NEW-CONCEPT NANOSTRUCTURED SOLAR CELLS

E. Vigil[a,b]

a) Facultad de Física, Univ. de La Habana, Ciudad de La Habana 10 400, Cuba. evigil@fisica.uh.cu
b) Instituto de Ciencia y Tecnología de Materiales (IMRE-UH)

Nuevos tipos de celdas solares, basadas en materiales nanoestructurados, son estudiadas intensamente en la actualidad debido a sus grandes perspectivas y novedoso principio de funcionamiento; el cual se debe esencialmente a la dimensión de las partículas en los nanomateriales utilizados. Eficiencias relativamente altas han sido obtenidas utilizando tecnologías que no emplean altas temperaturas y materiales que no requieren un alto grado de pureza., por lo que su bajo costo constituye un importante incentivo. Estos novedosos dispositivos fotovoltaicos se encuentran en evolución a partir de las celdas solares sensibilizadas (DSSC) buscándose un mejor comportamiento y características superiores, en particular, el tiempo de vida de las mismas. Se describen estas celdas solares así como su principio de funcionamiento basando el análisis en las más estudiadas, aunque aún no completamente explicadas, DSSC. Se examinan las implicaciones de la nanoestructura tridimensional en estos dispositivos. Unido al análisis de las tendencias de las investigaciones, se revisan los diferentes tipos de celdas solares sólidas cuyo principio de funcionamiento se basa en su nanoestructura tridimensional.

New types of solar cells based on nanostructured materials are intensively studied because of their prospective applications and interesting new working principle – essentially due to the particle size of nanomaterials used. Relatively high efficiencies have been obtained using low-temperature technology and materials that do not require high purity; therefore, their low cost represents an important incentive. Novel type photovoltaic devices have evolved from dye sensitized solar cells (DSSC) in the quest to improve their behavior and characteristics, particularly their lifetime. These solar cells are described and their working principle, not completely clear so far, is explained using the better known DSSC. An analysis is made of the implications of having a nano-sized three-dimensional structure in these solar cells. Different solid sensitized solar cells are briefly reviewed as well as actual and foreseeable research trends.

INTRODUCTION

Humanity faces a highly dangerous environmental crisis caused mainly by the employment of fossil fuels which are responsible for contamination in cities, acid rains and global warming accompanied by all its known devastating effects [1].

At the same time, a fuel crisis must occur in the not so distant future. According to the International Energy Agency (IEA) for almost 30 years oil new discoveries have been less than annual consumption [2]. Some predictions say we have already reached maximum possible yearly extraction (peak-oil) and a great majority says it will be reached before 2020 [3]. At the present moment, 85% of the energy used by the total population comes from fossil fuels: oil 34.6%, gas 23.4% and coal 27.6% [4]. Natural gas and coal will also peak, though later, especially coal - which is much more contaminant than oil.

It is urgent to develop a new energy infrastructure to avoid an environmental crisis and a fuel crisis. Sources for nuclear energy production are non-renewable and also contaminant. Renewable sources of energies like hydro, eolic, geothermal, solar, etc are not only renewable but affect the environment to a much lesser extent. Until recently, practically only hydro could compete in price with fossil fuels. Today

the situation is changing in spite that funds for renewable sources research have been insufficient and much less than those devoted to fossil fuels or nuclear energy [5]. Electricity coming from eolic or photovoltaic energy shows a very rapid growth. Photovoltaic is the fastest growing renewable energy market, specially its "grid-connected" application [6]. Direct solar energy conversion to heat also shows a significant increment in certain regions. Among all renewable energy sources, solar energy has by far the greatest potential and the wider distribution in the Planet. It is much larger than the present energy consumption and capable of covering future demands of world population [7]. Electricity coming from photovoltaic energy could also substitute needs of fuels for transportation if used to obtain hydrogen. One must conclude that it is urgent and highly convenient to develop photovoltaic energy.

Solar cells are the heart of photovoltaic systems. Interest in solar cells for terrestrial uses rouse because of the first oil crisis in the 70´s. Initial developments and applications were based on silicon solar cells which benefited from the microelectronic industry. Highly efficient AlGaAs solar cells developed for space applications were demonstrated for the

first time for terrestrial applications in 1981 using solar light concentrators at Ioffe Institute [8]. Solar cells that absorb the light more effectively allowing the use of thin films were also developed, though not as successfully as silicon solar cells. CdTe thin film solar cell with 6% efficiency was reported as early as 1966 [9]. In 1985, M. Green at the University of New South Wales, Australia, broke the 20% efficiency barrier for silicon solar cells under one sun; after developing one year earlier with S. Wenham the *LGBC* solar cell (laser-grooved buried-contact) [10].

In 1991 M. Grätzel and collaborators report the dye-sensitized photoelectrochemical solar cell (DSSC) [11] and in 1996 more than 10% efficiency is achieved [12]. The main advantage of the DSSC is its low cost together with a higher than 10% efficiency. Unfortunately, life-time is its Achilles' heel. This low cost is determined essentially by its different working principle. Because of it, they do not require high purity materials or highly cleaned rooms for their fabrication. Rather simple technologies can be used at room temperature or not very high temperature. This means less expensive technological equipments and much less energy used in their fabrication. It must be mentioned that their flexible options imply less weight, widening the range of possible uses. DSSC appearance and possible colors favor architectural and other applications where besides producing electricity, expensive decorative materials are substituted. Even though the use of photovoltaic energy is probably the most environmental-friendly form of renewable energy, materials and reagents used in their fabrication could have a small (though avoidable) contaminant effect. This could also be true when solar panels become old and have to be discarded (also avoidable through recycling). DSSC are the less contaminant of all different types of solar cells because they are based on innocuous materials.

Feltrin and Freundlich [13] estimate energy production limits for several mature photovoltaic technologies based on available global material reserves. DSSC stand out in that material shortages would not prevent their scale-up even to the terawatt range if the Sn conducting oxide contact is substituted.

Finally, regarding future market projection W. Hoffmann [14], president of the European Photovoltaic Industry Association (EPIA), predicts that by 2030 DSSC and "new concepts" solar cells production will surpass crystalline silicon (mono- and poly-) production.

