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Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 3–14

Journal of Photochemistry and Photobiology A:Chemistry

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Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells☆

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Received 25 November 2003; received in revised form 6 February 2004; accepted 6 February 2004

Abstract

The dye-sensitized solar cell (DSC) provides a technically and economically credible alternative concept to present day p–n junction photovoltaic devices. In contrast to the conventional silicon systems, where the semiconductor assumes both the task of light absorption and charge carrier transport the two functions are separated here. Light is absorbed by a sensitizer, which is anchored to the surface of a wide band gap oxide semiconductor. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the solid. Carriers are transported in the conduction band of the semiconductor to the charge collector. The use of sensitizers having a broad absorption band in conjunction with oxide films of nanocrystalline morphology permits to harvest a large fraction of sunlight. Nearly quantitative conversion of incident photon into electric current is achieved over a large spectral range extending from the UV to the near IR region. Overall solar (standard AM 1.5) to current conversion efficiencies of 10.6% have been reached. New electrolytes based on ionic liquids have been developed that show excellent stability both under prolonged light soaking and high temperature stress. There are good prospects to produce these cells at lower cost than conventional devices. Here we present the current state of the field, and discuss the importance of mastering the interface of the mesoporous films by assisting the self-assembly of the sensitizer at the surface of the oxide nanocrystals.

Keywords: Dye-sensitized solar cell; Nanocrystalline; Sensitizer

1. Introduction

Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism. To date this field has been dominated by solid-state junction devices, usually made of silicon, and profiting from the experience and material availability resulting from the semiconductor industry. The dominance of the photovoltaic field by inorganic solid-state junction devices is now being challenged by the emergence of a third generation of cells, based, e.g. on nanocrystalline oxide and conducting polymers films. These offer the prospective of very low cost fabrication and present attractive features that facilitate market entry. It is now possible to depart completely from the classical solid-state cells which are replaced by devices based on interpenetrating network junctions [1–4]. The presence of a bulk junction having an interface with a huge area endows these systems with intriguing optoelectronic properties. In the present review, we focus our attention on solar cells that contain inorganic oxides. The phenomenal progress realized recently in the fabrication and characterization of nanocrystalline materials has opened up vast new opportunities for these systems. Contrary to expectation, devices based on interpenetrating networks of mesoscopic semiconductors have shown strikingly high conversion efficiencies, which compete with those of conventional devices. The prototype of this family of devices is the dye-sensitized solar cell (DSC), which realizes the optical absorption and the charge separation processes by the association of a sensitizer as light-absorbing material with a wide band gap semiconductor of mesoporous or nanocrystalline morphology [1,2].

2. The operation principle of the dye-sensitized nanocrystalline solar cell (DSC)

A schematic presentation of the operating principles of the DSC is given in Fig. 1. At the heart of the system is a wide band gap oxide semiconductor which is placed in con-

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☆ Dedicated to Prof. Shozo Yanagida on the occasion of his retirement.

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doi:10.1016/j.jphotochem.2004.02.023

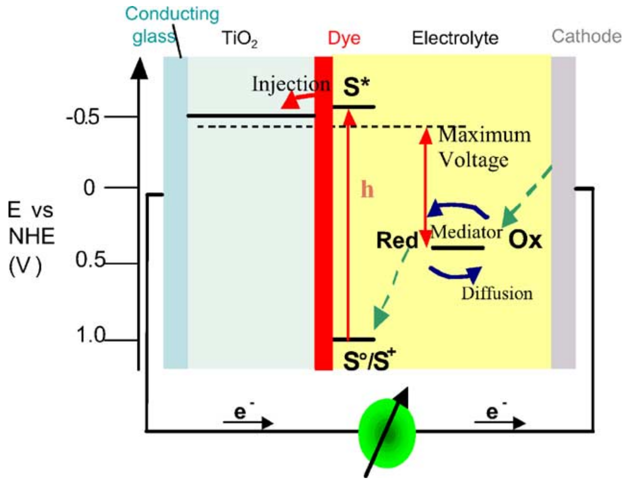

Fig. 1. Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell. Photoexcitation of the sensitizer (S) is followed by electron injection into the conduction band of an oxide semiconductor film. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter-electrode by electrons passed through the load. Potentials are referred to the normal hydrogen electrode (NHE). The open circuit voltage of the solar cell corresponds to the difference between the redox potential of the mediator and the Fermi level of the nanocrystalline film indicated with a dashed line. The energy levels drawn for the sensitizer and the redox mediator match the redox potentials of the doubly deprotonated N3 sensitizer ground state and the iodide/triiodide couple.

tact with a redox electrolyte or an organic hole conductor. The material of choice has been TiO_2 (anatase) although alternative wide band gap oxides such as ZnO [5], and Nb_2O_5 [6] have also been investigated. Attached to the surface of the nanocrystalline film is a monolayer of the charge transfer dye. Photo-excitation of the latter results in the injection of an electron into the conduction band of the oxide. The original state of the dye is subsequently restored by electron donation from the electrolyte, usually an organic solvent containing redox system, such as the iodide/triiodide couple. The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The iodide is regenerated in turn by the reduction of triiodide at the counter-electrode the circuit being completed via electron migration through the external load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte. Overall the device generates electric power from light without suffering any permanent chemical transformation.

