The Chemistry and Physics of Dye-Sensitized Solar Cells

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1. Introduction

Climate change is one of the major environmental problems that affect our society. At present annually more than 40 billons Tons of greenhouses gases are exhausted to atmosphere and the tendency is to the rise; the main reason for this situation is the high and uncontrolled use of fossil resource in energy generation. Development an environmental, friendly and reliable energy technology is a necessity. *Solar Energy* emerged as possible solution to confront this problem. This technology permits a direct conversion of sunlight into electrical power without exhaust of both greenhouse gases and another polluting agent. Actually silicon technology is market leader in photovoltaic technologies, however since a pioneering (Grätzel & O'Regan, 1991) dye-sensitized solar cells (DSSCs) have become in one important and promising technology in photovoltaic field. DSSCs given born to new solar cells generation replaced classical solid-state homo and hetero-junction device by a new concept with a nano-working electrode in photo-electrochemical cell. This technology offers a very low cost fabrication and easy industry introduction prospective; furthermore efficiencies near to 10% AM1.5 for DSSCs have been confirmed. DSSCs consists of three main components: A dye-covered nanoporous TiO_2 layer on a glass substrate coated with a transparent conductive oxide (TCO) layer, an redox electrolyte and a electrical contact deposited on conducting glass. Different parameters affect efficiency of the DSSCs: types of materials used as electrolyte, dye and electric contact, and synthesis method used to obtain these materials. In this chapter DSSCs components and different aspects related with photovoltaic principles and DSSCs performance will be studied. Special emphasis will put on to review physical, chemical and electrochemical principles of DSSCs operation.

2. Mechanism operation

All photovoltaic devices present two important steps to convert sunlight into electrical energy:
1. Radiation absorption with electrical excitation.
2. Charge carriers separation.
The way which radiation is absorbed and carriers are separated are two of the main differences between DSSCs and classical p-n junction. Conventional photovoltaic principle

relies on differences in work functions between the electrodes of the cell in which photo-generated carriers could be separated, an asymmetry through cell is necessary to obtain electrical power. In classical p-n junction of solid state device the separation of photo-generated carriers relies on separation through depletion region built at p-n interface materials (Neamen, 1997). A different process occurs in DSSCs. Figure 1 shows typical scheme for DSSCs. The working electrode of DSSCs is conventionally constituted by mesoporous network of TiO_2 nanocrystalline (5-15μm, thickness) covered with a dye monolayer (conventionally Ru complex); this working electrode is supported on conducting glass (transparent conducting oxide, TCO). Different materials as platinum, palladium and gold could be use as counter-electrode of the cell; finally the gap between the electrodes is typically filled with a molten salt which containing a redox couple (A/A-); this salt is a hole conductor. Most DSSCs studied so far employ redox couple as iodide/tri-iodide (I^-/I_3^-) couple as electrolyte because of its good stability and reversibility (Pooman & Mehra), however others hole conductors as solid and ionic electrolytes also can be used. In overall process, the DSSCs generate electric power from light without suffering any permanent chemical transformation (Kelly & Meyer, 2001)
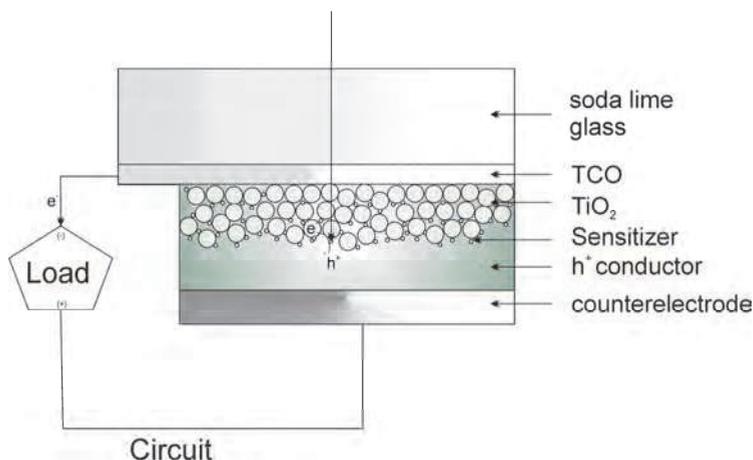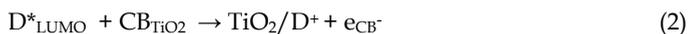

Fig. 1. General Structure of a dye-sensitized solar cell, the electron migration is showing.

In DSSCs, the basic photovoltaic principle relies on the visible photo-excitation of dye molecule; the esquematic reaction of overall process is follows:

