Current Trends in Materials for Dye Sensitized Solar Cells

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Abstract: Here, we intend to review those patents related with the technology of dye sensitized solar cells. In particular we discuss patents and papers that enable metal oxide layer to be more controllable and feasible for applications, and new and innovative dyes, sensitizers and electrolytes with promising features. Finally various methods were reviewed for fabricating semiconductor layers and complete DSSC devices focusing on the mass production of photovoltaic cells.

Keywords: DSSC, Grätzel, Nanotechnology.

1. INTRODUCTION

Using a principle inspired by natural photosynthesis, injection solar cells, in particular the dye sensitized solar cells (DSSCs), represent an alternative to solid-state p-n junction devices for energy conversion. Due to the nanoscopic and mesoscopic character of its materials DSSCs have become an excellent example in which nanomaterials have been used in technological applications, as it can be demonstrated by the increasing number of articles and patents. DSSCs kept the attention of the technological and scientific community for their promising additional properties, such as the flexibility and low fabrication costs. They are considered as third generation photovoltaic cells, in opposition to the silicon based solar cells, SSC, and the thin film solar cells, TFSC, which correspond to first and second generation cells, respectively. These two kinds of cells are dominated by solid-state devices taking the advantage from the experience gained through decades of studies and material availability resulting from the semiconductor industry.

Basically a solar cell, SC, consists of a junction of p- and n-type semiconductors. At the interface the Fermi levels of both semiconductors are the same, generating a depletion region, and therefore, a charge separation. When photons are absorbed in the p-type region, an electron-hole pair is created. Each electron is then injected in the n-type region and the hole goes across p-type region. In the case of TFSCs the amount of material for the SCs production is considerably less, thus it reduces costs. Some other advantages consist on the possibility of working with lighter materials and flexible substrates. As in the case of TFSCs, band gap semiconductor, attached to a dye submerged in a liquid electrolyte. See Fig. (1) for a complete scheme of the cell according to the first patent from Grätzel et al. [1]. The wide band gap mesoporous oxide is covering the conducting electrode, and it is composed by nanoparticles sintered together to allow electronic conduction. The most common material is anatase-TiO2, although other oxides such as ZnO [2], SnO2 [3] and Nb2O5 [4] have also been studied. The mesoporous film is then sensitized with organic and inorganic dyes which are responsible for the absorption of photons. In particular polypyrrolid complexes of ruthenium have shown the best performance in terms of efficiency and chemical stability [5].

The photo-excitation process results in an electron injection from dye into the conduction band of the semiconductor, thus it generates an electron-hole pair called excitons. A charge separation similar to a traditional p-n semiconductor junction is therefore induced. In order to restore the ground state of the dye, an electrolyte is used to close the circuit between positive and negative electrodes, donating one electron to the already charged dye. The most common electrolyte is composed by the I-/I3- redox couple dissolved in a liquid organic solvent. There are many efforts in finding alternatives for substituting this solvent by ionic liquids, gelled electrolytes and polymer electrolytes. Finally, iodide is regenerated by the reduction of I3- at the cathode and the electrical circuit is closed by electron migration through the external load.

DSSCs exhibit the highest conversion efficiency among organic and hybrid photovoltaic cells [5,6] which is over 10% [7-9]. A balance between advantages and disadvantages in their individual components, leads to the net power conversion efficiency, with an improvement in the general properties of the DSSC. In the case of nanocrystalline semiconductors, the high surface area is critical to allow an intense absorption of photons from the monolayer of the adsorbed sensitizer dye. The mesoporous film enhances the interfacial surface area, thus it increases the light absorbance.

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from the many successive monolayer of adsorbed dye in the optical path. Additionally, with a dye monolayer there is no requirement for electron-hole pair to diffuse through the dye/metal oxide interface. Thus it avoids the quenching of the excited states, often associated with thicker molecular films. However, the high surface area of the mesoporous films enhances the interfacial charge-recombination losses constituting an important drawback.

Regarding liquid electrolytes, high power conversion efficiency is achieved due to the highly mobility of ions into the solution. Moreover, it allows ions to rapidly compensate the coulomb interaction between photo-generated excitons (themselves). Thus this minimizes the recombination process at the interface. On the other hand, liquid electrolytes induce serious problems to DSSCs, such as chemical degradation of sealing polymers with subsequent losses of the electrolyte. It clearly conspires to the lifetime of the cell, and consequently many efforts are being focused on using solid or quasi-solid electrolytes. Up to now this point is still under development, being \( \eta = 4.5\% \) [8] the highest power conversion efficiency reported for a solid DSSC.

In this review we have focused on methods and materials for fabricating dye sensitized solar cells. The critical points for the improvement of DSSC photocurrent power efficiency consist in the control of sensitizers, electrolytes and thin film metal oxide layer, including its deposition techniques. On this basis we will present the current and future perspective of this technology.

2. SENSITIZERS

The dye sensitizer plays a key role in the overall photoelectric conversion efficiency of the DSSC. Since it is the solar energy absorber of the device, its properties directly affects the light harvesting efficiency. For this reason, a lot of effort is being made in the field of dyes engineering and design in order to tune its properties and thus it enhances the photovoltaic performance of the cells.

Considering its function in the device, the ideal dyes should absorb all the solar energy below a wavelength of about 920nm, and they should inject the photoinduced electrons into the semiconductor with a unit quantum yield. This is possible if the LUMO level of the dye is well matched to the lower level of the conduction band of the semiconductor, and if there is a good electronic coupling between both levels. In order to achieve the electron injection, the dye should be firmly grafted to the semiconductor surface. This is attained through suitable anchoring
groups such as: carboxylate, phosphonate or hydroxamate. These groups promote a good overlap between the dye molecule’s excited-state orbitals and the empty acceptor levels, i.e. the Ti IV-3d orbital manifold forming the conduction band of TiO2 [9]. In addition, the redox potential of the sensitizer should be high enough to enable the dye regeneration by means of electron donation from the electrolyte. Finally, and extremely important for applications, the regeneration by means of electron donation from the sensitizer should be high enough to enable the dye form (a di-tetrabutylammonium salt), is referred to N719 (Fig. 2), cis-diisothiocyanato - bis (2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium(II) bis- (tetrabutylammonium). Regarding functions, the -NCS group acts as the absorber of visible light, while the carboxylate group allows the anchoring to the TiO2 particles.

