Photovoltaic and photoelectrochemical conversion of solar energy

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The Sun provides approximately 100 000 terawatts to the Earth which is about 10 000 times more than the present rate of the world's present energy consumption. Photovoltaic cells are being increasingly used to tap into this huge resource and will play a key role in future sustainable energy systems. So far, solid-state junction devices, usually made of silicon, crystalline or amorphous, and profiting from the experience and material availability resulting from the semiconductor industry, have dominated photovoltaic solar energy converters. These systems have by now attained a mature state serving a rapidly growing market, expected to rise to 300 GW by 2030. However, the cost of photovoltaic electricity production is still too high to be competitive with nuclear or fossil energy. Thin film photovoltaic cells made of CuInSe or CdTe are being increasingly employed along with amorphous silicon. The recently discovered cells based on mesoscopic inorganic or organic semiconductors commonly referred to as 'bulk' junctions due to their three-dimensional structure are very attractive alternatives which offer the prospect of very low cost fabrication. The prototype of this family of devices is the dye-sensitized solar cell (DSC), which 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. Research is booming also in the area of third generation photovoltaic cells where multi-junction devices and a recent breakthrough concerning multiple carrier generation in quantum dot absorbers offer promising perspectives.

Keywords: renewable energy; solar energy conversion; photovoltaic cells;
thin film devices; bulk junction cells; dye-sensitized solar cells

1. Introduction

The Sun provides about 100 000 TW to the Earth, which is approximately 10 000 times greater than the world's present rate of energy consumption (13 TW). Photovoltaic (PV) cells are being used increasingly to tap into this huge resource and will play a key role in future sustainable energy systems. Our present needs could be met by covering 0.1% of the Earth's surface with PV installations that achieve a conversion efficiency of 10%.

2. How conventional p–n junction PV cells function

Figure 1 shows a simple diagram of how a conventional photovoltaic device works. The top and bottom layers are made of an n-doped and a p-doped silicon, where the charge of the mobile carriers is negative (electrons) or positive (holes), respectively. Upon contacting the two materials, spontaneous electron and hole transfer across the junction produces an excess positive charge on the side of the n-doped silicon (A) and an excess negative charge on the opposite p-doped (B) side. The resulting electric field plays a vital role in the photovoltaic energy conversion process. Absorption of sunlight generates electron–hole pairs by promoting electrons from the valence band to the conduction band of the silicon. Electrons are minority carriers in the p-type Si while holes are minority carriers in the n-type material. Their lifetime is very short as they recombine within microseconds with the oppositely charged majority carriers. The electric field helps to collect the photo-induced carriers because it attracts the minority carriers across the junction as indicated by the arrows in figure 1, generating a net photocurrent. As there is no photocurrent flowing in the absence of a field, the maximum photo-voltage that can be attained by the device equals the potential difference that is set up in the dark at the p–n junction. For silicon this is about 0.7 V.

3. Conversion efficiencies

The conversion efficiency of a solar cell is defined as the ratio of its electric power output to the incoming light intensity that strikes the cell. The internationally accepted standard test condition (STC) uses as a reference air mass (AM 1.5) sunlight (viewed at 48° to overhead) normalized to $1 \, kW \, m^{-2}$, with the temperature kept at 298 K. The conversion efficiency is determined by measuring the photocurrent (i.e. the electrical current induced by light) as a function of the cell voltage using the formula $\eta = J_{sc} V_{oc} FF / I_s$. Here J_{sc} is the short-circuit photocurrent density; V_{oc} is the open circuit voltage; I_s is the incident solar intensity ($1000 \, W \, m^{-2}$); and FF the fill factor defined as the electric power produced at the maximum power point of the J–V curve divided by the product $J_{sc} \times V_{oc}$. Figure 2 shows the history of confirmed 'champion' laboratory cell efficiencies. The performance of conventional solar cells is approaching a plateau; only incremental improvements have been accomplished in the last decade despite dedicated R&D effort. The efficiency of tandem cells based on III/IV semiconductors has progressed recently beyond 30%. However, the cost of these devices is very high, limiting their application to space and solar concentrators. In the latter case, sunlight is concentrated typically several hundred times by a mirror or a lens before striking the photovoltaic device. This will reduce the cost if the price per square metre of the solar concentrator is below that of the photovoltaic cell. However, solar concentrators need to track the Sun and work only well in direct sunlight in the absence of haze, limiting considerably their potential for practical applications.

