Molecular based consepts in PV towards full spectrum utilization

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Molecular based concepts offer the potential of low materials and processing costs in photovoltaics (PV), which is especially interesting if high efficiencies can be obtained. To accomplish high efficiencies a better utilisation of the solar spectrum is of high importance. The concept of two photon absorption in dye sensitized solar cells and full spectrum aspects of luminescent flat plates concentrators are being discussed in this paper. The two photon dye cell can be compared to a tandem solar cell on the molecular level. The luminescent concentrator offers the potential to employ full spectrum utilization in combination with static concentration of both direct and diffuse light.

1. Introduction

Molecular based concepts is one of the five activities of the European integrated project „FULLSPECTRUM: A new photovoltaics (PV) wave making more efficient use of the solar spectrum" [1]. The five activities will focus on enhancement of the performance of solar cells by making more efficient use of the solar spectrum. The work will be based on further developing proven concepts and by identifying new principles:

III–V multijuntion solar cells;

Thermophotovoltaics;

Intermediate band materials and cells;

Molecular based concepts and

Manufacturing technologies.

The area of molecular photovoltaics is not yet characterized by high conversion efficiencies. Nevertheless, ongoing scientific developments in this field continually lead to further progress in material quality with respect to their use in electronic components and the discovery of new properties. In general, molecular materials are interesting for use in photovoltaics if compared to bulk semiconductors, because of their distinct light absorption properties and distinct energy levels. Molecular based PV is believed to be compatible with low cost, large area, high throughput manufacturing technologies. In this respect, not only species chemically seen as molecules and polymers are included, but also quantum dots with discrete energy levels and absorption behaviour due to their size confinement. Also crystal lattices can be considered where the properties of the materials involved are dominated by the atomic levels, as for instance often is the case for rare earth ions in crystal lattices.

Molecular based photovoltaics has started with flat, two component systems, where one molecular layer acts as electron donor and the other molecular layer acts as electron acceptor. Due to limitations in exciton and charge carrier mobilities, typical useful material thickness is limited to approximately 10 nm. Significant efficiencies have not been reached for flat (bi-layer) systems so far. This has led to the development of threedimensional structures to circumvent the problem of limited charge carrier mobilities. The R&D efforts are directed in the field of engineering of molecular devices on the nanometer scale. Both the bulk heterojunction solar cells and the dye sensitized solar cell are examples of such nanostructures.

Besides the development in molecular photovoltaics towards engineering the nanometer scale, several scientific developments have led to a renewed interest in the molecular concept of the luminescent concentrator. Due to the ability to collect diffuse light in a flat plate, non static geometry, the flat-plate luminescent concentrator seems to be especially interesting for area's where diffuse light represents a large fraction on the solar energy flux, e.g. large parts of Europe, USA and Japan. The dye cell and the luminescent concentrator show interesting features for better use of the solar spectrum and these specific features will be under investigation in FULLSPECTRUM. The general concepts of the full spectrum aspects of a two photon dye solar cell and luminescent flat plate concentrator are discussed in this paper.

2. Dye sensitized solar cells

The dye sensitized solar cell or shortly dye cell (or Grätzel cell, after the inventors Brian O'Regan and Michael Grätzel [2]) is an interesting molecular based concept with respect to the potential of lowering the costs of photovoltaics. In a recent review paper, fundamentals, properties and technology are reviewed [3]. At present, practical applications are limited due to the relative poor stability under outdoor conditions. For long time, heat was considered a very important stress factor for dye cells, but recently good results have been achieved demonstrating stability in a 1000 h, 85°C oven test [4]. The maximum efficiency obtained so far for limited area dye sensitized solar cell is 11% [5] and 8.2% for a device exceeding 1 cm² [6].

