

THE THIRD GENERATION DYE-SENSITIZED SOLAR CELL

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ABSTRACT

In a traditional solid-state semiconductor, a solar cell is made from two doped crystals, one doped with n-type impurities (n-type semiconductor), which add additional free conduction band electrons, and the other doped with p-type impurities (p-type semiconductor), which add additional electron holes. When placed in contact, some of the electrons in the n-type portion flow into the p-type to "fill in" the missing electrons, also known as electron holes. Eventually enough electrons will flow across the boundary to equalize the Fermi levels of the two materials. The result is a region at the interface, the p-n junction, where charge carriers are depleted and/or accumulated on each side of the interface. In silicon, this transfer of electrons produces a potential barrier of about 0.6 to 0.7 Volt. When placed in the sun, photons of the sunlight can excite electrons on the p-type side of the semiconductor, a process known as photoexcitation. In silicon, sunlight can provide enough energy to push an electron out of the lower-energy valence band into the higher-energy conduction band. As the name implies, electrons in the conduction band are free to move about the silicon. When a load is placed across the cell as a whole, these electrons will flow out of the p-type side into the n-type side, lose energy while moving through the external circuit, and then flow back into the p-type material where they can once again re-combine with the valence-band hole they left behind. In this way, sunlight creates an electric current. In any semiconductor, the band gap means that only photons with that amount of energy, or more, will contribute to producing a current. In the case of silicon, the majority of visible light from red to violet has sufficient energy to make this happen. Unfortunately higher energy photons, those at the blue and violet end of the spectrum, have more than enough energy to cross the band gap; although some of this extra energy is transferred into the electrons, the majority of it is wasted as heat. Another issue is that in order to have a reasonable chance of capturing a photon, the n-type layer has to be fairly thick. This also increases the chance that a freshly ejected electron will meet up with a previously created hole in the material before reaching the p-n junction. These effects produce an upper limit on the efficiency of silicon solar cells, currently around 12 to 15% for common modules and up to 25% for the best laboratory cells (About 30% is the theoretical maximum efficiency for single band gap solar cells)

Keywords: *Solid-state semiconductor , Potential barrier , Photo-excitation etc..*

I. INTRODUCTION

The concept of DSSC was first presented in 1991 by Michael Grätzel and Brian O'Regan. Grätzel won the Millennium Technology Prize in 2010 for his work in the area of DSSCs. The DSSC is a photoelectron chemical device. Generally, a dye-sensitized solar cell consists of three main components: a dye coated nanocrystalline

TiO₂ layer on a transparent conductive glass substrate, an iodide/ triiodide redox couple in an organic solvent as an electrolyte, and a platinum film having high electrocatalytic activity coated on conductive glass as counter electrode; its operation is similar to that of photosynthesis. The operation of DSSC can be explained in three steps: first the dye molecule absorbs the photon and gets excited. The excited dye molecule is then given off to the conduction band of semiconductor and it gets oxidized. After that the transparent conducting oxide (TCO) layer collects the excited electron from the conduction band and the electrons flow from the external load to the counter electrode. Finally the oxidized dye molecule is reduced by gaining electrons from the electrolyte solution (Fig 1). DSSC is the only device that absorbs photon and converts them to electric charge without the need of intermolecular transport of electronic excitation. In conventional solar cells both light absorption and charge carrier transport were performed simultaneously, whereas in DSSC the two operations are performed separately. An energy conversion efficiency of more than 11 per cent has been achieved in DSSCs with an organic liquid-based electrolyte containing I₃⁻/I⁻ as a redox couple.