DYE SENSITIZED SOLAR CELLS

To understand advantages of using nanostructured materials in solar cells, it is convenient to know how dye sensitized solar cells work (DSSC, also sometimes called Grätzel's cells or DSC).
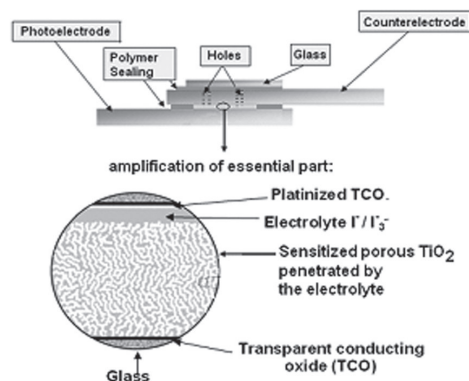

Figura 1: Component parts of a DSSC. The two electrodes are fixed together by the sealant that serves to contain the electrolyte and to avoid contact of the counter electrode with the TiO2.

A DSSC consists of the following essential parts: the photoelectrode formed by the electron-extracting electrode plus the dye-sensitized, mesoporous, nanocrystalline TiO2 penetrated by the electrolyte; and the counter electrode. These are shown in Fig. 1 that also shows

The electron-extracting electrode is usually a transparent conducting oxide (TCO) on glass in order to allow light penetration from that side. Surface resistivity of TCO used is between 8-15 Ω/square. The conducting oxide more frequently used is SnO_2:F (known as FTO) [15]. It behaves better than ITO (In_2O_3:Sn) whose conductivity decreases significantly during the thermal treatment of TiO_2 film at ca. 500⁰C. FTO is known to be thermally stable above this temperature. Studies are conducted to employ other substrates; especially for using high-throughput industrial roll-to-roll production of large area, flexible DSSC. Research includes conducting transparent plastic sheets [16], as well as non-transparent metallic foils with light penetrating from the other side [17].

TiO_2 is the mesoporous, nanocrystalline, wide bandgap metal oxide used in DSSC for best results (nanocrystalline anatase, bandgap E_G=3.2 eV). The TiO_2 layer thickness is typically between 5-15 μm and nanoparticles average size ranges from 15–30nm [18]. The porosity is approximately 50% [19], which together with particle size give rise to a real area or roughness factor of approximately 100-fold area enhancement per μm. This is very important to increase light absorption by the dye monolayer attached to the TiO_2 but also in determining a different working principle. There has been interest in replacing TiO_2 with other metal oxides such as SnO_2 [20] [21], $SrTiO_3$ [22] and ZnO [23], [24].

Dyes or sensitizers are chemisorbed onto the surface of the TiO_2. Sensitizers that have given best results so far are ruthenium bipyridyl complex with the general formula $RuL_xL_ySCN_z$, where L and L' are polypyridyl ligands. The 3 more frequently used complexes are known by their commercial names: red dye N-3, black dye N-749 and Z-907. The last two absorb a wider spectral range than the red dye N-3. Efforts have been made to find alternative less expensive sensitizing compounds. Na-

tural dyes have been studied [25], as well as sensitizers based on metal-free organic dyes [26]-[28]. Research reports on sensitizers are very abundant in the literature. Different goals have been and are been pursued as: improved molar absorption coefficients; longer-term stability; extension of the spectral absorption range; and sensitizers with different colors for special applications. It has also being reported [29] that the dye plays an important secondary role in passivating the semiconductor oxide surface and inhibiting the recombination with acceptors. The suitability of ruthenium bipyridyl complex then depends on both: the ligand and the nature of the oxide (TiO_2).

The electrolyte plays an essential role in DSSC [30]. The electrolyte typically used consists of the redox pair iodide-triiodide (I^-/I_3^-) dissolved in an organic solvent. No other redox pair has been found to give higher efficiencies than I^-/I_3^- even though there have been efforts to find less corrosive redox pairs, with lower light absorption and a more convenient redox potential energy [31], [32]. DSSC with highest efficiency employ a low-viscosity solvent, usually acetonitrile; but these electrolytes are not appropriate for achieving the best long-term stability characteristics, especially for outdoors. There are several reports regarding liquid electrolytes for DSSC [33]-[35] though there is no optimum solution. Solvent-free DSSC constitute an important direction of research and different solutions are studied for replacing the volatile liquid electrolyte with solid or quasi-solid hole conductors, such as p-type semiconductors, ionic liquid electrolyte and polymer electrolyte. It must be mentioned that in order to increase efficiency, liquid electrolytes also contain additives such as 4-tert-butylpyridine (TBP) or N-methylbenzimidazole (NMBI) [36] although their exact mechanism of action is not firmly established [37].

The counter-electrode is normally a conducting glass with a small amount of platinum adsorbed on the conducting-thin-film oxide that acts as catalyst in the I_3^- reduction; i.e., it facilitates electron exchange of the counter-electrode with the iodidie/triiodide redox couple. The TCO is used as electrode because the redox couple I^-/I_3^- corrodes many metals. Carbon materials [40] and polymers [41]-[43] have been employed as counter electrode although lower efficiencies have been obtained. These materials have the advantage that they are stable to corrosion and that they can be employed at low cost in roll-to-roll fabrication of flexible DSSC.

A hot melt polymer sealant serves to join together both electrodes. It is shaped to surround the sensitized TiO_2. The sealant is 25-50μm thick and it also serves to avoid contact of the sensitized TiO_2 with the counter-electrode.

DSSC working principle. In a traditional semiconductor-electrolyte interface a junction also forms (a depleted region where an electric field exists). It is due to charge transfer between the two contacting materials and it occurs in an analogous way as in the p-n junction; it is very similar to the semiconductor-metal junction produced by the contact of these two types of materials.
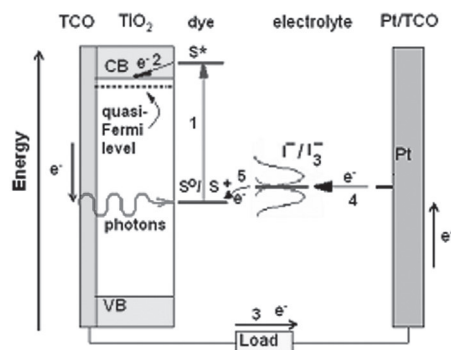

Figura 2. Energy levels in a DSSC under illumination. CB, conduction band. VB, valence band. S*, electron excited state in the dye. So/S+, electron HOMO state in the dye: SO is the ground state and S+ the state without an electron. The Gaussian distributions of iodide/triiodide (I⁻/I3⁻) species become equal at the redox potential Eredox that is practically equal to the Pt Fermi energy.

