Volume 2 Issue 1 | PDF 130 | Page 6
Edelweiss Applied Science and Technology
EDELWEISS PUBLICATIONS
OPEN ACCESS
Review Article ISSN: 2576-8484

Review on Dye-Sensitized Solar Cells (DSSCs)

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Citation: Andualem A, Demiss S. Review on Dye-Sensitized Solar Cells (DSSCs) (2018) Edelweiss Appli Sci Tech 2: 145-150
Received: Jan 09, 2018
Accepted: Feb 01, 2018
Published: Feb 07, 2018

Abstract
Our planet's community largely depends on a snug energy supply, and non-renewable energy such as fossil fuel has been serving as the most trustworthy energy source from its discovery time of 1673 till to the current century. However, non-renewable energy resources are rapidly decreased per year due to increasing the energy consumption rate. To address this issue, renewable energy chiefly photovoltaic energy has attracted much though, because it directly converts solar energy into electrical without environment pollution. For the past several years, different photovoltaic devices like inorganic organic, and hybrid solar cells are invented for different application purposes. Regardless of its high conversion rate of silicon based solar cells, the high module cost and complicated production process restricted their application. Research has been focused on alternative organic solar cells for their inherent low module cost and easy fabrication processes. From all organic solar cells, Dye-Sensitized Solar Cells (DSSCs) are the most efficient, low cost and easily implemented technology. This review paper focus on clarifying the technological meaning of DSSCs, Types of DSSCs materials, working principle, advantages, power full applications area of DSSCs, the efficiency and challenges for R&D of DSSCs to upgrade the current efficiency.

Keywords: Solar Cells; Global energy; Electrode.

Introduction
The consumption of global energy is increasing year by year. As the research progress show, in 1998, it was 12.7 TW, but in 2050, it is expected to be around 26.4 to 32.9 TW and in 2100, it will increase up to 46.3 to 58.7 TW [13]. The solar radiation from the sun is approximately 3×10^{24} J per year, which are ten times the current energy demands of the world [21,65].
As the storage of a fossil supply is ebbing every year the mankind must look for another source of energy [11,18,65]. The sun is a primary source of energy for most life forms in our planet. It is clear, abundant and renewable [14,65]. By fully grasping the power of the sun we can improve our way of life, reduce our dependence on fossil fuels or other types of energy sources and stimulate economy by bringing new jobs to all our planet industry.
Among sustainable and renewable energy resources, such as tidal power, solar thermal, hydropower and biomass, solar cell which is also known as photovoltaic cell is one of the promising options of renewable energy and the most efficient [22,23]. Among different categories of solar cell, the dye-sensitized solar cells (DSSC), which is invented by Professor M. Grätzel in 1991 (O'Regan & Grätzel, 1991) [18,26], is a most promising inexpensive route toward sunlight harvesting. DSSCs are belong to the thin film group, emerged as a new class of low cost energy conversion devices with simple manufacturing Procedures [13]. The good light-harvesting efficiency of the best desensitized solar cells (DSSCs) is the product of a dye with moderate extinction and a photo anode of high surface area (~1200 times the area of a flat electrode).This combination allows for ample absorbance over the majority of the visible spectrum with room for improvement in the red wavelengths [8,15,17].
The fundamental component of the DSC is a photo anode consisting of a monolayer of sensitizer (dye) adsorbed onto a mesoporous semiconductor oxide (typically TiO_2). In contrast to conventional solar cell systems, where the semiconductor assumes both the task of light absorption and charge carrier, in dye-sensitized solar cells light is absorbed by the anchored dye and charge separation takes place at the interface via photo induced electron injection from the dye into the conduction band of the solid [7,61].
In general highly efficient photovoltaic conversions, combined with ease of manufacturing and low production costs [6], make the DSC technology an attractive approach for large-scale solar energy conversion comparing to other forms of solar cell.
In this review paper, the general DSSCs benefits and application, DSSCs materials, working principles, efficiency increment due to new materials investigation that suit for DSSC and research challenges will be discussed.