Fig. 2 shows the first laboratory embodiment of the dye-sensitized solar cell which dates back to 1988 [7]. The photo-anode was a titanium sheet covered with a high surface area “fractal” TiO_2 film that was produced by a sol–gel method. The roughness factor of the film was about 150. The surface of the fractal film was

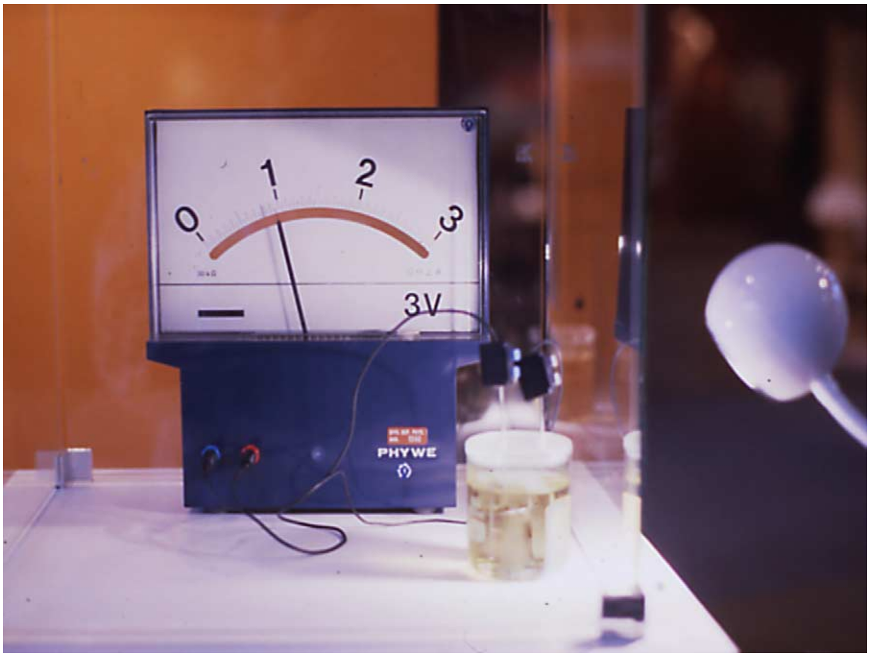

Fig. 2. The first laboratory embodiment of the dye-sensitized solar cell which dates back to 1988 [7]. The photo-anode was a titanium sheet covered with a high surface area “fractal” TiO_2 film that was produced by a sol–gel method. The scanning electron microscope picture of the film is shown in Fig. 3. The surface of the fractal film was derivatized with the yellow ruthenium dye RuL_3 (L = 2,2′-bipyridyl-4,4,-dicarboxylate). A cylindrical platinum wire mesh electrode served as a counter-electrode. The beaker was filled with slightly acidic (pH ca. 4.5) aqueous electrolyte containing bromide and small amounts of bromine. The open circuit voltage of the cell was 1 V under illumination with a halogen spotlight.

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3. The importance of the nanocrystalline film morphology

A photovoltaic conversion system based on light harvesting by a molecular absorber attached to a wide band gap semiconductor surface faces two dilemmas:

1. A monolayer of dye on a flat surface absorbs at most a few percent of light because it occupies an area that is much larger than its optical cross section. In quantitative terms the absorbance A of the dye covered film is given by:

   $$A = \Gamma\sigma \tag{1}$$

   where Γ (mol/cm^2) is the surface coverage of the sensitizer and σ (cm^2/mol) is the molar cross section for absorption of monochromatic light. The latter is the decadic molar extinction coefficient multiplied by 1000. Using a typical surface coverage of 1×10^{-10} mol/cm^2 and $s = 10^7$ cm^2/mol one obtains $A = 0.001$, i.e. the molecular sensitizer films adsorbed on a flat surface absorbs can only harvest a negligibly small fraction of the incoming light.

   The first embodiment of the dye-sensitized solar cell employed a TiO_2 film prepared by a sol–gel method, which had a surface roughness factor of about 150. The surface morphology is shown in Fig. 3. Light scattering within the porous film structure further enhanced the light harvesting. Thus, the dye derivatized fractal TiO_2 films captured practically all the incoming photons with wavelength close to 470 nm, where the RuL_3 sensitizer has its absorption maximum.
2. Compact oxide semiconductor films need to be n-doped to conduct electrons. However, the presence of conduction band electrons is undesirable as they can quench the excited sensitizer by energy transfer. This will inevitably reduce the photovoltaic conversion efficiency.

Present embodiments of the DSC employ dye-derivatized oxide nanocrystals as light harvesting units in [2]. This provides a strikingly simple and powerful method to overcome these problems, which till recently have rendered solar energy conversion devices based on the sensitization of wide band gap oxides notoriously inefficient. The films are made of a network of undoped (insulating) wide band gap oxide nanocrystallites producing a junction of huge contact area (Fig. 4). For a 10 μm thick oxide film the surface is enlarged over 1000 times allowing for efficient harvesting of sunlight by the adsorbed monolayer of sensitizer.

Thus, the fractal TiO_2 film prepared by sol–gel chemical methods, has been replaced with a nanostructure deposited from colloidal suspension. This evidently provides a much more reproducible and controlled porous high surface area

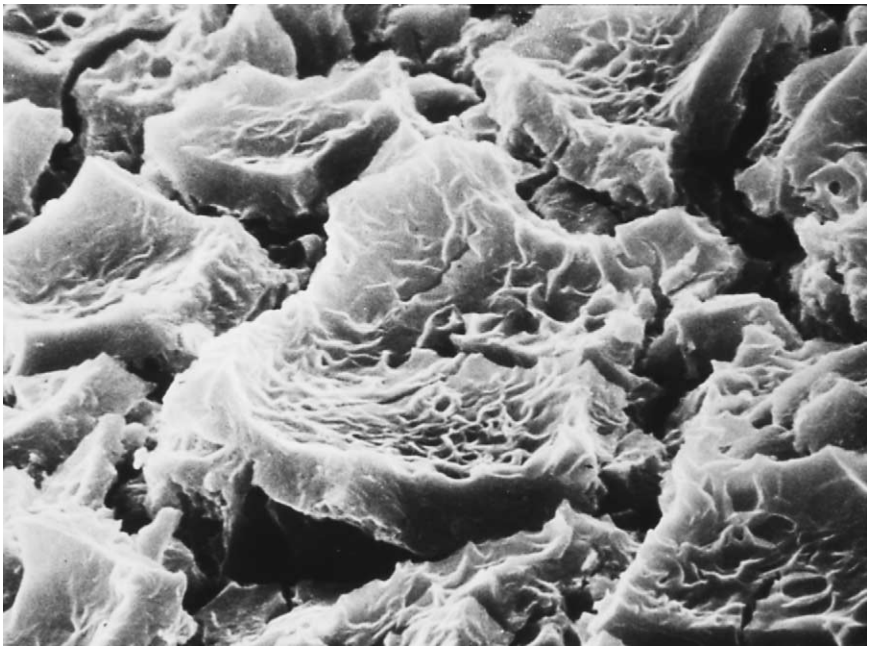


Fig. 3. Scanning electron microscope picture of the fractal TiO_2 film used in the first embodiment of the DSC.