The efficiencies reached with commercial solar cell modules are significantly lower than those of the best laboratory cells due to losses incurred during scale up. The typical size of 'champion laboratory cells' is in the square centimetre range or even below, facilitating the collection of photocurrent. All efforts are
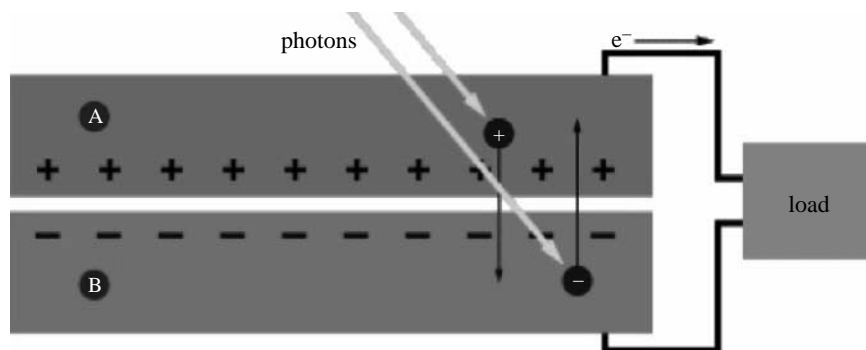
Figure 1. Schematic of how a conventional solid state photovoltaic device works.
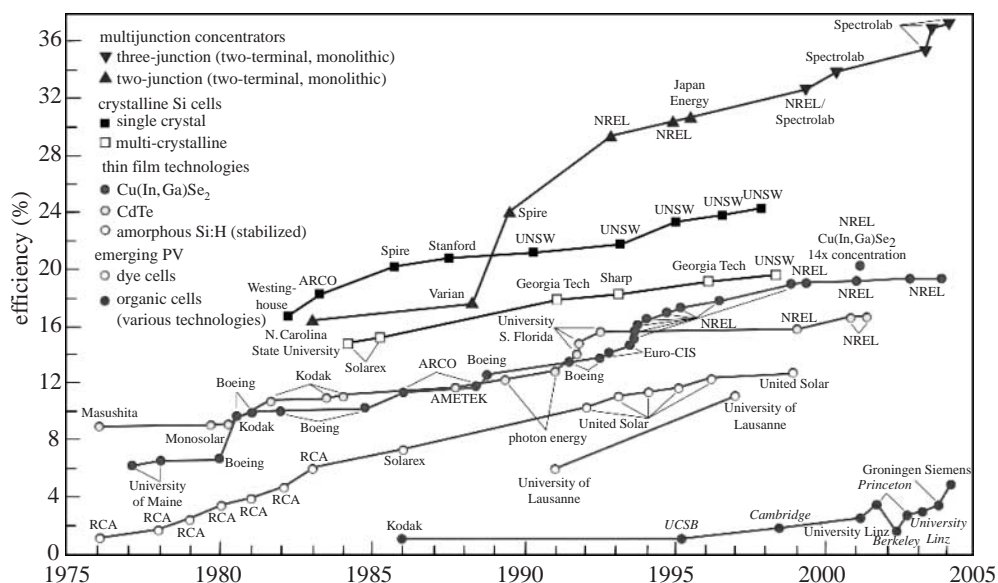

Figure 2. A history of best cell efficiencies. All plotted values have been confirmed and were measured under standard test conditions. Source A. J. Nozik, NREL, USA.

made to minimize resistive and optical losses increasing the power output although the methods used may not be applicable or are too expensive for production. Also, commercial criteria influence the choice of methods and materials used for large-scale production and compromises are often made in order to cut costs. Finally, large-scale modules need current collector grids or interconnects between individual cells, which reduce the exposed photoactive area of the cell decreasing the module conversion efficiency.