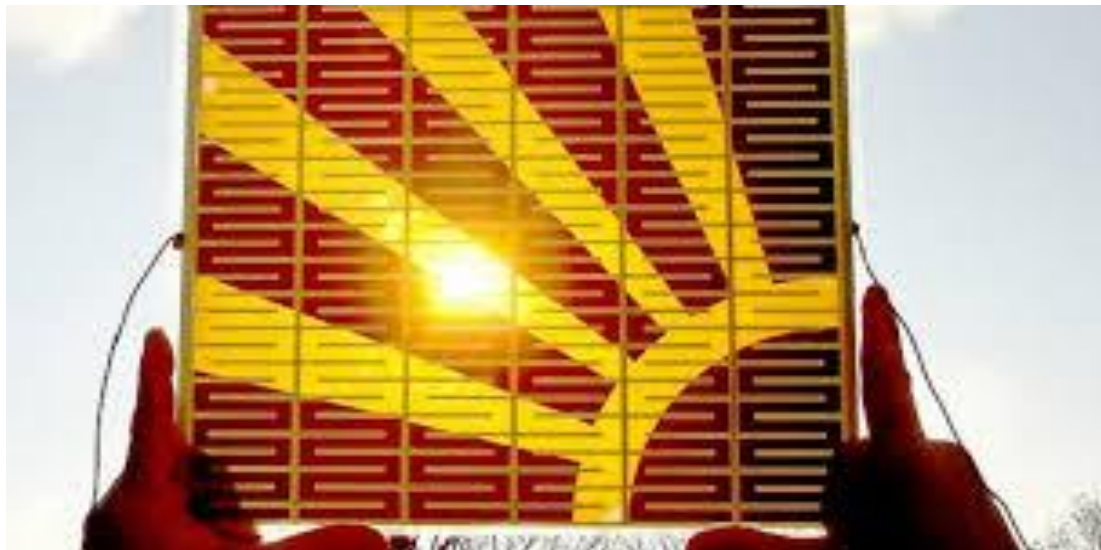


Fig .1 Dye-Sensitized Solar Cell

II. CONSTRUCTION

In the case of the original Grätzel and O'Regan design, the cell has 3 primary parts. On top is a transparent anode made of fluoride-doped tin dioxide (SnO₂:F) deposited on the back of a (typically glass) plate. On the back of this conductive plate is a thin layer of titanium dioxide (TiO₂), which forms into a highly porous structure with an extremely high surface area. TiO₂ only absorbs a small fraction of the solar photons (those in the UV). The plate is then immersed in a mixture of a photosensitive ruthenium-polypyridine dye (also called molecular sensitizers) and a solvent. After soaking the film in the dye solution, a thin layer of the dye is left covalently bonded to the surface of the TiO₂.

A separate plate is then made with a thin layer of the iodide electrolyte spread over a conductive sheet, typically platinum metal. The two plates are then joined and sealed together to prevent the electrolyte from leaking. The construction is simple enough that there are hobby kits available to hand-construct them. Although they use a number of "advanced" materials, these are inexpensive compared to the silicon needed for normal cells because

they require no expensive manufacturing steps. TiO₂, for instance, is already widely used as a paint base. One of the efficient DSSCs devices uses ruthenium-based molecular dye, e.g. [Ru(4,40-dicarboxy-2,20-bipyridine)₂(NCS)₂] (N3), that is bound to a photoanode via carboxylate moieties. The photoanode consists of 12 μm thick film of transparent 10–20 nm diameter TiO₂ nanoparticles covered with a 4 μm thick film of much larger (400 nm diameter) particles that scatter photons back into the transparent film. The excited dye rapidly injects an electron into the TiO₂ after light absorption. The injected electron diffuses through the sintered particle network to be collected at the front side transparent conducting oxide (TCO) electrode, while the dye is regenerated via reduction by a redox shuttle, I₃⁻/I⁻, dissolved in a solution. Diffusion of the oxidized form of the shuttle to the counter electrode completes the circuit.