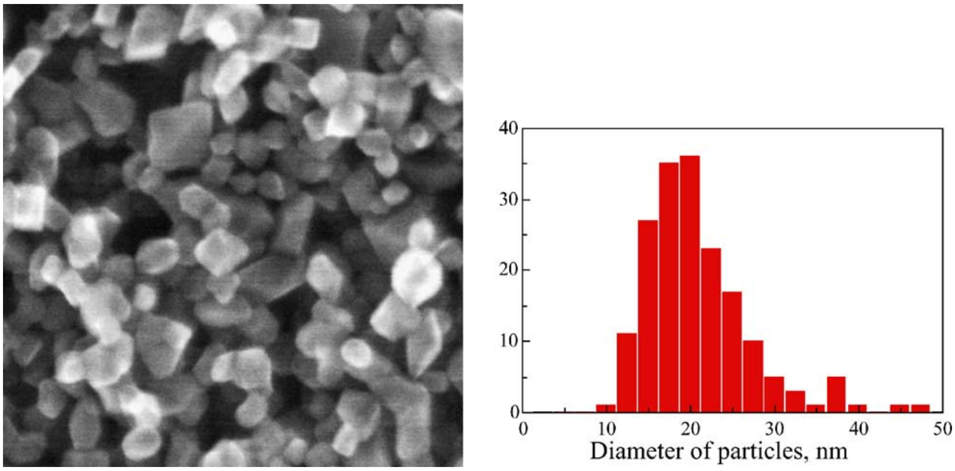


Fig. 4. Scanning electron micrograph and particle size distribution for a TiO_2 anatase colloid prepared at 230 °C, which has given optimal photovoltaic performance so far.

texture. Further, since it is compatible with screen-printing technology, it anticipates future production requirements. While commercially available titania powders produced by a pyrolysis route from a chloride precursor have been successfully employed, the present optimized material is the result of a hydrothermal technique, described by Brooks and coworkers [8]. A specific advantage of the procedure is the ease of control of the particle size, and hence of the nanostructure and porosity of the resultant semiconductor substrate. The synthesis involves the hydrolysis of the titanium alkoxide precursor producing an amorphous precipitate followed by peptisation in acid or alkaline water to produce a sol which is subjected to hydrothermal Ostwald ripening in an autoclave. The resulting TiO_2 particles consist of anatase or a mixture of anatase and rutile, depending on reaction conditions.

The temperature of the hydrothermal treatment has a decisive influence on the particle size. The standard sol, treated for about 12 h at 230 °C in the autoclave has an average particle diameter of 20 nm as shown in Fig. 4. The prevailing structures of the anatase nanoparticles are square-bipyramidal, pseudocubic and stablike. According to HRTEM measurements the (1 0 1) face is mostly exposed followed by (1 0 0) and (0 0 1) surface orientations [9]. The formation of the (1 0 1) face is favored by its low surface energy. The nanocrystalline TiO_2 film in Fig. 4 was deposited by screen printing on a glass sheet covered by a transparent conducting oxide (TCO) that serves as current collector. The film thickness is typically 5–20 μm and the TiO_2 mass about 1–4 mg/cm^2. Analysis of the layer morphology shows the porosity to be about 50–65%.

In contrast to a compact oxide layer there is no need to dope the oxide film since the injection of one single electron from the surface adsorbed sensitizer into a TiO_2 nanoparticle is enough to turn the latter from an insulating to a conductive state. In addition, there is no space charge limitation on the photocurrent as the charge of the injected electrons can be effectively screened by the electrolyte surrounding the oxide nanocrystal.

A striking and unexpected behavior of the mesoporous TiO_2 films is that the high surface roughness does not promote charge carrier loss by recombination. The reason for this behavior is that the electron and the positive charge find themselves within picoseconds after light excitation of the dye on opposite sides of the liquid–solid interface [10]. The carrier loss mechanisms are comparatively slow, and although conventionally referred to as recombination, by analogy with the solid-state process, the loss of a photo-excited electron from the semiconductor should be regarded as a recapture, by an oxidized dye species or a the oxidized form of the redox couple in the electrolyte. Either occurs on a micro- to millisecond time scale. Finally if a hole conductor is employed instead of the electrolyte the electrons and holes are injected in the nanocrystalline oxide film and hole conductor, respectively. Hence, their recombination can be controlled by the interface.

4. The choice of the sensitizer

The ideal sensitizer for a single junction photovoltaic cell converting standard global AM 1.5 sunlight to electricity should absorb all light below a threshold wavelength of about 920 nm. In addition, it must also carry attachment groups such as carboxylate or phosphonate to firmly graft it to the semiconductor oxide surface. Upon excitation it should inject electrons into the solid with a quantum yield of unity. The energy level of the excited state should be well matched to the lower bound of the conduction band of the oxide to minimize energetic losses during the electron transfer reaction. Its redox potential should be sufficiently positive that it can be regenerated via electron donation from the redox electrolyte or the hole conductor. Finally, it should be stable enough to sustain about 10^8 turnover cycles corresponding to about 20 years of exposure to natural light.

Much of the research in dye chemistry is devoted to the identification and synthesis of dyes matching these requirements, while retaining stability in the photo-electrochemical environment. The attachment group of the dye ensures that it spontaneously assembles as a molecular layer upon exposing the oxide film to a dye solution. This molecular dispersion ensures a high probability that, once a photon is absorbed, the excited state of the dye molecule will relax by electron injection to the semiconductor conduction band. However, as pointed out, above the optical absorption of a single monolayer of dye is weak, a fact which originally was cited as ruling out the possibility of high efficiency sensitized devices, as it was assumed that smooth substrate surfaces would be imperative in order to avoid the recombination loss mechanism associated with rough or polycrystalline structures in solid-state photovoltaics. This objection was invalidated by recognizing that the injection process produces electron in the semiconductor lattice, separated spatially from the positive charge carriers by the dye molecules, which are insulating in the ground state and hence provide a barrier for charge recombination. By now, the use of nanocrystalline thin film structures with a roughness factor of over 1000 has become standard practice.

