

Special Issue

The Advent of Mesoscopic Injection Solar Cells

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Mesoscopic injection solar cells operate in an entirely different fashion than conventional solar p-n junction devices. Mimicking the principles that natural photosynthesis has used successfully over the last 3.5 billion years in solar energy conversion, they achieve the separation of light harvesting and charge carrier transport. The semiconductors used in conventional cells assume both functions simultaneously imposing stringent demands on purity and entailing high material and production costs. The prototype of this new PV family is the dye-sensitized solar cell (DSC). The DSC has made phenomenal progress since its discovery was announced in the scientific literature only 14 years ago.¹ Conversion efficiencies of 11.3% and excellent stability have been reached rendering it a credible alternative to conventional p-n junction photovoltaic devices. The industrial development is advancing rapidly. Several enterprises currently produce modules and flexible cells on a pilot scale and commercial manufacturing of the DSC has recently been announced. It is asserted that this type of cell is a viable contender for large-scale future solar energy conversion systems on the bases of cost, efficiency, stability and availability, as well as environmental compatibility. Copyright © 2006 John Wiley & Sons, Ltd.

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1. INTRODUCTION

The field of photovoltaic cells has been dominated so far by solid state p-n junction devices made of crystalline or amorphous silicon, CdTe and copper indium gallium diselenide (CIGS) profiting from the experience and material availability of 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 due to their interconnected three-dimensional structure. These are formed, for example, from nanocrystalline inorganic oxides, ionic liquids and organic hole conductor or conducting polymer devices, which offer the prospect of very low cost fabrication without expensive and energy

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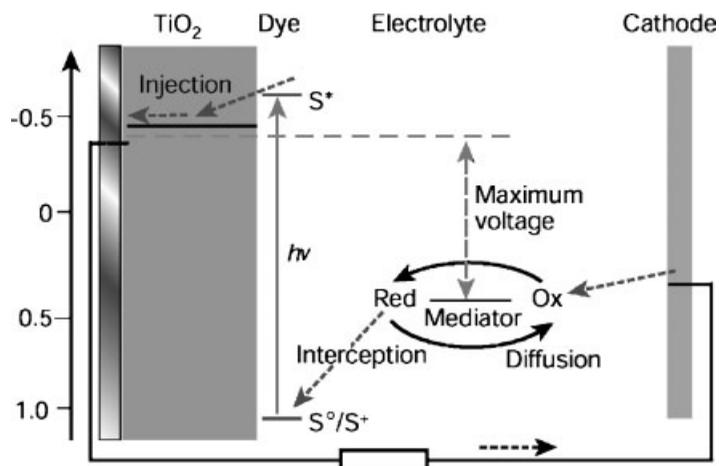


Figure 1. Energy band diagram of the DSC. Light is absorbed by a dye (S) or a semiconductor quantum dot that is located precisely at the interface between an electron conducting and hole transporting medium. The excited state (S^*) produced injects an electron into the conduction band of a n-type wide band gap oxide, such as TiO_2 , ZnO or SnO_2 . The sensitizer or quantum dot is regenerated by injecting a hole in the p-type conductor or redox electrolyte. The electrons diffuse across the oxide to the current collector and from there through the external circuit, performing electrical work. They re-enter the cell through the back contact (cathode) regenerating the hole conductor or redox mediator (Red) thereby closing the cyclic conversion of light to electricity

intensive high temperature and high vacuum processes. They can feasibly be produced employing flexible substrates and are compatible with a variety of embodiments and appearances to facilitate market entry, both for use in domestic devices as well as in architectural or decorative applications.

It is now possible to depart completely from the classical solid-state cells, replacing them by devices based on interpenetrating network junctions. The mesoscopic morphology produces an interface with a huge area endowing these systems with intriguing optoelectronic properties. Contrary to expectation, devices based on interpenetrating networks of semiconductors have shown strikingly high conversion efficiencies, competing with those of conventional devices. The prototype of this family is the dye-sensitized solar cell (DSC), invented in the author's laboratory at the Ecole Polytechnique Fédérale de Lausanne.¹ As shown below, this cell accomplishes the separation of 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.^{1–3}

The band diagram of the DSC is shown in Figure 1. Sunlight is harvested by a sensitizer that is attached to the surface of a large band gap semiconductor, typically an oxide such as TiO_2 film. Photo-excitation of the dye results in the injection of electrons into the conduction band of the oxide. The dye is regenerated by hole injection in an organic hole conductor or an electrolyte, such as an ionic liquid containing most frequently the iodide/triiodide couple as a redox system. This mediator intercepts the recapture of the conduction band electron by the oxidized state of the sensitizer S^+ . The redox system is regenerated in turn by the reaction with the electrons at the counter electrode which have passed through the external circuit. The voltage generated under illumination corresponds to the difference between the quasi-Fermi level of the electron in the solid and the redox potential of the electrolyte or the work function of the hole conductor. Thus, the device is regenerative, producing electricity from light without any permanent chemical transformation.