$$TiO_2/D + h\nu \leftrightarrow TiO_2/D^*_{LUMO} \tag{1}$$

$$D^*_{LUMO} + CB_{TiO2} \rightarrow TiO_2/D^+ + e_{CB^-} \tag{2}$$

$$Pt + [I_3]^- \rightarrow 3I^- \tag{3}$$

$$TiO_2/D^+ + 3I^- \rightarrow [I_3]^- + D \tag{4}$$

$$e_{CB^-} + D_{HOMO} \rightarrow D + CB_{TiO2} \tag{5}$$

$$e_{CB^-} + [I_3]^- \rightarrow 3I^- + CB_{TiO2} \tag{6}$$

Where CB_{TiO2} is TiO_2 conduction band and D is dye molecule. First, an electron is photoexcited from highest occupied molecular orbital (HOMO) level to lowest unoccupied molecular orbital (LUMO) level into dye molecule (eq. 1). Then, electron injection from excited dye (D*) into TiO_2 conduction band occurs (eq. 2), excitation of dye usually is a transition-metal complex whose molecular properties are specifically for the task is able to transfer an electron to TiO_2 by the injection process. After that, electron migrates through TiO_2 network toward the TCO susbtrate (fig. 2(a)). The physics of charge transfer and transport in molecular and organic materials is dominated by charge localization resulting from polarization of the medium and relaxation of molecular ions. As a result of weak intermolecular interactions, the carriers in these materials are strongly localized on a molecule, and transport occurs via a sequence of charge-transfer steps from one molecule to other, similar to the hopping between defects states in inorganic semiconductors or band gap states in amorphous inorganic semiconductors. A main difference between organic and inorganic disordered semiconductors is the shape of the density of states (DOS). In the inorganic semiconductors, the band gap states usually follow an exponential distribution. The energies of localized states in organic conductors are widely distributed due to several causes: the fluctuation of the lattice polarization energies, dipole interactions, and molecular geometry fluctuations (Bisquert & Quiñones, 2006).
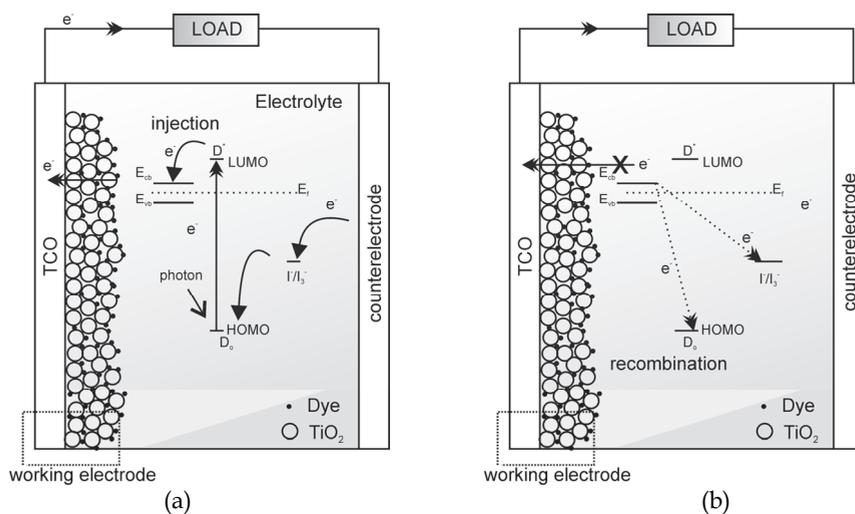

Fig. 2. (a) General schema for DSSCs, it is showed electron migration from dye molecule (D) through solar cell, (b) possible recombination process and, (c) Energy diagram for DSSCs.

Electron does a electric work at external load after go out from solar cell and then, come back through counterelectrode. Electrolyte transports the positive charges (holes) toward the counterelectrode and couple redox is reduced over its surface (eq. 3), on same time couple redox reduce the oxidized dye and regenerate the dye (eq. 4). Additionally In this process, some electrons can migrate from CB_{TiO2} to the HOMO level of the dye or electrolyte due to electron trapping effects; this process results in electron recombination (eq. 5, 6). These processes decrease the cell performance for affecting all its parameters (Fig. 2(b)); these process are presented because of differences on electron transfer rates between LUMO

level CB_{TiO2} and the electron transfer rate into CB_{TiO2} (Kay & Grätzel 2002, S.S. Kim et. al 2003, Grätzel 2004).To achieve a cell efficient operation, the electron injection rate must be faster than the decay of the dye excited state. Also, the rate of reduction of the oxidized sensitizer (D$^+$) by the electron donor in the electrolyte (eq. 4), must be higher than the rate of back reaction of the injected electrons with the dye cation (eq. 5), as well as the rate of reaction of injected electrons with the electron acceptor in the electrolyte (eq. 3). Finally, the kinetics of the reaction at the counter electrode must also guarantee the fast regeneration of redox couple (eq. 3) (Kalaignan & Kang, 2006). The oxidized dye must be regenerated by the redox couple at the speed of nanoseconds to kinetically compete with the metal oxide electrons for subsequent electron injection as well as to prevent the recombination, which depends on the energetic of metal oxide/dye/electrolyte interface (V. Thavasi et al, 2009).
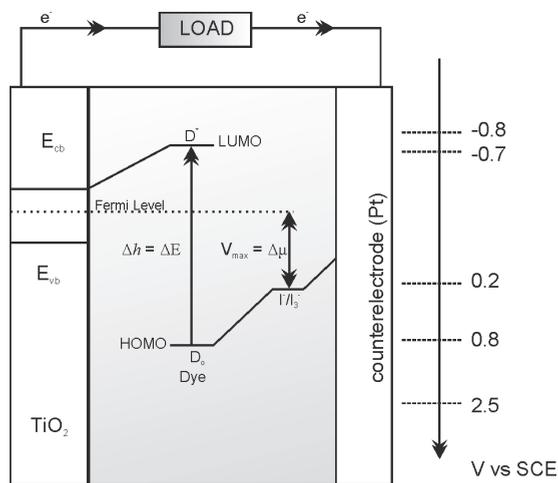

Fig. 3. General schema Energy diagram for DSSCs; and Voltage scale relative to SCE.

In terms of energetic levels shown in figure 3, electronic excitation in the dye (by light absorption) promotes the system into a high energy state, with associated electronic energy level, (LUMO level), simultaneously creating an electron deficient on low energy state (HOMO level). The electrons in these two states are separated by a difference in enthalpy *(h)*, as follows (Bisquert et al, 2004):

$$\Delta h = \Delta E = E_{LUMO} - E_{HOMO} \qquad (7)$$

$$\Delta E = E_C - E_V \text{ (in semiconductors)} \qquad (8)$$

The departure of the population of the states from their thermal equilibrium values implies a difference in their chemical potential ($\Delta\mu$) as follows:

$$\Delta\mu = \mu_{LUMO} - \mu_{HOMO} \qquad (9)$$

$$\Delta\mu = \mu_C - \mu_V \text{ (in semiconductors)} \qquad (10)$$

Efficient operation of DSSCs relies on both efficient electron injection and efficient dye regeneration. Additionally, the LUMO energy level should be sufficiently higher than the

TiO_2 conduction band (E_{CB}) for efficient electron injection. And the $\Delta\mu$ of the redox couple should be higher than the HOMO energy level for efficient dye regeneration and sustained photocurrent production (see fig. 3). The maximum voltage of a DSSCs under illumination corresponds to the difference of the TiO_2 Fermi level (E_f) and the $\Delta\mu$ of the electrolyte (relative to Standard Calomel Electrode, see figure 2(c)). In the DSSCs, the voltage is between 0.6-0.8V, and currents between 16-25mA/cm^2 can be achieved under standard operating conditions; the world record on efficiency is 10.4% (Wang 2010, Green 2010).