The dynamics of redox processes involved in the conversion of light to electric power by dye-sensitized solar cells are summarized in Fig. 5. The important feature that emerges from a whole series of experimental studies is that the initial events of electron injection and dye regeneration leading to photo-induced charge separation occur on a femto- to nanosecond time scale [10,11] while the redox capture of the electron by the oxidized relay and the electron migration across the nanocrystalline film take place within milliseconds or even seconds. The product of electron lifetime and diffusion coefficient determines its mean diffusion length. Both parameters depend on the light intensity. However, their product varies remarkably little over a large intensity range [12]. The result is that the mean electron diffusion length L is in the 10–20 μm range irrespective of the incident light level. Because this range is commensurate with the film layer thickness needed to harvest sunlight efficiently, the performance of the DSC is insensitive to changes in the electron lifetime. The latter can be prolonged by engineering the dye-derivatized semiconductor interface to retard the electron capture by the oxidized mediator present in the electrolyte. The use of self-assembly assisting agents is one very promising method to achieve this goal by enhancing the organization of the surface adsorbed sensitizer on the molecular level as will be shown below.

The best photovoltaic performance both in terms of conversion yield and long-term stability has so far been achieved with polypyridyl complexes of ruthenium and osmium. Sensitizers having the general structure $ML_2(X)_2$ where L stands for 2,2′-bipyridyl-4,4′-dicarboxylic acid M is Ru or Os and X presents a halide, cyanide, thiocyanate, acetyl acetonate, thiacarbamate or water substituent, are particularly promising. Thus, the ruthenium complex *cis*-$RuL_2(NCS)_2$, known as N3 dye, whose structure is shown in Fig. 5 has become the paradigm of heterogeneous charge transfer sensitizer for mesoporous solar cells. The fully protonated N3 has absorption maxima at 518 and 380 nm, the extinction coefficients being 1.3 and $1.33\times10^4\ M^{-1}$/cm, respectively. The complex emits at 750 nm the lifetime being 60 ns [13]. The optical

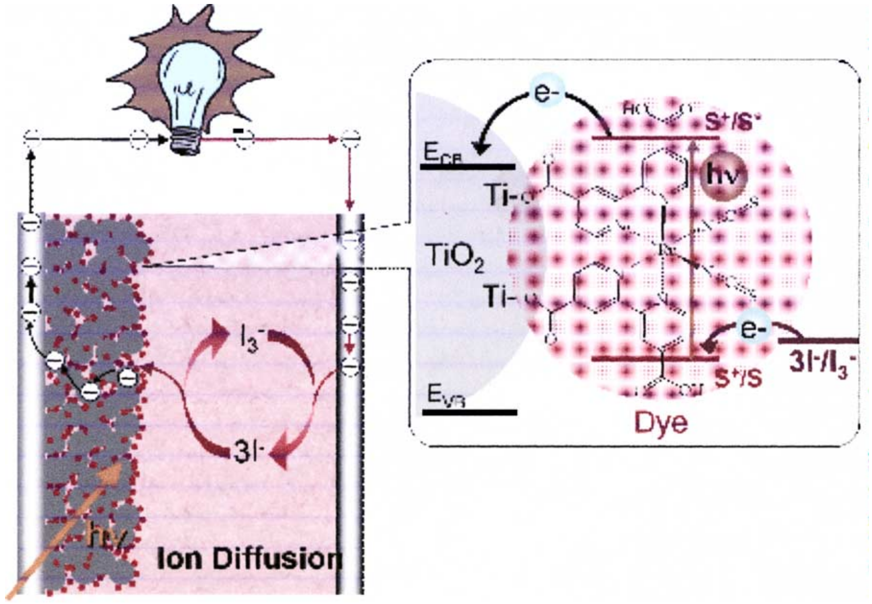


Fig. 5. Schematic drawing showing the currently used embodiment of the DSC. It employs dye-derivatized TiO_2 nanocrystals as light harvesting units. A scanning electron microscope picture of the film is shown in Fig. 4. The sensitizer is *cis*-$Ru(SCN)_2L_2$ (L = 2,2′-bipyridyl-4,4′-dicarboxylate). The redox system employed to regenerate the dye and transport the positive charges to the counter-electrode is the iodide/triiodide couple dissolved in an organic electrolyte or in a room temperature ionic liquid.

transition has MLCT (metal-to-ligand charge transfer) character: excitation oft the dye involves transfer of an electron from the metal to the π* orbital of the surface anchoring carboxylated bipyridyl ligand from where it is released within femto- to picoseconds into the conduction band of TiO_2 generating electric charges with unit quantum yield [14].

The sensitizer is grafted onto the semiconductor through anchoring groups, e.g. carboxylate, phosphonate or hydroxamate, that bind strongly to the oxide by coordination of surface titanium ions. The most widely used sensitizer for the DSC has been the N3 dye *cis*-$Ru(SCN)_2L_2$ (L = 2,2′-bipyridyl-4,4′-dicarboxylate) and the redox system use to regenerate the dye and transport the positive charges to the counter-electrode is the iodide/triiodide couple dissolved in an organic electrolyte or in a room temperature ionic liquid. Although this combination has the advantage to provide efficient, highly reproducible and stable cell performance, it does suffer from a mismatch between the redox level of the triioide/iodide (ca. 0.15 V versus SCE for a typical electrolyte composition) and that of the ground state N3 dye (ca. 0.85 V versus SCE for the protonated form the dye). As a consequence, the regeneration of the dye consumes about 0.7 eV constituting the main loss factor in the operation of this embodiment of the dye-sensitized solar cell. A driving force of 0.2–0.3 eV should be sufficient to ascertain regeneration of dye at a fast enough rate to intercept the recapture of the conduction band electron by the oxidized sensitizer. A better match of the redox systems should result in a net gain in the open circuit photovoltage. This has indeed been observed recently when the iodide/triiodide couple was replaced by a new cobalt complex [15] or a solid hole conductor yielding a gain in V_{oc} values of about 0.1–0.2 V higher in agreement with expectations. Ultimately an increase of the open circuit voltage by 0.4–0.5 V appears feasible which would result in doubling the conversion efficiency from currently 10 to 20%.