DSSCs Materials
The current DSSC construction involves a set of different layers of components, including glass substrate, transparent conducting layer,TiO_2 nanoparticles, dyes, electrolyte (I^-/ I^-_3 or Co II / Co III complexes), and counter electrode (Carbon or Pt) covered with sealing gasket. The typical construction of DSSC is shown in Figure 1.

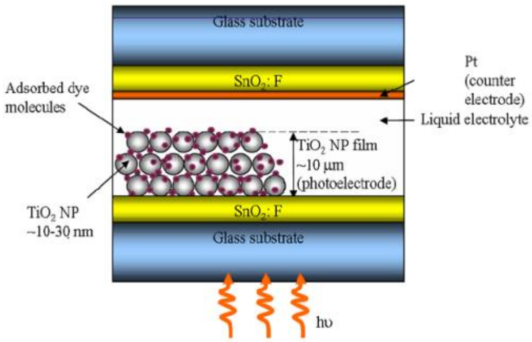

Figure 1: Typical design of a dye-sensitized solar cell [11].

The main in dye-sensitized solar cells components, including semiconductor films, dye sensitizers nonporous, redox electrolyte, conducting substrate and counter electrode [52].

Transparent and Conductive Substrate

DSSCs are typically constructed with two sheets of conductive transparent materials, which help a substrate for the deposition of the semiconductor and catalyst, acting also as current collectors [66]. Substrates necessarily are high transparent (transparency > 80%) to permit the passage of optimum sunlight to the effective area of the cell. Its electrical conductivity should also be high for efficient charge transfer and to decrease energy loss. These two characteristics of substrate dictate the efficiency of DSSCs [21,66].

Typically, FTO (fluorine tin oxide, SnO_2: F) and ITO (indium tin oxide, In_2O_3: Sn) are used as the conductive substrate. ITO and FTO and ITO substrates consist of soda lime glass coated with indium tin oxide layers and fluorine tin oxide, respectively. ITO films have a transmittance of above 80% and sheet resistance of 18 Ω/cm^2, while FTO films show a transmittance of about 75% in the visible region and sheet resistance of 8.5/cm^2 [21].

Nano Crystalline Semiconductor film Electrode

Semiconductor oxides used in dye-sensitized solar cell include SnO_2, Nb_2O_5, TiO_2, ZnO, and so forth, which serve as the carrier for the monolayers of the sensitizer using their high surface and the medium of electron transfer to the conducting substrate. Due to low-cost price, abundance in the market, nontoxicity, and biocompatibility, and as it is also used widely in health care products as well as in paints, TiO_2 becomes the best choice in semiconductor till now [52]. Titanium dioxide (TiO_2) films are covered on the conducting substrate such as metal foil, flexible polymer film and conducting glass.

Dye Sensitizer

Dye sensitizers serve as the solar energy absorber in DSC, whose proprieties will have much effect on the light harvesting efficiency and the overall photoelectric conversion efficiency. The ideal sensitizer for dye-sensitized solar cells should absorb all light just below a threshold wavelength of 920 nm and firmly grafted to the semiconductor oxide surface and inject electrons to the conduction band with a quantum yield of unity [11,52].Its redox potential should be sufficiently high that it can be regenerated rapidly via electron donation from the electrolyte or a hole conductor. Finally, it should be stable enough to sustain at least 108 redox turnovers under illumination corresponding to about 20 years of exposure to natural light [19].

The purpose of dye is to absorb light and exchange electrons to the conduction band of the semiconductor. It is chemically bonded to the porous surface of the semiconductor. An efficient photosensitizer should [21, 66]:

1. Show excellent absorption in the visible region (400nm to 700nm),
2. Adsorb strongly on the surface of the semiconductor,
3. Has a high extinction coefficient,
4. Be stable in its oxidized form allowing it to be reduced by an electrolyte,
5. Be stable enough to carry out ∼108 turnovers, which typically correspond to 20 years of cell operation,
6. Possess more negative LUMO than the CB of the semiconductor and more positive HOMO than the redox potential of the electrolyte.

