



## ZINC OXIDE PHOTO ANODE BASED SOLAR-CELL: A REVIEW

**Mrs. Lopamudra Pradhan**, Assistant Professor, Department of Electrical Engineering, Gandhi Institute of Technology And Management, Bhubaneswar, Odisha, India.

**Mrs. Deepti Priyanka Behera, Mr. Jyoti Prakash Jena, Mrs. Subhadarshini Misra**, Assistant Professor, Department of Electrical Engineering, Gandhi Institute of Technology And Management, Bhubaneswar, Odisha, India

### Abstract

Zinc oxide (ZnO) is gaining attention as a potential replacement for titanium dioxide (TiO<sub>2</sub>) in dye sensitized solar cells (DSSCs) due to its similar band gap, improved electron mobility, and flexible fabrication methods. Researchers have synthesized various ZnO films through methods like hydrothermal synthesis and sol-gel technique for DSSCs, employing the N3 dye as a sensitizer. The effectiveness of DSSCs heavily relies on the choice of dye, with natural dyes becoming popular due to their cost-effectiveness, availability, and eco-friendliness. However, the performance of natural dye-based DSSCs varies due to pigment characteristics and other factors. This review outlines the evolution and operation of DSSCs, highlighting the ongoing research on natural dye-based systems.

**Keywords:** sensitized solar-cells, natural dyes, ZnO films.

### Introduction

The increasing demand for fossil fuels and their environmental impact continue to stress the global energy infrastructure. Despite these challenges, considerable advancements have been achieved in renewable energy technologies like fuel cells, solar cells, and biofuels. Although these alternatives have historically been overlooked, there is optimism that ongoing technological progress will enhance their feasibility and competitiveness compared to fossil fuels, facilitating a transition away from them as the primary energy source.

Many people believe that solar energy is the best way to resolve the conflict between energy and the environment because it is a carbon-neutral energy source. Photovoltaic effect-driven solar-cell systems are used to convert solar radiation into electrical power. Many photovoltaic devices have been produced over the last fifty years, demonstrating significant advancements in the industry. However, cost and conversion efficiency pose two major obstacles to the widespread use of solar energy.

Research and development efforts are being made to address these issues, with a particular focus on lowering the cost and increasing the effectiveness of solar cells technology. To accomplish solar energy to reach its full potential and be widely adopted as a competitive alternative to fossil fuels, these obstacles must be removed.

One of the most well-established photovoltaic technologies is the mono crystalline silicon solar cell, which has been around for more than 50 years (Chapin et al., 1954). It currently controls the majority of the market, accounting for 94% of all solar cells installed. Monocrystalline silicon solar cells work on the basis of p-n junctions, which are created when p-type and n-type semiconductors are combined. When these junctions are exposed to light, these junctions' interface produces electrons and holes. The electric field across the p-n junction subsequently divides these charge carriers, and external circuits are used to collect them.

Theoretically, single-crystalline silicon semiconductors can convert energy up to 92% of the theoretically achievable amount; commercial devices have conversion efficiencies of about 20%. Nonetheless, thin-film solar cells have been created as a substitute to reduce costs associated with the product due to the high material costs connected with single-crystalline silicon [11].

Though less studied than TiO<sub>2</sub>, ZnO shows promise as a wide-band gap semiconductor oxide for dye-sensitized solar cells (DSSCs). Although its carrier mobility is substantially higher than that of TiO<sub>2</sub>, it shares similar energy levels making it more favorable for the collection of photo electrons [13]. After



TiO<sub>2</sub> based cells. ZnO nano-particles-built DSSCs have next highest efficiency [15]. Recently, single-crystal zinc oxide nano-tubes have been produced on transparent conductive substrates using a two-step process involving electrochemical deposition and chemical etching [24]. This electrochemical deposition technique offers benefits such as growth at low temperatures, precise control over morphology, and importantly, establishing effective electrical contact between nano-tube arrays and conductive substrates.