Discovered in 1993 [13] the photovoltaic performance of N3 has been unmatched for 8 years by virtually hundreds of other complexes that have been synthesized and tested. However, in 2001 the “black dye” tri(cyanato)-2.2′2″-terpyridyl-4,4′4″-tricarboxylate)Ru(II) achieved a record 10.4% (air mass 1.5) solar to power conversion efficiency in full sunlight [16]. This record has been broken only very recently by using the N3 dye in conjunction with guanidinium thiocyanate, a self-assembly facilitating additive allowing to increase substantially the open circuit voltage (V_{oc}) of the solar cell. These data will be discussed further below (Fig. 6).

Fig. 7 compares the spectral response of the photocurrent observed with the two sensitizers. The incident photon to current conversion efficiency (IPCE) of the DSC is plotted as a function of excitation wavelength. Both chromophores show very high IPCE values in the visible range. The conversion of incident light quanta to electric current is over 80% or close to 100% if the optical losses in the glass and the TCO film are accounted for. However, it is evident that the response of the black dye extends 100 nm further into the IR than that of N3. The photocurrent onset is close to 920 nm, i.e. near the optimal threshold for single junction converters. From there on the IPCE rises gradually until at 700 nm it reaches a plateau of over 80%. If one accounts for reflection and absorption losses in the conducting glass the conversion of incident photons to electric currents is practically quantitative over the whole visible domain. From the overlap in-

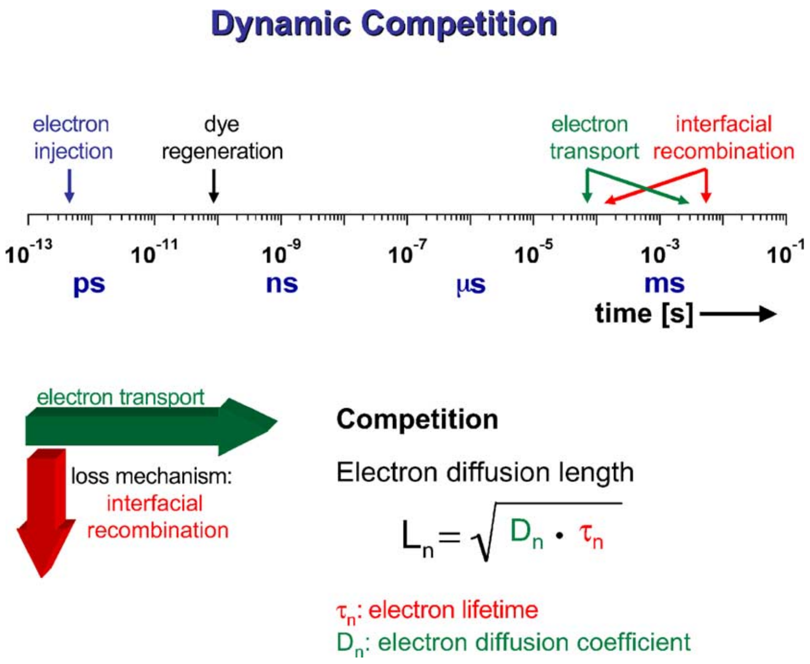
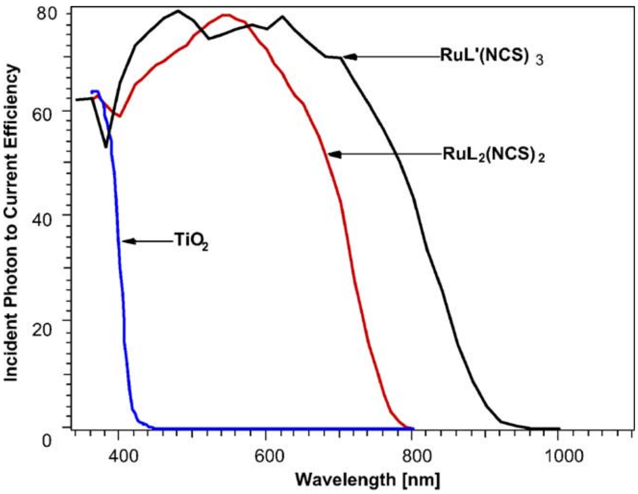


Fig. 6. Dynamics of redox processes involved in the conversion of light to electric power by dye-sensitized solar cells.



L = 4,4'-COOH-2,2'-bipyridine
L' = 4,4',4"-COOH-2,2':6',2"-terpyridine

Fig. 7. Photocurrent action spectra obtained with the N3 (ligand L) and the black dye (ligand L′) as sensitizer. The photocurrent response of a bare TiO_2 films is also shown for comparison. Detailed experimental conditions are given in [11].

tegral of the curves in Fig. 7 with the AM 1.5 solar emission one predicts the short circuit photocurrents of the N3 and black dye-sensitized cells to be 16.5 and 20.5 mA/cm^2, respectively, in agreement with experimental observations. The overall efficiency (η_{global}) of the photovoltaic cell is 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 ($I_{\text{s}} = 1000\,\text{W/m}^2$)

$$\eta_{\text{global}} = \frac{i_{\text{ph}} V_{\text{oc}} ff}{I_{\text{s}}} \qquad (2)$$

Judicious molecular engineering of the ruthenium dye structure will allow for further increasing the light harvesting in the 700–900 nm region. In this respect ruthenium complexes of quaterpyridyl derivatives show great promise [17]. The goal is to obtain a DSC having optical features similar to GaAs. A nearly vertical rise of the photocurrent close to the 920 nm absorption threshold would increase the short circuit photocurrent from currently 20.5 to about 28 mA/cm^2 raising the overall efficiency to about 15% even without changing the redox system.