In DSSC, nanocrystals are surrounded by electrolyte. According to calculations the electric field in the TiO2 nanocrystals-electrolyte interface is very small; it is not capable of separating charges as in conventional solar cells [44]. Because of nanocrystals size then, DSSC must be based on a different working principle if compared with traditional solar cells. It has been discussed to a great extent in the literature whether a macroscopic field to drive carriers toward the contact exists or not. There is a lot of evidence and it is widely accepted now that such field does not exist and that carriers move by diffusion, i.e., due to charge carriers concentration gradients in the device [45]-[47].

Which is the origin of photovoltage in DSSC then? In the electrolyte there are allowed energy ranges for reduced and for oxidized species. Their Gaussian probability distribution is exemplified in Fig. 2. Both distributions cross at the energy for which reduced and oxidized species are equally probable and therefore probability value is ½. This can be thought of as a "Fermi level" for redox species and it is called redox potential Eredox. In the dark all "Fermi energies" line up; as explained before for p-n junctions. When the device is illuminated, electrons in the dye absorb photons and occupy energy levels in the dye which lie above the TiO_2 conduction band empty states (process 1 in Fig. 2). Electrons are injected on a subpicosecond timescale [48] from the dye to the TiO_2 conduction band states that have lower energies (process 2 in Fig. 2). This process competes and it needs to be faster (higher probability) than the excited state decay, typically 100 ps –1 ns [49]. A quasi equilibrium state is reached for a constant light intensity, i.e., a quasi-equilibrium excess electron concentration appears in the TiO_2 conduction band and the electron distribution is no longer described by the Fermi energy but by the quasi-Fermi energy. In the dark, because of its wide bandgap, TiO_2 is practically an isolator; free electron concentration at room temperature is negligible. Therefore, majority carrier concentration increases due to concentration of electrons injected from the dye and QFL Fn is significantly different from the Fermi energy level in the dark. If the external circuit is open and no current flows, the *open-circuit photovoltage* V_{oc}, is given by the difference between the TiO_2 electrons QFL and the electrolyte redox potential:

$$eV_{oc} = F_n - E_{redox} \qquad (1)$$

The oxidized dye left behind by the electron injected to the TiO_2 (S+ in Fig. 2) is rapidly regenerated by the electrolyte (process 5 in Fig. 2). This process is essential in DSSC. When trying to substitute the I^-/I_3^- redox pair, it has been demonstrated that the lower efficiencies obtained were related to a slower dye regeneration rate [50]. I^- oxidizes to I_3^- while at the counter-electrode I_3^- is reduced to I^- (process 4 in Fig. 2). Therefore, I_3^- is produced at the photoelectrode and consumed at the counter-electrode (it is often considered as the "hole carrier" by analogy with traditional solar cells). I^- is produced at the counter-electrode and diffuses to the photoelectrode where it changes to I_3^- when it gives an electron to the dye.

The photocurrent appearance when the illuminated device is in a closed circuit can be understood from processes illustrated in Fig. 2. 1. An electron in the dye absorbs a photon occupying the excited state S*. 2. The electron in S* highest probability is to be injected to lower energy states in the nanocrystalline TiO_2 conduction band. 3. The electron is transported in the TiO_2, in the TCO, in the external circuit, arriving finally at the counter electrode. 4. The electron passes to the electrolyte reducing a triiodide ion to iodide. 5. The electron is returned to the dye by an iodide ion that oxidizes to triiodide. Notice that the energy that electrons can give, i.e. that can be converted to work in the external circuit, is equal to the energy difference between the electron QFL and the electrolyte redox potential (see Fig. 2). Also notice that equilibrium hole concentration in the TiO_2 does not change, contrary to what happens in traditional solar cells. Light is absorbed by the dye and absorption by the TiO_2 is negligible because it only absorbs photons in the violet and ultraviolet (E_G=3.2 eV, λ<387 nm). The absence of holes in non-equilibrium avoids electron-hole recombination in the semiconductor. This is a situation very different to that existing in p-n junctions where minority carriers must diffuse to the depletion region before recombining. That light is absorbed in one medium and electrons are transported in another medium determines the absence of minority carriers in non-equilibrium. This is the reason why semiconductor purity is not crucial in DSSC; there is no need to avoid impurities and defects that favor recombination.
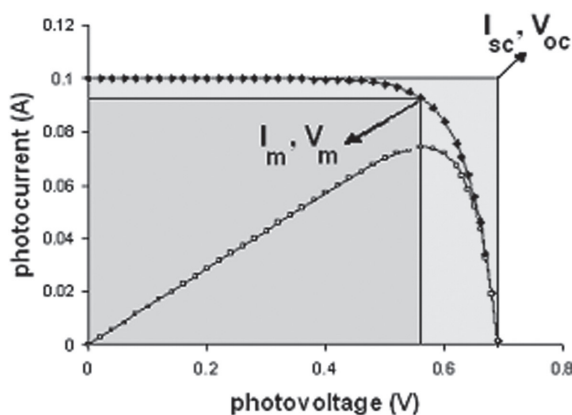

Figura 3: I-V characteristic for a solar cell. The product IV=P is also shown as a function of photovoltage. The ratio of the two rectangles gives the fill factor FF

The QFL position depends on light intensity but also on the external load. As the external load is changed for constant incident radiation intensity, a dependence of photocurrent on voltage is obtained. DSSC show I-V and P-V curves similar to those of conventional solar cells (see Fig. 3). The following known equations are also valid for DSSC:

$$I = I_0 \left[\exp(-eV/nKT) - 1 \right] - I_\Phi \qquad (2)$$

$$V_o = \frac{nKT}{e} \ln \frac{I_0}{I_\Phi} \qquad (3)$$

where I0 is the saturation current; n is the so-called ideality factor; K is the Boltzmann constant, T the temperature. The current corresponding to the short-circuit condition, R_L=0, is called short-circuit current I_{sc} and the voltage corresponding to open-circuit, R_L=∞, is called open-circuit photovoltage V_{oc}.

DSSC efficiency is obtained from the I-V dependence like in conventional solar cells. Efficiencies higher than 11% at one sun illumination have so far been obtained with DSSC [51]. The maximum efficiency is given by:

$$\eta_m = P_m / P_{in} = I_m V_m / P_{in} \qquad (4)$$

where P_{in} is the incident radiation energy per second. The fill factor FF, is the ratio of the areas of two rectangles defined by the points I_m, V_m and I_{sc}, V_{oc} with the coordinates axis (see Fig. 3). FF characterizes the shape of the I-V curve and it is related to its efficiency:

$$FF = I_m V_m / V_{oc} I_{sc} = P_m / V_{oc} I_{sc} \qquad (5)$$

Therefore:

$$\eta_m = V_{oc} I_{sc} FF / P_{in} \qquad (6)$$

NANO-SIZED THREE-DIMENSIONAL STRUCTURE

In a quest to obtain higher-efficiency, more stable, longer lived and cheaper solar cells, different types of nanostructured solar cells have come up after O'Reagan and Grätzel's first report in 1991 [11].