2. THE VIRTUES OF THE NANOSTRUCTURE

The nanocrystalline morphology of the semiconductor oxide film is essential for the efficient operation of the device. On a flat surface a monolayer of dye absorbs at most a small percentage of the impending light because

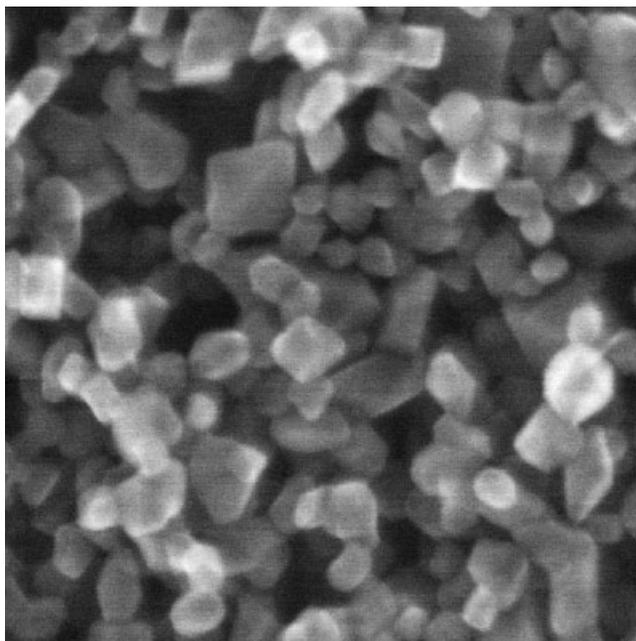


Figure 2. Transmission electron microscope picture of a mesoscopic TiO_2 (anatase) film. Note the bipyramidal shape of the particles having (101) oriented facets exposed. The average particle size is 20 nm

it occupies an area that is several hundred times larger than its optical cross section. Using multi-layers of sensitizer does not offer a viable solution to this problem. Only the molecules that are in direct contact with the oxide surface would be photoactive the remainder merely filtering the light. Apart from poor light harvesting, a compact semiconductor film would need to be n-doped to conduct electrons. In this case energy transfer quenching of the excited sensitizer by the electrons in the semiconductor would inevitably reduce the photovoltaic conversion efficiency.

Figure 2 is a scanning electron microscopy picture of a mesoscopic TiO_2 (anatase) layer. The particles have an average size of 20 nm and the facets exposed have mainly (101) orientation, corresponding to the anatase crystal planes with the lowest surface energy. Employing such oxide nanocrystals covered by a monolayer of sensitizer as light harvesting units allows overcoming the notorious inefficiency problems, which till the inception of the DSC in 1991 had haunted all solar energy conversion devices based on the sensitization of wide band gap semiconductors.

3. OPPORTUNITIES FOR DSC PERFORMANCE IMPROVEMENT

The DSC currently reaches 11.2% energy conversion efficiencies under standard reporting conditions (AM 1.5 global sunlight at 1000 W/m^2 intensity, 298 K temperature) in liquid junction devices⁴ rendering it a credible alternative to conventional p-n junction photovoltaic devices. Typical photovoltaic performance data are shown in Figure 3. Solid-state equivalents using organic hole-conductors have exceeded 4% efficiency⁵ whereas nanocomposite films comprising only inorganic materials, such as TiO_2 and CuInS_2 have achieved efficiencies between 5 and 6%.^{6,7} New dyes showing increased optical cross-section and capable of absorbing longer wavelengths are currently under development. Similarly, the performance of mesoscopic TiO_2 films employed as electron collectors is benefiting greatly from recent advances in nano-material research. Interfacial engineering to retard the interfacial back reaction of electrons injected into the nanocrystalline oxide with holes transferred from the dye to the redox electrolyte or the hole conductor will produce major gains in the open circuit voltage.⁸ Nevertheless, the most important gains to be expected in the near term will be in the short circuit photocurrent.

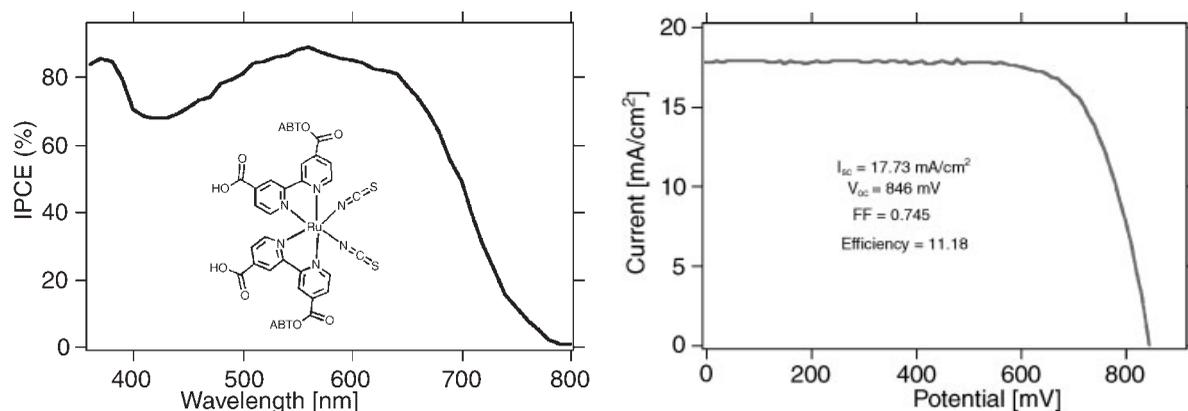


Figure 3. Photovoltaic performance of a state of the art DSC laboratory cell. Left: photo-current action spectrum showing the monochromatic incident photon to current conversion efficiency (IPCE) as function of light wavelength, inset: chemical structure of the N-719 sensitizer. Right: J-V curve of the same cell under AM 1.5 standard test conditions