5. Organic dyes and quantum dots as sensitizers

When considering organic dye structures, porphyrins and phthalocyanines attract particular attention, the former because of the analogy with natural photosynthetic processes. the latter because of their photochemical and phototherapeutic applications. However, porphyrins cannot compete with the N3 or black dye sensitizer due to their lack of red light and near IR absorption. Phthalocyanines do show intense absorption bands in this spectral region. However, problems with aggregation and the unsuitable energetic position of the LUMO level, which is too low for electron transfer to the TiO_2 conduction band have turned out to be intractable so far [18].

Recently the group of Arakawa and coworkers made a remarkable advance in developing new and very efficient organic dyes for the DSC [19,20]. Using coumarine or polyene type sensitizers, strikingly high solar to electric power conversion yields reaching up to 7.7% in full sunlight have been achieved.

Another strategy to obtain a broad optical absorption extending throughout the visible and near IR region is to use a combination of two dyes which complement each other in their spectral features. Such dye cocktails have already been applied to mesoporous TiO_2 films in the form of mixtures of porphyrines and phthalocyanines. The result was encouraging in as much as the optical effects of the two sensitizers were found to be additive. In particular, there was no negative interference between the co-adsorbed chromophores opening up the way for testing a multitude of other dye combinations [21].

Semiconductor quantum dots are another attractive option for panchromatic sensitizers. These are II–VI and III–V type semiconductors particles whose size is small enough to produce quantum confinement effects. The absorption spectrum of such quantum dots can be adjusted by changing the particle size. Thus, the band gap of materials such as InAs and PbS can be adapted to match the value of 1.35 eV, which is ideal for a single-junction solar quantum converter. During the last decade a wealth of information has been gathered on the physical properties of these materials and the research is being pursued very actively. One problem with this approach is the photo-corrosion of the quantum dots, which will almost certainly happen if the junction contact is a liquid redox electrolyte. However, they are expected to display higher stability in the solid-state heterojunction device [22]. The advantage of these sensitizers over conventional dyes is their very high extinction coefficient allowing for use of thinner films of the mesoporous oxide. This should reduce the dark current increasing V_{oc} and the overall efficiency of the cell.

6. Charge percolation

When the dye-sensitized nanocrystalline solar cell was first presented perhaps the most puzzling phenomenon was the highly efficient charge transport through the nanocrystalline TiO_2 layer. The mesoporous electrodes are very much different compared to their compact analogs because (i) the inherent conductivity of the film is very low, (ii) the small size of the nanocrystalline particles does not support a built-in electrical field and (iii) the electrolyte penetrates the porous film all the way to the back-contact making the semiconductor/electrolyte interface essentially three-dimensional. Charge transport in mesoporous systems is under keen debate today and several interpretations based on the Montrol–Scher model for random displacement of charge carriers in disordered solids [23] have been advanced. However, the "effective" electron diffusion coefficient is expected to depend on a number of factors such as trap filling and space charge compensation by ionic motion in the electrolyte. Therefore, the theoretical and experimental effort will continue as there is a need for further in depth analysis of this intriguing charge transport process. The factors controlling the rate of charge carrier percolation across the nanocrystalline film are presently under intense scrutiny. Intensity modulated impedance spectroscopy has proved to be an elegant and powerful tool [24,25] to address these and other important questions related to the characteristic time constants for charge carrier transport and reaction dynamics in dye-sensitized nanocrystalline solar cells. Very interestingly, recent pulsed laser-induced current transient measurements carried out in Prof. Yanagida's laboratory have revealed that dye adsorption onto nanoporous TiO_2 electrode can increase the electron diffusion coefficient compared with a bare surface [26].

7. Advanced mesoporous materials nanotubes and nanobrushes

On the material science side, research is currently been directed towards synthesizing structures with a higher degree of order than the random assembly of nanoparticles shown in Fig. 4. A desirable morphology of the films would have the mesoporous channels or nanorods aligned in parallel to each other and vertically with respect to the TCO glass current collector. This would facilitate charge diffusion in the pores and the mesoporous film, give easier access to the film surface, avoid grain boundaries and allow the junction to be formed under better control. One approach to fabricate such oxide structures is based on surfactant templates assisted preparation of TiO_2 nanotubes as described in paper by Adachi et al. [27]. Very recently a simple approach to prepare oriented nanobrushes of TiO_2 on titanium supports has been published [28]. The work of Alivisatos and coworkers [29] on hybrid solar cells consisting of blends of CdSe nanoparticles with polythiophene has confirmed the superior photovoltaic performance of nanorod films with regards to random networks of spherical particles.

8. Mastering the interface, a new record cell

The high contact area of the junction nanocrystalline solar cells renders mandatory the grasp and control of interfacial effects for future improvement of cell performance. The nature of the exposed surface planes of the oxide and the mode of interaction with the dye is the first important information to gather. For the adsorption of the N3 dye on TiO_2 this is now well understood. The prevalent orientation of the anatase surface planes is (1 0 1) and the sensitizer is adsorbed through two of the four carboxylate groups, at least one of them being in anchored via a bidentate configuration bridging two adjacent titanium sites [2]. Molecular dynamic calculations employing a classical force field have been carried out to predict the equilibrium geometry of the adsorbed sensitizer state [30]. More sophisticated first principle density functional calculations have also been launched recently [31] to model the surface interactions of TiO_2 with simple adsorbates as well as the surface reconstruction effects resulting from the adsorption. The latter approach is particularly promising and will provide an important tool for future theoretical investigations.

Synthetic efforts focus on the molecular engineering of sensitizers that enhance the charge separation at the oxide solution interface. The structural features of the dye should match the requirements for current rectification: in analogy to the photo-field effect in transistors, the gate for unidirectional electron flow from the electrolyte through the junction and into the oxide is opened by the photo-excitation of the sensitizer. The reverse charge flow, i.e. recapture of the electron by the electrolyte could be impaired by judicious design of the sensitizer. The latter should form a tightly packed insulating monolayer blocking the dark current. The gain in open circuit voltage can be calculated from the diode equation:

$$V_{\mathrm{oc}} = \frac{nRT}{F} \ln\left(\frac{i_{\mathrm{sc}}}{i_{\mathrm{o}}} - 1\right) \qquad (3)$$

where n is the ideality factor whose value is between 1 and 2 for the DSC and i_o is the reverse saturation current. Thus, for each order of magnitude decrease in the dark current the gain in V_{oc} would be 59 mV at room temperature. Work in this direction is indispensable to raise the efficiency of the DSC significantly over the 15% limit with the currently employed redox electrolytes.