The basic process of the dye cell (see Fig. 1) is light absorption by a dye adsorbed as monolayer onto a semiconductor surface, and subsequent energy and electron transfer to the semiconductor. An electron is returned to the oxidized dye via the electrolyte or hole conductor. Since the absorption by a single layer of dye molecules

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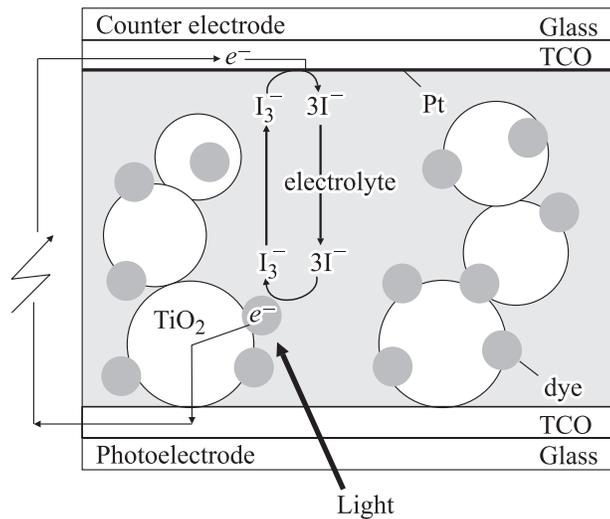
Figure 1. Schematic representation of the basic processes of the dye sensitized solar cell. Light is absorbed by a dye molecule. From the excited state of the dye, electron and energy are injected into a nanocrystalline, TiO_2, photoelectrode film of about $10 \mu m$ thickness. After transport through the TiO_2 film and lateral conduction through a thin (typically $1 \mu m$) transparent conductive oxide (TCO) on glass, the energy is available for work in the outer circuit. From the outer circuit the electrons are transferred to the iodine/iodide redox couple in the electrolyte via the counter electrode, which is another TCO layer on glass equipped with a miniscule amount of Pt catalyst. Through diffusion the redox ions reach the oxidized dye molecules and reduce them again to their original (ground) state (the actual reaction as shown releases not 1 but 2 electrons).

is limited, the invention by O'Regan and Grätzel provides a nanocrystalline electrode of a wide bandgap, transparent semiconductor, most often consisting of titanium dioxide, TiO_2. In this way, an up to $1000 \times$ surface enlargement is obtained as compared to flat layer devices. Typically, such a porous TiO_2 layer contains crystalline TiO_2 nanoparticles with a size of 15–20 nm in a layer of about $10 \mu m$ thickness. At present, highest efficiencies are obtained with a ruthenium compound as dye, an electrolyte employing the iodine/iodide redox couple, and TiO_2 as the semiconductor.

One strong point of the dye cell is that only majority charge carrier transport takes place (see Fig. 2), in contrast to semiconductor-based solar cells like crystalline silicon. In the dye cell, after absorption, an electron is injected into the TiO_2. Titanium dioxide is a (majority) photoconductor for electrons.

In crystalline silicon, after light absorption, the minority charge carriers (e.g., electrons in p-type silicon) have to diffuse to the junction before they can be collected, see Fig. 2. The maximum open circuit voltage (V_{oc}) in silicon is given

$$V_{oc}^{max} = h\nu - (\Delta V_1 + \Delta V_2)$$

where the potentials ΔV_1 and ΔV_2 are resulting from doping the silicon n- and p-type (potential losses); $h\nu = E_g$ is photovoltage equal to the Si energy gap E_g. High purity silicon is needed for sufficient minority carrier lifetimes, leading to high costs. In dye cells, materials constraints are less severe, allowing the use of relatively inexpensive materials and large area, low cost processing techniques such as screen printing.

The maximum theoretical performance of dye cells can be derived from the energy scheme, see Fig. 3. The absorption characteristics of the dye strongly influence voltage and current. The photocurrent is determined by the overlap of the dye absorption with the solar spectrum. If $h\nu$ is small, the number of photons absorbed will be high, but the voltage obtained is low, and vice versa. This is typical behaviour for solar cell with a single energy gap (Fig. 3, a), such as also is the case for crystalline silicon. For a single bandgap solar cell with an optimum bandgap, the maximum theoretical efficiency is 40.8%, not taking into account fundamental losses [7]. As for silicon, the maximum open circuit voltage V_{oc}^{max} (assuming perfect contacts etc.) of the dye cell is determined by the energy gap (photovoltage $h\nu = E_g$) minus the potential losses. In the dye cell, the maximum open circuit potential V_{oc}^{max} is given

$$V_{oc}^{max} = h\nu - (\Delta V_1 + \Delta V_2)$$

where ΔV_1 is the potential losses due to the energy differences between the redox electrolyte potential and the

Figure 2. Representation of carrier transport in crystalline silicon (c-Si, left) and dye sensitized solar cells (right). In p-Si, holes (square) are the majority carriers and have normal ohmic transport. Electrons (dot) are the minority carriers and have to diffuse to the junction. In the dye cell the electrons that are injected into TiO_2 are majority carriers and the ions in the electrolyte are majority carriers.