A new generation of sensitizers is presently being developed, having higher optical cross sections⁹ and enhanced near IR response. Shown in below in Figure 4 is the structure of a new dye coded K-19 which exhibits enhanced absorption due to extension of its π -system.

These dyes are expected to reach photocurrent densities of 25–27 mA/cm², which would allow pushing the overall conversion efficiency of the DSC above the 15% mark without changing the currently used non-volatile redox system. A road map to achieve this goal within the next 2 years has been elaborated and will serve to coordinate synthetic efforts of several groups on the international scale.

4. TANDEM CELLS

An advantage that makes the DSC particularly attractive for tandem cell application is that its optical transmission and short circuit photocurrent can be readily adjusted by changing the film thickness, pore size, the nature of the dye, and the dye loading. This, along with the ease of forming layered structures, for example by producing the mesoscopic oxide films using screen printing or doctor blading methods, renders the DSC particularly well suited for the fabrication of tandem solar cell structures for an optimal utilization of the solar spectrum. Several previous publications have dealt with the use of stacked DSC configurations where two dyes absorbing different parts of the solar spectrum were employed as sensitizers.^{10–14} We demonstrated recently that a tandem device

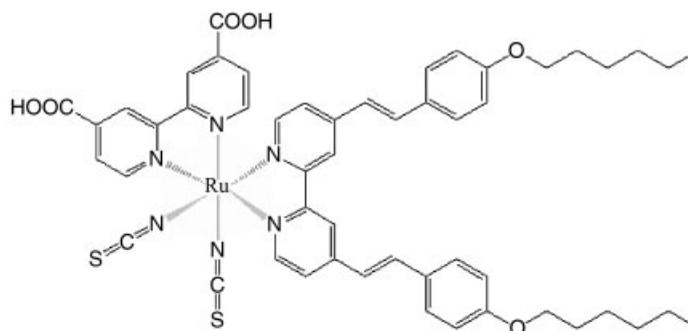


Figure 4. The K19 dye molecular structure

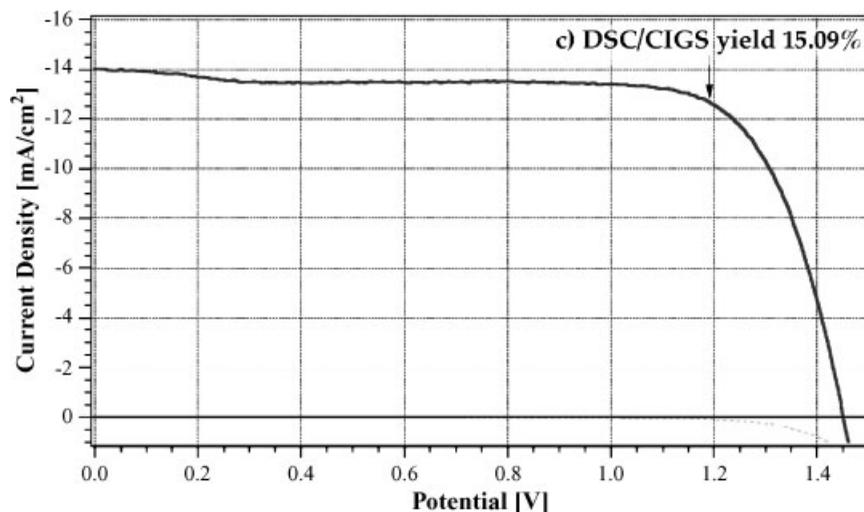


Figure 5. Photocurrent density-voltage characteristics under AM 1.5 full sunlight (100 mW/cm^2) for a two-terminal tandem DCS/CIGS cell. The DSC top cell gave $J_{sc} = 13.66 \text{ mA/cm}^2$; $V_{oc} = 0.8 \text{ V}$; $FF = 0.75$ and $\eta = 8.2\%$. For the CIGS bottom cell in the stack $J_{sc} = 14.3 \text{ mA/cm}^2$; $V_{oc} = 0.65 \text{ V}$ and $FF = 0.77$ while the DSC/CIGS tandem cell produced $J_{sc} = 14.05 \text{ mA/cm}^2$; $V_{oc} = 1.45 \text{ V}$; $FF = 0.74$ and conversion efficiency = 15.09%

comprising a DSC as a top cell for high energy photons and a copper indium gallium selenide (CIGS) thin film bottom cell capturing the red and near IR solar emission produces AM 1.5 solar to electric conversion efficiencies greater than 15% without any significant efforts to optimize current matching and minimize optical losses.¹⁵