In general there are three classes of photosensitizers: metal-free organic sensitizers, natural sensitizers and metal complex sensitizers [66].

Metal Complex Sensitizers

Metal complex sensitizers comprise of both Anchoring Ligands (ACLs) and Ancillary Ligands (ALLs). The adhesion of photosensitizers to the semiconductor is highly dependent on the properties of ACLs. While ALLs can be used for the tuning of the overall nature of sensitizers, polypyridine complexes of d6 metal ions possess very high Metal To Ligand Charge Transfer (MLCT) bands in the visible region which is shown by polypyridine complexes of d6 metal ions [21].

Metal - Free Photo Sensitizers

Metal free organic sensitizers have been used both to replace the expensive ruthenium based sensitizers and to improve the electronic properties of devices. Even though, the efficacy of these sensitizers is still low when compared to devices based on ruthenium-based dyes, the efficacy and performance can be improved by the proper selection or tuning of the designing components.

Natural Sensitizers

Natural dyes have also been used in DSSCs due to their low cost, easy extraction, nontoxicity, and the environmentally benign nature [22] (Figure 2).

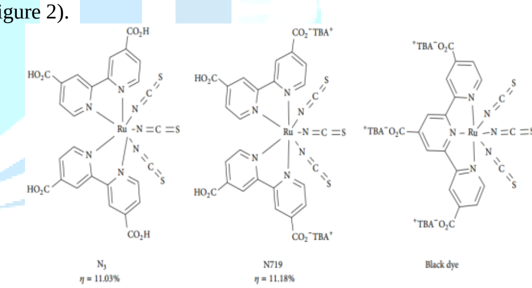

Figure 2: Structure of some efficient Ru-based photosensitizers adapted from [21].

Electrolyte

The purpose of the electrolyte is to regenerate the dye after it injects electrons into the conduction band of the semiconductor. It also acts as a charge passage medium to transfer positive charges toward the counter electrodes. The long-functional life time stability of DSSCs strongly depends on the properties of electrolyte. Thus, the electrolyte must have the following characteristic [21,19].

1. Excellent electrical conductivity and low viscosity for faster diffusion of electrons.
2. Good interfacial contact with the nanocrystalline semiconductor and the counter electrode.
3. It should not be the cause of desorption of the dye from the oxidized surface and the degradation of the dye.
4. It should not absorb light in the visible region.

Electrolytes for DSSCs are classified into three types: solid state electrolytes, liquid electrolytes, and quasi solid state electrolytes.

Liquid Electrolytes

Liquid electrolytes are basically classified into two types: organic solvent based electrolytes and room temperature ionic liquid electrolytes (RTIL) based on the solvent used.

Organic Electrolytes: Each component of organic electrolytes such as the redox couple, solvent, and additives affects the performance of DSSCs. The major component of organic electrolyte is the redox couple. Many types of redox couples such as Br−/Br_3, SCN−/ $(SCN)_2$, SeCN−/$(SeCN)_2$ [21,24], and substituted bipyridyl cobalt (III/II) [52] have been investigated. But I3−/I− is considered an ideal redox couple because of its excellent solubility, rapid dye regeneration, low absorbance of light in the visible region, suitable redox potential, and very slow recombination kinetics between injected electrons into the semiconductor and triiodide [13].

Ionic Electrolytes: RTIL have been employed successfully for reduction of a high evaporation rate due to high volatility of liquid electrolytes. They are a group of organic salts containing captions such as pyridinium, imidazolium, and anions from the halide or pseudohalide family [19]. They act simultaneously as an iodine source and as a solvent.