Figure 3. Energy schemes, in which VB is the titanium dioxide valence band, E_F is the Fermi level in TiO$_2$ (just below the conduction band) and U_{RE} is the redox potential of the electrolyte. In 3, *a*, representative for the normal dye sensitized solar cell, photons with minimum energy $h\nu$ are absorbed by the dye. Fig. 3, *b* represents the energy scheme for the two-photon dye cell concept.

ground state of the dye and ΔV_2 is loss between the excited state of the dye and the Fermi level of the wide bandgap semiconductor TiO$_2$, see Fig, 3, *a*.

As can be seen from Fig. 3, *a*, the energy gap of the wide bandgap semiconductor (typically > 3 eV) allows for a broader use of the solar spectrum than normally obtained through single photon absorption. A two photon absorption process has been proposed [8]. In Fig. 3, *b*, schematically potential energy levels for this concept are shown. The proposed mechanism is that a first absorption step $(h\nu_1)$ is followed by an electron and energy transfer after which a second absorption step $(h\nu_2)$ should take place. The maximum V_{oc} equals

$$V_{oc}^{max} = h\nu_1 + h\nu_2 - (\Delta V_1 + \Delta V_3 + \Delta V_2)$$

where ΔV_1 is potential loss between electrolyte redox potential and ground state of the dye moiety 1; ΔV_3 is loss between excited state of the dye moiety 1 and ground state of dye moiety 2; ΔV_2 is loss between excited state of the dye moiety 2 and the Fermi level in TiO$_2$. One of the boundary conditions is that the intermediate state has sufficient lifetime to allow the second absorption step to occur. In two-photon processes where the second absorption is done from the excited state, without energy and electron transfer to an intermediate state, the absorption cross sections are normally extremely low and can only be accomplished by strong lasers. Therefore, the electron and energy transfer to a stable intermediate is a very important part of the model.

In this way a tandem-like approach is accomplished on a molecular scale. As for other tandem-based solar cell devices, both absorption steps have to generate the same current for optimal performances, and the absorbers will have to be tailored to this requirement. If, however, both steps have an identical energy transition, it is also possible to interpret this as an upconversion process, through which it would for instance be possible to add absorption from the infrared to the normal dye absorption, see Fig. 4. In comparison to the single absorption case of the dye cell, the two-photon process does not increase the number of electrons generated and the (maximum) current thus remains unchanged. The efficiency enhancement by two-photon absorption is the result of a fundamental increase in voltage, as is also the case in semiconductor tandems. This can not be accomplished with the commonly used iodide/⟨iodine redox⟩ couple, since this would result in an unchanged voltage. Other redox couples or hole
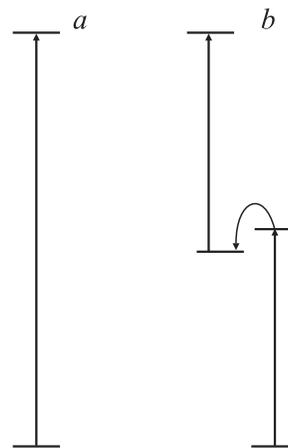
Figure 4. Schematic representation of how a two-photon dye (*b*) could be used as upconverter (e. g. for infrared radiation), together with a normal dye (*a*). Both could be absorbed on TiO$_2$ leaving the voltage unchanged.
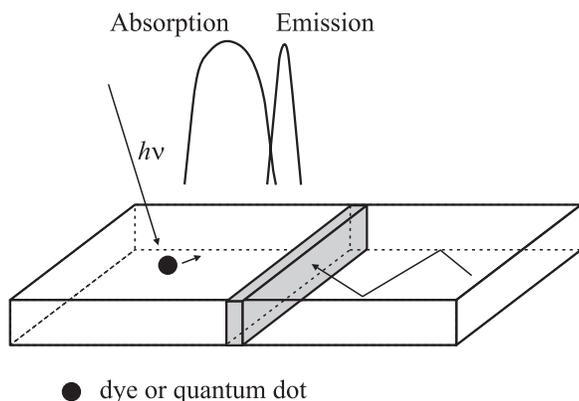
Figure 5. Schematic representation of a luminescent flat plate concentrator. Direct and diffuse sunlight are absorbed by luminescent materials, e. g. organic dye molecules or quantum dots. The luminescent materials emit light at lower energy in all directions, of which the largest part is reflected at the interface between plate and air. In this way, it is concentrated and can be collected at the edges. In the graph, a bifacial solar cell is used in between the edges of two luminescent plates.

