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Highlight Review

Mesoscopic Solar Cells for Electricity and Hydrogen Production from Sunlight

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Abstract

The quality of human life depends to a large degree on the availability of energy sources. The present annual worldwide energy consumption has already attained a level of over 400 exajoules and is expected to further augment steeply from the increase in world population and the rising demand of energy in the developing countries. This implies enhanced depletion of fossil fuel reserves leading to further aggravation of the environmental pollution. Quality of life on earth is threatened unless renewable energy resources can be developed in the near future. Chemistry is expected to make important contributions to identify environmentally friendly solutions of the energy problem. One attractive strategy discussed in this article is the development of systems that mimic natural photosynthesis in the conversion solar energy. The task to be accomplished by these systems is to harvest sunlight and convert it to electricity or drive an uphill chemical reaction. Learning from the concepts used by green plants, we have developed a molecular photovoltaic device whose overall efficiency for solar energy conversion to electricity has already attained 11%. The system is based on the sensitization of nanocrystalline oxide films by charge-transfer sensitizers. The underlying fundamental processes of light trapping by the sensitizer, heterogeneous electron transfer from the electronically excited chromophore into the conduction band of the semiconductor oxide and the percolative migration of the injected electrons through the mesoporous film to the collector electrode, will be described below in detail. The low cost and ease of production of the new cell should benefit large scale applications. These systems will undoubtedly promote the acceptance of renewable energy technologies, not least by setting new standards of convenience and economy. The nanocrystalline semiconductor junctions developed first for dye sensitized solar cells have meanwhile found a realm of other applications ranging from electrochromic and electroluminescent displays to high power lithium insertion batteries. They are also used in tandem cells for the cleavage of water into hydrogen and oxygen by sunlight.

◆ Introduction

The idea of converting light to electric power or chemical fuels has infatuated mankind for many centuries. The dream is to capture the energy that is freely available from sunlight and turn it into the valuable and strategically important asset that is electric power or to generate directly chemical fuels, such as hydrogen. To date photovoltaics has been dominated by solid-state junction devices, usually in silicon, crystalline or amorphous, and profiting from the experience and material availability resulting from the semiconductor industry. However, there is an increasing awareness of the possible advantages of devices based on mesoscopic inorganic or organic semiconductors commonly referred to as "bulk" junctions because of their bicontinuous three dimensional structure. These are formed for example from nanocrystalline inorganic oxides, ionic liquids and organic hole conductor or conducting polymer devices[1–9] which offer the prospect of very low cost fabrication without expensive and energy intensive high temperature and high vacuum processes, compatibility with flexible substrates and a variety of presentations and appearances to facilitate market entry, both for domestic devices and in architectural or decorative applications. It is now possible to depart completely from the classical solid-state cells, which are replaced by devices based on interpenetrating network junctions. The presence of a bulk junction having an interface with a huge area endows these systems with intriguing optoelectronic properties. 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), invented in our laboratory at the Ecole Polytechnique Fédérale de Lausanne.[1] This accomplishes 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.[1–4]

The development of these new types of solar cells is promot-

Figure 1. The top ten problems mankind will face during the next 50 years according to Nobel laureate Richard Smalley.

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ed by the increasing public awareness that the earth's oil reserves will run out during this century. As the needs of the planet will at least double within the next 50 years the stage is set for a major shortage of energy supply unless renewable sources can cover the substantial deficit that fossil fuels can no longer furnish. Nobel laureate R. Smalley at a recent conference in Washington cited energy as the top problem that mankind will face in the near future, Figure 1.

Public concern has heightened recently because of the disastrous environmental pollution arising from all too frequent oil spills and the frightening climatic consequences of the green house effect caused by the combustion of fossil fuels. Fortunately, the supply of energy from the sun to the earth is gigantic, i.e., 3×10^{24} joule a year or about ten thousand times more than what mankind consumes currently. In other words covering only 0.1% of the earth's surface with solar cells with an efficiency of 10% would suffice to satisfy our current needs. To tap into this huge energy reservoir of the sun remains, nevertheless, a major challenge for mankind.

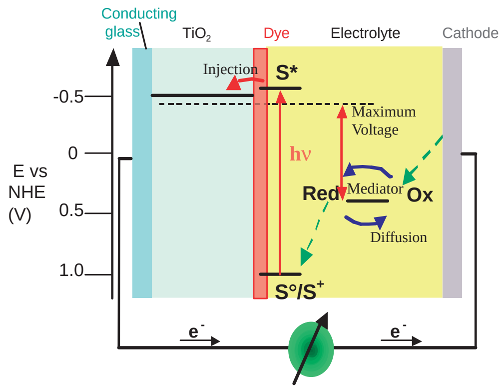

Figure 2. Principle of operation of the dye-sensitised nanocrystalline solar cell. Photoexcitation of the sensitizer (S) is followed by electron injection into the conduction band of an oxide semiconductor film. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter electrode by electrons passed through the load. Potentials are referred to the normal hydrogen electrode (NHE) The energy levels drawn match the redox potentials of the N3 sensitizer ground state and the iodide/triiodide couple shown in Figure 4.