Solid-State Electrolyte

Leakage is the main problem in liquid-electrolyte based DSSCs, which drastically minimize the long-term stability of solar cells. In order to upgrade the performance and stability, solid state electrolytes have been developed. They replace the liquid electrolyte with a p-type semi-conductor [21].

Counter Electrode

The counter electrode is used for the regeneration of the electrolyte. The oxidized electrolyte diffuses towards the counter electrode where it receive electrons from the external circuit. A catalyst is needed to accelerate the reduction reaction and platinum (Pt) is considered a preferred catalyst due to its high exchange current density, good catalytic activity, and transparency. The performance of the CE depends on the method of Pt deposition on TCO substrate [19, 22].

Working Principles of DSSC

The basic operational principles of DSSC solar cells in comparison with conventional semiconductor solar cells are different. In semiconductor solar cells light absorption and charge carrier transport are not the separate task. In DSSC these two tasks are separate. Charge separation is done by photo-induced injection to the conduction band and such created carriers are transported to charge collector [11]. By using dyes the solar cell is capable to harvest large fraction of sunlight due to its high broad absorption band. Figure 3 shows the energy band structure of the DSSC device and principal carrier transfer channels [1].

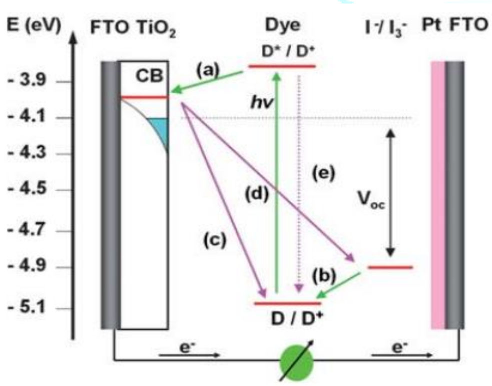

Figure 3: Energy band structure and major electron transfer processes in DSSCs [1].

The sensitizer dye absorbs light ($h\nu$), by which an electron is excited from the HOMO to the LUMO of the dye and the photo generated electron will be injected from the LUMO of the dye to the CB of TiO_2 (channel (a) in Fig. 1). About 40 % of the electrons are injected from the triplet state and about 60 % from the singlet state. The corresponding injection rate constants are in the femtosecond range (singlet state) and about one order of magnitude slower for the triplet state [57]. The energy level of the triplet state is only slightly above the conduction band edge of TiO_2 thus both the driving force for electron injection and the electron transfer probability is lower, which is the cause of relatively slow injection rate.

electron will further transfer to the Photo Anode Fluorine-Doped Tin Oxide (FTO), through the external load, the cathode FTO, the Pt layer, the HOMO of the redox couples, and finally back to the HOMO of the dye (channel(b)).

There are many other undesirable carrier transfer channels including charge recombination of the injected electrons from the TiO_2 CB (defined as the injected electron) to cations of the dyes (c) and to redox couples (d), and direct decay from the LUMO to the HOMO of the dye (e).

The general chemical reactions, which take part in all the processes, described as follow [11,13,18]:

$$TiO_2/D + h\nu \rightarrow TiO_2/D^* \quad ....1$$

$$TiO_2/D^* \rightarrow TiO_2/D^+ + e^- \quad ....2$$

$$TiO_2/D^+ + e^- \rightarrow TiO_2/D \quad ....3$$

$$TiO_2/D^+ + \tfrac{3}{2}I^- \rightarrow TiO_2/D + \tfrac{1}{2}I_3^- \quad ....4$$

$$\tfrac{1}{2}I_3^- + e^- \rightarrow \tfrac{3}{2}I^- \quad ....5$$

$$I_3^- + 2e^- \rightarrow 3I^- \quad ....6$$

Where D represents dye sensitizer.