Nanocrystals in DSSC in the range 10-50 nm do not generally show the confinement effect present in quantum dots of size ca. 1-10nm. In these nano-crystals the electron wave functions are strongly confined, so that the electron energy levels are discrete and their separation is determined by the crystal size. Nonetheless, the nanocrystalline character of the metal oxide in DSSC determines a different working principle. Let us summarize the implications of having a nano-sized three-dimensional (3D) structure in DSSC.

Light absorption by the sensitizer or dye is enormously enhanced since the real internal area of the semiconductor-oxide with the attached dye is orders of magnitude larger than the visibly apparent area.

It allows the electrolyte to penetrate and surround the semiconductor-oxide nanocrystals. Therefore, a 3D semiconductor-electrolyte interface is formed. It is not a 3D heterojunction, i.e., there is no macroscopic electric field at this 3D interface, so only diffusion current exists. There are no drift currents as in traditional solar cells.

It allows charge carriers to be transported in media different from the medium in which photon absorption creates them.

It is a majority carrier device. There are no excess minority carriers in the oxide-semiconductor where electrons are transported. Electron-hole recombination in the semiconductor does not play an important role in decreasing efficiency as in traditional solar cells. Therefore, no highly perfect and highly pure materials are required. This leads to the most important characteristic of DSSC: they are cheaper than traditional solar cells while having efficiency above 10%. This is not only because raw materials required are cheaper but also technological procedures: very high temperature processes are not needed; clean-room conditions are less necessary (high purity materials are not employed); technological equipment is not as expensive.

Notice that the electrolyte creates a perfect 3D interface because it can penetrate very well the pores and interstices. This is a great advantage of the liquid electrolyte. But, on the other hand, a perfect seal has not been accomplished; i.e., a sealant resistant to the highly reactive electrolyte to prevent leakage and/or evaporation of the solvent for several years. Also permeation of water or oxygen molecules that react with the electrolyte worsens cell performance. Therefore, a great disadvantage of DSSC is that they do not last long due to electrolyte and dye degradation. They have passed 1000h stability test at 55°C in a solar simulator (100 mW/cm²) maintaining 94% of its initial performance [52].

SOLID AND QUASI-SOLID SENSITIZED SOLAR CELLS (SSSC)

Difficulties caused by the liquid electrolyte in DSSC has motivated research to replace it with solid or quasi-solid hole conductors, such as ionic electrolytes, p-type semiconductors or polymers. A brief review follows of some published reports on solid nanostructure sensitized solar cells (SSSC).

Ionic liquid electrolytes. Ionic liquids constitute the source of both, the redox pair and the solvent. Although most of them are in the liquid state at room temperature, they have good chemical and thermal stability, as well as negligible vapor pressure; thus decreasing problems encountered with organic solvents.

Several ionic liquid electrolytes have been reported while imidazolium compounds have been the most frequently employed [53], [54]. High viscosity imidazolium iodides have yielded high stability cells with efficiencies around 6%. Very

viscous and solid electrolytes with low ion mobility and low conductivity[1] represent an obstacle for developing ionic electrolyte SSSC with high conversion efficiency. Some polymers [55], gelators [56], and composites [57] have been used as framework materials to solidify ionic liquid-based electrolyte; they also favor triiodide/iodide diffusion.

Power conversion efficiency ca. 8% has been achieved for SSSC with the lower-viscosity 1-ethyl-3 -methylimidazolium selenocyanate (EMISeCN), a $SeCN^-/(SeCN)_3^-$ based ionic electrolyte under AM 1.5 sunlight [58].

P type semiconductors. High band-gap inorganic semiconductors have been used as hole conductors to replace the liquid electrolyte. Technologically this is a much harder task than with liquid electrolytes. It must be guaranteed that the hole conductor penetrates pores all along the thickness of the mesoporous TiO_2 in order to contact the sensitizer but it must not contact the electron-extracting conducting electrode. CuI was the first p-type semiconductor to be used in a SSSC [59] These CuI SSSC are not very stable [60]. Also incorporation of small quantity of 1-methyl-3-ethylimidazolium thiocyanate (MEISCN) improved the stability and 3.8 % efficiency was obtained [61].

Other p-type semiconductor used as hole conductor is CuSCN. It has been found to give more stable and durable SSSC but efficiencies obtained are lower than with CuI [62], [63].

NiO has been reported as hole conductor in SSSC [64], [65], as well as, $CuAlO_2$ [66].Complete pore filling represents a problem if available fabrication techniques were to be used for wide-bandgap p-type oxides.

Organic p-type semiconductors are used as substitutes of inorganic ones for different devices in microelectronics and optoelectronics. They have also been studied as hole conductors in SSSC [67]-[69]. Efficiency values of 3.2% have been obtained using 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9'90-spirobifluorene (spiro-OMeTAD) [70]. There are several organic hole-conductors that have been utilized: pyrrole or polypyrrole [71],[72]; thiophene and polythiophene [73], [74]; poly(3,4-ethylenedioxythiophene, PEDOT [75], [76]; the polyanilines (PANIs) [77], [78].

Polymer electrolytes. Polymer electrolytes have the advantages of relatively high ionic conductivity and easy solidification. They have been used before in lithium batteries and in redox type laminated supercapacitors. In SSSC the polymer plays the role of the organic solvent in DSSC; the I^-/I_3^- redox couple is used dissolved in the polymeric medium [79]. Polymerization must occur in the presence of iodine and at an adequate temperature for the dye not to decompose. The two polymers that have been more frequently used in polymer electrolytes for SSSC are poly(ethylene glycol) (PEO) [80]-[82] and poly(epichlorohydrin-co-ethylene oxide), Epichlomer-16 [83]-[85]. Studies continue to improve results obtained with

electrolytes based on these polymers, as well as on other polymers [86]-[91].