The “black dye” (Fig. 2c), tri(cyanato)-2,2’2”-terpyridyl-4,4’4”-tricarboxylate-Ru(II), shows solar to power conversion efficiency of \(\eta=10.4%\) [11, 12] (air mass 1.5) in full sunlight, thus it enhances the spectral response in the red and near-IR region. This efficiency has been improved using the N3 dye in combination with guanidinium thiocyanate, which is absorbed with the N3 anions and reducing the lateral coulombic repulsion in the sensitizer. This allows the self-assembly of a compact dye monolayer and consequently improves the cell voltage by a reduction of dark current. Using this combination the conversion efficiency under illumination of AM 1.5 simulated sun light [5] is \(\eta=10.6\%\).

Recently, many modifications to the Ru-complexes have been proposed and evaluated and some examples are shown in Table 1. The results demonstrate that a considerable amount of them permitted similar or even improved DSSCs overall efficiencies when compared with the N719 dye. The compounds produced by Chen C-L et al. [13] Fig. (3), Klein C et al. [77,78] and Lin J-T’ et al. [79], are shown as examples. Particularly, interesting results were obtained using the I-2 dye, whose structure is presented in Fig. (3b).

Another type of inorganic dyes, based on metal-phthalocyanines, have been extensively used in several studies as a sensitizer. Recently, Ihm et al. [14] reported a cross linked polyphthalocyanine, which exhibits excellent resistance to light, heat and chemical degradation. This compound seems to be suitable for its use as a near infrared absorber, having a high absorption power from about 750 nm to about 1100 nm.

2.2. Organic Dyes

In general, organic dyes have lower conversion efficiencies in comparison with inorganic dyes. This is mainly due to the formation of aggregates on the semiconductor surface, and the recombination of the conduction-band electrons with triiodide. In order to avoid these problems several structural modifications have been proposed.

Fig. (2). Structures of inorganic dyes N3 (a), N719 (b), and “black dye” (c).
Kim S. et al. [15] have engineered and synthesized organic dyes comprising donor, electron-conducting, and anchoring groups achieving an incident photon to current efficiency (IPCE) of 91%, and overall conversion efficiency of $\eta=8.01\%$ under standard AM 1.5 sunlight. The sensitizers are 3-{5-[N,N-bis(9,9-dimethylfluorene-2-yl)phenyl]-thiophene-2-yl}-2-cyano-acrylic acid (JK-1) and 3-{5´-[N,N-bis-(9,9-dimethylfluorene-2-yl)phenyl]-2,2´-bisthiophene-5yl}-2-cyano-acrylic acid (JK-2). Both consist of the bis-dimethylfluoreneaniline moiety acting as electron donor, and the cyanoacrylic acid moiety acting as acceptor, the two functions being connected by thiophene which acts as the electron-conducting bridge. The dimethylfluoreneaniline provides resistance to degradation under light, and due to its non-planar structure it avoids molecular aggregation. The thiophene ensures conjugation between donor and anchoring groups broadening the absorption spectrum of the dye on the TiO$_2$ surface [16]. Finally, chemical stability studies indicate that dyes stand for $5 \times 10^6$ turnovers without any noticeable decrease in performance.

Another series of organic sensitizers have been designed and synthesized by Hagberg et al. [17], 3-(5-(4-diphenylamino)styryl)thiophen-2-yl)-2-cyanoacrylic acid (D5), 3-(5-bis(4-diphenylamino)styryl)thiophen-2-yl)-2-cyanoacrylic acid (D7), 5-(4-(bis(4-methoxyphenylamino)styryl)thiophen-2-yl)-2-cyanoacrylic acid (D9), and 3-(5-bis(4,4'-dime-thoxydiphenylamino)styryl)thiophen-2-yl)-2-cyanoacrylic acid (D11). The structure of these compounds is shown in Fig. (4). The relevant current-voltage parameters obtained for these dyes are illustrated in Table 2, and Table 3. When referring to the TiO$_2$ film thicknesses, the nomenclature is x $\mu$m (transparent) + 5 $\mu$m (scattering) TiO$_2$ layers. Authors demonstrated the effect of donor groups on the optical and photovoltaic properties of the dye. Donor groups prevent triiodide, which is present in the electrolyte, from recombination with injected electrons in the TiO$_2$, thus it leads to an increase in the open-circuit potential. According to this work, the short-circuit current density ($J_{sc}$) and overall efficiency ($\eta$) increased. This is due to the fact that thicker TiO$_2$ films offer larger surface areas in which dyes could anchor.

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>ff (%)</th>
<th>$\eta$ (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(II)-LL'(NCS)2]</td>
<td>17 ± 0.5</td>
<td>720 ± 50</td>
<td>0.75 ± 0.05</td>
<td>8.8 ± 0.5</td>
<td>[77]</td>
</tr>
</tbody>
</table>
|  L = 4,4'-bis(carboxylic acid)-2,2'-bipyridine  
L’ = 4,4'-bis(dodecan-12-ol)-2,2'-bipyridine | 18 ± 0.5 | 640 ± 50 | 0.75 ± 0.05 | 8.64 ± 0.5 | [78] |
| I’- 1 | 16.56** | 670 ** | 0.65** | 7.20** | [79] |
| cis-di(thiocyanato)-N,N’-bis(2,2'-bipyridyl-4,4’-dicarboxylic acid)ruthenium(II) | 8.22 * | 780* | 0.64* | 4.09* | [13] |
| bis(benzyltributylammonium) (I-1) | 9.42* | 790* | 0.62* | 4.54* | [13] |
| cis-di(thiocyanato)-N,N’-bis(2,2'-bipyridyl-4,4’-dicarboxylic acid)ruthenium(II) | 8.46* | 800* | 0.64* | 4.33* | [13] |
| bis(benzyltriethylammonium) (I-2) | 6.98* | 680* | 0.63* | 3.00* | [13] |
| cis-di(thiocyanato)-N,N’-bis(2,2'-bipyridyl-4,4’-dicarboxylic acid)ruthenium(II)bis(1-dodecylpyridinium) (I-4) | 7.84* | 810* | 0.65* | 4.12* | [13] |
| tris(benzyltriethylammonium) (I-5) | 7.99* | 750* | 0.62* | 3.74* | [13] |
| cis-di(thiocyanato)-N,N’-bis(2,2'-bipyridyl-4,4’-dicarboxylic acid)ruthenium(II)tetakis(benzyltriethylammonium) (I-6) | 7.36mA/cm$^2$ | 760mV | 0.61 | 3.38% | [13] |
| ** Comparative example using N719 produces the following outputs: $J_{sc}$=16.39mA/cm$^2$, Voc=690mV, ff=0.63, $\eta $(% )=7.12. |
Fig. (3). Chemical structures for I'-1 (a) and I-2 dye (b).