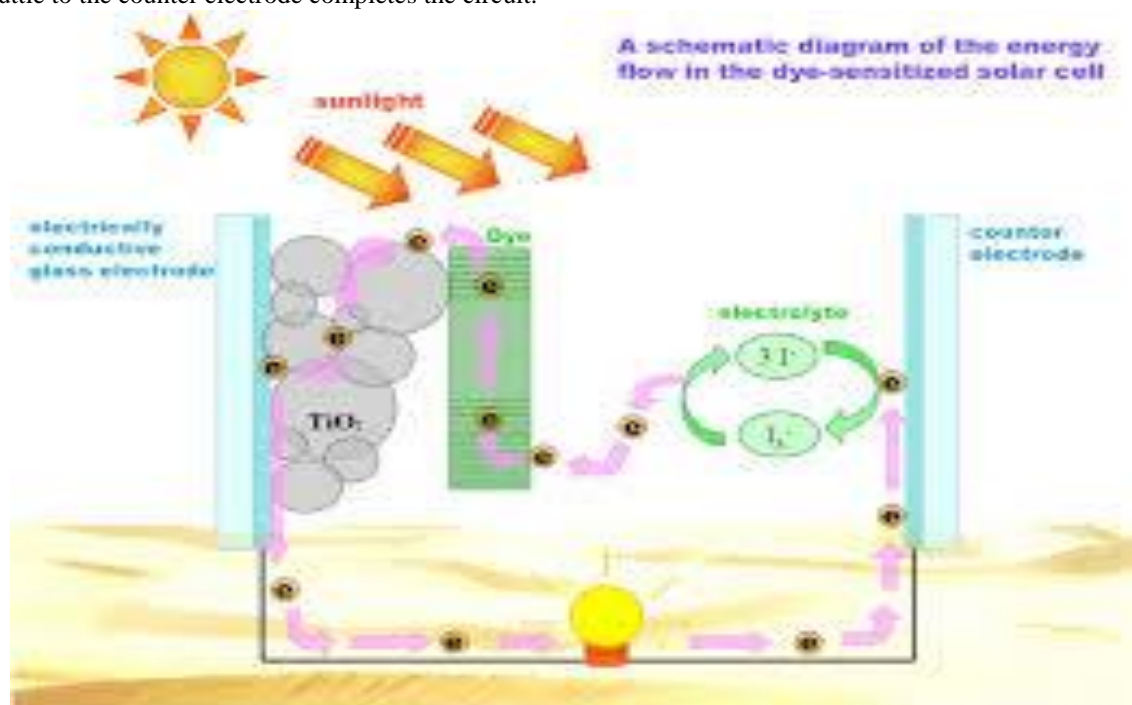


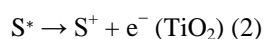
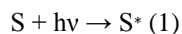
Fig 2: The Schematic Diagram of a Dye-Sensitized Solar Cell

• **Mechanism of DSSCs**

The main processes that occur in a DSSC

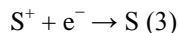
Step 1: The following primary steps convert photons to current:

1. The incident photon is absorbed by Ru complex photosensitizers adsorbed on the TiO₂ surface.
2. The photo-sensitizers are excited from the ground state (S) to the excited state (S*). The excited electrons are injected into the conduction band of the TiO₂ electrode. This results in the oxidation of the photo-sensitizer (S⁺).

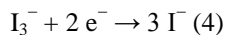


3. The injected electrons in the conduction band of TiO₂ are transported between TiO₂ nanoparticles with diffusion toward the back contact (TCO). And the electrons finally reach the counter electrode through the circuit.

4. The oxidized photo-sensitizer (S⁺) accepts electrons from the I⁻ ion redox mediator leading to regeneration of the ground state (S), and the I⁻ is oxidized to the oxidized state, I₃⁻.



5. The oxidized redox mediator, I_3^- , diffuses toward the counter electrode and then it is reduced to I^- ions.



The efficiency of a DSSC depends on four energy levels of the component: the excited state (approximately LUMO) and the ground state (HOMO) of the photosensitizer, the Fermi level of the TiO_2 electrode and the redox potential of the mediator (I^-/I_3^-) in the electrolyte.

• Nanoplant-like morphology

In DSSC, electrodes consisted of sintered semiconducting nanoparticles, mainly TiO_2 or ZnO . These nanoparticles DSSCs rely on trap-limited diffusion through the semiconductor nanoparticles for the electron transport. This limits the device efficiency since it is a slow transport mechanism. Recombination is more likely to occur at longer wavelengths of radiation. Moreover sintering of nanoparticles requires a high temperature of about 450 °C, which restricts the fabrication of these cells to robust, rigid solid substrates. It has been proved that there is an increase in the efficiency of DSSC, if the sintered nanoparticle electrode is replaced by a specially designed electrode possessing an exotic 'nanoplant-like' morphology.

• Operation

Sunlight enters the cell through the transparent $SnO_2:F$ top contact, striking the dye on the surface of the TiO_2 . Photons striking the dye with enough energy to be absorbed create an excited state of the dye, from which an electron can be "injected" directly into the conduction band of the TiO_2 . From there it moves by diffusion (as a result of an electron concentration gradient) to the clear anode on top. Meanwhile, the dye molecule has lost an electron and the molecule will decompose if another electron is not provided. The dye strips one from iodide in electrolyte below the TiO_2 , oxidizing it into triiodide. This reaction occurs quite quickly compared to the time that it takes for the injected electron to recombine with the oxidized dye molecule, preventing this recombination reaction that would effectively short-circuit the solar cell. The triiodide then recovers its missing electron by mechanically diffusing to the bottom of the cell, where the counter electrode re-introduces the electrons after flowing through the external circuit.

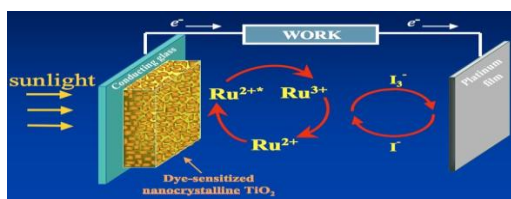


Fig 3: The Working of a Dye-Sensitized Solar Cell

III. ADVANTAGES

DSSCs are currently the most efficient third-generation solar technology available. Other thin-film technologies are typically between 5% and 13%, and traditional low-cost commercial silicon panels operate between 14% and 17%. This makes DSSCs attractive as a replacement for existing technologies in "low density" applications like rooftop solar collectors, where the mechanical robustness and light weight of the glass-less collector is a major advantage. They may not be as attractive for large-scale deployments where higher-cost higher-efficiency cells are more viable, but even small increases in the DSSC conversion efficiency might make them suitable for some of these roles as well. There is another area where DSSCs are particularly attractive. The process of