Conversion efficiencies of solar cells under real conditions can differ significantly from the values measured at STC. One reason for this discrepancy is that in full sunlight the temperature of a module rises within minutes to over 60°C. Since the efficiency of silicon solar cells drops by 0.5% per °C, a module

with a specified efficiency, say 12% at STC, would exhibit less than 10% efficiency in real sunshine. The temperature dependence of efficiency means that a cell located in a cloudy, temperate zone could actually be more efficient than one in a sunny desert although the absolute power produced would of course be lower than in direct sunshine.

4. The rapidly growing PV market

So far, solid-state junction devices based on crystalline or polycrystalline silicon (Si) have dominated photovoltaic solar energy converters, with 94% of the market share. These systems have benefited from the experience and the material availability generated by the semiconductor industry and they are at a mature state of technical development in a rapidly growing market. Figure 3 shows the photovoltaic peak power installed annually from 1988 to 2003. In 2004 and 2005 the trend has continued, the installed peak powers being 1.15 and 1.5 GW, respectively.

By 2010 the module output sales are expected to quadruple again, reaching 6 GW. This impressive growth is being fuelled by attractive feed-in tariffs, amounting to € 0.5/kW h in Germany, where such encouragement has been strongest. Revenues are predicted to increase from US$ 8.3 billion in 2004 to US$ 36.1 billion in 2010, with pre-tax profits rising from US$ 1.2 to 6.4 billion over the same period (Rogol 2005). By 2030 the yearly PV module output is expected to attain 300 GW (EUR 2005). However, this is still too little to make a major impact because the world's energy consumption will by then approach 20 TW; in addition, photovoltaic power figures are expressed in peak-watts, i.e. the output reached only in full sunshine at $1 \, \text{kW m}^{-2}$ incident light intensity. The real power averaged over day and night and the four seasons is approximately 3–10 times lower (depending on geographical location as well as direction and angle of exposition of the panels). Nevertheless, based on the recent growth rates, it has been predicted (Zweibel 2005) that by 2065 all the world's energy needs could be met by photovoltaic cells.

5. Cost and feedstock supply problems

While the growth of the PV market over the last decade has been impressive, the cost of photovoltaic electricity production is still too high to be competitive with fossil fuels. For the best systems installed at well-chosen sites, the price per kilowatt hour is at present US$ 0.25–0.65 (EUR 2005) compared with US$ 0.05/kWh for current wholesale electricity. To descend to the latter value, the cost for the total installed PV system should decrease below US$ 1/W. The module itself would have to contribute less than US$ 0.5/W to this price, a target that seems difficult if not impossible to meet with present silicon technology.