Fig. (4). Chemical structures of: D5, D7, D9 and D11 sensitizers synthesized by Hagberg et al. [17].
allowing better light harvesting. On the other hand, the increase of the thickness induces further polarization at the semiconducting surface, reducing the open circuit voltage ($V_{oc}$). Since the fill factor (ff) is inversely proportional to the product between $J_{sc}$ and $V_{oc}$, this parameter remains almost constant for the whole series. The D9 and D11 dyes present broader IPCE curves, in comparison with D3 and D5. This fact explains the high $J_{sc}$ values and the high efficiencies achieved. In particular, the high value of $V_{oc}$ for D11 is explained in terms of the increased lifetime of the electrons in the conduction band of the TiO$_2$.

As it was mentioned before, the photocurrent increases with the thickness of the TiO$_2$ nanocrystalline layer. On the one hand, the surface area is larger allowing better light harvesting but on the other hand, it allows the possibility for injected electrons to recombine with the oxidized redox species triiodide. The $V_{oc}$ of a DSSC is determined by the difference between the quasi-Fermi level ($nE_F$) in the TiO$_2$ under illumination and the Fermi level of the electrolyte (redox potential). The reasons for the increase of $V_{oc}$ with the TiO$_2$ film thickness could be explained by two mechanisms. The first one is the delay in the recombination between injected electrons and oxidized species in the electrolyte. The second one is the band edge movement with respect to the redox potential. IPCE and electron life-times are directly implied in the determination of $V_{oc}$ parameter.

Recently, Xu and coworkers [18] presented organic compounds which show cell efficiencies similar to that of corresponding cells using noble metal complexes as sensitizers (up to 10%). Fig. (5) shows the general structure of these compounds. In this formula, “a” stands for an acceptor group: cyano, acyl, aldehyde, carboxyl, acylamino, sulfonic, nitryl, haloform and quaternary ammonium, and “b” is selected from carboxyl, phosphorus acid, sulfonic acid, acylamide, boric acid, and squaric acid, including deprotonated forms of the aforementioned and represents the anchoring group. The R1, R2, R3, R4, R5 and R6 are selected from H, alkyl, alkoxyl, aromatic hydrocarbon or heterocycle and they may be substituted or not with one or more heteroatoms, and wherein one or more of R3, R4, R5 and R6 may also be halogens. Finally, R consists of up to ten successive moieties selected from 20 polyethylene-thiophene based compounds which were reported by these authors [18]. Table 4 summarizes the photovoltaic parameters obtained with the above mentioned organic sensitizers. Fig. (6) shows the chemical formula of the dyes. The best results were obtained for the “X” compound with a cell efficiency of $\eta=10.2\%$.

### 2.3. Quantum Dots (QDs)

Quantum dots consist of nanoparticles of II-VI and III-V type semiconductors whose size is small enough to produce quantum confinement effects. The band gap of such quantum dots can be adjusted by changing the particle size. QDs’s main disadvantage is the photocorrosion that they experience when contacting with liquid redox electrolytes. However, they still have motivating advantages such as very high extinction coefficients and the possibility of multiple excitons generation from the absorption of a single photon [19]. As an example, the photo carrier generation efficiency (IPCE) of 12% has been reached by Robel et al. [20] using a TiO$_2$-CdSe composite as photoanode, with MDA (malondialdehyde) and MPA (mercaptopropionic acid) as linker molecules. While a stable photocurrent was obtained at low excitation intensity, it decays at higher excitation intensities.
during the initial excitation period. Scattering and recombination at internal grain boundaries was found to be responsible for that behavior.

Liu Y. et al. [21] have recently reported that PbS-N719 sensitizer increases the open circuit voltage and enhances the efficiency of the cell from 5.95% (corresponding to N719 on TiO2) to 6.35%. The alignment of a conduction band edge (Ec) of the Pb QDs in between the excited state of the dye and the Ec of TiO2 allows the electron injection from PbS QDs to TiO2 and prevents the charge recombination between TiO2 and the electrolyte. Additionally, the electron injection from the LUMO dye orbital to the semiconductor conduction band takes place in two steps instead of one. Consequently, the relative position of Ec of the PbS QDs to the LUMO of the dye and the Ec of TiO2 clearly influence the overall electron injection efficiency.

### 3. ELECTROLYTES

One of the major problems that present the DSSCs lies in the fact that liquid electrolytes are usually unstable, volatile and highly corrosive. The highest conversion efficiencies obtained by DSSCs is η=11% using an electrolyte that contains triiodide/iodide as a redox pair. This redox pair suffers from two major disadvantages: electrolytes containing triiodide/iodide corrode electrical contacts made of silver and triiodide partially absorbs in the visible light spectrum. All of these affect negatively the construction and stability of the devices, especially those with large surfaces, representing one of the major problems to be solved in order to promote this technology as a reliable commercial product. The most widely used electrolyte for the construction of this type of solar cells is the I/I3 redox couple dissolved in an organic solvent. This pair is the most widely distributed and has shown the best results up to now [22-25].

The use of organic solvents for the electrolyte is a common practice, presenting good performances for DSSC, since they can be designed to enhance the ionic conductivity of electrolyte solutions [23,24]. These solvents should be chosen to exhibit relatively low viscosity and high chemical and photo-electrochemical stability. While nitrile-based solvents are the most used, other examples are acetonitrile, propionitrile, and pionitrile methoxy acetonitrile. Another widely used solvent, that has shown a decrease in the resistance of electrolyte solutions, is the 1,2-dimethyl-3-propylimidazolium iodide (DMPImI). However, the volatility of the organic solvents is a major issue for the implementation in long-life devices [22, 25, 26, 80]. This aspect should be taken into account in order to design devices that can demonstrate a reasonable stability during operation under extreme conditions. As an example, the temperature that can be reached at the surface of the cell arises at c.a. 60°C, causing thermal expansion with loss (leakage) of electrolyte and the deactivation of the device. Therefore, intensive efforts are being carried out in order to solve these problems: some of them are presented below.