injecting an electron directly into the TiO_2 is qualitatively different from that occurring in a traditional cell, where the electron is "promoted" within the original crystal. In theory, given low rates of production, the high-energy electron in the silicon could re-combine with its own hole, giving off a photon (or other form of energy) and resulting in no current being generated. Although this particular case may not be common, it is fairly easy for an electron generated in another molecule to hit a hole left behind in a previous photo-excitation. In comparison, the injection process used in the DSSC does not introduce a hole in the TiO_2 , only an extra electron. Although it is energetically possible for the electron to recombine back into the dye, the rate at which this occurs is quite slow compared to the rate that the dye regains an electron from the surrounding electrolyte. Recombination directly from the TiO_2 to species in the electrolyte is also possible although, again, for optimized devices this reaction is rather slow. On the contrary, electron transfer from the platinum coated electrode to species in the electrolyte is necessarily very fast. As a result of these favorable "differential kinetics", DSSCs work even in low-light conditions. DSSCs are therefore able to work under cloudy skies and non-direct sunlight, whereas traditional designs would suffer a "cutout" at some lower limit of illumination, when charge carrier mobility is low and recombination becomes a major issue. The cutoff is so low they are even being proposed for indoor use, collecting energy for small devices from the lights in the house. A practical advantage, one DSSCs share with most thin-film technologies, is that the cell's mechanical robustness indirectly leads to higher efficiencies in higher temperatures. In any semiconductor, increasing temperature will promote some electrons into the conduction band "mechanically". The fragility of traditional silicon cells requires them to be protected from the elements, typically by encasing them in a glass box similar to a greenhouse, with a metal backing for strength. Such systems suffer noticeable decreases in efficiency as the cells heat up internally. DSSCs are normally built with only a thin layer of conductive plastic on the front layer, allowing them to radiate away heat much easier, and therefore operate at lower internal temperatures.

IV. DISADVANTAGES

The major disadvantage to the DSSC design is the use of the liquid electrolyte, which has temperature stability problems. At low temperatures the electrolyte can freeze, ending power production and potentially leading to physical damage. Higher temperatures cause the liquid to expand, making sealing the panels a serious problem. Another disadvantage is that costly ruthenium (dye), platinum (catalyst) and conducting glass or plastic (contact) are needed to produce a DSSC. A third major drawback is that the electrolyte solution contains volatile organic compounds (or VOC's), solvents which must be carefully sealed as they are hazardous to human health and the environment. This, along with the fact that the solvents permeate plastics, has precluded large-scale outdoor application and integration into flexible structure. Replacing the liquid electrolyte with a solid has been a major ongoing field of research. Recent experiments using solidified melted salts have shown some promise, but currently suffer from higher degradation during continued operation, and are not flexible.

V. APPLICATIONS

The use of highly ordered transparent TiO_2 nanotube arrays in dye-sensitized solar cells (DSCs). Highly ordered nanotube arrays of 46-nm pore diameter, 17-nm wall thickness, and 360-nm length were grown perpendicular to a fluorine-doped tin oxide-coated glass substrate by anodic oxidation of a titanium thin film. After

crystallization by an oxygen anneal, the nanotube arrays are treated with $TiCl_4$ to enhance the photogenerated current and then integrated into the DSC structure using a commercially available ruthenium-based dye. Although the negative electrode is only 360-nm-thick, under AM 1.5 illumination the generated photocurrent is 7.87 mA/cm^2 , with a photocurrent efficiency of 2.9%. Voltage-decay measurements indicate that the highly ordered TiO_2 nanotube arrays, in comparison to nanoparticulate systems, have superior electron lifetimes and provide excellent pathways for electron percolation. Our results indicate that remarkable photoconversion efficiencies may be obtained, possibly to the ideal limit of $\sim 31\%$ for a single photosystem scheme, with an increase of the nanotube-array length to several micrometers.



Fig .4 Applications of Dye-Sensitized Solar Cell

V.CONCLUSIONS

The dye-sensitized nanocrystalline electrochemical photovoltaic system has become a validated and credible competitor to solid-state junction devices for the conversion of solar energy into electricity. It is the prototype of a series of optoelectronic and energy technology devices exploiting the specific characteristics of this innovative structure for oxide and ceramic semiconductor films. Recent developments in the area of sensitizers for these devices have lead to dyes which absorb across the visible spectrum leading to higher efficiencies. The recent development of an all solid-state heterojunction dye solar cell holds additional potential for further cost reduction and simplification of the manufacturing of dye solar cells.

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