EXTREMELY THIN ABSORBER (ETA) SOLAR CELLS

This solar cell type is similar to the p-type semiconductor SSSC. The difference is that also the sensitizer is replaced by a semiconductor. The eta solar cell consists of an extremely thin light-absorbing semiconductor sandwiched between two transparent, highly interpenetrated, nanostructured semiconductors – an n-type and a p-type [92]. Nanostructure wide-bandgap mesoporous oxide semiconductors are used also in eta solar cells, mainly TiO_2. Good coverage of the nanostructure electrode by the extremely thin film absorber, as well as, the filling of the pores with the hole-transporting semiconductor is essential for device efficiency. The absorber must be extremely thin so that electron-hole pairs are created by photons next to the wide-band gap semiconductors or extremely close; i.e., so that electron-hole pairs do not recombine before been injected to the wide-bandgap semiconductors. Different narrow bandgap semiconductors have been proposed as light absorbers like CdTe [93], CdSe [94], CuO [95], $CuInS_2$ [92], [96]. Several wide bandgap semiconductors have been studied as hole conductors, e.g., CuI [97], CuSCN [98], [99], NiO [100], $CuAlO_2$ [101]. Efficiency so far is below 4% [102], [103].

OTHER TRENDS IN THE DEVELOPMENT OF NANOSTRUCTURED SOLAR CELLS

DSSC efficiency value of ca. 11% is acceptable if it were accompanied by solar cell long life. As mentioned before, the very reactive liquid electrolyte plus dye degeneration attempt against it. SSSC and eta solar cells show higher stability in general but lower efficiency. Charge transport in their respective hole conductors is not as efficient as in the electrolyte; either because of the viscosity of the solvent if ions are transported (ionic and polymer SSSC) or the poor pore filling and contact in the case of electronic conductivity (p-type semiconductor SSSC and eta solar cells). These problems lead to incomplete dye regeneration and low charge generation efficiencies [104]. An appropriate morphology of the porous wide-bandgap n-type semiconductor (TiO_2 most frequently) can help to minimize these difficulties. Therefore, different structures are been studied like nanorods [105], nanowires [106] and nanotubes [107]-[109]. All cases may ease penetration of the hole conductor in the mesopores and its contact with the sensitizer.

At present studies of quantum dots as sensitizers are being conducted. The energy bandgap value depends on quantum dot size; so the optical absorption spectrum can be tailored to obtain different color solar cells. Besides, they may have a large extinction coefficient which implies good light absorption efficiency. Different semiconductors with energy bandgap adequate for absorbing a significant part of the solar spectrum have been studied: CdSe [110]-[112]; CdTe [113], [114]; PbS [115],[116]; and CdS, that although it has a less appropriate bandgap value, it nicely renders nanocrystals of controlled size [117]-[119].

In traditional solar cells, ohmic metal-semiconductor contacts used to extract photogenerated carriers are very important. In DSSC not much attention has been given to electrical contact between the TiO_2 and the conducting glass (TCO) [120], [121], which is used instead of a metal contact to extract electrons. In Fig. 2 one must look in more detail to what happens between process 2 and 3, i.e. to electron transfer from the TiO_2 to the TCO. In this TiO_2-TCO interface two loss mechanisms can be present: First, recombination of electrons in the TCO with species in the electrolyte. Since the TiO_2 is porous, the electrolyte can penetrate and contact the TCO allowing this recombination to occur. Second, a barrier exists at this interface due to differences in oxides work functions and affinity values [121]-[122]. Defects at this interface would affect this barrier. Therefore, contact resistivity could be affected. Conducting oxide type (ITO, FTO, etc), TiO_2 crystal structure and morphology, as well as, the technology used when forming the TiO_2/TCO contact, should influence electron extraction efficiency at the TiO_2-TCO interface. For example, a different electrical contact to the TCO is to be expected according to the TiO_2 porosity (electron recombination with the electrolyte changes) and adherence (contact resistivity plus electron recombination with the electrolyte change). Layers obtained by "doctor blading" a nanocrystalline TiO_2 suspension are porous as required but they do not adhere so well as sprayed films [123] or TiO_2 films obtained using MW-CBD [124][125][126][127], for example. Because of all this, the use of double layer TiO_2 structures has also received attention lately. The purpose is to avoid the recombination of electrons in the TCO with acceptor species in the electrolyte, [128][129], as well as, to improve electrical contact of the TiO_2 with the TCO [120]. The use of double layer structures has been considered essential in solid dye sensitized solar cells [130].

SUMMARY

New-concept nanostructured solar cells show great prospective among different solar cell types that are called to guarantee a significant percentage of electric energy used in the not too distant future. Their working principle, based on their three dimensional nanostructure, implies that no highly pure materials have to be used hence contributing to their low cost. Electron-hole pairs are created and transported by different materials thus avoiding recombinations. Diffusion due to charge-carriers-concentration gradients is responsible for charge transport since the nano-character of the semiconductor is not compatible with the existence of electric-field-driven current. Highest efficiency values have been found with liquid electrolytes corresponding to highest mobility value in the hole-extracting medium. At the same time, the liquid electrolyte causes short lifetimes. Different solutions to overcome this problem are under study given rise to different types of solid solar cells based on a three dimensional nanostructure which have been described along with research trends.

[1] IPCC, 2007: Summary for Policymakers. In: Climate Change 2007: Impacts, Adaptation and Vulnerability. Con-tribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, M.L. Parry, O.F. Canziani, J.P. Palutikof, P.J. van der Lin-den, C.E. Hanson, Eds., Cambridge University Press, Cam-bridge, UK, 7-22

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[2] International Energy Agency, World Energy Outlook 2005, November 2005, page 132

[3] R. L. Hirsch, Peaking of World Oil Production: Recent Forecasts. DOE NETL-2007/1263, February 2007

[4] Report #: DOE/EIA-0484(2009), May 2009

[5] IEA Energy Technology R&D Statistics Service, 2007, http://www.iea.org/stats/rd.asp

[6] W. Hoffmann, Solar Energy Materials & Solar Cells 90, 3285 (2006)

[7] Set for 2020 - Solar Photovoltaic Electricity: A mainstream power source in Europe by 2020- Executive Summary, Eu-ropean Photovoltaic Industry Association (EPIA), 2009, www.setfor2020.eu

[8] Zh.I. Alferov, V.M. Andreev, Kh.K. Aripov, V.R. Larionov, V.D. Rumyantsev, Geliotechnika No 6 (1981), p. 3. Translated into English in: Applied Solar Energy No 6 (1981).