Figure 5 shows the J-V curve obtained under AM-1.5 for one of the first embodiments of a two-terminal tandem device. The DSC top cell produced $J_{sc} = 13.66 \text{ mA/cm}^2$; $V_{oc} = 0.798 \text{ V}$; $FF = 0.75$ and $\eta = 8.18\%$ while the CIGS bottom cell in the stack gave $J_{sc} = 14.3 \text{ mA/cm}^2$; $V_{oc} = 0.65 \text{ V}$; $FF = 0.77$. For the DSC/CIGS tandem cell $J_{sc} = 14.05 \text{ mA/cm}^2$; $V_{oc} = 1.45 \text{ V}$; $FF = 0.74$ and $\eta = 15.09\%$. The performance of the tandem was clearly superior to that of the individual cells, despite the fact that the short circuit currents of the two cells were not perfectly matched entailing the observed shoulder in the J-V curve. Likewise, no effort was made to minimize the optical losses. This leaves no doubt that further rapid efficiency gains reaching well beyond the 20% mark can be expected from the fructuous marriage of these two thin film PV technologies.

5. STABILITY

Contrary to amorphous silicon, which suffers from degradation due to the well-known Staebler-Wronski effect, the intrinsic stability of the DSC has been confirmed by extensive accelerated light soaking tests carried out over the last decade. One major issue that has been settled during this period is that the sensitizers employed in the current DSC embodiments can sustain 20 years of outdoor service without significant degradation. However, as new more advanced dye structures emerge in the future, and in order to avoid repeating these lengthy tests every time the sensitizer is modified, kinetic criteria have been elaborated allowing prediction of its long-term performance. Figure 6 illustrates the catalytic cycle that the sensitizer undergoes during cell operation. Critical for stability are side reactions that occur from the excited state S^* or the oxidized state of the dye (S^+), which would compete with electron injection from the excited dye into the conduction band of the mesoscopic oxide and with the regeneration of the sensitizer. These destructive channels are assumed to follow first or pseudo-first order kinetics and are assigned the rate constants k_1 and k_2 .

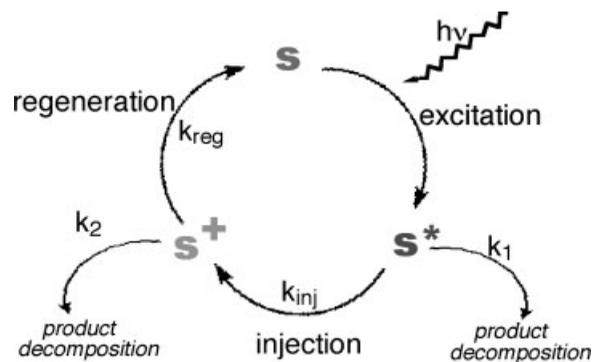


Figure 6. The catalytic cycle of the sensitizer during DSC operation

By introducing the two branching ratios, $P_1 = k_{inj}/(k_1 + k_{inj})$ and $P_2 = k_{reg}/(k_2 + k_{reg})$ where k_{inj} and k_{reg} are the first order or pseudo-first order rate constants for the injection and regeneration process, respectively, the fraction of the sensitizer molecules that survives one cycle is given by the product $P_1 \times P_2$. A simple calculation shows that the sum of the two branching ratios should not exceed 1×10^{-8} in order for the lifetime of the sensitizer to reach at least 20 years. The turnover frequency of the dye, averaged over seasons and day-night time, is about 0.16 s^{-1} .

For most of the common sensitizers the rate constant for electron injection from the excited state to the conduction band of the TiO_2 particles is in the femtosecond range. Assuming $k_{inj} = 1 \times 10^{13} \text{ s}^{-1}$, any destructive side reaction should have $k_1 < 10^5 \text{ s}^{-1}$. Ruthenium sensitizers of the N-719 or K-19 type readily satisfy this condition as the bleaching from the excited state level occurs at a much lower rate than the 10^5 s^{-1} limit. Precise kinetic information has also been gathered for the second destructive channel involving the oxidized state of the sensitizer, the key parameter being the ratio k_2/k_{reg} of the rate constants for the degradation of the oxidized form of the sensitizer and its regeneration. The S^+ state of the sensitizer can be readily produced by chemical or electrochemical oxidation and its lifetime determined independently by absorption spectroscopy. A typical value of k_2 is around 10^{-4} s^{-1} while the regeneration rate constant is at least in the 10^5 s^{-1} range. Hence, the branching ratio is well below the limit of 10^{-8} , which can be tolerated to achieve the 100 million turnovers and a 20 year lifetime for the sensitizer.