One of the strategies to solve these problems corresponds to the replacement of the ionic liquid electrolytes for solid hole-conducting materials, such as organic/inorganic polymeric conductors or semiconductors [27]. Examples of

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**Table 4. Current-Voltage Characteristics Obtained with the Organic Dyes I-X Under AM 1.5 Full Sunlight (100mW/cm²) [18]**

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (mV)</th>
<th>ff</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>13.35</td>
<td>776.6</td>
<td>0.749</td>
<td>7.8</td>
</tr>
<tr>
<td>II</td>
<td>13.98</td>
<td>778.2</td>
<td>0.726</td>
<td>8.4</td>
</tr>
<tr>
<td>III</td>
<td>12.66</td>
<td>773.6</td>
<td>0.784</td>
<td>8.0</td>
</tr>
<tr>
<td>IV</td>
<td>14.65</td>
<td>780.3</td>
<td>0.731</td>
<td>8.5</td>
</tr>
<tr>
<td>V</td>
<td>15.93</td>
<td>772.1</td>
<td>0.719</td>
<td>9.6</td>
</tr>
<tr>
<td>VI</td>
<td>14.84</td>
<td>782.9</td>
<td>0.734</td>
<td>8.7</td>
</tr>
<tr>
<td>VII</td>
<td>14.55</td>
<td>777.9</td>
<td>0.744</td>
<td>8.8</td>
</tr>
<tr>
<td>VIII</td>
<td>16.70</td>
<td>774.7</td>
<td>0.711</td>
<td>9.9</td>
</tr>
<tr>
<td>IX</td>
<td>16.54</td>
<td>765.2</td>
<td>0.738</td>
<td>9.7</td>
</tr>
<tr>
<td>X</td>
<td>16.78</td>
<td>779.8</td>
<td>0.712</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Note: See Fig. (6) for description of the chemical structure.
widely used solid electrolytes are: 2,2’,7,7’-tetrakis-(N,N-di-p-methoxyphenylamine) 9,9’-spirobifluorene (OMeTAD), polyvinylpyrrolidone, CuSCN, CuBr and CuI [28,31]. The main problem with this type of technology lies in the difficulty in establishing good quality solid-to-solid interfaces. Additionally, polymers with molecular weights greater than c.a. 8000 show extremely low penetration into the semiconductor mesoporous film. All these disadvantages limit critically the use of these solvents [29] since the efficiencies are significantly lower than those obtained using ionic liquid electrolytes.

One possible alternative to liquid electrolytes is the use of quasi-solid electrolytes. This has been reported in the patent entitled “Electrolyte composition for dye-sensitized solar cell, dye-sensitized solar cell including same, and method of preparing same” [30], where authors present a polymer gel electrolyte. This gel is the mixture of two polymers, one of them with an average molecular weight less than c.a. 500 and the other one with a molecular weight above c.a. 2000. The gel is further modified by incorporation of substances with the aim of increasing ionic conductivity and providing a redox coupling. In the first case, inorganic nanoparticles not only provide ionic conduction, but also provide a better light dispersion by the medium. In the case of redox couple, there are many possibilities including the well known I/ I3 pair. According to authors, the best configuration combines a power conversion efficiency of about η=8.8%, together with long term stabilities.

One of the functions of the low molecular weight polymer is to increase ionic conductivity, also acting as interfacial contact surface, thus facilitating penetration into the pores of the semiconductor film. Additionally, it works as a plasticizing agent, decreasing the crystallinity of the second polymer. Some common polymers are polyalkylene oxide, polypropylene oxide, polyethylene glycol dimethyl ether, polyacrylonitrile, polyalkylether, polyalkyleneimine and polyalkylene sulphide, all of them with molecular weights below c.a. 500. A high molecular weight polymer may support the dissociation of the redox couple, thus providing adequate mechanical properties through the gelation of the electrolyte. Many of these solid polymers are based on the analogous liquids with modification in the molecular weights in the range of 5000-1000000. Other examples are polyvinylidene halides. The inorganic nanoparticles decrease the crystallinity of the solid polymer and increase the ionic conductivity. They also work as “scattering centers” for the incident radiation, thus improving photovoltaic current. Some examples include carbonaceous nanoparticles and metallic oxides, with sizes ranging from 10 nm to 1 μm. The redox derivative comprises a redox pair, such as I/ I3 couple, allowing the electron transfer between the electrodes. The authors claim that polymeric electrolytes present high ionic conductivities, because gelation is achieved by the second solid phase polymer, and the gel can permeate through the pores of the metal oxide film minimizing contact problems. Additionally, there are improvements in the mechanical strength of the cells, thus reducing problems of volatility and leakage.

Another variant is described in an earlier patent from Kang et al. [31], entitled “Gel electrolyte and dye-sensitized solar cell using the same”, in which solidification is obtained by self assembly of ionic gel electrolyte. The gel electrolyte must contain a non-volatile polymer solvent consisting of one or two polymers, with average molecular weight below 2000 and at least two sites for establishing hydrogen bonds, in order to achieve good polymerization. Finally, the preparation is completed with the addition of a redox pair, such as I/ I3, prepared by adding iodine and iodized salts. The ionic conductivity and gelation properties can be adjusted controlling the number of hydrogen bonding sites of the hydrogen bonding groups. According to the authors, this kind of cells enables efficiencies up to η=6.4%.

Another alternative corresponds to the work by Snaith et al. [32], in the patent entitled “Liquid transporting charge material”. In this work authors present a methodology for building optoelectronic and electrochemical devices, in particular DSSCs, using organic liquids as charge carrier. This alternative allows the optimization of devices incorporating organic semiconductors, particularly those that present an interface between semiconductor and semiconductor mesoscopic organic solids. Authors successfully explored the possibility of modifying organic materials, so that they are liquid at the time of filling the device, and solid in normal conditions. Authors set a value of c.a. 180ºC as upper bound for melting point, or glass transition temperature. All of these allow better interfacial contact between the semiconductor and the solid electrolyte. In particular, liquid viscosities of solid electrolytes should be less than 15000 cP, and should be present in amorphous form. While using a mixture of charge carriers would be a reasonable option, different chemical species show different charge transport properties, thus limiting the net transport of the medium. Among the possible precursors for organic charge transport liquid material we can identify derivatives of phenylene, vinylene, fluoride, phenylene, naphtylene, anthracene, pentacene, indenofluorene, phenanthrenyl, perylene, fullerene, thiophene and acrylate. The modification of the melting point is achieved by the functionalization of the parent molecules, through the addition of hydrocarbons residues. These residues can be carbon chains of 1 to 30 units, ramified or not. Besides that, the residues could be substituted with one or more heteroatoms, such as oxygen and fluorine.

Additionally, fine tuning of the melting point can be achieved by adding room temperature molten salts to the charge transport liquid material. The power conversion efficiency of devices using this kind of electrolytes presents typical values of η=2.9%.