3. Constituents of DSSCs

3.1 Working electrode (TiO_2)

TiO_2 thin films are extensively studied because of their interesting chemical, electrical and optical properties; TiO_2 film in anatase phase could accomplish the photocatalytic degradation of organic compounds under the radiation of UV. Therefore, it has a variety of application prospects in the field of environmental protection (Quiñones & Vallejo, 2010). TiO_2 thin film in rutile phase is known as a good blood compatibility material and can be used as artificial heart valves. In addition, TiO_2 films are important optical films due to their high reflective index and transparency over a wide spectral range (Mechiakh et. al, 2010). Despite the existence of other types of oxide semiconductor with high band-gap and band gap positions as SnO_2 and ZnO, the TiO_2 thin films are the most investigated material as photo-electrode to be used in DSSCs; because of the efficiency DSSCs constructed with TiO_2 electrodes yield the highest values of Isc, Voc, η and the IPCE (Bandaranayake, 2004). In this section we will review the main characteristics of TiO_2 thin film used as photoelectrode.

3.1.1 Structural properties of TiO_2

Titanium dioxide presents three mainly different crystalline structures: *rutile, anatase,* and *brookite* structures; and other structures as *cotunnite* has been synthesized at high pressures; in table 1 are listed some physical and chemical properties for three major structures of TiO_2. Despite their three stable structures, only rutile and anatase play any role on DSSCs, the unit cell for anatase and rutile structures are shown in figure (4a,b); in both structures the building block consists of a titanium atom surrounded by six oxygen atoms in a more or less distorted octahedral configuration. In each structure, the two bonds between the titanium and the oxygen atoms at the aspices of the octahedron are slightly longer (U. Diebold , 2003). In figure 5 is shown a typical X-ray diffraction pattern (XRD) of TiO_2 thin film (about 14µm of thickness) deposited by Atomic Pressure Chemical Vapor Deposition (APCVD) method; the bigger peak observed at 2θ=25.16° corresponds to preferential crystalline plane (110) of the crystalline phase anatase. It is important take into account that crystalline structure depends on deposition method and synthesis conditions used to obtain TiO_2 thin films; and different methods have been used to deposit TiO_2 thin films. Among these are the Sol–gel method by hydrolysis of Ti(OiPr)$_4$ followed by annealing at 500–600 ∘C, chemical vapor deposition (CVD), physical vapor deposition, chemical bath deposition (CBD), reactive sputtering and atomic layer deposition (ALD) (Quiñones & Vallejo, 2010).

3.1.2 Electrochemical properties of TiO_2

It is broadly accepted that DSSCs efficiency is mainly governed by the kinetics of charge transfer at the interface between TiO_2, the dye, and the hole transport material.
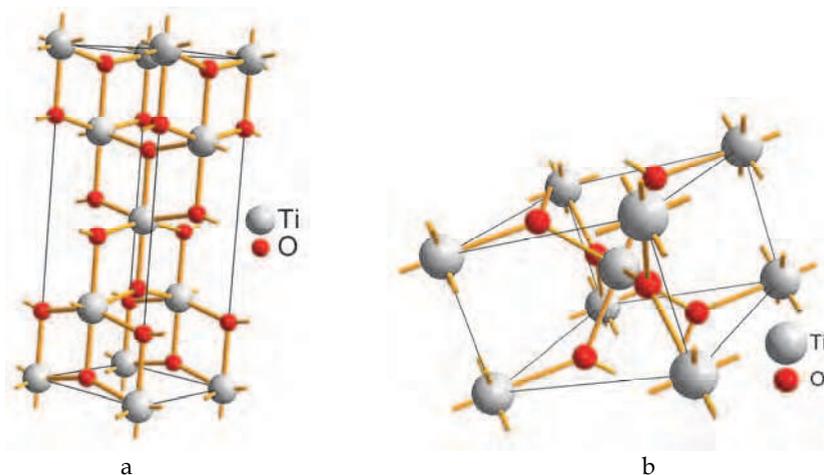
a   b
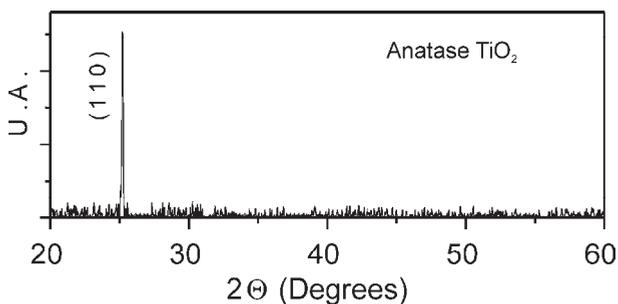
Fig. 4. Unit cell for: (a) anatase TiO₂ and (b) rutile TiO₂.

Fig. 5. XRD pattern of TiO$_2$ thin film, (take it on Shimadzu 6000 diffractometer with Cu-K$_\alpha$ radiation (λ = 0.15418 nm) source.

Crystal Structure	System	Space Group	Lattice constant (nm)			
			A	B	c	c/a
Rutile	Tetragonal	$D_{4h}^{14} - P4_2 / mnm$	0.4584	--	0.2953	0.644
Anatase	Tetragonal	$D_{4h}^{19} - I4_1 / amd$	0.3733	--	0.937	2.51
Brookite	Rhombohedral	$D_{2h}^{15} - Pbca$	0.5436	0.9166	0.5135	0.944
Density (Kg/m³)		Band gap Energy (eV)		Standard heat capacity (J/mol °C)		
Rutile	4240	3.0 Indirect		55.06		
Anatase	3830	3.2 Indirect		55.52		
Brookite	4170	----		298.15		

Table 1. TiO₂ bulk properties

The initial steps of charge separation in a DSSCs are the injection of an electron from a photoexcited dye to the conduction band of the TiO_2 and subsequently, the transfer of an electron from the hole transport molecule to the dye (Figure 2). The first process is usually completed within 200 ps, and the latter, the regeneration of the oxidized dye, is completed within the nanosecond time scale for liquid electrolyte DSSCs containing an (I^-/I_3^-) redox couple (Bisquert & Quiñones, 2006). It is very important to study this phenomenon with an appropriate analytical technique. Electrochemical impedance spectroscopy (EIS) is an experimental method of analyzing electrochemical systems; this method can be used to measure the internal impedances for the electrochemical system over a range of frequencies between mHz-MHz (Wang et al, 2005); additionally EIS allows obtaining equivalent circuits for the different electrochemical systems studied. Figure 6(a) shows a typical equivalent circuit for DSSCs; this model has four internal impedances. The first impedance signal (Z_1) related to the charge transfer at the platinum counter electrode in the high-frequency peak (in kHz range) and the sheet resistance (R_h) of the TCO in the high frequency range (over 1 MHz); the second signal (Z_2) related to the electron transport in the TiO_2/dye/electrolyte interface in the middle-frequency peak (in the 1–100 Hz), and the third signal (Z_3) related to the Nernstian diffusion within the electrolyte in the low-frequency peak (in the mHz range); in figure 6(b) is shown Nyquist diagram of a DSSCs from the result of a typical EIS analysis. Finally, the total internal impedance of the DSSCs is expressed as the sum of the resistance components (R_1, R_2, R_3, and R_h). High performance of the DSSCs is achieved when this total internal resistance is small (Shing et al, 2010).