Many long-term tests have been performed with the N3-type ruthenium complexes confirming the extraordinary stability of these charge transfer sensitizers. For example, a European consortium financed under the Joule program¹⁶ has confirmed cell photocurrent stability during 10 000 h of light soaking at 2.5 suns corresponding to ca 56 million turnovers of the dye without any significant degradation. These results corroborate the projections from the kinetic considerations made above. A more difficult task has been to reach stability under prolonged stress at higher temperatures, i.e., 80–85°C. Recent stabilization of the interface by using self-assembly of sensitizers in conjunction with amphiphilic coadsorbents has been particularly rewarding by allowing the DSC to meet for the first time the specifications laid out for outdoor applications of silicon photovoltaic cells.¹⁷ For example, the new amphiphilic sensitizer K-19, shows increased extinction coefficients due to extension of the π conjugation of the hydrophobic bipyridyl and the presence of electron donating alkoxy groups. Taking advantage of the enhanced optical absorption of this new sensitizer and using it in conjunction with decylphosphonic acid (DPA) as coadsorbent and a novel electrolyte formulation, a $\geq 8\%$ efficiency DSC has been realized showing strikingly stable performance under both prolonged thermal stress and light soaking.¹⁸

While impressive progress has been made in the development of stable, non-volatile electrolyte formulations the conversion yields obtained with these systems are presently in the 7–10% range, i.e., below the 11% reached with volatile solvents. Future research efforts will be dedicated to bridge the performance gap between these systems. The focus will be on hole conductors and solvent-free electrolytes such as ionic liquids. The latter are

a particularly attractive choice for the first commercial modules, due to their high stability negligible vapor pressure and excellent compatibility with the environment.

6. SOLID STATE DSC

Research on the solid state DSC has gained considerable momentum recently as this embodiment is attractive for realizing flexible PV cells in a roll to roll production.¹⁹ The *spiro*-OMeTAD has been the most successful p-type organic conductor (HTM) employed. Its work function is about 4.9 eV and the hole mobility $2 \times 10^{-4} \text{ cm}^2/\text{s}$. The structure of the *spiro*-OMeTAD is shown in Figure 7 along with a energy diagram of the solid stated DSC. Reported first in 1998, the conversion yields have increased dramatically over the last few years, i.e. from a fraction of a per cent² to over 4%.²⁰ The main draw back of these cells has been fast interfacial electron-hole recombination reducing the diffusion length of the conduction band electrons to a few microns²¹ as compared to 20–100 microns for the electrolyte based DSC. As a consequence, the film thickness employed in these cells is only 2 microns which is insufficient to harvest the sunlight by the adsorbed sensitizer, thus reducing the resultant photocurrent. The dye monolayer itself blocks this back reaction because it is electrically insulating.²² Hence current efforts are being directed towards molecular engineering of the interface to improve the compactness and order of monolayer and prevent in this fashion the charge carriers from recombining. Another difficulty encountered has been the filling of the porous network with the hole conductor. This impediment may be overcome by developing oxide films having regular mesoporous channels aligned in a perpendicular direction to the current collector. On the other hand, the V_{oc} values obtained with solid state DSCs are high, reaching nearly 1 V, due to a better match of the hole conductor work function than that of the electrolyte with the redox potential of the sensitizer. The future of these solid hole conductor systems, thus looks very bright if the recombination and pore filling problems can be addressed.

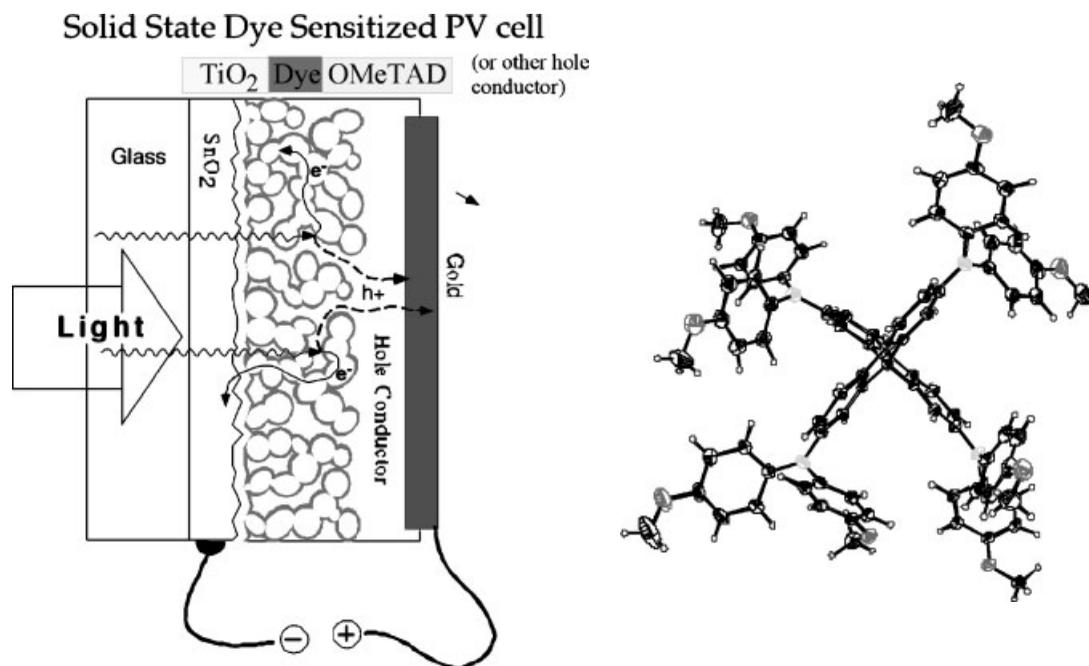


Figure 7. Cross sectional view of a solid state DSC using the hole conductor *spiro*-OMeTAD whose structure is indicated on the right side (left drawing by courtesy of Brian O'Regan)

