



Review

Dye-sensitized solar cells

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Abstract

The dye-sensitized solar cells (DSC) provides a technically and economically credible alternative concept to present day p–n junction photovoltaic devices. In contrast to the conventional systems where the semiconductor assume 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 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 (IPCE) over 10% have been reached. There are good prospects to produce these cells at lower cost than conventional devices. Here we present the current state of the field, discuss new concepts of the dye-sensitized nanocrystalline solar cell (DSC) including heterojunction variants and analyze the perspectives for the future development of the technology.

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Keywords: Solar light energy conversion; Dye-sensitized solar cells; Nanocrystalline oxide semiconductor films; Organic hole conductors; Ionic liquids; Ruthenium charge transfer sensitizers

Contents

1. Introduction	145
2. Operation principle of the dye-sensitized nanocrystalline solar cell (DSC)	146
3. Historical background	147
4. Present DSC research and development	147
4.1. Panchromatic sensitizers	147
4.2. Organic dyes, quantum dot as sensitizers	149
4.3. Mesoporous oxide film development	149
4.4. Higher cell voltage and conversion efficiency through molecular engineering of the interface	150
4.5. Photovoltaic performance stability	150
4.6. Solid-state dye-sensitized solar cells	151
5. Conclusions	152
Acknowledgements	152
References	152

1. Introduction

Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different con-

duction 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, for example, on nanocrystalline

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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 junction device, by replacing the contacting phase to the semiconductor by an electrolyte, liquid, gel or solid, thereby forming a photo-electrochemical cell. 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, 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 nanocrystalline morphology [1].

2. 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 mesoporous oxide layer composed of nanometer-sized particles which have been sintered together to allow for electronic conduction to take place. The material of choice has been TiO_2 (anatase) although alternative wide band gap oxides such as ZnO [2], and Nb_2O_5 [3] have also been investigated. Attached to the surface of the nanocrystalline film is a

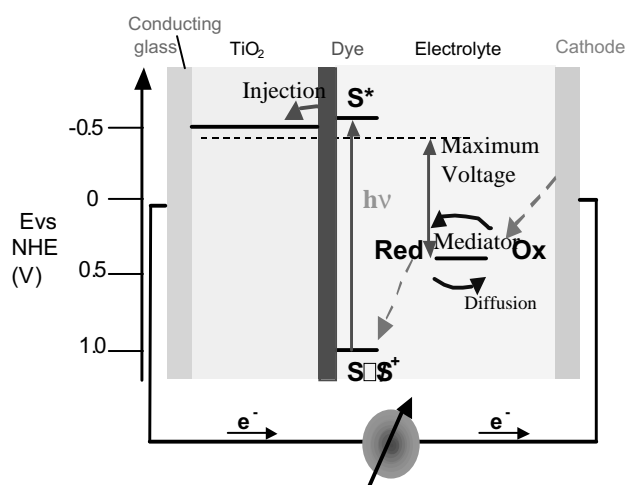


Fig. 1. Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell. Photo-excitation of the sensitizer (S) is followed by electron injection into the conduction band of the mesoporous oxide semiconductor. The dye molecule is regenerated by the redox system, which 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.

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 counterelectrode 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 scanning electron micrograph of a typical TiO_2 (anatase) film deposited by screen printing on a conducting glass sheet 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%, the average pore size being 15 nm. 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.

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 [4,5] or organic [6] and of p-type polarity. The prior photo-electrochemical variant, being further advanced in development, has an AM 1.5 solar conversion

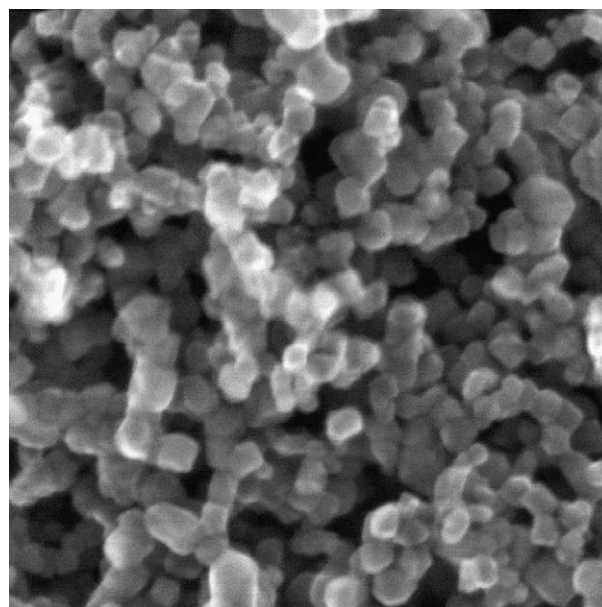


Fig. 2. Scanning electron microscope picture of a nanocrystalline TiO_2 (anatase) film used in the dye-sensitized solar cell (DSC).

efficiency of over 10%, while that of the solid-state device is, as yet, significantly lower.