♦ The Operational Principle of the Dye Sensitized Solar Cell (DSC)

A schematic presentation of the operating principles of the DSC is given in Figure 2. At the heart of the system is a mesoscopic oxide semiconductor film which is placed in contact 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, and Nb_2O_5 have also been investigated. Attached to the surface of the nanocrystalline film is a monolayer of the sensitizer. Photoexcitation of the latter results in the injection of an electron into the conduction band of the oxide. The dye is regenerated 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.

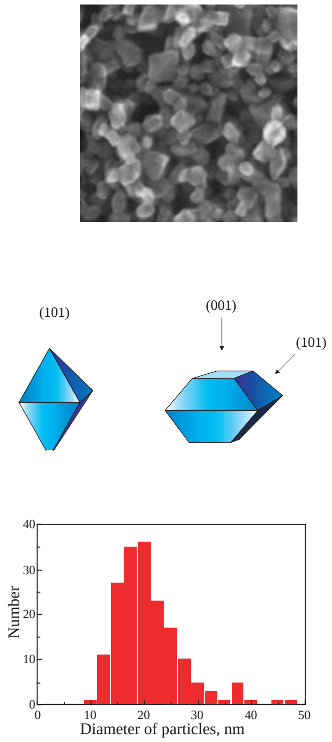

Figure 3. Scanning electron mircograph of a nanocrystalline TiO_2 (anatase film). The average size of the particles is about 20 nm and the facets have mainly (101) orientation.

The first laboratory embodiment of the dye-sensitized solar cell which dates back to 1988.[10] The photoanode 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 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 aqueous electrolyte containing bromide and small amount of bromine. The open circuit voltage of the cell was 1 V under illumination with a halogen spotlight. The device converted more than 60% of the incident photons to electric current at the absorption maximum of the sensitizer near 470 nm and the overall conversion efficiency in full sunlight was between 1–2%.

♦ Present Day Embodiments of the Dye Sensitized Solar Cell

Present embodiments of the DSC employ nanometer sized dye-derivatized oxide particles as light harvesting units in ref 1. This provides a simple and powerful method to achieve efficient

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harvesting of sunlight by the adsorbed monolayer of sensitizer. Figure 3 shows a scanning electron microscope picture of such a film. The real surface area of films having a thickness of 10 micron is about 1000 times larger than that of a flat film.

To enhance the light harvesting capacity of the dye-sensitized film in the red or near infrared region, larger anatase particles of 200–400 nm radius are either mixed in the film or printed as an overlayer on top of the smaller particles.

The most widely used sensitizer for the DSC has been *cis*-$Ru(SCN)_2L_2$ (L = 2.2′-bipyridyl-4,4′-dicarboxylate) abbreviated as N3[3] and the redox system used to regenerate the dye and transport the positive charges to the counter electrode has been the iodide/triiodide couple dissolved in an organic electrolyte or in a room-temperature ionic liquid. Figure 4 shows an operational diagram of the cell using these constituents, which form the main embodiment of the DSC to date.

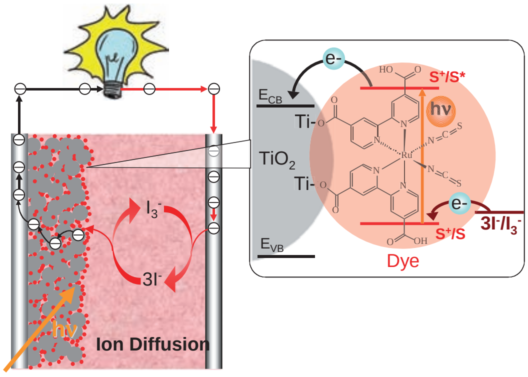

Figure 4. Schematic drawing showing the currently used embodiment of the DSC. It employs dye-derivatized TiO_2 nanocrystals as light harvesting units. The sensitizer is *cis*-$Ru(SCN)_2L_2$ (L = 2.2′-bipyridyl-4,4′-dicarboxylate) The redox system employed to regenerate the dye and transport the positive charges to the counter electrode is the iodide/triiodide couple dissolved in an organic electrolyte or in a room-temperature ionic liquid.