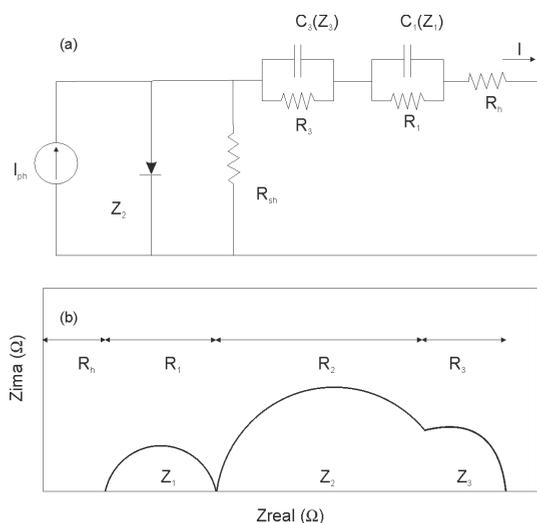Fig. 6. Scheme of: (a) Equivalent circuit model for DSSCs and (b) Nyquist plot of the DSSCs from EIS analysis (adapted from Shin, 2010).

When you compared the equivalent circuit for DSSCs and conventional pn-junction solar cells, appears two large capacitance elements C_1 (in 10 µF/Cm² range) and C_3 (in 1F/Cm² range). Additionally R_{sh} can be described as (Islam & Han, 2006):

$$R_s = R_h + R_1 + R_3 \qquad (11)$$

Under direct current conditions, the equivalent circuit for DSSCs is similar to conventional equivalent circuit for conventional solar cells, although the working mechanism is very different.

3.2 Sensitizer

One drawback with DSSCs is the high band gap of the core materials, e.g. TiO_2 particles <50–70nm in size (3.2 eV, wavelength <385nm in the ultraviolet range), compared to other semiconductors, which is illustrated by its absorption of UV light but not visible light. In the case of solar ultraviolet rays, only 2–3% of the sunlight (in the UV spectrum) can be utilized (Lee & Kang, 2010). To solve this, it appears the main characteristic of DSSCs: the dye, one of the most important constituents of the DSSCs. Some of the requirements that an efficient sensitizer has to fulfill include:

- A broad and strong absorption, preferably extending from the visible to the near-infrared.
- Minimal deactivation of its excited state through the emission of light or heat.
- Irreversible adsorption (chemisorption) to the surface of the semiconductor and a strong electronic coupling between its excited state and the semiconductor conduction band.
- Chemical stability in the ground as well as in the excited and oxidized states, so that the resulting DSSCs will be stable over many years of exposure to sun light.
- A reduction potential sufficiently higher (by 150–200mV) than the semiconductor conduction band edge in order to bring about an effective electroninjection.
- An oxidation potential sufficiently lower (by 200–300mV) than the redox potential of the electron mediator species, so that it can be regenerated rapidly.

A variety of transition-metal complexes and organic dyes has been successfully employed as sensitizers in DSSCs thus far, however the most efficient photosensitizers are ruthenium(II) polypyridyl complexes that yielded more than 11% sunlight to electrical power conversion efficiencies. The first two sensitizers used in DSSCs were N3 and N719. These are showed in figure 7. The molecular difference between these two compounds is the presence of tetrabutylammoniun ion to form two esters groups in N719. N3 and N719, affording DSSCs with overall power conversion efficiencies of 10.0% and 11.2 %respectively, harvest visible light very efficiently with their absorption threshold being at about 800 nm; figure 7 shows also the UV/VIS curve for N3 and N719 dyes, this profile is typical for al Rutenium complex used as dyes in DSSCs. Other important issue concerning dyes is their cost. Ruthenium, for instance, which is currently the most commonly utilized metal in metal-containing dyes for DSSCs, is a rare metal with a high price. Despite the fact that the contribution of the sensitizer to the total cell cost is limited, as efficient light harvesting requires a monolayer of sensitizer molecules, stable long-living ruthenium-based dyes are always highly desirable. Efficient, ruthenium-free sensitizers could also lead to such a cost decrease (Vougioukalakis et al, 2010).

Since the first Grätzel report, special attention has been paid to a number of details in the development of sensitizers in order to improve the photoelectric conversion efficiency and stability. A series of modifications of these early Ru(II) complexes have, among others, led to sensitizers with amphiphilic properties and/or extended conjugation. These amphiphilic new dyes try to achieve some of the following properties:

- A higher ground state pK_a of the binding moiety thus increasing electrostatic binding onto the TiO_2 surface at lower pH values.

- The decreased charge on the dye attenuating the electrostatic repulsion in between adsorbed dye units and thereby increasing the dye loading.
- Increasing the stability of solar cells towards water-induced dye desorption.
- The oxidation potential of these complexes is cathodically shifted compared to that of the N3 sensitizer, which increases the reversibility of the ruthenium III/II couple, leading to enhanced stability.
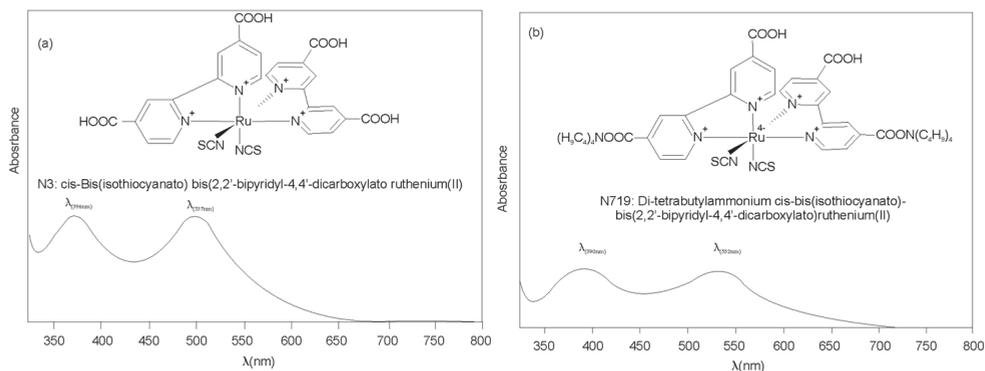