3. Historical background

The history of the sensitization of semiconductors to light of wavelength longer than that corresponding to the bandgap has been presented elsewhere [7,8]. It is an interesting convergence of photography and photo-electrochemistry, both of which rely on photo-induced charge separation at a liquid–solid interface. The silver halides used in photography have band gaps of the order of 2.7–3.2 eV, and are therefore insensitive to much of the visible spectrum, just as is the TiO₂ now used in these photo-electrochemical devices.

The first panchromatic film, able to render the image of a scene realistically into black and white, followed on the work of Vogel in Berlin after 1873 [9], in which he associated dyes with the halide semiconductor grains. The first sensitization of a photo-electrode followed shortly thereafter, using a similar chemistry [10]. However, the clear recognition of the parallelism between the two procedures, a realization that the same dyes in principle can function in both [11] and a verification that their operating mechanism is by injection of electrons from photo-excited dye molecules into the conduction band of the n-type semiconductor substrates [12] date to the 1960s. In subsequent years the idea developed that the dye could function most efficiently if chemisorbed on the surface of the semiconductor [13,14]. The concept emerged to use dispersed particles to provide a sufficient interface [15], then photo-electrodes where employed [16].

Titanium dioxide became the semiconductor of choice. The material has many advantages for sensitized photochemistry and photo-electrochemistry: it is a low cost, widely available, non-toxic and biocompatible material, and as such is even used in health care products as well as domestic applications such as paint pigmentation. The standard dye at the time was *tris*(2,2'-bipyridyl-4,4'-carboxylate) ruthenium(II), the function of the carboxylate being the attachment by chemisorption of the chromophore to the oxide substrate. Progress thereafter, until the announcement in 1991 [1] of the sensitized electrochemical photovoltaic device with a conversion efficiency at that time of 7.1% under solar illumination, was incremental, a synergy of structure, substrate roughness and morphology, dye photophysics [17] and electrolyte redox chemistry. That evolution has continued progressively since then, with certified efficiency now over 10%.

4. Present DSC research and development

4.1. Panchromatic sensitizers

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 high 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 10⁸ 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, 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 (Fig. 3). This objection was invalidated by recognizing that the injection process produces electron in the

The dilemma of light harvesting by surface immobilized molecular absorbers

A monolayer of dye on a flat surface absorbs at most a few percent of light because its size is much larger than its optical cross section

Compact semiconductor films need to be n-doped to conduct electrons. As a consequence there is energy transfer quenching of the excited sensitizer by the electrons in the semiconductor.

Light harvesting by nanocrystalline TiO₂ films

- Light is absorbed by a dye derivatized mesoporous film made of a network of undoped (insulating) TiO₂ nanocrystallites
- The sensitizer is grafted onto the TiO₂ surface through suitable anchoring groups, e.g. carboxylate, phosphonate or hydroxamate.
- Light induced electron injection from the adsorbed dye into the nanocrystallites renders the TiO₂ conductive.

Fig. 3. The dilemma of using flat surfaces for dye-sensitized photovoltaic cells and the advantages of light harvesting by nanocrystalline films.