◆ Photovoltaic Performance

The astounding performance of nanocrystalline semiconductor junctions is illustrated in Figure 5 where we compare the photoresponse of a single crystal anatase electrode with that of a mesoporous TiO_2 film, both electrodes being sensitized by the N3 dye. The incident photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. The IPCE value obtained with the single crystal electrode is only 0.13% near 530 nm, where the sensitizer has an absorption maximum while it reaches 88% with the mesoporous electrode. As a consequence, in sunlight the photocurrent augments more than 1000 times when passing from a single crystal to a nanocrystalline electrode. This striking improvement defies expectations as such large area junctions should fare poorly in photovoltaic energy conversion the presence of defects at the disordered surface enhancing recombination of photogenerated charge carriers.

Very high incident photon to electric current conversion efficiencies can also be achieved with organic dyes. Figure 6 shows data obtained with a laboratory cell using a green prophyrin dye, which was provided to us by Prof. David Officer from the Massey University, New Zealand. The sensitizer is endowed with a cyanoacrylate group enhancing light absorption in the red region of the spectrum and anchoring the sensitizer at the surface

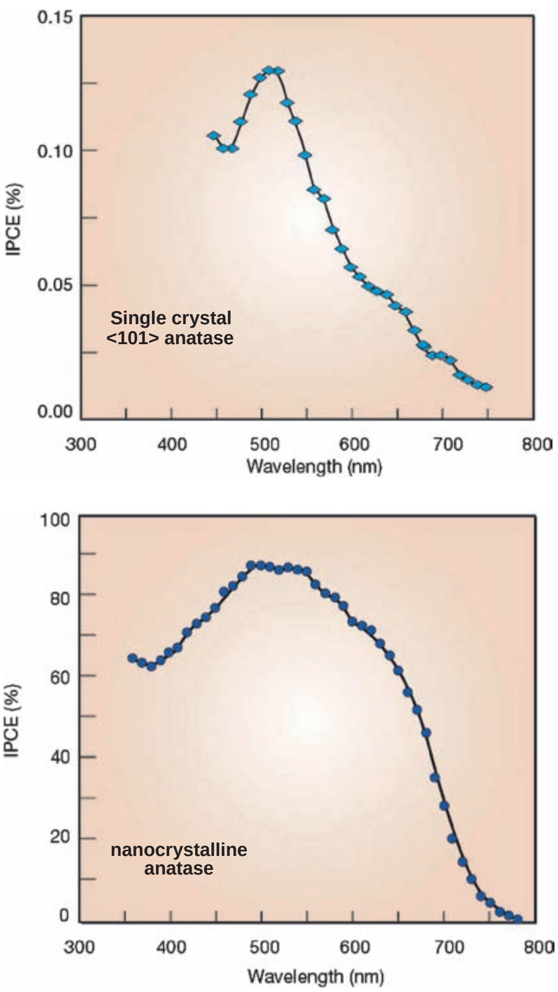

Figure 5. Conversion of light to electric current by dye-sensitized solar cells. The incident photon to current conversion efficiency is plotted as a function of the excitation wavelength. Top: single crystal anatase cut in the (101) direction. Bottom: nanocrystalline anatase film. The electrolyte consisted of a solution of 0.3 M LiI and 0.03 M I_2 in acetontrile.

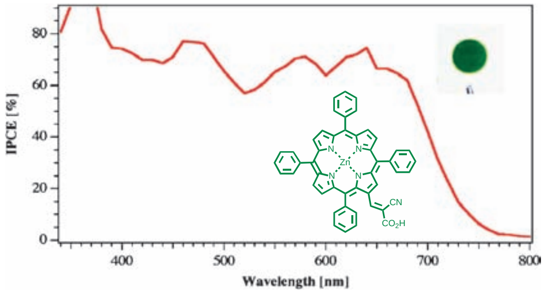

Figure 6. Photocurrent action spectrum obtained with a newly developed green porphyrin dye endowed with a cyanoacrylate group that red shifts the absorption spectrum of the porphyrine and serves to anchor the sensitizer at the TiO_2 surface.