In principle, the energy conversion efficiency of a DSSC is the product of the short-circuit photocurrent, J_{sc}, the open-circuit photovoltage V_{oc}, as well as the fill factor [1, 11]. Referring to the energy band structure and the carrier transfer processes in Fig. 1, the V_{oc} is calculated by the following equation.

$$V_{oc} = \frac{E_{CB}}{q} + \frac{kT}{q}\ln\left(\frac{n}{N_{CB}}\right) - \frac{E_{redox}}{q}$$

Where n is the number of the electrons in TiO_2, N_{CB} is the effective density of states at conduction band, E_{redox} is the HOMO level of the redox couples, and q is the unit charge in coulomb. In general, working principles of DSSCs are distinct from other classes of solar cells as the three key processes, i.e., light absorption and the subsequent generation of electric charges, electron transport, and hole transport are directed through three materials, thereby making them highly interfacial devices [54].

Efficiency of DSSCs

Tremendous research efforts have been invested to improve the efficiency of solar energy conversion which is generally determined by the light harvesting efficiency, electron injection efficiency and undesirable charge recombination degree. Pursuing high efficiency is always the core task for photovoltaic devices. For DSSC, overall energy conversion efficiency (η) of 11.0% has been achieved at AM 1.5 [7] .In order to further enhance the energy conversion efficiency of DSSCs, it is critical to improve the V_{oc} by (1) reduce the charge recombination between redox couple and the injected electrons in the TiO_2 CB; (2) reduce charge recombination between the oxidized sensitizer and the injected electrons in the TiO_2 CB; (3) increase the electron injection efficiency; (4) increase the TiO_2 ECB; (5) downshift the Eredox; (6) tandem DSCs.[1]. To reduce charge recombination, the following factors about sensitizers should be considered. First, it should form a compact blocking layer on the TiO_2 surface. Secondly, the undesirable complexation between the sensitizer and iodide should be prevented. Thirdly, the electron donor unit should be separated from the TiO_2 surface to impede charge recombination between the injected electrons and the oxidized sensitizer. To improve electron injection efficiency, molecular aggregation should be prevented and the LUMO of the sensitizer should overlap well with that of TiO_2. Finally, to broaden the absorption spectra of the sensitizer, strong electron donor and acceptor groups might be a good choice. Furthermore, multiple electron donor substituents are encouraged under the condition that the oxidized sensitizer can be reduced effectively by the redox couple. The fast-developing organic sensitizers are promising for reinforcing the V_{oc} and efficiency by exquisite molecular tailoring. The DSSC performance also depends on the film morphology Nanoparticles are essential to increase surface area, and hence, amount of dye, while large particles are required to enhance absorption of red light through light scattering. It is impossible to increase surface area and light scattering simultaneously, because they oppose each other. Therefore, there must be a balance between them. Such a balance was well controlled by tuning the layer structure, and an energy conversion efficiency of 10.2% was obtained using a multilayer structure. The multilayer structure is also suitable for other dyes in terms of improving light harvesting efficiency, and hence, photocurrent. In order to scatter the red light more efficiently, a more sophisticated multilayer structure with gradually increased particle size from the most-inner layer is desirable [53].

The performance of a DSSC is explained by its I-V characteristics which is attained from parameters such as short-circuit current I_{sc} and open circuit voltage V_{oc} and Fill factor (FF) . The ff can be given by the equation:

$$FF = \frac{(VI)_{\max}}{I_{SC} \times V_{OC}} = \frac{P_{\max}}{I_{SC} \times V_{OC}}$$

Where V_{oc}; open circuit voltage, I_{sc}; short circuit current. I_{max} and V_{max} are the maximum cell current and voltage respectively at the maximum power point, $P_{max} = I_{max} \times V_{max}$.