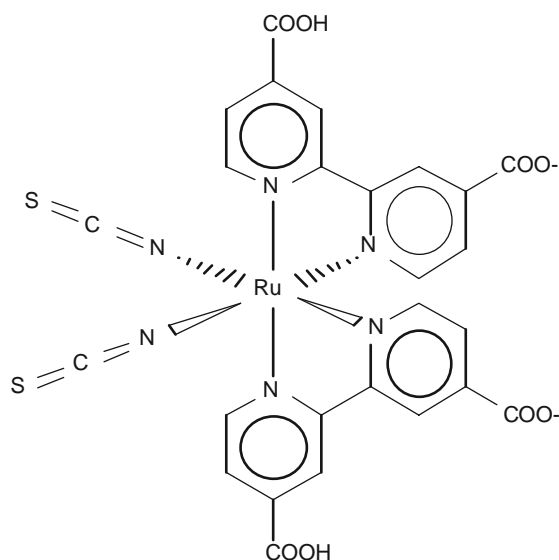
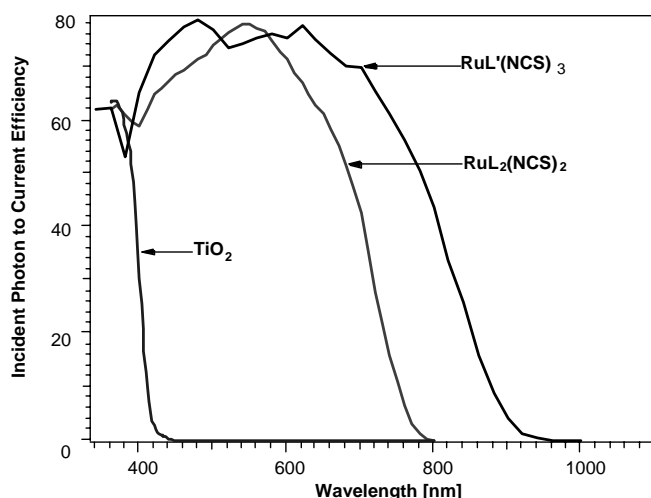


Fig. 4. Chemical structure of the N3 ruthenium complex used as a charge transfer sensitizer in dye-sensitized solar cells.

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 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, thiocarbamate or water substituent, are particularly promising. Thus, the ruthenium complex *cis*- $RuL_2(NCS)_2$, known as N3 dye, shown in Fig. 4 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 $1.33 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The complex emits at 750 nm the lifetime being 60 ns. The optical transition has metal-to-ligand charge transfer (MLCT) character: excitation of the dye involves transfer of an electron from the metal to the p^* 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 [18].

Discovered in 1993 [19] 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 [20]. This record has been broken only very recently by using the N3 dye in conjunction



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

Fig. 5. 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 [19].

with guanidinium thiocyanate, a self-assembly facilitating additive allowing to increase substantially the open-circuit voltage of the solar cell. These data will be discussed further below.

Fig. 5 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. However, 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 ca. 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 integral of the curves in Fig. 5 with the AM 1.5 solar emission one predicts the short circuit photocurrents of the N3 and black dye-sensitized cells to be 16 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 ($I_s = 1000 \text{ W}/\text{m}^2$)

$$\eta_{\text{global}} = \frac{i_{\text{ph}} \times V_{\text{oc}} \times \text{ff}}{I_s} \quad (1)$$

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 [21]. 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 currently from 20.5 to 28 mA/cm² raising the overall efficiency to about 15%.

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.

4.2. Organic dyes, quantum dot 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 TiO₂ conduction band have turned out to be intractable so far.

A remarkable advance in the use of organic dyes for DSC was recently made by the group of Hara et al. [22,23]. Using coumarin or polyene type sensitizers, strikingly high solar to electric power conversion efficiencies 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 TiO₂ films in the form of mixtures of porphyrins 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 [24].

Semiconductor quantum dots are another attractive option for panchromatic sensitizers. These are II–VI and III–V type semiconductor 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 hetero-junction device [25]. 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.

4.3. Mesoporous oxide film development

When the dye-sensitized nanocrystalline solar cell was first presented perhaps the most puzzling phenomenon was the highly efficient charge transport through the nanocrystalline TiO₂ 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 [26] 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 percolation process. The factors controlling the rate of charge carriers percolation across the nanocrystalline film are presently under intense scrutiny. Intensity modulated impedance spectroscopy has proved to be an elegant and powerful tool [27,28] 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.

On the material science side, future research will be directed towards synthesizing structures with a higher degree of order than the random fractal-like assembly of nanoparticles shown in Fig. 2. 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 pore diffusion, 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 TiO₂ nanotubes as described in recent paper by Adachi et al. [29]. These and the hybrid nanorod-polymer composite cells developed by Huynh et al. [30] have confirmed the superior photovoltaic performance of such films with regards to random particle networks.