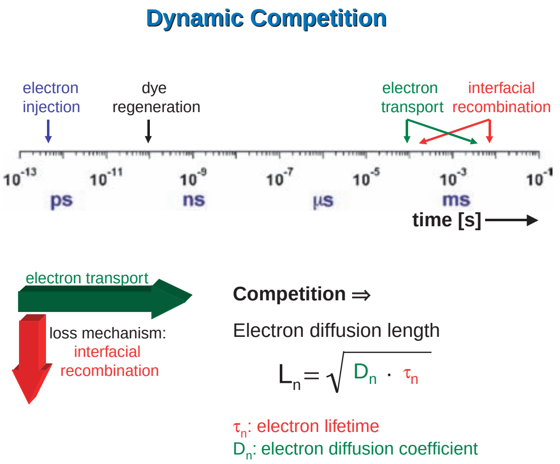

Figure 7. Dynamics of redox processes involved in the conversion of light to electric power by dye-sensitized solar cells.

of the mesoscopic TiO_2 film. Organic sensitizers that come close to matching the efficiency of the N3 dye have recently been developed in Japan.[11,12]

These extraordinary findings are due to the specific kinetic features of the interfacial charge-transfer processes summarized in Figure 7. The initial events of electron injection and dye regeneration leading to photoinduced charge separation occur on a femto- to nanosecond time scale[13,14] 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.[15] The result is that the mean electron diffusion length L is in the 10–20 micrometer range irrespective of the incident light level. Because this range is commensurate with the film layer thickness needed to harvest sunlight efficiently all photogenerated electrons can be collected.

The overall conversion efficiency of the dye-sensitized cell is determined by the photocurrent density measured at short circuit (I_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (ff) and the intensity of the incident light (I_s)

$$\eta \text{ global} = I_{sc} \times V_{oc} \times ff/I_s \tag{1}$$

Under full sunlight (air mass 1.5 global intensity $I_s = 1000\,\text{watt/m}^2$) short circuit photocurrents ranging from 16–22 mA/cm^2 are reached with state of the art ruthenium sensitizers, while V_{oc} is 0.7 to 0.86 V and the fill factor values 0.65–0.75. A certified overall power conversion efficiency of 10.4% was attained[16] in 2001. A new record efficiency of 11% was achieved recently and Figure 8 shows current–voltage curves obtained with this cell.

While this efficiency figure now makes dye-sensitized cells fully competitive with the better amorphous silicon devices, a commercially even more significant parameter is the dye lifetime achieved under working conditions. A recent stability test during 12000 h of continuous full intensity light exposure has confirmed that this system does not exhibit any inherent instability,[17] in contrast to amorphous silicon, which due to the Stabler–Wronski effect undergoes photodegradation. Recently a heat resistant quasisolid state electrolyte based on imidazolium iodide 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.[18] Other laboratories have also presented systematic verifications of the cell stability carried out independently.

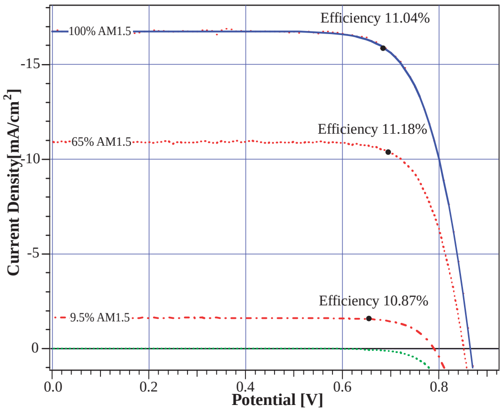

Figure 8. Photocurrent–voltage curve of a DSC at different light intensities. The conversion efficiency in full AM 1.5 sunlight was 11.04%. It increased to 11.18% at 65% full sunlight.

Tandem Cells for Water Cleavage by Visible Light

The advent of nanocrystalline semiconductor systems has rekindled interest in tandem cells for water cleavage by visible light, which remains the "holy grail" of photoelectrochemical research. The "brute force" approach to achieve this goal is to employ a set of four in series connected silicon photovoltaic cells to generate electricity that is subsequently passed into a commercial-type water electrolyzer. Solar to chemical conversion efficiencies obtained are about 7%. Higher efficiencies of 12% have recently been reported for tandem cells based on III–V semiconductors.[19] However, the cost of these single crystal materials is too high for large-scale terrestrial applications.