A major dilemma that the PV industry currently faces is a shortage of raw materials. The silicon for today's PV cells originates primarily from waste produced by the chip industry. Alarmingly, the cost of solar-grade silicon leapt from US$9 per kilo in year 2000 to US$60 in 2005. Demand will outstrip supply at least for the next 5 years maintaining the module price at over US$ 5/W
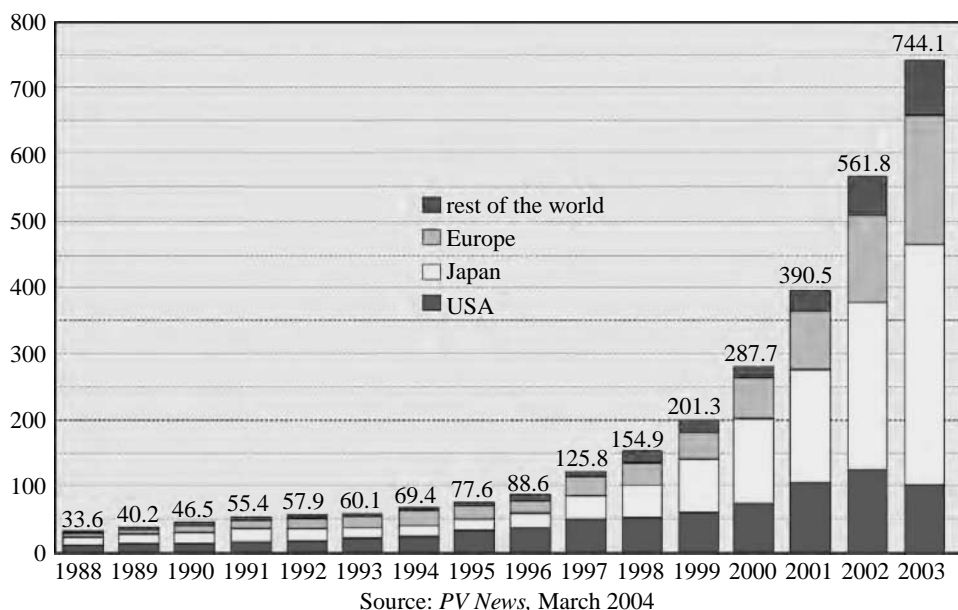
Figure 3. The increase in worldwide production of PV modules (MW) during the last 15 years. The market growth rate in the last decade has been over 30%.

(http://www.photon-consulting.com/executive_summary.htm, Photon-consulting 'Solar annual 2006'). Clearly, a change in economics is required for photovoltaics to become fully cost-competitive.

6. Thin film PV cells

Since the 1970s, a second generation of thin film PV cells has emerged and the main examples are listed in table 1. Their market share is expected to grow significantly from the current 5%. Cells made of CuInSe (copper indium selenide) or CdTe (cadmium telluride), along with amorphous silicon are being increasingly employed and the industrial production of dye-sensitized solar cells (DSCs) has started. The conversion yields of commercial devices are still significantly below the 12–17% attained by polycrystalline and single-crystal silicon but the energy pay-back time is shorter, i.e. 3 years as compared with 4.5 years. Pay-back times for the dye-sensitized solar cells and organic thin film PVs are expected to be below 1 year.

CuIn(Ga)Se and CdTe devices are attractive due to their high conversion efficiency, reaching 15–20% for the best laboratory demonstrations, figure 2. However, they are unlikely to become large-scale suppliers of solar electricity due to the scarcity of indium, tellurium and selenium, and the high toxicity of cadmium (Green 2006). The prices of these elements have decoupled recently and are now 1000, 180 and 150 US$/kg for In, Te and Se, respectively. Although much smaller material quantities are needed for thin-film PV devices, i.e. approximately 100 mg W^{-1} (Keshner & Arya 2004) compared with 13 g W^{-1} for silicon, low availability and environmental concerns remain a problem.

Table 1. Examples for first and second generation solar cells.

first generation	second generation (low cost, mainly thin films)
single crystal polycrystalline (silicon)	amorphous Si thin-film Si $CuIn(Ga)Se_2$, CdTe dye-sensitized nanocrystalline cells (DSC) organic PV (molecular and polymeric)

Most of the annual 50–70 MW thin-film market is currently served by amorphous silicon (a-Si) solar cells. These give lower efficiencies, i.e. 5–7%, instead of 7–11% obtained with CdTe and CuInSe based devices and are subject to performance degradation. The need for high vacuum production methods and their lower efficiency make them as expensive as crystalline silicon cells on a per peak-watt basis.