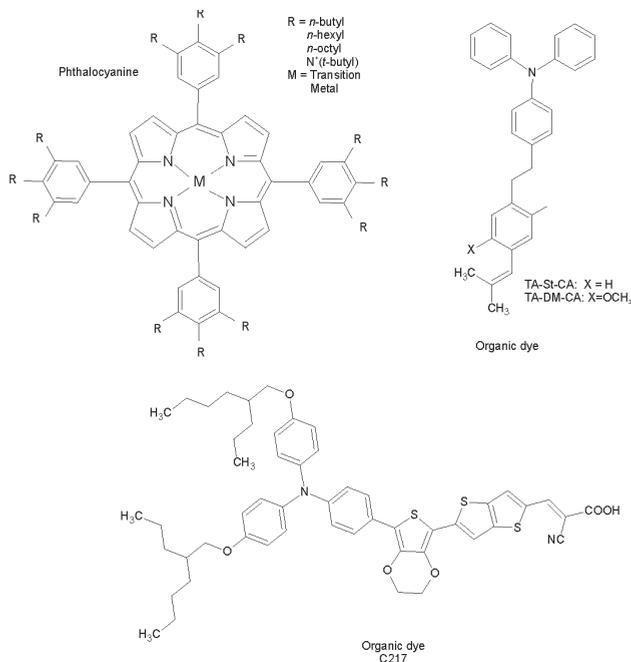Fig. 7. Molecular structure of: (a) N3 and (b)N719.

Fig. 8. The molecular structures of tetrakis(4-carboxyphenyl)porphyrin (Phthalocyanine) and two organic dyes (adapted from Vougioukalakis et al, 2010).

With respect to metal polypyridine complexes, organic dyes have been less investigated for sensitization of wide band gap semiconductors. Apart from the coumarin derivative, organic dyes such as porphyrins, phthalocyanines, perylene bis-amides, xanthenes and polyenes show low photon to electron conversion efficiencies. The understanding of the factors that determine these low performances could lead to the development of new efficient dyes, cheaper to manufacture than transition metal complexes (Argazzi et al, 2004). Figure 8 (a) shows some typical molecular structure of a basic phthalocyanine, (special polypyridine complexes); in this figure, R means a radical like: *t*-butl, *n*-hexil, *n*-octyl, in some cases R can be a substituted amine, and M means a metallic cation. Figure 8(b) shows some organic dye sensitizers used in DSSCs; TA-St-CA nad TA-TM-TA dyes contain a p-conjugated oligo-phenylenevinylene unit with an electron donor–acceptor moiety for intramolecular charge transfer, and a carboxyl group as an anchoring unit for the attachment of the dye onto TiO_2 nanoparticles; efficiences about 9% have been reported for DSSCs based in organic dyes. Additionally, C217 dye employing a lipophilic dihexyl oxy-substituted triphenylamine electrondonor, a cyanoacrylic electron acceptor, a distinguishable feature of this new amphiphilic D–π–A chromophore consists in a binary π-conjugated spacer. Here, an electron-rich 3,4-ethylenedioxythiophene unit is connected to electron-donor to lift the energy of the highest occupied molecular orbital (HOMO), while thienothiophene conjugated with A leads to a suitable lowest unoccupied molecular orbital (LUMO) energy; DSSCs based on C217 dye have reported efficiencies about 9.8%.

3.3 Electrolyte solution
3.3.1 Volatile Organic Solvents (VOS)

A typical DSSCs consists of a dye-coated mesoporous TiO_2 nano-particle film sandwiched between two conductive transparent electrodes, and a liquid electrolyte traditionally containing the (I^-/I_3^-) couple redox to fill the pores of the film and contact the nano-particle. The electrolyte, as one of the key components of the DCCS, provides internal electric ion conductivity by diffusing within the mesoporous TiO_2 layer and is an important factor for determining the cell performance (Wang, 2009). Volatile organic solvents (VOS) are commonly used as electrolyte (hole conductor), and nowadays, high efficiencies can be obtained for DSSCs using electrolytes based on VOS. When you compare the IPEC peak of a DSSCs construed with different types of electrolyte solutions, the biggest values are obtained with VOS; conventionally it IPEC peak value is about (74-78%) whilst others as ionic electrolytes present values about 53% and less solar efficiency. Typical VOS are acetonitrile, propionitrile, methoxyacetonitrile, and methoxypropionitrile, which present a high degree of ion conductivity, relatively high dielectric constant and ability to dissolve electrolytes; figure 9 shows the chemical strucuture of some typical VOS used in DSSCs.
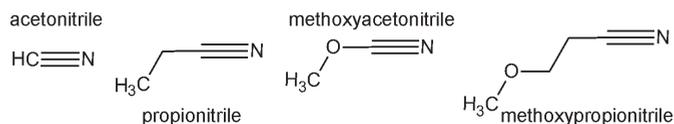

Fig. 9. Chemical strucuture of some typical VOS used in DSSCs.

Despite the relative high efficiency values of VOS in DSSCs (about 10%), the usage of these VOS electrolytes seriously limits a large scale implementation of this technology due to the poor long-term stability of the cells and the necessity of a complex sealing process (Wachter

et al, 2010). Today this is one of the major drawbacks of DSSCs to implementation in a factory production line, and a new field research tries to replace the VOS in DSSCs by new type of electrolytes as: ionic liquid electrolytes, p-type inorganic semiconductors and polymer electrolytes. In principle, all materials with p-type semiconducting behavior, capable of accepting holes from the dye cation, are potential candidates to replace the liquid electrolyte in DSSCs. We will review main aspects of these possible substitutes.

3.3.2 Ionic liquid electrolytes

As an alternative to VOS, the use of room temperature ionic liquids (RTIL) and low molecular weight organic solvents with polar ligand have received considerable attention in recent decades. RTIL have several superior properties such as the non-volatility, chemical stability, not inflammability and high-ionic conductivity at room temperature. Nevertheless, the viscosity of the non-volatile solvents is usually higher than those of conventional volatile solvents, leading the energy conversion efficiency, which does not reach those of DSSCs employing conventional VOS electrolytes. The viscosity of typical ionic liquids is about 100 times larger than conventional VOS, and also 30 times larger than water at room temperature. Photocurrents in such systems are affected by the series resistances of the electrolytes, which are usually in proportion to the viscosity.