conductors will be necessary. The theoretical maximum efficiency for a series connected tandem is 55.5%, not taking into account fundamental losses [7].

3. Luminescent concentrator

The luminescent concentrator has been under study since the seventies of the last century [9,10]. The concept is based on incorporating in a transparent matrix materials that are absorbing (to absorb the sunlight) as well as luminescent. The refractive index of the transparent matrix is chosen larger than the surrounding medium (mostly air). As the luminescent materials emit light in all directions, part of the emitted light will be internally reflected at the matrix/air interface. By designing geometries for which the length and width of the transparent matrix are larger than its thickness (such as for a plate configuration), geometric concentration is accomplished. The emitted light is totally internally reflected and will be concentrated within the matrix where it can be harvested at the edges of the matrix. There, it can be transformed into electricity by solar cells, see Fig. 5.

In the flat plate luminescent concentrator, light from all incoming angles is collected. Because of this property, the luminescent concentrator is a static, non-moving form for the concentration of solar light. However, it is also an indirect form of photovoltaics, since the sunlight is first absorbed and subsequently emitted by luminescence. Therefore, in order to obtain high overall efficiencies, the luminescence efficiency also has to be high. Since light is collected from all angles, the luminescent concentrator is sensitive to diffuse light. The fact that it is both static and sensitive to diffuse light makes the flat plate concentrator interesting for building integrated applications, especially in

areas with a relatively large contribution of diffuse light to the total incoming energy. For instance, in The Netherlands the diffuse part of the incoming solar energy annually is about 50% and therefore quite significant. If it is possible to obtain reasonable overall system efficiencies based on inexpensive materials, flat plate luminescent concentrators can thus be an interesting low cost photovoltaic option.

In the work that has been done some thirty years ago, the overall system efficiencies that have been achieved were limited to around 5% only [11]. One of the problems for the organic luminescent materials that were used, was probably [12] that the luminescent wavelengths were only slightly higher than the absorption wavelengths. Under those conditions a significant part of the emitted light is lost by re-absorption. For organic materials that are used in luminescent concentrators, luminescence is based on the Stokes shift. The Gaussian distribution around the absorption maximum is shifted to a higher wavelength (lower energy) where the Gaussian distribution of the luminescence occurs. Since the shift is relatively small, the tails of the Gaussians overlap. For this reason, an important part of the light that is emitted by the luminescence process is re-absorbed, thereby diminishing its performance. Another problem was the relative instability of the luminescent organic materials under operation conditions.

The appealing concept of the luminescent concentrator is now revisited because of several interesting developments in materials science by which the overall system efficiency can be enhanced, e. g. luminescent materials, photonic materials and up- and downconversion, but also in the area of stability, potentially allowing the use of organic and polymeric materials for long term outdoor applications.

In recent years, new materials have shown interesting luminescent properties. For use in luminescent concentrators, especially quantum dots are considered [12,13]. The quantum dots of interest are based on nanocrystalline semiconductor particles. The luminescence process is similar to the organic materials, based on the Stokes shift. However, the Stokes shift can be enlarged as it is influenced by particle size and particle size distribution. The resulting overlap between absorption and luminescent emission can thus be reduced. An additional advantage of quantum dots is that the absorption width is larger as compared to organic materials, so a larger part of the solar spectrum can be absorbed. By varying the size, the absorption wavelength of the quantum dots can be tuned and by combining various materials, larger part of the solar spectrum can be covered. Other materials that have shown interesting luminescence properties are rare earth and polymeric materials.