7. QUANTUM DOT SENSITIZERS

Semiconductor quantum dots (QDs) can replace dyes as light harvesting units in the DSC.^{23,24} Light absorption produces excitons or electron-hole pairs in the QD. The electron is subsequently injected within femtoseconds into the semiconducting oxide support while the hole is transferred to a hole conductor or an electrolyte present in the pores of the nanocrystalline oxide film. Efficient and rapid hole injection from PbS quantum dots into triarylamine hole conductors has already been demonstrated and IPCE values exceeding 50% have been reached without attempting to optimize the collector structure nor to retard interfacial electron hole recombination.²³ QDs have much higher optical cross sections than molecular sensitizers, depending on their size. However, they also occupy a larger area on the surface of the mesoporous electrode decreasing the QD-concentration in the film. Nevertheless, the value of the absorption length is significantly shorter than that observed for the dye loaded films.

8. MULTI-EXCITON GENERATION AND CHARGE CARRIER MULTIPLICATION

A very recent exciting discovery shows that multiple excitons can be produced from the absorption of a single photon by a quantum dot via impact ionization (IMI) if the photon energy is three times higher than its band gap.²⁵ The challenge is now to find ways to collect the excitons before they recombine. As recombination occurs on a picosecond time scale, the use of mesoporous oxide collector electrodes presents a promising strategy, because the electron transfer from the quantum dot to the conduction band of the oxide collector electrode occurs within femtoseconds.²³ This opens up research avenues that ultimately may lead to photo-converters reaching external quantum efficiencies values of several hundred percent. A calculation based on Henry's model²⁶ shows that the maximum conversion efficiency of a single junction cell could be increased from 34 to 44% by exploiting IMI effects.

9. THE FIRST DSC MODULES

A few years after the inception of the DSC in 1991 the first monolithic Z-type interconnected modules were made by Dr Andreas Kay in our laboratory following a procedure, which has been published since then.²⁷ A photograph of a 6-cell module is shown in Figure 8a along with a smaller module that is turned on its back for visualization of the carbon-based back contact. Under illumination by a desk lamp the electric power generated by the cell serves to spin a fan quite rapidly, illustrating the successful photovoltaic conversion process. Note that this module was produced manually using screen-printing to deposit the nanocrystalline TiO₂ film and avoiding any costly materials or fabrication steps. A test at the NREL PV calibration laboratory produced the J-V curve shown in Figure 8b. Even though a mismatch in the output of the individual cells produced a step in the current plateau, a respectable total aperture area conversion efficiency of 5.29% was obtained. Meanwhile much larger modules have been developed principally by industrial enterprises reaching significantly higher efficiencies of around 7%.²⁸

10. PILOT PRODUCTION OF MODULES AND OUTDOOR FIELD TESTS

Figure 9 shows two prototypes of the monolithic Z-type interconnected modules, fabricated by Aisin Seiki in Japan. Note that the same low cost embodiment is employed as in the device shown in Figure 8. Field tests of such modules have already started several years ago and the results of these tests revealed advantages of the DSC with regards to silicon panels under realistic outdoor conditions. Thus, for equal rating under standard test conditions (STC) the DSC modules produced 20–30% more energy than the poly-crystalline silicon (pc-Si) modules.²⁸ A photograph of the test station comparing the two types of PV technologies is shown in Figure 10. The superior performance of the DSC can be ascribed to the following factors.