Quite recently, Wang et al. [33] presented a new disulfide/thiolate redox couple that has negligible absorption in the visible spectral range, which is a very attractive feature for flexible DSSCs. Using this novel, iodide-free redox electrolyte, in conjunction with a sensitized heterojunction, unprecedented efficiencies of 6.4% can be obtained under standard illumination test conditions.

4. SEMICONDUCTOR THIN FILM OXIDE

As it was previously mentioned the thin film oxide is a wide band gap semiconductor, with high surface area deposited generally over a transparent conducting plate, which is
usually a fluorine doped tin oxide (FTO) or an indium tin oxide (ITO) layer. Regarding film oxide, titanium dioxide is the common choice because of its advantages for sensitized photochemistry and photovoltaic chemistry since it is a low-cost, widely available, non-toxic and bio-compatible material. The progress thereafter was incremented through synergy on structure, substrate roughness and morphology as was demonstrated by O’Regan & Grätzel [34], showing how a sensitized electrochemical photovoltaic devices can achieve conversion efficiencies of $\eta=7.1\%$ under solar illumination. That evolution has continued progressively since then, with certified efficiencies now over $\eta=11\%$ [34].

The semiconductor properties should match multiple conditions for the semiconductor/dye/electrolyte system. First, the open circuit voltage ($V_{oc}$) corresponds to the difference between the pseudo-gap of the semiconductor and the redox potential of the electrolyte. Second, the bottom of the conduction band of the semiconductor should match the LUMO level of the dye in order to achieve efficient electron injection. The band gap and energy levels alignment can be modified through doping and pH control of the electrolyte.

Commonly, TiO$_2$ films present the following typical properties: thickness in the range of 5–20 μm, mass ratio of 2 mg/cm$^2$, film porosity 50–65%, average pore size 15 nm, particle diameter of 20 nm. Since the common procedure involves the use of a paste which is spread over the conductive plate, the final mesoporous semiconductor is a random assembly of nanoparticles. Controlling the morphology pore structure of the film allows the diffusion of the dye and the electrolyte, resulting in a better performance over conventional disordered nanocrystalline assembly of PV cell [35]. An excellent example corresponds to the work of Jiu et al.
decreases the lifetime of the PV cell, since \( I_\text{-}I_3 \) conversion efficiency. In addition, the use of metal sheet other counter electrode, with a net decrease of the photo-

problem with metal foils is that light must be introduced by the other counter electrode, with a net decrease of the photo-conversion efficiency. In addition, the use of metal sheet decreases the lifetime of the PV cell, since \( I_\text{-}I_3 \) pair is highly corrosive, and the use of other inert metals clearly increase the price of the cell. In a recent patent from K. Murofushi et al. [37], authors claim that using a mixture of metal oxide fine particles, a binder (poly N-vinylacetamide, N-vinylacetamide/sodium acrylate copolymer, acrylamide/sodium acrylate copolymer and polytetrafluoroethylene) and a solvent, improves the process of depositing films over a sheet-shaped electrode. This procedure involves a semiconductor/bind mixture that is applied over the film by spray methods. After that, the solvent is removed by slow heating. The use of mixed alkoxy/halide/oxide allows sintering temperature to be lowered up to the range of 80-200°C.

Another way to get a better performance is to work with a semiconductor film deposited on an increased surface conductive layer [38]. Fig. (7) shows a sketch of the system, where nanowires and nanorods are formed on the first conductive substrate and then a plurality of metal-oxide nanoparticles are deposited. Since the surface area increases, the cell efficiency is promoted. The nanorods are formed on the conductive layer by sputtering or thermal evaporation using ITO, FTO, aluminum doped zinc oxide (AZO) and antimony doped tin oxide (ATO). The nanorods length is between 5 - 500 \( \mu \text{m} \), with diameters in the range of 5 - 60 nm. Metal oxide nanoparticles with diameters in the range of 5 - 20 nm are deposited by dip coating or sputtering, and then sintered at temperatures in the range of 400 - 550 °C. Importantly, this work presents the improvement in efficiency in comparative terms, without showing the improvement in absolute terms.

It is clear that optimization of the photocurrent conversion efficiency requires firstly to control stability and repro-
ducibility of DSSC. The performance is thus highly affected by the physical properties of all its components, and especially in the performance of the metal oxide layer. Conventional methods for deposition of the semiconductor layer, such as screen-printing, often result in film thickness variation in ±5%, due to residual blocked or dirty screen cells, adhesion to the screen during separation from the substrate surface and trapped bubble expansion during drying because of the incompletely out-gassing of the viscous paste. Others methods, such as doctor-blade, suffer from the inability of providing uniform thick metal oxide layer. According to Ishida et al. [39] it is possible to improve the quality of the metal oxide layer, producing DSSCs by forming a plurality of adjacent metal oxide cells, spaced from one another, yielding localized heating across the metal oxide cells. Over a conductive layer a bank structure is fabricated forming a matrix of square pixel cell, using a photo-reactive acrylic polymer masked, then exposed to ultraviolet radiation to promote cross-linking. Then the unexposed region is chemically removed and thermally cured at 130°C. After that, a spatially controlled metal oxide layer is deposited by ink-jet printing. The colloidal TiO\(_2\) is then subjected to localized heating using microwave 28 GHz radiation with 1 kW power output for periods of 5 min, or laser 364 nm with 1W power output for periods of 1 min. All of these things allow an accurate control in the drying and sintering process for the metal oxide layer deposition. While conventional DSSCs fabricated according to Grätzel et al. [1] present an energy conversion (\( \eta \)), open circuit voltage (\( V_{\text{oc}} \)), short circuit current (\( I_{\text{sc}} \)) and fill factor (\( \text{ff} \)) of 5%, 0.48 V, 15 mA/cm\(^2\) and 52 % respectively, by using microwave heating the obtained values correspond to: 4.8%, 0.46 V, 13 mA/cm\(^2\) and 52 %. All of this demonstrates that this method allows a controlled fabrication of DSSCs.