In recent times, there has been growing interest in self-powered systems that can generate electricity from ambient sources, enabling the operation of electrical devices without relying on external power [29]. Our research group has recently demonstrated the use of piezoelectric zinc oxide nano-wires to capture mechanical energy from ambient sources. This approach holds promise for powering pH and UV sensors without the need for batteries [32]. In our current study, zinc oxide nano-rods were first electrochemically deposited, followed by chemical etching of their central portion to create aligned zinc oxide nano-tube arrays. The electrode position process facilitates easy control over the morphology of the nano-tubes. Using these 5.1  $\mu\text{m}$  nano tubes as photo anodes for dye-sensitized solar cells (DSSCs) resulted in an overall conversion of light into energy.

### **Dye-Sensitized Nano-Crystalline Solar Cell (DSC)**

Dye-sensitized solar cell (DSSC) consists of an electrode fabricated from a wide-band gap semiconductor like TiO<sub>2</sub> or ZnO, which is sensitized with a suitable dye. They also include a redox electrolyte and a counter electrode. In recent years, DSSCs have attracted considerable interest because of their various benefits, including low cost, reduced toxicity. [8]. When light hits the working electrode, the dye attached to the semiconductor absorbs the incoming light. The generated photoelectron is then transferred from the excited state of the dye to the conduction band of the semiconductor, and proceeds to move through the electrode into the external circuit. The electrolyte aids in electron transport and regenerates the sensitizer by reducing the tri-iodide ion at the counter electrode and at the dye oxidizing the iodide ion [9].

The efficiency of electron transport and power conversion in DSSCs relies on several factors, with the surface morphology of the working electrode and the selection of dye being particularly significant [11]. In comparison to nano-crystalline semiconductors, DSSCs based on hierarchical patterns like nano-rods and flower-like structures present a promising alternative for efficiently converting solar energy into electricity on a large scale [23].

Considerable research has been undertaken on dye-sensitized solar cells (DSSCs) as a viable substitute for traditional inorganic solid solar cells. These DSSCs employ nano-crystalline TiO<sub>2</sub> as photo electrodes sensitized with ruthenium poly-pyridine complexes or metal-free organic dyes as photo-electrodes [22]. Photovoltaic cells employing TiO<sub>2</sub> nano-particles with sizes ranging from 10 to 30 nm as photo-anodes have demonstrated a photovoltaic conversion efficiency of up to 11% [17].

However, the effectiveness of DSSCs is impeded by sluggish electron movement through interconnected nano-particles and the recombination of charges between injected electrons and electron acceptors, such as I<sup>-3</sup> ions, within the electrolyte [18]. As a result, considerable efforts have been directed towards developing more efficient photo-anode materials, including structured materials with ordered mesostructures [19] and one-dimensional materials like nanorods, nanowires, and nanotube [20]. Particularly promising are meticulously ordered arrays of TiO<sub>2</sub> nanotubes, which have demonstrated enhanced power conversion efficiency [20].

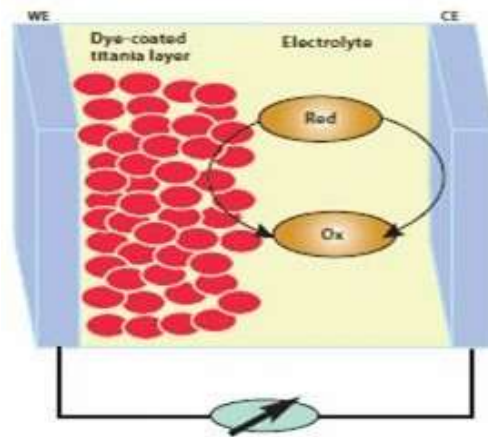


Figure 1 shows a dye-sensitized thin-layer solar cell schematically

### The Dye-Sensitized Solar Cell's Structure

The major components of dye-sensitized solar cells (DSSC) with a single connection are shown. The transparent conducting electrode, the counter-conducting electrode, the nano-structured wide-band gap semiconductor layer, the dye molecules (sensitizer) and the electrolyte are the four fundamental components of the cell. A thin transparent and conductive layer, such as fluorine-doped tin dioxide (SnO<sub>2</sub>), is applied to both the transparent conducting electrode and the counter-electrode