Theoretically, the luminescent concentrator offers very good possibilities for full spectrum utilization. In principle each part of the solar spectrum can be addressed by a different material, see Fig. 6. By using quantum dots and molecular materials almost the complete wavelength regime of the solar spectrum can be covered, from ultraviolet light into deep infrared. In practice, however, this will be limited by the overlap between absorption and emission spectra
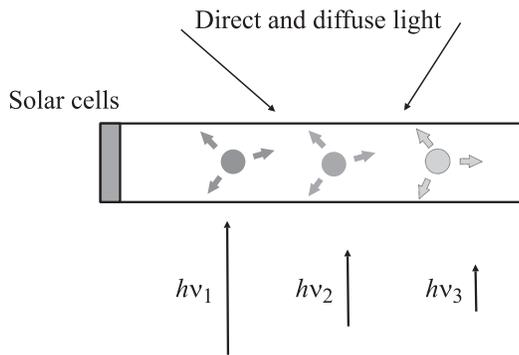
Figure 6. Schematic representation of a luminescent flat plate concentrator, indicating that different luminescent materials can be integrated to cover different parts of the solar spectrum. In principle, for each emitted wavelength a different solar cell is needed.
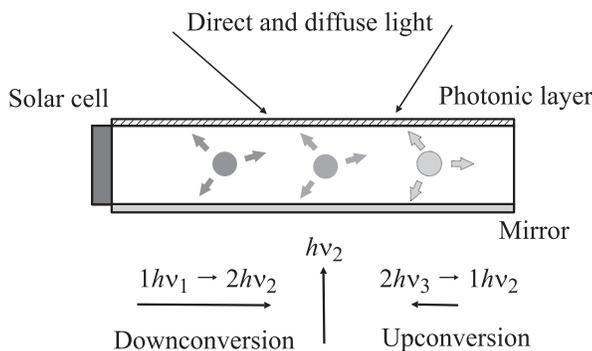
Figure 7. Representation of an idealized luminescent concentrator. All photons of the solar spectrum are transformed into a single wavelength. By a downconversion process, 1 high energy photon ($h\nu_1$) is converted into 2 lower energy photons of energy $h\nu_2$. A second part of the solar spectrum is absorbed by a regular luminescent material and emitted at $h\nu_2$. An upconverter material converts 2 lower energy photons $h\nu_3$ into 1 photon with energy $h\nu_2$. A photonic layer on the top acts as a mirror for specifically $h\nu_2$. At the bottom a normal mirror can be used. At the edge a single solar cell can be used.

of the various materials. One way to overcome this is to incorporate each absorber in an individual transparent matrix, separated by air (for instance) to ensure total internal reflection in each to these matrices. Theoretically, in this way the maximum efficience (unconstrained) for three colour centres is 63.8%, not taking into account fundamental losses [7].

To reach the maximum theoretical efficiency is far from trivial. The geometric concentration factors that can be reached are reasonably high. For a hypothetical concentrator plate of e.g. $100 \times 100 \times 5$ mm, executed in double with a bifacial solar cell of 100×5 mm (Fig. 5), the geometrical concentration is $40\times$. The system, however, will be strongly limited by the optical efficiency or, in other words, optical losses. An important loss factor, as already mentioned, is the re-absorption of the emitted light [12]. Another optical loss factor is intrinsically determined by the operation principle

of the luminescent concentrator, namely the principle of total internal reflection. The angle under which light is totally internally reflected is dependent on the difference in refractive index between the transparent matrix and the surrounding air. Typical refractive indexes of transparent polymers are in the order of 1.5 and for this reason tens of percents are lost. An aspect that is also of influence on the overall system efficiency is that monochromatic efficiencies for most solar cells (that are used to collect the concentrated light at the edges) are well below 100%.