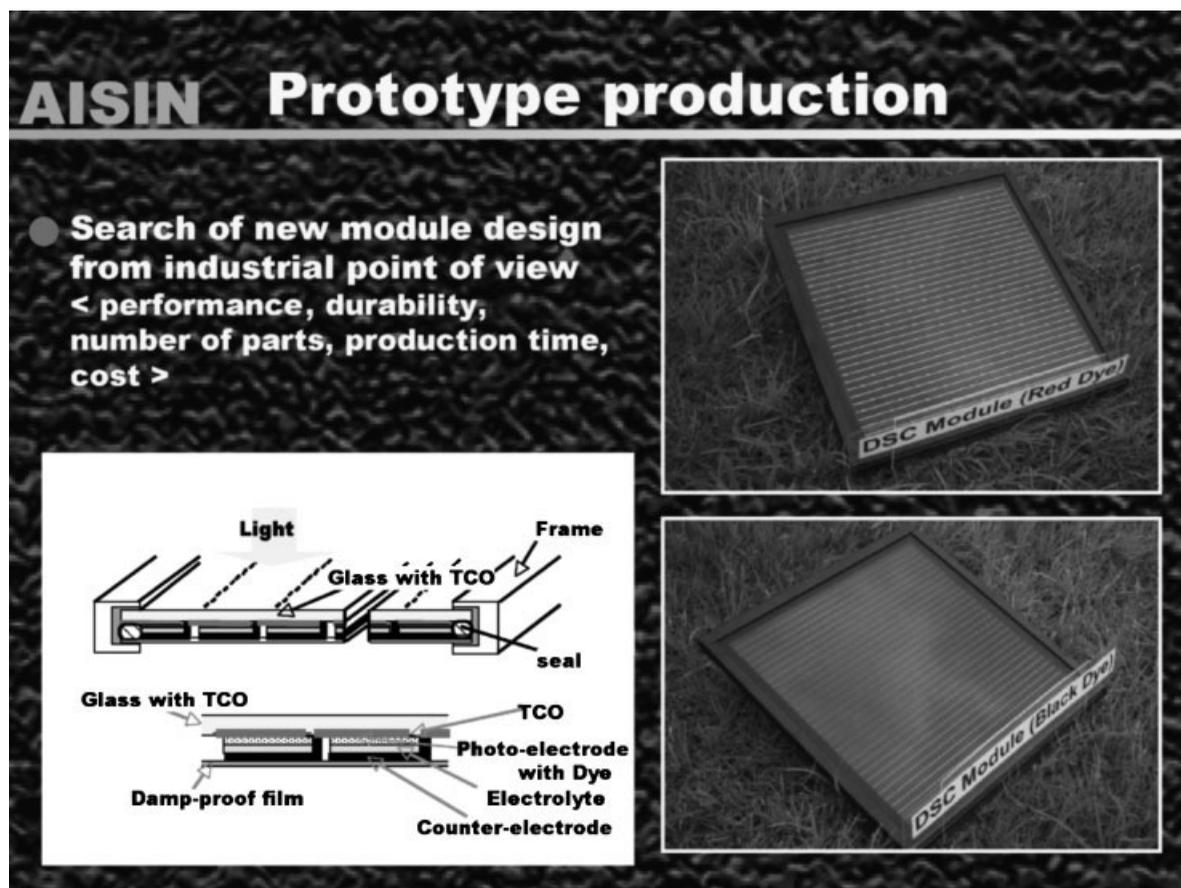


Figure 9. Production of DSC prototypes by Aisin Seiki in Japan. Note the monolithic design of the PV modules and the use of carbon as interconnect and counter electrode material. The red dye is related to N-719 while the black dye has the structure $\text{RuL}'(\text{NCS})_3$ where $L' = 2, 2', 2''$ -terpyridyl, 4,4',4''-tricarboxylic acid

to absorb incident photons in selective spectral regions of the solar emission, while maintaining high transparency in the remaining wavelength range. Thus, see-through cells can assume different colors or be totally transparent in the visible absorbing only near IR and UV light. An example for the latter case is the DSC based on a phthalocyanine sensitizer whose structure and photocurrent action spectrum is shown in Figure 11. This dye absorbs selectively in the 550–750 nm region leaving a window in the rest of the visible domain. Cells of this type are transparent with a beautiful blue tinge rendering them very attractive for architectural applications.

Efficiencies of over 5% can be readily reached with such power windows, values which are at least twice as high as competing amorphous silicon thin film solar devices that achieve partial transparency only by leaving part of the glass uncovered. Figure 12 shows an example of an electric power producing transparent glass.

DSC panels have also been installed in the walls of the Toyota 'Dream House' shown in Figure 13, offering a building integrated source of solar power to the inhabitants. Very recently Dyesol has announced the building of the first large scale DSC manufacturing plant in Greece.³¹

12. OUTLOOK

Using a principle derived from natural photosynthesis, mesoscopic injection solar cells and in particular the DSC have become a credible alternative to solid-state p-n junction devices. Conversion efficiencies over

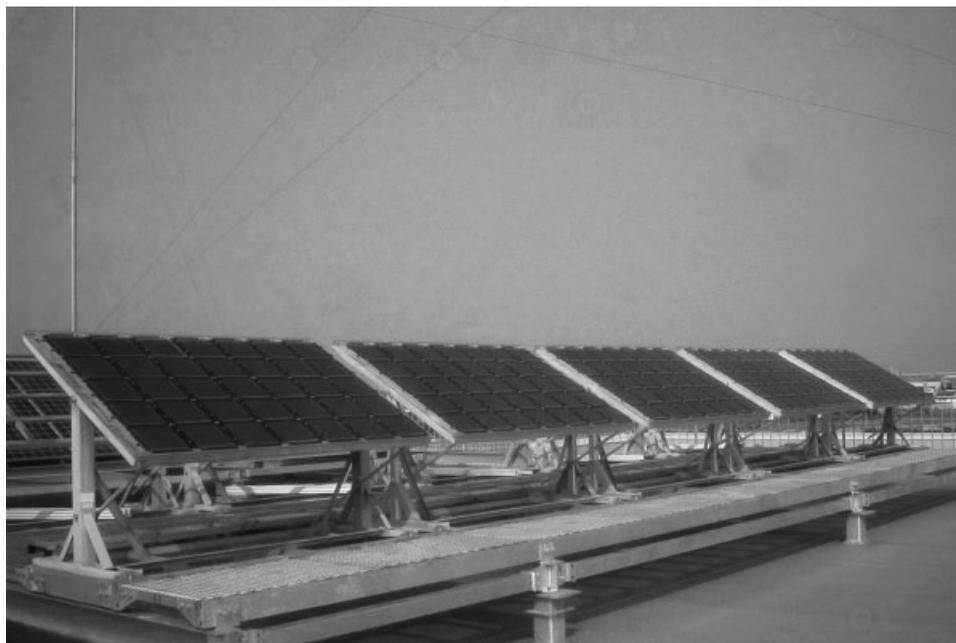


Figure 10. Outdoor field tests of DSC modules in Kariya City Japan at lat. $35^{\circ}10'N$, Azimuthal angle: 0° Facing due south, Tilted at 30° . Note the pc-Si modules in the second row