7. Mesoscopic solar cells

These new solar cells employ films composed of an interpenetrating network of inorganic or organic semiconductor particles of mesoscopic (2–50 nm) size forming junctions of very high contact area instead of the flat morphology used by conventional thin-film cells. They are commonly referred to as 'bulk' junction cells due to their three-dimensional structure. The prototype of this family of devices is the dye-sensitized solar cell (DSC), which accomplishes optical absorption and charge separation by combining a light-absorbing material (the sensitizer) with a wide band gap semiconductor of nanocrystalline morphology (O'Regan & Graetzel 1991; Keshner & Arya, 2004). The DSC is used in conjunction with electrolytes (Graetzel 2001), ionic liquids (Wang 2005a), polymer electrolytes (Haque *et al.* 2003) or organic (Bach *et al.* 1998) as well as inorganic hole conductors (O'Regan 1997; Perera *et al.* 2003). Other strategies employ blends of organic materials, such as polymeric (Halls *et al.* 1995) or molecular semiconductors (Peumans & Forrest 2001) as well as hybrid cells using a p-type semiconducting polymer (such as poly 3-hexylthiophene), in conjunction with a fullerene (Brabec *et al.* 2003) or CdSe 'nanorods' (Huynh *et al.* 2002).

These new dye-sensitized solar cells may be fabricated without expensive and energy-intensive high temperature and high vacuum processes. They are compatible with various supporting materials and can be produced in a variety of presentations and appearances to enter markets for domestic devices and architectural or decorative applications. The DSC conversion efficiency validated at STC is currently 11.1% (Chiba *et al.* 2006). Excellent stability under long-term illumination and high temperatures has been reached fostering industrial applications.

Figure 4 compares the energy band diagrams for a dye-sensitized solar cell with that of a conventional p–n junction photovoltaic device.
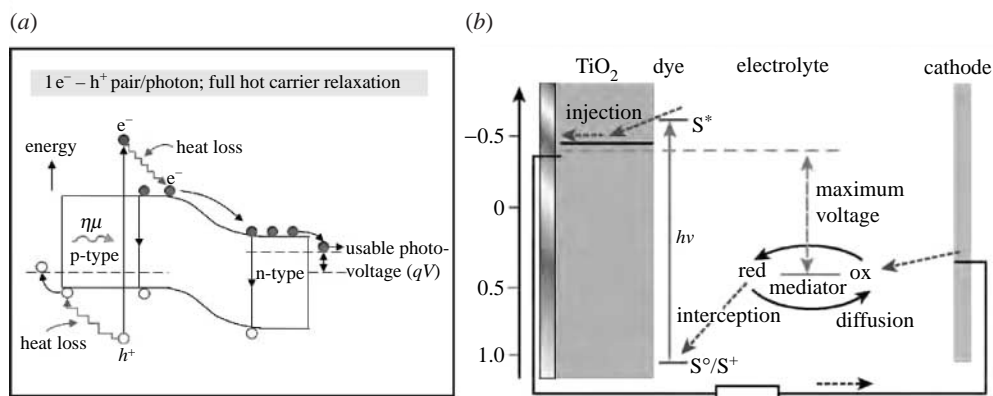
Figure 4. Band diagrams for a conventional photovoltaic device (*a*) and a dye-sensitized solar cell (*b*). The band bending at the p–n junction is produced by spontaneous dark current flowing in order to reach electronic equilibrium imparting a negative and positive excess space charge to the p- and n-side, respectively, as was discussed in figure 1. Absorption of a photon produces a single electron–hole pair, any excess energy being transferred to the lattice as heat. Note that the semiconductor on the left assumes two functions simultaneously: it absorbs sunlight and transports electric current. In order to collect all the charge carriers generated by light excitation, the materials must be very pure and should not contain lattice imperfections or grain boundaries accelerating electron–hole recombination. A critical device parameter is the diffusion length of the minority charge carriers (conduction band electrons for the p-doped Si and valence band holes for the n-doped side) which should be larger than the thickness of the film. By contrast, in the dye-sensitized cell (DSC), the light absorption and charge carrier transport are separated and there are no minority charge carriers involved in the photo-conversion process. Light is absorbed by a dye molecule attached to the surface of a nanocrystalline titanium dioxide film, which is selected because it is stable and environmentally friendly. During operation, the sensitizer transfers an electron to the semiconductor. The dye molecule, now positively charged, is regenerated by the electrolyte or a p-type hole conductor while the latter recovers an electron from the external circuit. The conversion efficiency of the DSC is currently above 11% while silicon champion cells have attained 24%, the maximum being approximately 30% for both devices. The use of solvent-free electrolytes in the DSC gives very stable performance.