Fig. 10. Chemical strucuture of some typical ionic liquid electrolytes used in DSSCs (adapted from Zafer et al, 2009).

The low mass transport of redox couples is a limiting factor of applicability of these solvents in DSSCs. Therefore, high concentration of redox couples is required to obtain considerable conductivity in the electrolyte medium; however, in this case, the dark current may be increased owing to the high concentration of redox couples near to dye-attached to TiO_2 and the photocurrent generation is also interrupted by the absorption of visible light into the electrolyte medium (Kang et al, 2008). Currently, RTIL based on 1,3-dialkilimidazolium salts, have been studied as a electrolyte components for DSSCs. Relatively high viscosity of these type electrolytes appears to limit their applications. In order to improve charge transport properties, di-cationic bis-imidazolium based Ionic liquid electrolytes (ILs) with alkyl and polyether chains have been successfully investigated. Polyether groups improve the self organization of molecules in electrolyte which increase the charge transfer and the wetting capacity of the TiO_2 surface. Overall light-to-electric conversion efficiencies of 5.6%

have been achieved by dicationic bis-imidazolium iodide under simulated sunlight (Zafer et al 2009). It is of great interest that the fill factors of ionic liquid electrolytes-based DSSCs easily reach extremely high values of over 75% even in full sunlight. Dilution of the same ionic liquid with a low-viscosity organic solvent often decreases the fill factor. Figure 10 shows the chemical strucuture of some typical ionic liquids electrolytes used in DSSCs.

3.3.3 P-type semiconductors

The most common approach to fabricate solid-state DSSCs is by using p-type semiconductors. Several aspects are essential for any p-type semiconductor in a DSSCs:

- It must be able to transfer holes from the sensitizing dye after the dye has injected electrons into the TiO_2; that is, the upper edge of the valence band of p-type semiconductors must be located above the ground state level of the dye.
- It must be able to be deposited within the porous nanocrystalline layer.
- A method must be available for depositing the p-type semiconductors without dissolving or degrading the monolayer of dye on TiO_2 nanocrystallites.
- It must be transparent in the visible spectrum, or, if it absorbs light, it must be as efficient in electron injection as the dye.

Many inorganic p-type semiconductors satisfy several of the above requirements. However, the familiar large-band gap p-type semiconductors such as SiC and GaN are not suitable for use in DSSCs since the high-temperature deposition techniques for these materials will certainly degrade the dye. After extensive experimentation, a type of inorganic p-type semiconductor based on copper compounds such as CuI, CuBr, or CuSCN was found to meet all of these requirements (Li et al, 2006).

3.3.4 Polymer electrolytes

According to the physical state of the polymer, there are two types of polymer electrolytes used in DSSCs: (1) solid polymer electrolytes and (2) gel polymer electrolytes.

3.3.4.1 Solid polymer electrolytes

Compared with inorganic p-type semiconductors, organic p-type semiconductors (i.e. organic hole-transport materials) possess the advantages of having plentiful sources, easy film formation and low cost production. However, the conversion efficiencies of most of the solid-state DSSCs employing organic p-type semiconductors are relatively low particularly under high light irradiation. This is due to the low intrinsic conductivities of organic hole-transport material (HTMs), the high frequencies of charge recombination from TiO_2 to HTMs, and the poor electronic contact between dye molecules and HTMs, because of incomplete penetration of solid HTMs in the pores of the mesoporous TiO_2 electrodes. The ionic conductivity of solid polymer electrolytes is dependent on molar ratio of the polymer and the iodide salt due to the transfer efficiency of charge carriers and complex formation between metal cations and polymer atoms.

3.3.4.2 Gel polymer electrolytes (GPE)

Compared to other types of HTM, GPE are constructed by trapping liquid electrolytes, which usually contain organic solvents and inorganic salt ssuch as propylene (PC), Ehylene Carbonate (EC) or acetonitryle, lithium iodide (LiI), sodium iodide (NaI) and potassium iodide (KI). Compared to the corresponding parameters of the DSSCs based on liquid electrolytes, after gelation the decrease of J_{SC} (short-circuit density) due to the comparatively

lower conductivity and the increase of VOC (open-circuit voltage) because of the suppression of dark current by polymer chains covering the surface of TiO_2 electrode result in the almost same efficiency for the DSSCs with GPE and with liquid electrolytes. Achieved by ''trapping'' a liquid electrolyte in polymer cages formed in a host matrix, GPE have some advantages, such as low vapor pressure, excellent contact in filling properties between the nanostructured electrode and counter-electrode, higher ionic conductivity compared to the conventional polymer electrolytes. Furthermore GPE possess excellent thermal stability and the DSSCs based on them exhibit outstanding stability to heat treatments. There was negligible loss in weight at temperatures of 200°C for ionic liquid-based electrolytes of poly (1-oligo(ethyleneglycol) methacrylate-3-methyl-imidazoliumchloride) (P(MOEMImCl). Thus the DSSCs based on GPE have outstanding long-term stability. Therefore, GPE have been attracting intensive attentions and these advantages lead to broad applications in the DSSCs Nowadays, several types of GPEs based on different types of polymers have already been used in the DSSCs, such as poly(acrolynitrile), poly(ethyleneglycol), poly(oligoethylene glycol methacrylate), poly(butylacrylate), the copolymers such as poly(siloxane-co-ethyleneoxide) and PVDF-HFP (Wang, 2009).