Another way consists in the deposition of blocking layer onto substrates, application includes a method for making metal oxide patterns by atomic layer deposition (ALD) on different substrates such as glass, metal and polymeric electrodes [40]. ALD generally refers to a method of producing thin films over a substrate in which a thin film is formed by surface-initiated chemical reaction. According to authors, ALD provides good bond contact with controlled patterning of selective areas that may be supported on polymer, glass and metal foils, allowing a continuous fabrication. Patterning

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[36] where TiO\(_2\) nanotubes are growing by surfactant-template assistance. While this work corresponds to deposition of semiconductors over FTO or ITO plates, it is clear that using light weight, conductive and flexible electrodes will benefit in the production and cost reduction of PV cells. There are several reports involving methods for sintering metal oxide at high temperatures using metal foil as a sheet electrode and a method in which anodization is directly performed by a chemical oxidation method [37]. The problem with metal foils is that light must be introduced by the other counter electrode, with a net decrease of the photocurrent conversion efficiency. In addition, the use of metal sheet decreases the lifetime of the PV cell, since \( I_\text{-}I_3 \) pair is highly corrosive, and the use of other inert metals clearly increase the price of the cell. In a recent patent from K. Murofushi et al. [37], authors claim that using a mixture of metal oxide fine particles, a binder (poly N-vinylacetamide, N-vinylacetamide/sodium acrylate copolymer, acrylamide/sodium acrylate copolymer and polytetrafluoroethylene) and a solvent, improves the process of depositing films over a sheet-shaped electrode. This procedure involves a semiconductor/bind mixture that is applied over the film by spray methods. After that, the solvent is removed by slow heating. The use of mixed alkoxy/halide/oxide allows sintering temperature to be lowered up to the range of 80-200°C.

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**Fig. (7).** (a) Conductive matrix with a pixeled polymeric matrix for easily ink-jet printing of metal oxide layer. (b) Extended nanowires structure for increasing conducting surface for metal oxide nanoparticles deposition.
is performed using a masking agent, as was described Ishida et al. [39], excluding the deposition of the metal oxide onto the surface.

4.1. Semiconductor Nanocrystalline Electrodes

Morphology, crystallinity and composition of the nanostructures that conforms the semiconductor film are critical to the performance of the photoelectrodes. A desirable architecture is one that ensures large surface area, good electrical transport, and low charge carrier recombination. Several techniques have been performed in order to achieve films architectures with improved properties. The most common deposition methods are doctor blade, screen printing, spin coating and dip coating. There are many groups working on the paste formulation, in order to simplify the deposition of TiO2 on the substrate and to avoid cracks and peeling-up from the substrate during the posterior annealing [41-44]. Ito S. et al. [41] exhaustively described a screen-printing technique from commercially-available TiO2 for the preparation of nanocrystalline films, and cell assembly, obtaining efficiencies up to 9.2%, reducing the preparation time and making the process more suitable for industrial applications. They proposed a fabrication scheme where the TiO2 is grinded with acetic acid, followed by a few grindings with water and ethanol. Afterwards, the mixture is magnetically stirred and then sonicated adding of terpineol and ethyl cellulose. Finally, the ethanol is evaporated and the paste is passed through a final grinding. They observed that water and/or ethanol were necessary to achieve the stability of the porous TiO2 layers (over 10μm thickness). They concluded that more transparent films can be prepared with 100% nanoparticles made by fumed TiCl4 synthesis which will lead to more efficient DSSCs.

Anodization methods are also extensively used for growing aligned nanostructure arrays [42]. A decrease of the free electron scattering, that enhances the electron mobility, is produced due to an increase of the structural order at the contact between two crystalline particles with respect to nanoparticles arrays. Other techniques such as electrophoretic deposition [43,44], flat-flame chemical vapor condensation [45] and sputtering have also been used.

4.2. Morphology

As reviewed comprehensively by Chen X. et al. [46], different attempts have been made to change the nanostructures morphology in order to improve the performance of photoelectrodes. Zukalova et al. [47] demonstrated that ordered mesoporous TiO2 films show better solar conversion efficiencies than randomly oriented anatase nanocrystalline films of the same thickness. They found an important increase of the short circuit photocurrent in the case of ordered mesoporous nanocrystalline films associated to the better accessibility of the surface area to the dyes and the electrolyte.

The TiO2 nanotubes were also used to construct nanocrystalline electrodes even in a disordered fashion [48] or vertically ordered arrays [49]. Both exhibit improvements compared with those made of commercial TiO2 nanoparticles based on an increase in the electron density in these electrodes by keeping longer electron lifetimes, leading to a high open circuit voltage [50]. Interesting results have been reached using anodization in order to grow vertically oriented TiO2, high aspect ratio nanostructures, nanotubes and nanowires arrays as photoelectrodes, being the nanotube architectures the most extensively investigated of these two options [49]. The nanotubes were grown perpendicular to an FTO glass substrate [51], allowing the orthogonalization of charge separation and transport minimizing the scattering of free electrons.

Different mechanisms of crystallization of the nanotubes have been tested. In this aspect, a two step annealing at low-temperatures was proposed based on a pretreatment of the Ti foil in H2O2 containing electrolytes, followed by a potentiostatic anodization in a fluoride based media [52]. Annealing at low temperatures prevents the formation of a thick barrier (which is disadvantageous as it favors the recombination losses) and prevents incompatibility with polymeric substrates.

4.3 Composition

Regarding the nanocrystalline films, TiO2 is the most widely used semiconductor in DSSCs, being anatase the polymorph which shows better results. However, Han and coworkers found that hybrid anatase-rutile nanocrystalline electrodes had a better performance than the ones made of pure anatase [53,54]. Also, it is worth noting that although TiO2 is the most commonly used oxide, other semiconductors such as ZnO [55], SnO2 [56], Nb2O5 [57] and BaSnO3 [58] have also been used as photoanodes in DSSCs. In particular, ZnO attracts more attention due to its similarities in photochemical properties to TiO2. Efficiencies up to 5.4% (when irradiated by AM 1.5 sunlight with a power density of 100mW/cm2) have been reached when using a film composed by polydisperse nearly spherical ZnO aggregates (ranging from several tens to several hundreds of nanometers) of agglomerated nanocrystallites [59].

Modifications to the semiconductor composition, in particular to semiconductor nanotubes, have been performed trying to modify its electronic properties. In order to decrease its wide electronic gap approaches like doping using quantum dots heterojunctions and combining oxides with different band gaps were examined in addition to sensitization by anchored dyes. In spite of the improvement achieved narrowing the electronic gap by cation doping using transition metals, an increase of instability and a decrease in carrier lifetime, limits the overall photo-conversion efficiencies [60,61] and it is a drawback for this approach. On the other hand, there is not yet an agreement in the literature about the effects of anionic doping using nitrogen, carbon, and fluorine, on the electronic band structure of the semiconductor.

