("CO-Breathing Ruthenium and Rhodium Clusters", Y. Izumi and Y. Iwasawa, *Chemtech*, 1994, **24**, (7), 20–27). The ruthenium cluster, $(NMe_3CH_2Ph)^+(Ru_6C[CO]_{16}Me)^-$, which has a μ_6-carbido ligand inside the octahedra Ru_6 framework, was examined during ethene hydroformylation. The stability of this cluster is attributable to binding between the framework and the carbido carbon, and perhaps to metal-support interactions.

The reactions were followed by extended X-ray absorption fine structure. It was observed, when supported on basic oxides, that the metal core framework of the surface-attached ruthenium species shrank on loss of CO ligands; while expansions in the framework were induced by CO uptake. When CO was released again, either by evacuation or decreasing the CO pressure, the expanded cluster shrank. This process can be called "CO breathing". The μ_6-carbido carbon inside the cluster acted, in effect, like a central spring, making the cluster framework expand and shrink.

Also on supports, a switchover in the reaction path was observed during carbon monoxide hydrogenation as carbido carbon was inserted into the Ru_6 cluster framework, from dissociative to oxidative carbon monoxide hydrogenation, the latter having higher turnover frequencies and selectivities. Products changed from hydrocarbons and methane to methanol, dimethyl ether and formaldehyde, respectively. Electronic effects of the carbido carbon and cluster metal framework were also found, and inverse isotope effects for hydrogen, dependent on support, were observed for the supported clusters.

Two other supported rhodium and ruthenium clusters show structural chemical control by μ_6-ligands; and elements, such as carbon and nitrogen inside metal cluster frameworks behave as a new type of catalytic promoter, not interacting with reactant molecules, but affecting the catalytic properties without blocking the catalysis. These promoters also act like a central spring making the cluster flexible at the surface. This feature could be used with a wide range of main and transition metal elements.