[9] D. Cusano, Solid State Electron. 6, 217 (1963)

[10] V. Petrova-Koch in: High-Efficient Low-Cost Photovoltaics Recent Developments, p. 1, edited by Vesselinka Petrova-Koch, Rudolf Hezel, Adolf Goetzberger, Springer (2008)

[11] B. O'Regan, M. Gratzel, Nature 353, 737 (1991)

[12] M. Gratzel, Prog. Photovolt. 8, 171 (2000)

[13] A. Feltrin, A. Freundlich, Renewable Energy 33, 180 (2008)

[14] W. Hoffmann, Solar Energy Materials & Solar Cells 90, 3285 (2006)

[15] B. Yoo, K. Kim, S. H. Lee, W. M. Kim, N-G Park, Solar Energy Materials & Solar Cells 92, 873 (2008)

[16] C. Longo, J. Freitas, M.-A. De Paoli, J. Photochem. & Pho-tobiol. A-Chemistry 159, 33 (2003)

[17] K. Onoda, S. Ngamsinlapasathian, T. Fujieda, S. Yoshika-wa, Solar Energy Materials & Solar Cells 91, 1176 (2007)

[18] F. O. Lenzmann and J.M. Kroon, Advances in OptoElec-tronics 2007, 65073 (2007)

[19] R. Solarska, J. Augustynski, K. Sayama, Electrochimica Acta 52, 694 (2006)

[20] A. N. M. Green, E. Palomares, S. A. Haque, J. M. Kroon, J. R. Durrant, J. Phys. Chem. B 109, 12525 (2005)

[21] S. Chappel, A. Zaban, Solar Energy Materials & Solar Cells 71, 141 (2002)

[22] F. Lenzmann, J. Krueger, S. Burnside, K. Brooks, M. Grätzel, D. Gal, S. Rühle, D. Cahen, J. Phys. Chem. B 105, 6347 (2001)

[23] K. Keis, E. Magnusson, H. Lindström, S-E. Lindquist, A. Hagfeldt, Solar Energy Materials & Solar Cells 73, 51 (2002)

[24] Y. Yoshida, S. Tokashiki; K. Kubota, R. Shiratuchi, Y. Yamaguchi, M. Kono, S. Hayase, Energy Materials & Solar Cells 92, 646 (2008)

[25] R. Espinosa, I. Zumeta, J. L. Santana, F. Martinez-Luzardo, B. Gonzalez, S. Docteur, E. Vigil, Solar Energy Materials & Solar Cells 85, 359 (2005)

[26] G. Boschloo, T. Marinado, K. Nonomura, T. Edvinsson, A. G. Agrios, D. P. Hagberg, L. Sun, M. Quintana, C. S. Karthikeyan, M. Thelakkat, A.Hagfeldt, Thin Solid Films 516, 7214 (2008)

[27] W. H. Howie, F. Claeyssens, H. Miura, L. M Peter, J. Am. Chem. Soc. 130, 1367 (2008)

[28] X. M. Ma, J. L. Hua, W. J. Wu, Y. H. Jin, F. S. Meng, W. H. Zhan, H. Tian, Tetrahedron 64, 345 (2008)

[29] P.V.V. Jayaweera, A.G.U. Perera, K. Tennakone, Inorganica Chimica Acta 361, 707 (2008)

[30] F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo, A. Hagfeldt, Solar Energy Materials & Solar Cells 87, 117 (2005)

[31] H. Nusbaumer, J.-E. Moser, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel, J. Phys. Chem. B 105, 10461 (2001)

[32] B.A. Gregg, F. Pichot, S. Ferrere, and C. L. Fields, J. Phys. Chem. B 105, 422 (2001)

[33] Z. Kebede, S.-E. Lindquist, Sol. Energy Mater. Sol. Cells 57, 259 (1999)

[34] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Ara-kawa, Sol. Energy Mater. Sol. Cells 70, 151 (2001)

[35] A. Fukui, R. Komiya, R. Yamanaka, A. Islam, L. Han, Solar Energy Materials & Solar Cells 90, 649 (2006)

[36] C. Shi, S. Dai, K. Wang, X. Pan, F. Kong, L. Hu, Vibra-tional Spectroscopy 39, 99 (2005)

[37] G. Boschloo, L. Haggman, A. Hagfeldt, J. Phys. Chem. B 110, 13144 (2006)

[38] K. Imoto, K. Takahashi, T. Yamaguchi, T. Komura, J. I. Nakamura, K. Murata, Sol. Energy Mater. Sol. Cells 79, 459 (2003)

[39] W. J. Lee, E. Ramasamy, D. Y, Lee, J. S. Song, J. Photo-chem. Photobio. A-Chem. 194, 27 (2008)

[40] Z. Huang, X. Liu, K. Li, D. Li, Y. Luo, H. Li, W. Song, L. Chen, Q. Meng, Electrochem. Comm. 9, 596 (2007)

[41] X. Fang, T. Ma, M. Akiyama, G. Guan, S. Tsunematsu, E. Abe, Thin Solid Films 472, 242 (2005)

[42] W. Hong, Y. Xu, G. Lu, C.Li, G. Shi, Electrochem. Comm. 10 1555 (2008)

[43] J-G. Chen, H-Y. Weib, K-C. Hoa, Solar Energy Materials & Solar Cells 91 1472 (2007)

[44] A. Hagfeldtt, M. Grätzel, Chem. Rev. 95 49 (1995)

[45] M. J. Cass, F. L. Qiu, Alison B. Walker, A. C. Fisher, and L. M. Peter, J. Phys. Chem. B 107, 113 (2003)

[46] N. Kopidakis, E. A. Schiff, N.-G. Park, J. van de Lagemaat, A. J. Frank, J. Phys. Chem. B 104, 3930 (2000)

[47] S. Ruhle, T. Dittrich, J. Phys. Chem. B 109, 9522 (2005)

[48] M. Grätzel, J. Photochem. Photobio. A-Chem. 164, 3 (2004)

[49] J. R. Durrant, S. A. Haque, E. Palomares, Coord. Chem. Rev. 248, 1247 (2004)

[50] G. Oskam, B.V. Bergeron, G.J. Meyer, P.C. Searson, J. Phys. Chem. B 105 6867 (2001)

[51] J. M. Kroon, N. J. Bakker, H. J. P. Smit, P. Liska, K. R. Thampi, P. Wang, S. M. Zakeeruddin, M. Grätzel, A. Hinsch, S. Hore, U. Würfel, R. Sastrawan, J. R. Durrant, E. Palomares, H. Pettersson, T. Gruszecki, J. Walter, K. Sku-pien, G. E. Tulloch, Prog. Photovolt, Res. Appl. 15, 1 (2007)