As an alternative, combinations of several oxides have also been used. Shankar et al. [42] have investigated ternary oxides Cu-Ti-O and Fe-Ti-O in nanotubes architectures, in which TiO2 offers structural support and chemical stability to the narrow band gap material. They reach good visible response, pointing that it is not necessary the formation of a homogeneous solution of the oxides. These architectures were constructed by depositing co-sputtered films of the adequate composition on a conductive glass followed by anodization in fluoride ion containing media.
4.4. Buffer or Blocking Layers

Besides, as a way of reducing electron losses, avoiding electron recombination from the TCO with species in the electrolyte a blocking thin dense TiO$_2$ layer is used. Regarding this layer, as an example, microwave-activated chemical-bath deposition (MW-CBD) was proposed by Zumeta and coworkers [62] as a way of improving TiO$_2$-conductive glass contact. Buffer layers had been previously introduced and used by several research groups to prevent recombination losses. As an example, a TiO$_2$-WO$_3$ (15-75 mol%) composite materials were used by Kang et al. [63] enhancing both, open-circuit voltage and short-circuit photocurrent.

4.5. Novel Architectures

In order to decrease the electron-hole recombination 3D electrodes have been developed. Joanni and coworkers produced photoelectrodes growing indium-tin oxide (ITO) nanowires on glass and covering these wires with sputtered TiO$_2$ [64]. The ITO nanowires act as TCO current collectors anchored to the substrate allowing a 3-D DSSC. Although they achieved low efficiencies they succeeded in demonstrating the feasibility of a 3-D cell concept claiming the flexibility of independent optimization of the active and the electron-gathering layers provided by this kind of architectures.

Recently another example of a 3-D electrode was provided by Pei-Ling Hung and coworkers [65]. They synthesized ITO nanowires electrode via a template-free electrophoretic process within anodized TiO$_2$ nanotubes. The conversion efficiency could not been improved in this way due to the discontinuity of ITO nanowires and the incomplete filling of the nanotubes channels.

**Core-shell Structured Nanocrystalline Electrodes**

Improvements in dye absorption and photocurrents have been achieved via coating of nanocrystalline TiO$_2$ electrodes with a thin layer of insulating oxides such as ZnO, SiO$_2$, ZrO$_2$, MgO, Al$_2$O$_3$ and Y$_2$O$_3$. Another approach used to fabricate these core-shell electrodes is synthesising core-shell nanostructures and then forming the nanostructured film onto the substrate. The metal oxides overlayers act as an energy barrier for interfacial electron transfer processes [66]. The shell oxide should have more negative potential forming the conduction band which prevents the reaction of the electrons present in TiO2 with the oxidized dye or the electrolyte.

**Illumination Geometry Aspects**

The illumination geometry was also studied using non-plane substrates as a way of trapping the light such that the reflected light then reaches another point in the same electrode, limiting optical losses. The probability of absorption is increased by forcing the light to pass several times through the semiconductor. Fabrication of arrays of TiO$_2$ nanotubes on curved titanium surfaces as tubes and half tubes using anodization modified process were presented by Shankar et al. [53]. They investigated the absorption as a function of the aspect ratio of the pipe (ratio of the length of the pipe to its inner diameter). They observed the best photocconversion efficiency for a pipe aspect ratio of 1.7 using a fixed inner diameter of 3.75 mm, representing a 60% over the efficiency of a flat geometry device (0.150% vs. 0.094% under AM 1.5% illumination). They indicated that large aspect ratio pipes have relatively poor quality nanotubes arrays at their center, likely due to restricted access to fresh electrolyte during anodization. As aspect ratio increases there is an increase in dark current due to an increase in surface area. They suggested that the amount of light absorption is maximized after a single reflection, being negative a subsequent increase in aspect ratio. In the case of anodized half pipes, they found a maximum efficiency of 0.126% which is better than the obtained with flat substrates but it is lower that the maximum efficiency obtained by the above mentioned 1.7 aspect ratio pipe. The capture of specularly reflected light in both geometries seems to be beneficial for improving the performance of the devices.

Also, using geometry optimization, a DSSC fabricated inside a glass tube to form a Dye-Sensitized Solar Tube (DSST) was recently fabricated by Tachan et al. [67]. They synthesized and deposited fluorine-doped tin oxide in the inner side of a glass tube of 14mm of inner diameter using spray pyrolysis. Then a mesoporous TiO$_2$ film was deposited by electrophoresis deposition (EPD). As in the case of flat cells, this tube was sintered, sensitized with N3 and immersed into redox electrolyte. As a counter electrode an FTO-coated glass rod was used and a Pt layer was sputtered on it. In this geometry, the area that requires sealing is reduced and the sealing process is simplified. The possibility to incorporate a current collector without blocking the direct sunlight, diminish the wind resistivity in panels allowing the air flow between the tubes and the more efficient collection of diffuse radiation, could be mentioned as advantages for this shape. They demonstrated the feasibility of this idea obtaining a conversion efficiency of 2.8% for the initial prototypes.

5. CONDUCTIVE FILMS

Transparent electrode materials are widely used in the manufacture of various optoelectronic devices, including devices for thin film photovoltaics (TFPV). Currently, the use of indium tin oxide (ITO) is by far the most widely used for this purpose but other metal oxides can also be used such as the fluorine tin oxide (FTO) which is, in fact, used worldwide but in much smaller proportion as it is less effective. Thin films of these materials are used to manufacture these electrodes to fulfill the dual role of being transparent conductors, allowing the passage of solar radiation into the cell and closing the circuit conducting the charges generated in them. However, these materials have some important disadvantages. In the case of ITO, the main disadvantage is the limited availability of indium, a relatively rare element on Earth and not directly mined - its annual production is less than 500 tons per year-. Additionally, it is a fact that indium is constantly used in new devices, increasing its demand and consequently its cost. In the case of DSSCs, and because of their nature, other disadvantages are the chemical instability of these compounds, the possible ionic diffusion from them through the layers of other components of the cell, and particularly in the case of FTO, the appearance of leakage currents due to the virtually inevitable presence of imperfections in their crystal structures. Another important disad-
vantage of these materials is that they show low transmittance in the near infrared, which limits its potential applications to explore the use of broad spectral ranges.

All this means that other alternatives are being considered to allow substitute materials. One of the replacement alternatives that generate higher expectations for earlier commercial applications is the use of graphene (a single atom thick, two dimensional arrangements of carbon atoms). This is based on the very interesting and promising properties of this material, such as electron transport, mechanical properties and high surface area among others.