4.4. Higher cell voltage and conversion efficiency through molecular engineering of the interface

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 TiO₂ this is now well understood. The prevalent orientation of the anatase surface planes is (101) and the sensitizer is adsorbed through two of the four carboxylate groups, at least one of them being anchored via a bidentate configuration bridging two adjacent titanium sites [18]. Molecular dynamic calculations employing a classical force field have been carried out to predict the equilibrium geometry of the adsorbed sensitizer state [31,32]. More sophisticated first principle density functional calculations have also been launched recently [33] to model the surface interactions of TiO₂ 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:

$$V_{oc} = \left(\frac{nRT}{F} \right) \ln \left[\frac{i_{sc}}{i_o} - 1 \right] \quad (2)$$

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 TiO₂ 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 10.6% was achieved recently and Fig. 6 shows current voltage curves obtained with these cells.

4.5. 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 TiO₂ film, the sensitizer, the electrolyte, the counterelectrode and the sealant has therefore been subjected to close scrutiny. The stability of the TCO glass and the nanocrystalline TiO₂ film being unquestionable investigations have focused on the four other components.

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 10⁸ 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 TiO₂ occurs in the femto-second 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 N3⁺ 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 under these conditions. 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 has led to cell failure [34].

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 TiO₂ rendering these solvents unsuitable for practical usage.

These were therefore replaced by a highly polar and nonvolatile solvents, such as methoxypropionitrile (MPN) which do not exhibit this undesirable property. Using a MPN based electrolyte in conjunction with a surfactant ruthenium dye, the critical 1000 h stability test at 80 °C was recently passed for the first time with a dye-sensitized solar cell [35].

Room temperature molten salts based on imidazolium iodides have revealed very attractive stability features. Despite their high viscosity impressive overall conversion efficiencies exceeding 6% have been obtained so far [36]. This has been attributed to a Grothus mechanism which increases the diffusion coefficient of the triiodide ions in the melt and to a



Cell Name: PL0705/bb1_May 12#32

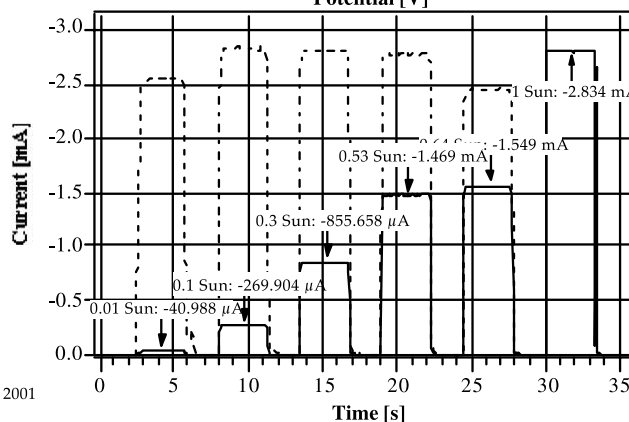
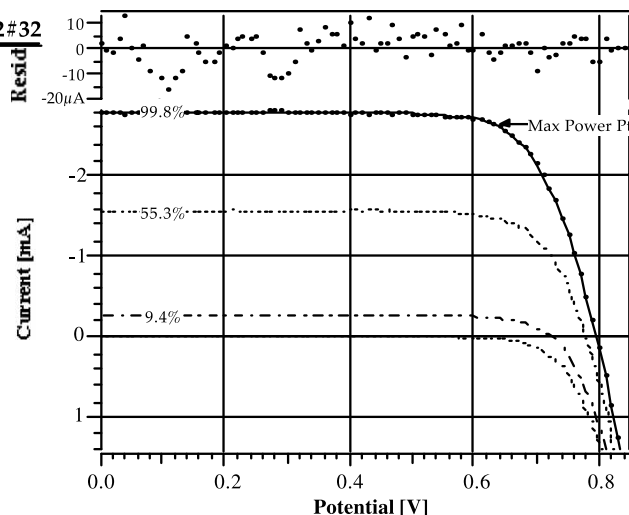
Measurement Date : Mon, May 12, 2003 / 11:14:29 PM
 Type of cell : PC; tipex + AR
 Cell Active Area : 0.158 cm²
 Light Source : Xe 450W @ AM1.5G
 Dye Sensitiser : N719
 Additional Remarks : 111.. old rec.; 24h
 Electrolyte 1316 : 1376 mod.0.1M GRh; 85% ACN..
 Working Temperature : 298 K
 Semiconductor Layer : 16/4+ TiCl₄>; 20nm; + AR
 Layer Thickness, Porosity : 12 μm, 0.68 %
 Working Electrode Glass : LOF 15/cm
 Counter Electrode Type : LOF 15/Pt[∞]/Ag
 Data File Name : PL0705/bb1_May 12#32
 Current Compliance : 2 mA
 Settling Time, Voltage Step : 0.1 s, 10 mV0 s