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

[53] P. Wang, S.M. Zakeeruddin, J.E. Moser, M. Grätzel, J. Phys. Chem. B 107 13280 (2003)

[54] H. Paulsson, M. Berggrund, E. Svantesson, A. Hagfeldt, L. Kloo, Sol. Energy Mater. Sol. Cells 82 345 (2004)

[55] A.F. Nogueira, M.-A. De Paoli, I. Montanari, R. Monkhou-se, J. Nelson, J.R. Durrant, J. Phys. Chem. B 105, 7517 (2001)

[56] J. Xia, F. Li, C. Huang, J. Zhai, L. Jiang, Solar Energy Ma-terials & Solar Cells 90, 944 (2006)

[57] B. Muthuraaman, S. Murugesan, V. Mathew, S. Ganesan, B. J. Paul, J. Madhavan, P. Maruthamuthu, S. A. Suthanthi-raraj, Solar Energy Materials & Solar Cells 92, 1712 (2008)

[58] P. Wang, S.M. Zakeeruddin, J. Moser, R. Humphry-Baker, M. Grätzel, J. Am. Chem. Soc. 126, 7164 (2004)

[59] K. Tennakone, G. Kumara, A.R. Kumarasinghe, K.G.U. Wijayantha, P.M. Sirimanne, Semicond. Sci. Technol. 10, 1689 (1995)

[60] P.M. Sirimanne, T. Jeranko, P. Bogdanoff, S. Fiechter, H. Tributsch, Semicond. Sci. Technol. 18, 708 (2003)

[61] Q.B. Meng, K. Takahashi, X.T. Zhang, I. Sutanto, T.N. Rao, O. Sato, A. Fujishima, H. Watanabe, T. Nakamori, M. Uragami, Langmuir 19, 3572 (2003)

[62] J. Bisquert, V. S. Vikhrenko, J. Phys. Chem. B 108, 2313 (2004)

[63] B. C. O'Regan, F. O. Lenzmann, J. Phys. Chem. B 108, 4342 (2004)

[64] L. Bandara, H. Weerasinghe, Sol. Energy Mater. Sol. Cells 85, 385 (2005)

[65] Y-M Lee, C-H. Hsu, H-W. Chen, App. Surf. Sc. 255, 4658 (2009)

[66] J Bandara and J P Yasomanee, Semicond. Sci. Technol. 22, 20 (2007)

[67] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, M. Grätzel, Nature 395, 583 (1998)

[68] J. Kruger, R. Plass, L. Cevey, M. Piccirelli, M. Grätzel, U. Bach, Appl. Phys. Lett. 79, 2085 (2001)

[69] F. Fabregat-Santiago, J. Bisquert, E. Palomares, S. A. Haque, J. R. Durrant, J. Appl. Phys. 100, 034510 (2006)

[70] J. Kruger, R. Plass, M. Grätzel, H.J. Matthieu, Appl. Phys. Lett. 81, 367 (2002)

[71] K. Murakoshi, R. Kogure, Y. Wada, S. Yanagida, Sol. Energy Mater. Sol. Cells 55, 113 (1998)

[72] T. Kitamura, M. Maitani, M. Matsuda, Y. Wada, S. Yana-gida, Chem. Lett.30, 1054 (2001)

[73] G. P. Smestad, S. Spiekermann, J. Kowalik, C. D. Grant, A. M. Schwartzberg, Solar Energy Materials & Solar Cells 76, 85 (2003)

[74] W. S. Shin, S. C. Kim, S-J. Lee, H-S Jeon, M-K. Kim, B. V. K. Naidu, S-H. Jin, J-K. Lee, J. W. Lee, Y-S. Gal, J. Polymer Sc. Part A: Polymer Chem. 45, 1394 (2007)

[75] Y. Saito, N. Fukuri, R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, Electrochem. Commun. 6, 71 (2004)

[76] E.M.J. Johansson, A. Sandell, H. Siegbahn, H. Rensmo, B. Mahrov, G. Boschloo, E. Figgemeier, A. Hagfeldt, S.K.M. Jönsson, M. Fahlman, Synthetic Metals 149, 157 (2005)

[77] S. Tan, J. Zhai, B. Xue, M. Wan, Q. Meng, Y. Li, L. Jiang and D. Zhu, Langmuir 20 2934 (2004)

[78] G.K.R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, J. Photochem. Photobiol. A-Chem. 164 61 (2004)

[79] A. F. Nogueira, C. Longo, M.-A. De Paoli, Coord. Chem. Reviews 248 1455 (2004)

[80] F. Croce, G. B. Appetecchi, L. Persi, B. Scrosati, Nature 394, 456 (1998)

[81] Y. J. Ren, Z. C. Zhang, S. B. Fang, M. Z. Yang, S. M. Cai , Sol. Energy Mater. Sol. Cells 71, 253 (2002)

[82] M. S. Kang, J. H. Kim, Y. J. Kim, J. Won, N. G. Park, Y. S. Kang, Chem. Commun., 889 (2005)

[83] A. F. Nogueira, M. A. De Paoli, Sol. Energy Mater. Sol. Cells 61, 135 (2000)

[84] A. F. Nogueira, J. R. Durrant, M. A. De Paoli , Adv. Ma-ter. 13, 826 (2001)

[85] S. A. Haque, E. Palomares, H. M. Upadhyaya, L. Otley, R. J. Potter, A. B. Holmes, J. R. Durrant, Chem. Commun., 3008 (2003)

[86] M. Matsumoto, Y. Wada, T. Kitamura, K. Shigaki, T. Inoue, M. Ikeda, S. Yanagida, Bull. Chem. Soc. Japan 74, 387 (2001)

[87] G. Katsaros, T. Stergiopoulos, I. M. Arabatzis, K. G. Papadokostaki, P. Falaras, J. Photochem. Photobiol. A-Chem. 149, 191 (2002)

[88] E. Stathatos, P. Lianos, U. Lavrencic-Stangar, B. Orel, Adv. Mater. 14, 354 (2002)

[89] Y. Shibata, T. Kato, T. Kado, R. Shiratuchi, W. Takashima, K. Kaneto, S. Hayase, Chem. Commun., 2730 (2003)