To improve the total amount of emitted light that is directed towards the solar cells at the edges, recent developments in the area of photonic materials can potentially be used. Photonic crystals are known to act as a mirror for a single wavelength. This property could be used by applying a photonic crystal layer on top of the luminescent concentrator, see Fig. 7. The photonic crystal has to be tuned in such a way that it reflects exactly the emitted, luminescent wavelength. In this way, also the light that would not be reflected by total internal reflection can be reflected and will be concentrated to the edges. The photonic layer will not only reflect the light from within the luminescent concentrator, but will also function as a mirror for that part of the incoming sunlight. This will be a minor loss factor if the wavelength region for the photonic material and the overlap with the absorption of the luminescent materials are small. At the back of the luminescent concentrator a standard low-cost mirror can be used.

Another principle that can be used to increase the overall system efficiencies is the use of up- and downconversion of photons, see Fig. 7. By the downconversion process, a high energy photon can be transformed into two (or more) lower energy photons. By the upconversion process, two lower energy photons can by „upconverted" to higher energies, e.g. from infrared to visible. If all photons of the solar spectrum can be transformed into a single wavelength, only a single solar cell is needed to collect the light at the edges, compared to three solar cells if three colour centres were used.

A final remark on luminescent concentrators is that it has the interesting feature that it transforms incoming, perpendicular light into reflected, lateral light. This division in perpendicular and lateral light can be used as an interesting engineering tool. For example, if the luminescent concentrator is not equipped with a mirror on the back, in principle it is transparent for all the light that is not absorbed. If for instance only the visible light would be absorbed, the infrared could be transmitted (or vice versa) and used for other purposes (e.g. for a thermal collector, room heating, ets.).

4.   Conclusions

The general concepts of a full spectrum approach with two photon processes in dye cells and flat plate luminescent concentrator are discussed. For further advancement in

these area's these general concepts need to be refined and elaborated, as is under progress in the FULLSPECTRUM project [1].

References

[1] A. Luque, A. Martí, A.W. Bett, V.M. Andreev, C. Jaussaud, J.A.M. van Roosmalen, J. Alonso, A. Räuber, G. Strobl, W. Stolz, C. Algora, B. Bitnar, A. Gombert, C. Stanley, P. Wahnon, J.C. Conesa, W.G.J.H.M. van Sark, K. Barnham, R. Danz, T. Meyer, I. Luque-Heredia, R. Kenny, C. Christofides, G. Sala, P. Benítez. *Proc. 19th Eur. Photovolt. Specialists Conf.* (Paris, France, 2004), in press.

[2] B. O'Regan, M. Grätzel. Nature, **353**, 737 (1991).

[3] J.M. Kroon, B.C. O'Regan, J.A.M. van Roosmalen, W.C. Sinke. *Handbook of Photochemistry and Photobiology* (American Scientific Publishers, 2003) v. 1, p. 1.

[4] P. Wang, S.M. Zakeeruddin, J.E. Moser, M.K. Nazeeruddin, T. Sekiguchi, M. Grätzel. Nature Mater., **2**, 402 (2003).

[5] M.A. Green, K. Emery, K. Bücher, D.L. King, S. Igari. Progr. Photovolt.: Res. Appl., **6**, 35 (1998).

[6] A. Hinsch, J. Kroon, R. Kern, I. Uhlendorf, R. Sastrawan, A. Meyer. *Proc. 17th Eur. Photovolt. Solar Energy Conf.* (2001) p. 51.

[7] M.A. Green. *Third generation photovoltaics. Advanced solar energy conversion* (Springer, 2003) p. 61.

[8] J.A.M. van Roosmalen. *The Path to Ultra-High Efficient Solar Cells. First Workshop* (JRC ISPRA, Italy, 2001).

[9] W.H. Weber. J. Lambe. Appl. Opt., **15**, 2299 (1976).

[10] A. Goetzberger, W. Greubel. Appl. Phys., **14**, 123 (1977).

[11] V. Wittwer, A. Goetzberger, K. Heidler, A. Zastrow. J. Luminesc. **24/25**, 873 (1981).

[12] A.J. Chatten, K.W.J. Barnham, B.F. Buxton, N.J. Ekins-Daukes, M.A. Malik. Sol. Energy Mater. Solar Cells, **75**, 363 (2003).

[13] K.W.J. Barnham, J.L. Marques, J. Hassard, P. O'Brien. Appl. Phys. Lett., **76**, 1197 (2000).

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