Important progress to control the self-assembly of the N3 dye at the TiO_2 interface was achieved recently in our laboratory. The strategy employed was to add guanidinium thiocyanate to the electrolyte. The guanidinium cations are adsorbed along with the N3 anions at the interface, screening the lateral Coulombic repulsion of the sensitizer and facilitating in this fashion the self-assembly of a compact dye monolayer. This results indeed in a remarkable improvement of the cell voltage due to a reduction in dark current. Using this approach, a new record conversion efficiency of 11% was achieved recently and Fig. 8 shows current voltage curves obtained with these cells.

9. Photovoltaic performance stability

A photovoltaic device must remain serviceable for 20 years without significant loss of performance. The stability of all the constituents of the nanocrystalline injection solar cells, that is: the conducting glass the TiO_2 film, the sensi-

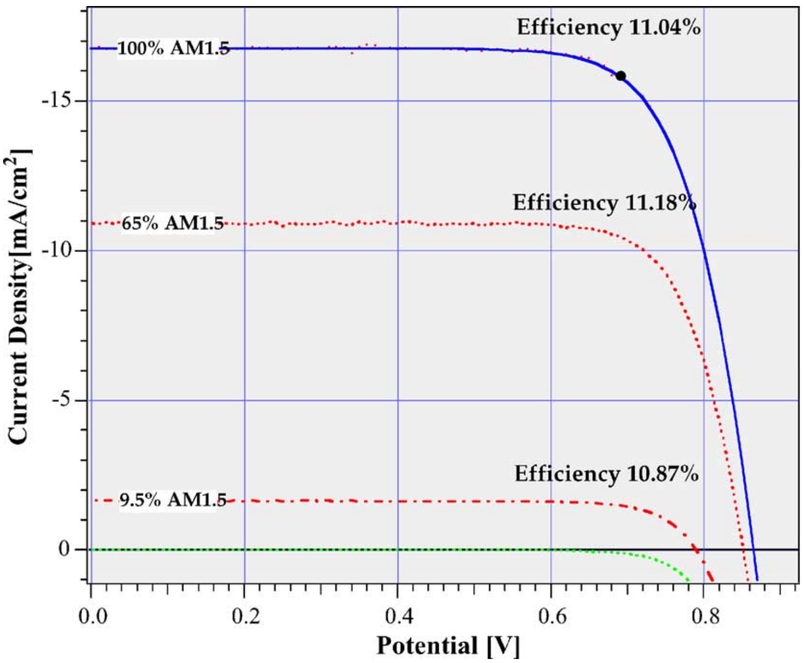


Fig. 8. Photocurrent–voltage curve of a solar cell based on an electrolyte containing guanidinium thiocyanate as self-assembly facilitating agent. The sensitizer was passed three times over a Sephadex column for purification. The cell was equipped with an anti-reflecting coating. The conversion efficiency in full AM 1.5 sunlight was 11.04%. It increased to 11.18% at 65% full sunlight.

tizer, the electrolyte, the counter-electrode and the sealant has therefore been subjected to close scrutiny. The stability of the TCO glass and the nanocrystalline TiO_2 film being unquestionable, investigations have focused on the other components, in particular the sensitizer, the redox electrolyte and the sealant.

As a pure solid the N3 dye is stable even in air up to 280 °C where decarboxylation sets in. Upon long time illumination it sustained 10^8 redox cycles without noticeable loss of performance corresponding to 20 years of continuous operation in natural sunlight. The reason for this outstanding stability is the very rapid deactivation of its excited state via charge injection into the TiO_2, which occurs in the femtosecond time domain. This is at least eight orders of magnitude faster than any other competing channels of excited state deactivation including those leading to chemical transformation of the dye. The oxidized state of the dye produced by the electron injection is much less stable although the $N3/N3^+$ couple shows reversible electrochemical behavior in different organic solvents indicating that the lifetime of $N3^+$ is at least several seconds [32]. However, when maintained in the oxidized state the dye degrades through loss of sulfur. Regeneration of the N3 in the photovoltaic cell should therefore occur rapidly, i.e. within nanosecond or microseconds to avoid this unwanted side reaction. Lack of adequate conditions for regeneration of the dye may lead to dye degradation [33].

Long-term light soaking tests on sealed cells have progressed significantly over the last few years. These tests are very important, as the redox electrolyte or the sealing, may fail under long-term illumination. A recent stability test during 12 000 h of continuous full intensity light exposure has confirmed that this system does not exhibit any inherent instability [34], in contrast to amorphous silicon, which due to the Stabler–Wronski effect undergoes photo-degradation. These tests are very important, since—apart from the sensitizer—other components of the device, such as the redox electrolyte or the sealing, may fail under long-term illumination. Indeed, a problem emerged with electrolytes based on cyclic carbonates, such as propylene or ethylene carbonate, which were found to undergo thermally activated decarboxylation in the presence of TiO_2 rendering these solvents unsuitable for practical usage.

Maintaining stable cell operation under thermal stress has been a major challenge for the DSC. Upon exposure for prolonged periods to higher temperatures, i.e. 80–85 °C degradation of performance was frequently observed. Only recently a heat resistant quasi-solid state electrolyte based on a mixture of imidazolium iodide, methoxypropionitrile and a fluorinated polymer was introduced. When used in conjunction with the amphiphilic ruthenium dye Z-907, it was possible to pass for the first time the critical 1000 h stability test at 80 °C with a dye-sensitized solar cell [35].

10. Ionic liquids

Room temperature ionic liquid electrolytes have been actively pursued as non-volatile electrolytes of DSC [36,37] and Prof. Yanagida's group has made pioneering contributions in this field [38]. Molten salts based on imidazolium iodides have revealed very attractive stability features [39–41]. Despite their high viscosity, linear photocurrent response up to full solar light intensities has been observed. This has been attributed to a Grotthus exchange mechanism, which increases the effective diffusion coefficient of the triiodide ions in the melt [42]. Overall efficiencies exceeding 7% have been obtained recently in our laboratory under full sunlight with solvent-free ionic liquids.