8. The benefits of the mesostructure

The mesoscopic morphology of materials used in these new thin film PV devices is essential for their efficient operation. For the DSC, the nanocrystalline structure of the oxide semiconductor used to support the sensitizer has the following benefits.

(i) It renders possible efficient light harvesting by the surface absorbed sensitizer (Nanu *et al.* 2004). On a flat surface a monolayer of dye absorbs at most a few per cent of light because 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 because only those molecules that are in direct contact with the oxide surface can sensitize the semiconductor, the remainder acting as a filter. The huge amplification of the interfacial area enhances the light absorption resulting in a 1000-fold increase in the photocurrent compared with a DSC having a flat surface morphology.

   (ii) The TiO_2 nanocrystals do not have to be electronically doped to render them conducting because the injection of one electron from the sensitizer into a 20 nm sized TiO_2 particle suffices to switch the latter from an insulating to a conductive state. This photo-induced conductivity of the particle films allows collecting the electrons without significant ohmic loss. By contrast, a compact semiconductor film would need to be n-doped to conduct electrons. In this case, energy transfer from the excited sensitizer to the conduction band electrons of the semiconductor would inevitably reduce the photovoltaic conversion efficiency.

  (iii) The small dimension of the TiO_2 particles allows for efficient screening of the negative charge of the electrons by the electrolyte or hole conductor present in the pores. As a result there the photocurrent is not impaired by the repulsive interactions between electrons diffusing through the particle network.

Figure 5 shows a scanning electron microscopy image of a mesoscopic TiO_2 (anatase) layer and the molecular structure of the most frequently used sensitizer (light harvester). The particles have an average size of 20 nm (20 billionths of a metre). By coating the oxide nanocrystals with a monolayer of sensitizer it is possible to produce far more efficient solar energy conversion devices.

9. Opportunities for performance improvement

The DSC currently reaches over 11% energy conversion efficiency at STC (Graetzel 2005; Chiba *et al.* 2006). Photovoltaic performance data for a 'champion' cell are shown in figure 6. Solid-state equivalents using organic hole-conductors have attained 4.2% efficiency (Schmidt-Mende *et al.* 2005) whereas nanocomposite films comprising only inorganic materials, such a TiO_2 and $CuInS_2$ have achieved efficiencies between 5 and 6% (Nanu *et al.* 2004, 2005), significantly more than the recently reported CdTe/CdSe particle-based heterojunctions (Gur *et al.* 2005). Organic PV cells based on blends of a fullerene derivative with poly(3-hexylthio-phene) have a confirmed conversion efficiency of 4.8% (Schilinsky *et al.* 2006). So far, no certified efficiencies for organic solid-state PV cells based on small molecules, e.g. perylene imides and phthalocyanines, have been published.

To further improve the DSC performance, new dyes or combinations showing increased optical cross-sections (Wang *et al.* 2005*b*) and capable of absorbing wavelengths in the near IR region are under development. The near-term goal is to increase the photocurrent densities to 25–27 mA cm^{-2}, which should allow the overall conversion efficiency of the DSC to reach 15%, without changing the currently used stable non-volatile redox electrolyte. A roadmap to achieve this goal within the next 2 years has been established and will serve to coordinate synthetic efforts of several international groups. DSCs based on the new sensitizer have also shown excellent stability both under long-term light soaking and thermal stress (Wang *et al.* 2005*c*).