[90] J. H. Kim, M-S Kang, Y. J. Kim, J. Won, N-G Park, Y. S. Kang, Chem. Commun., 1662 (2004)

[91] H. Han, U. Bach, Y-B Cheng, R. A. Caruso, Appl. Phys. Lett. 90, 213510 (2007)

[92] I. Kaiser, K. Ernst, Ch-H. Fischer, R. Könenkamp, C. Rost, I. Sieber, M. Ch. Lux-Steiner, Solar Energy Mater. Solar Cells 67, 89 (2001)

[93] R. Tena-Zaera, A. Katty, S. Bastide, C. Levy-Clement, B. O'Regan, V. Munoz-Sanjose, Thin Solid Films 483, 372 (2005)

[94] C. Lévi-Clément, R. Tena-Zaera, M. A. Ryan, A. Katty, G. Hodes, Adv. Mater. 17, 1512 (2005)

[95] E. Vigil, B. González, I. Zumeta, C. Domingo, X. Dome-nech, J. A. Ayllon, Thin Solid Films 489, 50 (2005)

[96] M. Nanu, J. Schoonman, A. Goossens, Adv. Mater. 16, 453 (2004)

[97] T. Taguchi, X. T. Zhang, I. Sutanto, K. Tokuhiro, T. N. Rao, H. Watanabe, T. Nakamori, M. Uragami, A. Fujis-hima, Chem. Commun. 19, 2480 (2003)

[98] K. Ernst, A. Belaidi, R. Könenkamp, Semicond. Sci. Technol. 18, 475 (2003)

[99] P. M. Sirimanne, T. Jeranko, P. Bogdanoff, S. Fiechter, H. Tributsch, Semicond. Sci. Technol. 18, 708 (2003)

[100] J. Bandara, H. C. Weerasinghe, Sol. Energy Mater. Sol. Cells 85, 385 (2005)

[101] J. Bandara, J. P. Yasomanee, Semicond. Sci. Technol. 22, 20 (2007)

[102] R. Tena-Zaera, M. A. Ryan, A. Katty, G. Hodes, S. Bas-tide, C. Levy-Clement, C. R. Chim. 9, 717 (2006)

[103] O. Niitsoo, S. K. Sarkar, C. Pejoux, S. Rühle, D. Cahen, G. Hodes, J. Photochem. Photobiol. A-Chem. 181, 306 (2006)

[104] L. Schmidt-Mende, M. Grätzel, Thin Solid Films 500, 296 (2006)

[105] M. Y. Song, Y. R. Ahn, S. M. Jo, D. Y. Kim, J-P. Ahn, Appl. Phys. Lett. 87, 113113 (2005)

[106] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, P. Yang, Nature Mat. 4, 455 (2005)

[107] J. R. Jennings, A. Ghicov, L. M. Peter, P. Schmuki, A. B. Walker, J. Am. Chem. Soc. 130, 13364 (2008)

[108] G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, C. A. Grimes, Appl. Phys. Lett. 91, 152111 (2007)

[109] K. Shankar, G. K. Mor, H. E. Prakasam, O. K. Varghese, C. A. Grimes, Langmuir 23, 12445 (2007)

[110] J. Chen, J. L. Song, X. W. Sun, Appl. Phys. Lett. 94, 153115 (2009)

[111] S-Q. Fan, D. Kim, J-J. Kim, D. W. Jung, S. O. Kang, J. Ko, Electro-chem. Comm. 11, 1337 (2009)

[112] L. J. Diguna, Q. Shen, J. Kobayashi, T. Toyoda, Appl. Phys. Lett. 91, 23116 (2007)

[113] X-F. Gao, H-B. Li, W-T. Sun, Q. Chen, F-Q. Tang, L-M. Peng, J. Phys. Chem. C 113, 7531 (2009)

[114] G-Y. Lan, Z. Yang, Y-W. Lin, Z-H. Lin, H-Yi Liao, H-T. Chang, J. Mater. Chem. 19, 2349 (2009)

[115] R. J. Ellingson, M. C. Beard, J. C. Johnson, P. R. Yu, O. I. Micic, A. J. Nozik, A. Shabaev, A. L. Efros, Nano Lett. 5, 865 (2005)

[116] W. Lee, J. Lee, S. K. Min, T. Park, W. Yi, S-H. Han, Mater. Sc. & Eng. B 156, 48 (2009)

[117] W. Lee, J. Lee, S. Lee, W. Yi, S-H. Han, B. W. Cho, Appl. Phys. Lett. 92, 153510 (2008)

[118] C-H. Chang. Y-L. Lee, Appl. Phys. Lett. 91, 53503 (2007)

[119] S-C. Lin, Y-L. Lee, C-H. Chang, Y-J. Shen, Y-M. Yang, Appl. Phys. Lett. 90, 143517 (2007)

[120] I. Zumeta, J.A. Ayllon, B. Gonzalez, X. Domenech, E. Vigil, Solar Energy Materials & Solar Cells 93, 1728 (2009)

[121] H. J. Snaith, M. Grätzel, Adv. Mater. 18, 1910 (2006)

[122] S. Rühle, D. Cahen, J. Phys. Chem. B. 108, 17946 (2004)

[123] L. Kavan, M. Grätzel, Electrochim. Acta 40, 643 (1995)

[124] E. Vigil, L. Saadoun, J. A. Ayllón, X. Domènech, I. Zu-meta, R.Rodríguez-Clemente, Thin Solid Films 365, 12 (2000)

[125] E. Vigil, B. González, I. Zumeta, S. Docteur, A. M. Peiró, D. Gutié-rrez–Tauste, C. Domingo, X. Doménech, J. A. Ayllón, J. Crystal Growth 262, 366 (2004)

[126] E. Vigil, J. A. Ayllón, A. M. Peiró, R. Rodríguez-Clemente, X. Domè-nech, J. Peral, Langmuir 17, 891 (2001)

[127] I. Zumeta, R. Espinosa, J.A. Ayllón, E. Vigil, Semicond. Sci. Technol. 17, 1218 (2002)

[128] P. J. Cameron, L. M. Peter, J. Phys. Chem. B 109, 7392 (2005)

[129] T. Sreethawong, Y. Suzuki, S. Yoshikawa, S. Ngamsinla-pasathian, Solar Energy Materials & Solar Cells 86, 269 (2005)

[130] B. Peng, G. Jungmann, C. Jäger, D. Haarer, H-W. Schmidt, M. The-lakkat, Coordination Chemistry Reviews 248, 1479 (2004)