Very intriguing is the observation of high fill factors with ionic liquid electrolytes based DSCs, which readily reach values of over 0.75 even in full sunlight. Dilution of the same ionic liquid with a low-viscosity organic solvent often decreases the fill factor. This unexpected behavior is likely to arise from the effective screening of the electric charges that are produced under light illumination in the mesoporous films. The very high density of ions present in these molten salts appears to facilitate charge separation although the mechanism by which the screening is achieved remains obscure to date.

11. Solid-state dye-sensitized solar cells

A recent alternative embodiment of the DSC concept is the sensitized heterojunction usually with an inorganic wide band gap nanocrystalline semiconductor of n-type polarity as electron acceptor, the charge neutrality on the dye being restored by a hole delivered by the complementary semiconductor, inorganic [43,44] or organic [45] and of p-type polarity. The prior photoelectrochemical variant, being further advanced in development, has an AM 1.5 solar conversion efficiency of over 10%, while that of the solid-state device is, as yet, significantly lower (Fig. 9).

Since the sensitizing dye itself does not provide a conducting functionality, but is distributed at an interface in the form of immobilized molecular species, it is evident that for charge transfer each molecule must be in intimate contact with both conducting phases. It is evident that this applies to the porous wide bandgap semiconductor substrate into which the photo-excited chemisorbed molecules inject electrons. It is also evident that in the photo-electrochemical format of the sensitized cell the liquid electrolyte penetrates into the porosity, thereby permitting the intimate contact with the charged dye molecule necessary for charge neutralization 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 so easily be established that an immobilized molecule at their interface can exchange charge carriers with both. However, results are promising. The charge transport materials are deposited by spin coating from the liquid phase in order to achieve the necessary intimate contact, thereby introducing a solution of the conducting compound into the previously sensitized nanostructure. The charge transfer material currently used is a spirobifluorene, whose structure is shown in Fig. 10.

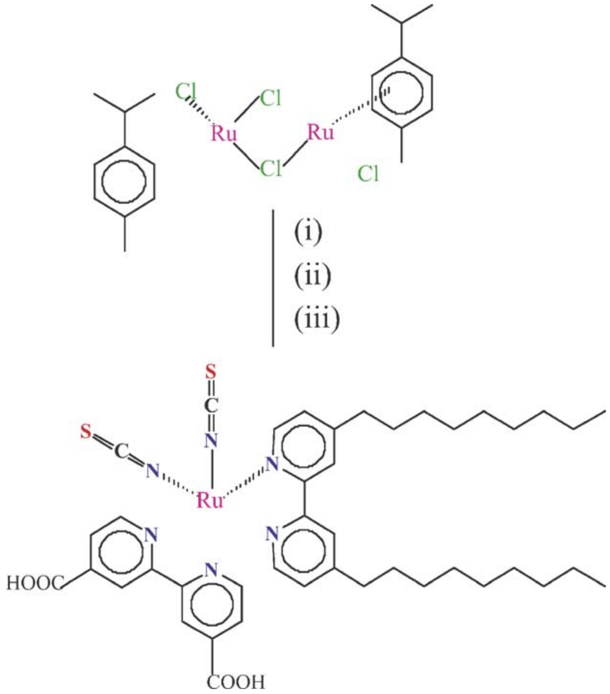


Fig. 9. Structure of the amphiphilic ruthenium dye Z-907 and synthesis route from a ruthenium xylene precursor complex.

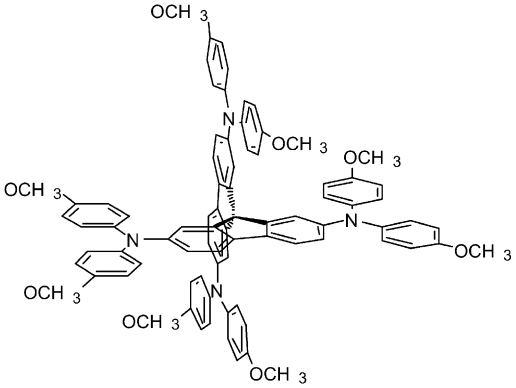


Fig. 10. Structure of the spiro-bisfluorene triarylamine type hole conductor.

Since the first report on this system in 1998, its photovoltaic conversion efficiency has been improved considerably and stands presently at 3.2% [46]. An even higher efficiency of 3.8% was recently achieved by Fujishima and coworkers [47] using a dye-sensitized solar cell containing CuI as a hole conductor instead of a liquid electrolyte.

12. Conclusions

The dye-sensitized nanocrystalline electrochemical photovoltaic system has become a validated and credible competitor to solid-state junction devices for the conversion of solar energy into electricity. An advantage of the DSC with respect to competing technologies is that its performance is remarkably insensitive to temperature change. Thus, raising the temperature from 20 to 60 °C has practically no effect on the power conversion efficiency. In contrast, conventional silicon cells exhibit a significant decline over the same temperature range amounting to ca. 20%. Since the temperature of a solar cell will reach readily 60 °C under full sunlight this feature of the injection cell is particularly attractive for power generation under natural conditions. Other advantages are the lower sensitivity to angle of light incidence and shorter energy pay back time as compared to silicon-based cells. These factors do render the system attractive for practical applications.

The DSC is the prototype of a series of optoelectronic and energy technology devices exploiting the specific characteristics of this innovative structure for oxide and ceramic semiconductor films. Recent developments in the area of sensitizers for these devices have lead to dyes which absorb across the visible spectrum leading to higher efficiencies. The recent development of an all solid-state heterojunction dye solar cell holds additional potential for further cost reduction and simplification of the manufacturing of dye solar cells.

Acknowledgements

Recognition is due to the members of the EPFL electrochemical photovoltaics development team, some of whose work is referenced below; to those industrial organizations whose interest in this PV system has induced them to license the concept and thereby support our research; to EPFL; and to OFEN (Swiss Federal Office of Energy) and to the US Airforce European Research Office for past encouragement and support.

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