10. Field tests of DSC modules

The industrialization of the DSC is progressing and field tests of DSC modules under realistic outdoor conditions started more than 3 years ago. While the
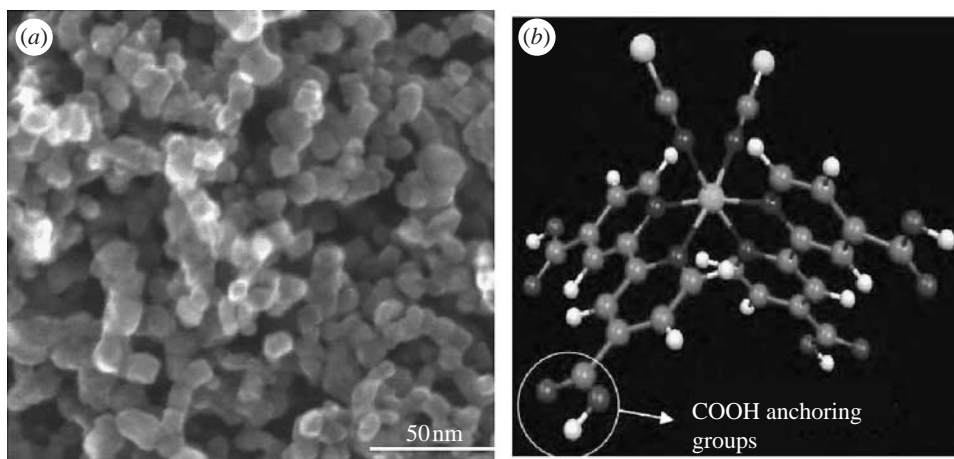
Figure 5. (*a*) Scanning electron microscopy picture of a nanocrystalline TiO$_2$ film used in the DSC. (*b*) Molecular structure of a compound (*cis*-Ru(2,2′-bipyridyl-4,4′-dicarboxlyate)$_2$(SCN)$_2$) that is widely used as a sensitizer.
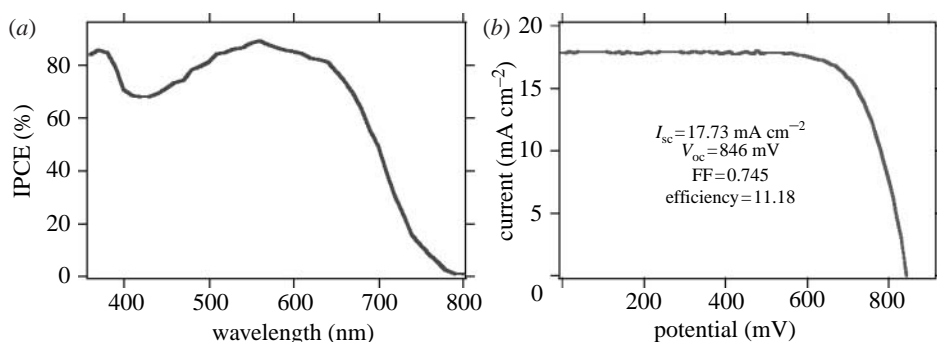

Figure 6. Photovoltaic performance of a 'state of the art' DSC laboratory cell. (*a*) Photo current action spectrum showing the monochromatic incident photon to current conversion efficiency (IPCE) as function of light wavelength obtained with the N-719 sensitizer. (*b*) *J–V* curve of the same cell under AM 1.5 standard test conditions.

efficiency of these modules under STC is currently still about a factor of two lower than that of silicon panels, these tests have revealed significant advantages of the DSC under real outdoor conditions. Thus, DSC modules that would be equally rated to silicon cells under STC produced 20–30% more energy than the polycrystalline silicon (pc-Si) modules (Motohiro 2005). A photograph of a test station comparing the two types of PV technologies is shown in figure 7. The superior performance of the DSC can be ascribed to the following facts.

— The DSC efficiency is practically independent of temperature in the range 25–65°C whereas that of pc-Si declines by approximately 20% over the same range.
— The DSC collects more solar energy during the day than pc-Si due to a lower sensitivity of the light harvesting to the angle of incidence.

— The DSC shows a higher conversion efficiency than pc-Si in diffuse light or cloudy conditions.