3.4 Redox couple

It is well known that the iodide salts play a key role in the ionic conductivity in DSSCs. Moreover, the basis for energy conversion is the injection of electrons from a photoexcited state of the dye sensitizer into the conduction band of the TiO_2 semiconductor on absorption of light. However, despite of its qualities; (I^-/I_3^-) couple redox has some drawbakcs, such as the corrosion of metallic grids (e.g., silver or vapor-deposited platinum) and the partial absorption of visible light near 430 nm by the I_3^- species. Another drawback of the (I^-/I_3^-) couple is the mismatch between the redox potentials in common DSSCs systems with Ru-based dyes, which results in an excessive driving force of 0.5~0.6 eV for the dye regeneration process. Because the energy loss incurred during dye regeneration is one of the main factors limiting the performance of DSSCs, the search for alternative redox mediators with a more positive redox potential than (I^-/I_3^-) couple is a current research topic of high priority. In order to minimize voltage losses, due to the Nernst potential of the iodine-based redox couple, and impede photocurrent leakage due to light absorption by triiodide ions, other redox couples have been also used, such as $SCN^-/(SCN)^3$; $SeCN^-/(SeCN)^{3-}$, (Co^{2+}/Co^{3+}), (Co^+/Co^{2+}), coordination complexes, and organic mediators such as 2,2,6,6-tetramethyl-1-piperidyloxy (Min et al, 2010). Notwithstanding of different options and alternatives to replace (I^-/I_3^-) couple redox: this system presents highst solar cell efficiency. Additional, alternatives have been proposal to improve the efficiency of this type of DSSCs, as the adition of organic acid to electroylte solution or others aditives but until now best effiency has been reached with (I^-/I_3^-) couple redox.

3.5 Counter electrode

In DSSCs, counter-electrode is an important component, the open-circuit voltage is determined by the energetic difference between the Fermi-levels of the illuminated transparent conductor oxide (TCO) to the nano-crystalline TiO_2 film and the platinum counter-electrode where the couple redox is regenerated (McConnell, 2002). Platinum counter-electrode is usually TCO substrate coated with platinum thin film. The counter-electrode task is the reduction of the redox species used as a mediator in regenerating the sensitizer after electron injection, or collection of the holes from the hole conducting

materials in DSSCs (Argazzi et al, 2004). Electrochemical impregnation from salts and physical deposition such as sputtering are commonly employed to deposit platinum thin films. Chemical reduction of readily available platinum salts such as H_2PtCl_6 or $Pt(NH_3)_4Cl_2$ by $NaBH_4$ is a common method used to obtain platinum electrodes. Platinum has been deposited over or into the polymer using the impregnation–reduction method (Yu et al, 2005). It is known that the final physical properties of Pt thin films depend on deposition method. Figure 11 shows SEM images of platinum thin films deposited by sputtering and electrochemical method as function of substrate type. Figure 11(a) corresponds to TCO substrate without platinum thin film, and Figure 11(b) shows a platinum thin film on TCO substrates deposited by electrochemical method. It is clear that TCO substrate grain size is smaller than platinum thin film grain size; this figure shows different size grain and Pt particles distribute randomly through out the substrate surface; this image shows some cracks in some places of the substrate. Furthermore, figure 11(c) shows platinum thin films deposited on TCO by sputtering method, it shows that platinum thin films have better uniformity than platinum thin film deposited by electrochemical method and the size grain is greater than size grain of thin film deposited by electrochemical method. In fig. 11(c) the Pt particles are distributed randomly through out the substrate without any crack; this is different to the electrochemical method, and indicates that the surface is uniformly coated. This thin film is less rough and corrects imperfections of substrate. Finally platinum thin film grown on glass SLG shows both smaller size grain particles and lower uniformity than platinum thin film deposited on TCO (Quiñones & Vallejo, 2011).
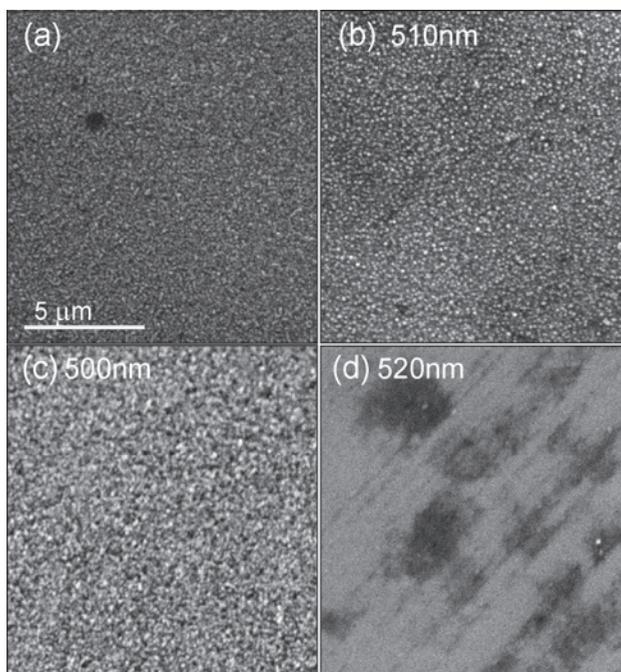

Fig. 11. SEM images (20000x) from: (a) TCO substrate; (b) Pt/TCO by electrochemical method; (c) Pt/TCO by sputtering; (d) Pt/SLG by sputtering (Quiñones & Vallejo et al, 2011).

Despite Pt has been usually used as counter electrode for the I_3^- reduction because of its high catalytic activity, high conductivity, and stability, Pt counter-electrode is one of the most expensive components in DSSCs. Therefore, development of inexpensive counter electrode materials to reduce production costs of DSSCs is much desirable. Several carbonaceous materials such as carbon nanotubes, activated carbon, graphite, carbon black and some metals have been successfully employed as catalysts for the counter electrodes. The results shows that carbonaceous materials not only gave ease in creating good physical contact with TiO_2 film but also functioned as efficient carrier collectors at the porous interface (Lei et al, 2010). Some possible substitutes to Pf thin films counter-electrode are:

3.5.1 Metal counter electrodes

Metal substrates such as steel and nickel are difficult to employ for liquid type DSSCs because the $I-/I_3-$ redox species in the electrolyte are corrosive for these metals. However, if these surfaces are covered completely with anti-corrosion materials such as carbon or fluorine-doped SnO_2, it is possible to employ these materials as counter-electrodes. Metal could be beneficial to obtain a high fill factor for large scale DSSCs due to their low sheet resistance. Efficiencies around 5.2% have been reported for DSSCs using a Pt-covered stainless steel and nickel as counter-electrode (Murakami & Grätzel, 2008).