A low-cost tandem device that achieves the direct cleavage of water into hydrogen and oxygen by visible light was developed recently.[2] This is based on the in series connection of two photosystems as shown in Figure 9 in the electron flow diagram. A thin film of nanocrystalline tungsten trioxide[20] or iron oxide serves as the top electrode absorbing the blue part of the solar spectrum. The valence band holes (h^+) created by band gap excitation of the film oxidize water to oxygen:

$$4h^+ + 2H_2O = O_2 + 4H^+ \tag{2}$$

while the conduction band electrons are fed into the second photosystem consisting of the dye-sensitized nanocrystalline TiO_2 cell discussed above. The latter is placed directly under the WO_3 film, capturing the green and red parts of the solar spectrum that is transmitted through the top electrode. The photovoltage generated by the second photosystem enables the generation of hydrogen by the conduction band electrons:

$$4H^+ + 4e^- = 2H_2 \tag{3}$$

The overall reaction corresponds to the splitting of water by visible light. There is close analogy to the *Z*-scheme operative in

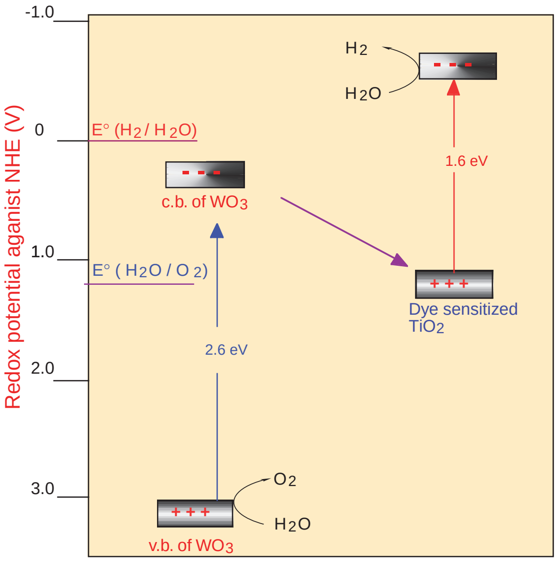

Figure 9. The *Z*-scheme of photocatalytic water decomposition by a tandem cell.

the light reaction of photosynthesis in green plants. The advantage of the tandem approach is that higher efficiencies than with single junction cells can be reached if the two photosystems absorb complimentary parts of the solar spectrum. At present, the overall AM 1.5 solar light to chemical conversion efficiency achieved with this device has reached already over 6%.[21] Recently a tandem cell having 8% conversion efficiency in simulated sunlight was even reported.[22] A photograph of such a cell is shown below. The light beam traverses the cell from the left to the right. The tungsten trioxide film at the fron Wall of the cell where oxygen is evolved absorbs the blue and ultraviolet parts of the spectrum. The electrons produced by photoexcitation of the WO_3 are passed through the dye-sensitized solar cell mounted on the back of the cell wall and which absorbs the yellow and red portions of the sunlight. This increases the energy of the electrons to the extent that they can produce hydrogen when reintroduced in the cell through a platinum wire.

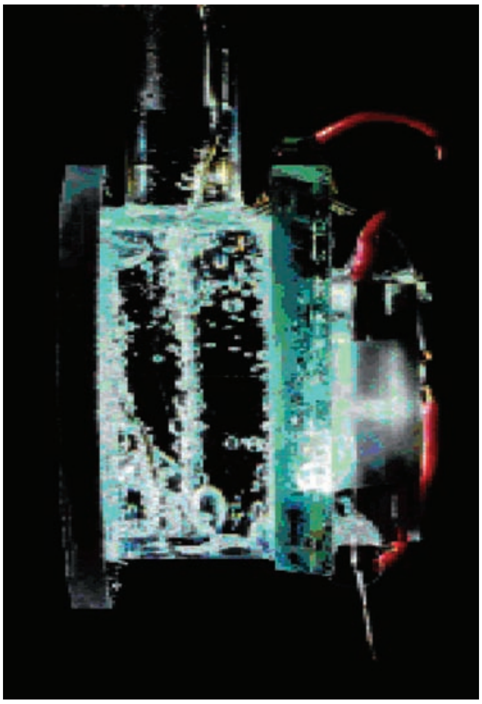

Figure 10. Tandem cell for the photocleavage of water by visible light.

Figure 11. Dye-sensitized solar glass panels integrated in the wall of the CSIRO research building in New Castle, Australia.

♦ First Large Scale Field Tests and Commercial Developments

During recent years industrial interest in the dye sensitized solar cell has surged and first commercial products have appeared. A number of industrial corporations, such as Konarka (www.konarkatech.com) in the U.S.A., Aisin Seiki and Hitachi Maxell in Japan, and well as RWE in Germany and Greatcell in Switzerland are actively pursuing the development of new products. Particularly interesting are applications in building integrated photovoltaic elements such as electric power producing transparent glass tiles. The Australian company Sustainable Technologies International (www.sta.com.au) has produced such tiles on a large scale for field testing and a first building has been equipped with a wall of this type as shown in Figure 11.

♦ Acknowledgement

Recognition is due to the members of the EPFL electrochemical photovoltaics development team, some of whose work is referenced below and to those industrial and public organizations whose interest in this new system has induced them to support our research.

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