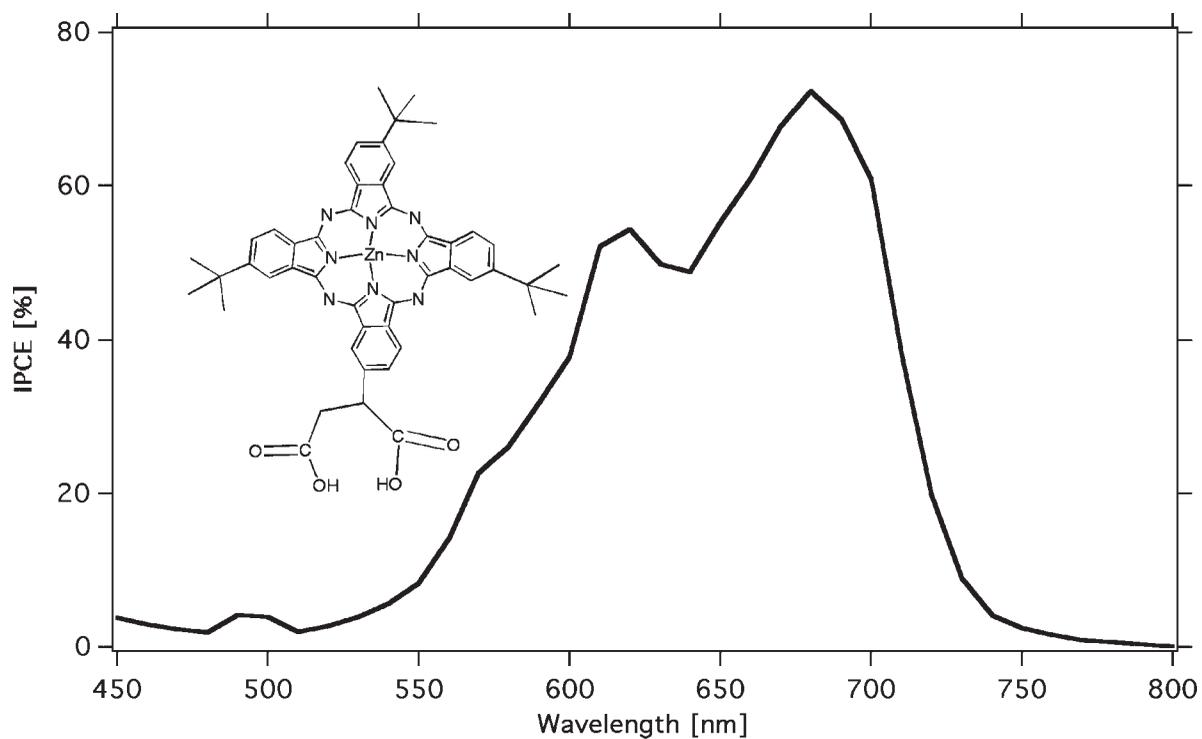


Figure 11. Photocurrent action spectrum of a phthalocyanin-sensitized transparent DSC³⁰



Figure 12. see-through DSC producing electric power from diffuse light to drive a fan



Figure 13. The Toyota 'Dream House' featuring DSC panels made by Aisin Seiki. For details see web announcement http://www.toyota.co.jp/jp/news/04/Dec/nt04_1204.html

11% and 15% have already been obtained with single junction and tandem cells, respectively, on the laboratory scale, with ample room for further amelioration. Future research will focus on improving the J_{sc} by extending the light response of the sensitizers in the near IR spectral region. Substantial gains in the V_{oc} are expected from introducing ordered oxide mesostructures and controlling the interfacial charge recombination by judicious engineering on the molecular level. Hybrid cells based on inorganic and organic hole conductors are

an attractive option in particular for the flexible DSC embodiment. Nanostructured devices using purely inorganic components will be developed as well. The mesoscopic cells are well suited for a whole realm of applications ranging from the low power market to large-scale applications. Their excellent performance in diffuse light gives them a competitive edge over silicon in providing electric power for stand-alone electronic equipment both indoor and outdoor. Application of the DSC in building integrated PV has already started and will become a fertile field of future commercial development. Almost one hundred years ago, at the 1912 IUPAC conference in Washington the famous Italian photochemist Professor Giacomo Ciamician from the University of Bologna predicted that mankind will unravel the secrets of photosynthesis and apply the principles used by plants to harvest solar energy in glass buildings. His visionary thoughts appear now to be a reality.

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