3.5.2 Carbon counter electrode

First report of carbon material as counter electrode in DSSCs was done by Kay and Grätzel. In this report they achieved conversion efficiency about 6.7% using a monolithic DSSCs embodiment based on a mixture of graphite and carbon black as counter electrode (Kay & Grätzel, 1997).
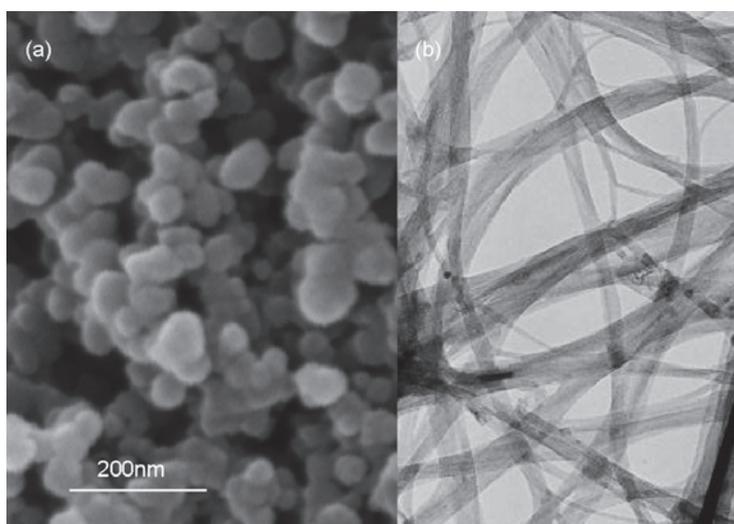

Fig. 12. SEM images (30000x) from: (a) Carbon nanoparticles and (b) Carbon nanotubes.

The graphite increases the lateral conductivity of the counter electrode and it is known that carbon acts like a catalyst for the reaction of couple redox ($I_3-/I-$) occurring at the counter

electrode. Recently, carbon nanotubes have been introduced as one new material for counter electrodes to improve the performance of DSSCs (Gagliardi et al, 2009). The possibility to obtain nanoparticles and nanotubes of carbon permits investigation of different configuration in synthesis of counter electrode fabrication, to improve the DSSCs efficiency. In figure 12 are showing the scanning electron microsocopy images of nanoparticles and nanotubes of carbon.

4. Efficiency and prospects

From first Grätzel report, the efficiency of DSSCs with nano-porous TiO_2 has not changed significantly. Currently, the world record efficiency conversion for DSSCs is around 10.4% to a solar cell of 1 cm² of area; in table 2 are shown the confirmed efficiencies for DSSCs.

The high efficiency (table 2) of DSSCs has promoted that many institutes and companies developed a commercial research on up-scaling technology of this technology. The Gifu University in Japan, developed colorful cells based on indoline dye and deposited with zinc oxide on large size of plastic substrate. The Toin University of Yokohama in Japan fabricated the full-plastic DSSCs modules based on low-temperature coating techniques of TiO_2 photoelectrode. Peccell Technologies in Japan, and Konarka in US, practiced the utility and commercialization study about flexible DSSCs module on polymer substrate. Léclanche S.A, in Switzerland, developed outer-door production of DSSCs. INAP in Germany gained an efficiency of 6.8% on a 400 cm² DSSCs module. However, despite prospective of DSSCs technology, the degradation and stability of the DSSCs are crucial topics to DSSCs up-scaling to an industrial production (Wang et al, 2010).

Device	Efficiency (%)	Area (cm²)	V_{oc} (V)	J_{sc} (mA)	FF	Test center
DSSCs$_{cell}$	11.2 +/-0.3	0.219	0.738	21	72.2	AIST*
DSSCs$_{cell}$	10.4+/-0.3	1.004	0.729	22.0	65.2	AIST
DSSCs$_{ubmodule}$	9.9+/-0.4	17.11	0.719	19.4	74.1	AIST

*Japanese National Institute of Advanced Industrial Science and technology.

Table 2. Confirmed terrestrial DSSCs efficiencies measured under the global AM1.5 spectrum (1000W/m²) at 25°C (Green et al 2010).

According to the operation principle, preparation technology and materials characteristics of DSSCs, they are susceptible to:

• Physical degradation: the system contains organic liquids which can leak out the cells or evaporate at elevated temperatures. This could be overcome using appropriate sealing materials and low volatiles solvents.

• Chemical degradation: The dye and electrolyte will photochemically react or thermal degrade under working conditions of high temperature, high humidity, and illumination. The performance DSSCs will irreversible decrease during the process causing the life time lower than commercial requirements (>20 years)

Unfortunately, there are not international standards specific in DSSCs. Nowadays, most of the performance evaluation of DSSCs is done according to International electrotechnical commission (IEC), norms (IEC-61646 and IEC-61215), prepared for testing of thin film photovoltaic modules and crystalline silicon solar cells. Most of the on up-scaling technology was made with these IEC international standards (Wang et al, 2010).

5. Conclusion

In this Chapter, the physics and chemistry of the dye sensitizer solar cells were reviewed using own studies and some of the last reports in the area. Different aspects related with basic principle and developments of each component of the solar cell was presented. This type of technology presents different advantages with its homologues inorganic solar cells, and nowadays DSSCs are considered one economical and technological competitor to pn-junction solar cells. This technology offers the prospective of very low cost fabrication and easy industry introduction. However, the module efficiency of DSSCs needs to be improved to be used in practical applications. It is necessary to achieve the optimization of the production process to fabricate photoelectrodes with high surface area and low structural defects. It is necessary to solve problems asociated to encapsulation of (I⁻/I₃⁻) redox couple in an appropiate medium such Ionic liquid electrolytes, p-type semiconductors, Solid polymer electrolytes, Gel polymer electrolytes and the deposited stable and cheap counterelectrode. If this problems are solved is possible that in near future DSSCs technology will become in a common electrical energy source and widely used around the world.

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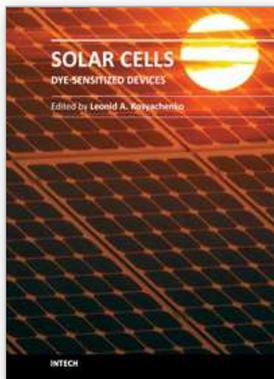
Solar Cells - Dye-Sensitized Devices

Edited by Prof. Leonid A. Kosyachenko

The second book of the four-volume edition of "Solar cells" is devoted to dye-sensitized solar cells (DSSCs), which are considered to be extremely promising because they are made of low-cost materials with simple inexpensive manufacturing procedures and can be engineered into flexible sheets. DSSCs are emerged as a truly new class of energy conversion devices, which are representatives of the third generation solar technology. Mechanism of conversion of solar energy into electricity in these devices is quite peculiar. The achieved energy conversion efficiency in DSSCs is low, however, it has improved quickly in the last years. It is believed that DSSCs are still at the start of their development stage and will take a worthy place in the large-scale production for the future.

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