In particular, according to some of these studies, it is feasible to manufacture ultra-thin films of high quality graphene, optically transparent, very good conductors of electricity, heat-stable and technically possible to be scaled.

This material may solve some of the disadvantages of the metal oxides, such as cost, sustainability, chemical and mechanical resistance and transparency in the near IR. There are several methods for producing graphene, including chemical vapor deposition (CVD), chemical or thermal reduction and exfoliation of graphene oxide (GO), exfoliation-intercalation-expansion, arc-discharge, mechanical cleavage, bottom-up organic synthesis, exfoliation of sulfuric acid-graphite intercalates in organic solvents, plasma-enhanced chemical vapor deposition, exfoliation in organic solvents [68-72]. Wang et al. [69] presented an interesting approach in the preparation of graphene ultrathin films. The researchers presented a way of preparing graphene films by dip coating of an aqueous GO dispersion, managing to control their thickness by controlling the temperature and the number of immersions.

As it is an aqueous dispersion, hydrophilic substrates are needed and the GO film obtained is reduced in a controlled atmosphere heat. By this method these researchers were able to prepare films which show very good electrical conductivities, ultra smooth surfaces and controlled thickness.

The conductivity increased with the annealing temperature for 10 nm thick films and such films showed a sheet resistance (R_s) maximum in approximately 1.8 kΩ/sq and an average conductivity of 550 S/cm. This conductivity depends on the thickness of the film and decreases when it increases.

The measured transmittance of these films was 70.7 %, using a wavelength of 1000 nm, which is lower than that of FTO (82.4%) and ITO (90%). Despite the above, the transmittance can be increased by reducing the thickness of the film, with the additional advantage of being transparent to IR radiation, in contrast to the ITO and FTO films, which present a strong absorption in the spectrum band between 0.75 and 3 μm. There are many other works that explore how the properties of the films are affected - uniformity, thickness, roughness, conductivity, transmittance, etc.- in relation to the variation of the experimental conditions of preparation [70]. Such is the case of the work by Blake et al. [71] where the authors start from a suspension of graphene obtained by graphite exfoliation using sonication in DMP deposited by spray or spin-coating. Becerril et al. [72] and Xu et al. [73] explored the effect of different parameters such as concentrations of GO in solution, reducing conditions, temperature, atmosphere, reducing agent, on the resulting film properties.

Recently, Liang et al. [74] showed how the presence of acetylene during the thermal reduction process, can greatly improve the conductivity of the resulting film -1425 S/cm-. This interesting result is explained by the action of acetylene to provide carbon atoms while the oxygen atoms are being removed acting as a repairing agent of the crystalline defects present in the graphene sheets.

6. COUNTER ELECTRODES

A deposit of Pt over a transparent conductive layer, such as FTO, is usually used as counter electrode for allowing the I _2_ reduction because of its high catalytic activity, high conductivity and stability. However, Pt is one of the most expensive materials for the DSSCs construction, thus generating a lot of work around it in order to obtain cheaper alternatives for counter electrodes. Carbon allotropes such as graphite, fullerenes and nanotubes have been studied seriously for DSSCs purposes since they are in general good catalysts with a relatively low cost [75-78]. Another alternative to carbon material is the use of carbon black or activated carbon since they offer good surface-to-volume ratio. In particular activated carbon present higher surface-to-volume ratio in comparison with carbon black. Imoto et al. [81] reported better photocurrent conversion efficiency using activated carbon in comparison with Pt as a counter electrode. Another step was reached by Murakami et al. [82] using carbon black reached an efficiency of 9 %. Kay et al. [75] reported an important conversion efficiency of 6.67 % by substituting Pt for a mixture of carbon black, TiO_2_ and graphite, significantly reducing the fabrication costs of the device. The mixture of carbonaceous species with metal-oxide particles improves the strength of the film allowing a subsequent regulation of electrode impedance by adjusting the ratio of both and thickness.

Besides the economical implications of using Pt as material for electrodes, there exist technical problems with their use in very thick films. Kay et al. [75] reported that a small amount of Pt can be dissolved by oxidation and complex formation with I _2_ when it is in contact the iodide/triiodide electrolyte. This clearly compromises the performance of DSSC over the time. Many strategies have been proposed to solve the problem, one of them consist in the deposition of a metal oxide film on top of the Pt film as reported by Chou et al. [76]. According to this work deposition of NiO not only reduces the dissolution of the electrode but the structure of the deposit increases its catalytic activity. The power conversion efficiency changes from 3.16% (Pt) to 4.28 % when the NiO/Pt deposit was used.

CURRENT & FUTURE DEVELOPMENTS

Although DSSCs have demonstrated their potential for solid-state p-n junction devices with power conversion efficiencies over 11% they are still far from other technologies such as multi-junction collectors where efficiencies over 41% have been registered. These efficiencies differences are vast, so that the main advantage for the technological application of DSSCs should be based on the simplicity of the fabrication and the promise of a low cost technology. However, more research should be undertaken to improve
the power conversion efficiencies in order to turn this technology into a very competitive option in worldwide photovoltaic solar cells market.

Future research will have to focus on improving the short-circuit current by extending the light response of the sensitizers in the near-IR spectral region. It is very important to achieve power conversion in this region as a regular technology since it would be a very remarkable difference in favor of DSSCs.

Steps towards different dye combinations, sensitive to different wavelength, should be taken in another effort to improve DSSCs efficiencies. For this reason, research should be carried out to find new and cheaper dyes suitable for this kind of cells, free of high-cost and low abundant metals.

Design aspects in DSSCs should be drawn to attention since this is another potential advantage that this technology could offer compared to others with higher power conversion efficiencies. Innovative work involving variations in the transparent electrodes and other components of the cells could be performed with the purpose of obtaining flexible and shape adaptable DSSCs. Hybrid cells based on solid-state inorganic and organic-hole conductors are an attractive option in particular for the flexible DSSCs embodiment.

Mesoscopic dye-sensitised cells are well suited for a whole realm of applications ranging from the low-power market to large-scale applications. Their excellent performance in diffuse light gives them a competitive edge over silicon in providing electric power for stand-alone electronic equipment both indoors and outdoors. DSSCs are already being applied in building-integrated PV and this will become a fertile field of future commercial development.

Finally, substantial gains in the open-circuit voltage are expected from introducing order oxide mesostructures and controlling the interfacial charge recombination by judicious engineering on the molecular level.

The next decade certainly will show the final answer to the question whether this technology is competitive and find its place in the global market. Today a prediction that this technology into a very competitive option in worldwide photovoltaic solar cells market.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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