	9.4% Sun	55.3% Sun	99.8% Sun
Thermopile _{ref}	Nan Sun	Nan Sun	Nan Sun
Current _{ref}	-364.346 μA	-2.136 mA	-3.851 mA
Power _{in}	9.439 mW/cm ²	55.331 mW/cm ²	99.762 mW/cm ²
Norm. Std. Dev.	0.19	0.33	0.27
Module U _{oc}	722.52 mV	778.56 mV	795.65 mV
Cell U _{oc}	722.52 mV	778.56 mV	795.65 mV
I _{sc}	-269.369 μA	-1.563 mA	-2.801 mA
I _{sc} ^{norm}	-1.72 mA/cm ²	-11.45 mA/cm ²	-17.77 mA/cm ²
U _{pmax}	594.88 mV	632.06 mV	629.87 mV
I _{pmax}	-1.6 mA/cm ²	-9.4 mA/cm ²	-16.8 mA/cm ²
Power _{out}	972.19 μW/cm ²	5.94 mW/cm ²	10.55 mW/cm ²
Total Power _{out}	153.61 μW	938.16 μW	1.67 mW
Fill Factor	0.789	0.771	0.748
Efficiency η	10.30%	10.73%	10.58%

IPCE @ 550 nm : 160.11 %
 Slope V_{oc}/ln(I_{sc}) : 31.172 mV
 Ideality Factor @ 1 Sun : 1.73
 Series Resistance @ 1 Sun : 14.69 ± 0.96 %, (2.32 / cm²)

Calibration File: Solar Lab I:Igor Applications:DataScan Data:cal_Thu, Oct 11, 2001

© RAHB: KIDAQ Measured by Paul



Date: Tue, May 13, 2003

Fig. 6. Photocurrent–voltage curve of a solar cell based on an electrolyte containing guanidinium thiocyanate as self-assembly facilitating agent. The cell was equipped with an antireflecting coating. The conversion efficiency in full sunlight was 10.6%.

very effective mode of charge screening which is operative in this ionic liquids.

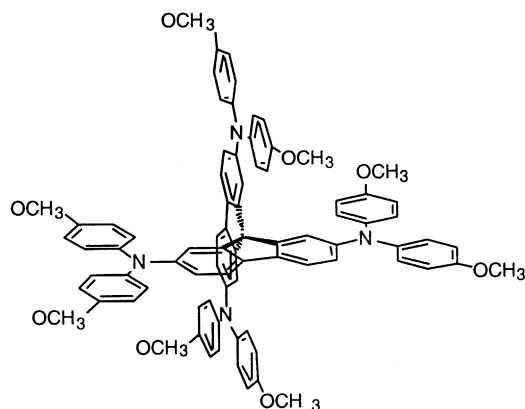
Long-term light soaking tests on sealed cells have also progressed significantly over the last few years. These tests are very important, as the redox electrolyte or the sealing, may fail under long-term illumination. A recent stability test 12,000 h of continuous full intensity light exposure has confirmed that this system does not exhibit an inherent instability [37], in contrast to amorphous silicon which due to the Stabler–Wronski effect undergoes photodegradation.

4.6. Solid-state dye-sensitized solar cells

One alternative which offers itself to confront the sealing problem is the replacement of the redox electrolyte by a solid p-type semiconductor interpenetrating the nanocrystalline TiO₂ structure which would permit the charge neutralisation of dye molecules after electron injection by its hole transport properties.

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 neutralisation after the electron loss by exchange with the redox system in solution. It is not immediately evident that an interpenetrating network of two conducting solids can 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:



Since the first report on this system in 1998 its photovoltaic conversion efficiency has been improved considerably and stands presently at 3.2% [38]. An even higher efficiency of 3.8% was recently achieved by Meng et al. using a dye-sensitized solar cell containing Cu(I) as a hole conductor instead of a liquid electrolyte [39].

5. 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. It 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 led 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.

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