Although it is up to the commercial supplier to set the price of completed modules, it is clear that the DSC shares the cost advantage of all thin-film devices. In addition, it uses only cheap and readily available materials[1] and in contrast to amorphous silicon, avoids cost-intensive high vacuum production steps. Given these additional advantages at comparable conversion efficiencies, module costs well below € 1 are realistic targets for large-scale production plants.

11. Industrial DSC development

The potential of the dye-sensitized solar cell as a practical device is supported by commercial interest, with several industries taking patents and using prototype applications. First applications in building integrated photovoltaics have been found. The DSC panels shown in figure 7 have been installed in the walls of the Toyota dream house (http://www.toyota.co.jp/jp/news/04/Dec/nt04_1204. html) offering an integrated source of solar power to the inhabitants. American, Australian and Japanese development engineers are exploiting the potential for incorporation into flexible substrates (www.konarka.com). A 20 MW plant to produce flexible cells on metal foils has been established by G24I Innovation, Inc. in Wales (www.G24I.com). There are also projects in Australia (www.dyesol. com) and Japan to erect and evaluate large-area systems.

12. Third generation photovoltaic cells

Intensive research is currently being performed in the field of third-generation photovoltaic cells which encompass devices whose maximum conversion efficiency is above the 33% limit for single junction converters in AM 1.5 sunlight (Henry 1980). The systems under investigation comprise multi-gap tandem cells, hot electron converters, cells, quantum dot (carrier multiplication) solar cells and mid-band gap state (3 level) PV. A recent breakthrough concerning charge carrier multiplication offers great promise. Enormous excitement has followed the prediction (Nozik 2004), discovery (Schaller & Klimov 2004) and confirmation (Nozik 2005; Hanna & Nozik 2006) that several excitons can be produced from the absorption of a single photon by very small semiconductor particles, called 'quantum dots' because their electronic properties are different from those of bulk-size materials due to the confinement of the electron–hole pairs produced by optical excitation. This effect occurs if the photon energy is several times higher than the semiconductor band gap. In a bulk semiconductor the excess energy would be converted into heat, while in a quantum dot a change in the selection rules allows several electron–hole pairs to be generated by a single photon. The challenge is now to find ways to collect the excitons before they recombine. As recombination occurs on a picosecond

[1] It may be argued that the ruthenium based sensitizer adds high material cost. However the contribution is less than € 0.01/pWatt given the small amount employed. Also purely organic sensitizers have reached practically the same yield as ruthenium complexes.

Figure 7. Outdoor field tests of DSC modules produced by Aisin Seiki in Kariya City. Note the pc-Si modules in the second row (photograph courtesy of Aisin Seiki).

time-scale, the use of mesoporous oxide electrodes to support the quantum dot presents a promising strategy, because transfer of the electron from the quantum dot to the conduction band of the oxide collector electrode can occur within femtoseconds (Plass *et al.* 2002). This opens up research avenues that ultimately may lead to photo-converters reaching external quantum efficiencies of several hundred per cent. A calculation shows that the maximum conversion efficiency of a single junction cell could be increased from 34 to 44% by exploiting IMI effects.

13. Summary

While the present photovoltaic market is dominated by single crystal and polycrystalline silicon cells, we will be looking to the second and third generation cells to contribute the lion's share of the future terawatt-scale output in solar module production, which is required to make a major contribution towards the huge future demands for renewable energy. Mesoscopic cells are well suited for a whole realm of applications, ranging from the low-power market to viable large-scale applications. Thus, their excellent performance in diffuse light gives them a competitive edge over silicon in providing electric power for stand-alone electronic equipment, both indoors and outdoors. Application of the DSC in building integrated PV cells has already started and will become a fertile field of future commercial development. With the ongoing expansion of the PV market and with the escalation of fossil fuel prices as well as environmental considerations, there is high expectation that mesoscopic cells will play a significant role in providing solar power in competition with conventional devices and other innovations.

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