The incident photon conversion efficiency (IPCE) of DSSC is an incident energy-dependent quality. It is a measure of the useful range of the cell. The IPCE is given by

$$IPCE = \frac{P_{IN}}{I_{SC}} * \frac{e\lambda}{hc}$$

Where λ is wavelength, P_{IN} incident optical power, *e* is the fundamental electron charge, *h* Planck's constant and *c* is the speed of light in vacuum. The global power conversion efficiency of energy to electricity conversion efficiency (η) of a cell with Pout electrical power under standard illumination conditions is given by

$$\eta = \frac{P_{out}}{P_{in}} = I_{SC}V_{OC}\frac{FF}{P_{in}}$$

Research and Development Challenges in DSSCs improvement

As the different researcher progress work on DSSC shows, it has currently have low conversion efficiency. Many researchers have attempted to resolve this problem, by increasing the surface area of TiO_2 photo-electrodes used in the DSSC [62].

Low efficiency and low stability are the major challenges for the commercial deployment of DSSCs [21].The main causes of low efficiency in DSSCs are

1. Low red and near-IR absorption.
2. Low extinction coefficient requires high surface area.
3. Only I^- / I_3^- redox couple has slow recombination kinetics, but it has unnecessarily large over potential.
4. Poor contact between the electrodes
5. Degradation of electrolyte properties due to UV absorption of light.

Improving the environmental stability of cells is the most important issue in studying these cells [60]. Stability refers to the performance of individual processes or the entire solar cell at any time relative to the initial time. Good stability leads to long lifetimes [59]. The critical issue regarding to stability and robustness of DSSCs are

1. Liquid electrolyte is undesirable, but solid state hole conductors give lower efficiency.
2. Achieving DSSC module lifetimes of more than 20 years requires 10^8 turnovers for dye molecules and high quality encapsulation to prevent leakage of the electrolyte and ingress of water [59].
3. I^- / I_3^- Is corrosive.

Advantages of DSSCs

Dye-sensitized solar cells have the following main advantages:

Capable of production in a simple way: Dye-sensitized solar cells require no vacuum system for manufacturing, and thus have an essential advantage in terms of production cost [63]. It reduces manufacturing cost by 1/5 to 1/10 as compared to silicon solar cells production cost [22, 23 and 55].

Colorable, transparent: The use of dye allows wide selection of colored cells and transparent cells. The transparency and varied color of DSSCs could be utilized for decorative purposes like window and sunroof [58].

Flexible and thin structure: By using aggregates of fine particles of photoelectric conversion materials, the solar cells can be formed as flexible thin films.

Generation characteristics of insusceptible to the incident angle and intensity of the sunlight: Even though the light condition is very week generation characteristics can be maintained, such as under faint light in the morning and evening and when indoors.

Lighter weight: Plastic substrates can be used to minimize the weight of solar cells and panels. Dou to its light weight, dye-sensitized solar cells can be installed in locations where appearance is important and other solar cells are not applicable, such as the glass panes and outer and inner walls of a building, the sunroof and outer panels of an automobile, and the enclosure of a hand phone. This allows the creation of new markets with high demand [55,56.58] (Figure 4).

Figure 4: Prototype Models of Dye-Sensitized Solar Cell Panels for decoration purpose [56].

Environmentally friend and recyclable

Dye-sensitized solar cells do not have harmful substance as a cell component material. The materials are comparatively easy to separate and get back, which is advantageous in view of a recycling and reuse framework for solar cell panels [63].

Conclusion

In conclusion, the world's nonrenewable energy degrades time by time and the consumption rate increases inversely. To weaken these two controversies, new environmental friend green renewable energy resources are highly needed to our planet. Among different types of renewable green energy resources, solar energy is regarded as one of the perfect energy resources.

There has been a continuous effort in searching for affordable organic solar energies among which dye-sensitized solar cells (DSCs) thus far demonstrate the highest energy conversion efficiency, and have been regarded as the most prospective technology in the near future. Dye-sensitized solar cells have gained widespread attention in recent years because of their low production costs, easy of fabrication, its lighter weight property, environmentally friend and recyclable advantages and tunable optical properties, such as color and transparency regardless of its low efficiency output comparing to silicon solar cell.

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