### Transparent Substrate For Conducting And Counter Electrode

Because clear glass substrates are widely available, reasonably priced, and have a high optical transparency in the visible and near-infrared portions of the electromagnetic spectrum, they are frequently used as substrates. A conductive substance is applied to one side of the substrate, typically in the form of a thin coating of transparent conductive oxide (TCO). Very little electrical resistance is guaranteed per square unit with this conductive material. These films typically have a resistance of 10 to 20 ohms per square at room temperature. On the conductive side of the substrate, the nano-structured wide-band gap oxide semiconductor, which serves as the electron acceptor is then produced, printed, or applied. The counter electrode needs to be coated with a catalysing layer, like a layer of graphite, as it will be discussed later. Before the cell is assembled to assist the electron donation process to the electrolyte.

It is crucial to remember that, once the conductive film has been applied, the transparent conducting electrodes transparency levels are not quite throughout the visible and near-infrared portions of the solar spectrum. In actuality, the electrodes transparency is usually decreased with the deposition of nano-structured material.

### Photo Electrode With Nanostructure

The photo electrodes in earlier iterations of photo electrochemical solar cells (PSCs) were usually composed of bulky semiconductor materials like Si, GaAs, or CdS. Nevertheless, when exposed to light, these kinds of photo electrodes are vulnerable to photo corrosion, which reduces the stability of the photo electrochemical cell. Because of their resistance to photo corrosion, sensitized wide-band gap semiconductors like ZnO or TiO<sub>2</sub> have improved the chemical stability of the cell.

Bulky single or polycrystalline wide- band gap materials have a poor light- to -current conversion efficiency, which is mainly because of insufficient sensitizer molecule absorption brought on by the electrode's small surface area. A good way to increase the light-harvesting efficiency (LHE) and, consequently, the light-to-current conversion efficiency is to increase the surface area (roughness factor) of the sensitized photo electrode. There has been a lot of interest in nanostructure materials because of the notable changes in their mechanical, electrical, magnetic, optical, and chemical properties when compared to their bulk counterparts [7].

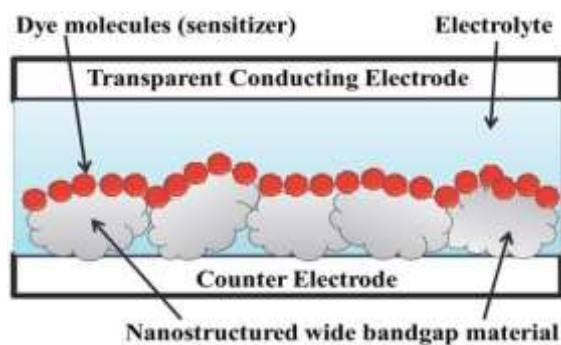


Figure 2: Diagram showing the dye-sensitized solar cell's structural components

Furthermore, a dye monolayer absorbs very little light since a single dye molecule occupies a larger area than its optical cross-section for light capture. It has been shown that superior photovoltaic efficiency requires the use of a nanostructured layer with a very high roughness factor as opposed to a flat layer of semiconductor or wide-band gap semiconductor oxide surface. As a result, Gratzel and his associates used a nonporous layer of titanium dioxide ( $\text{TiO}_2$ ) in lieu of the thicker layer as a photo-electrode. They also produced effective photo sensitizers, including novel Ru complexes, that could absorb a large range of the visible and near-infrared parts of the solar spectrum, producing outstanding results for photovoltaic cells [17].

One method is to anneal, or sinter, the deposited  $\text{TiO}_2$  layer for around 15 minutes at  $450^\circ\text{C}$  in a well-ventilated room in order to get the nano-porosity of the  $\text{TiO}_2$  paste (or colloidal solution).

Redox mediators may easily diffuse across the nanostructure  $\text{TiO}_2$  layer due to its high porosity (>50%), which facilitates their reactivity with sensitizers that are bonded to the surface. A technique for creating a room-temperature, nanostructure porous layer of semiconductor material was presented. This porous layer is pressed onto a conducting glass or plastic substrate in order to use it in a dye-sensitized nano-crystalline solar cell [33].

### Photo Electrochemical Cell Components

The concept of sensitization in photo electrochemistry has a rich history, dating back over a century to Moser's pioneering work in 1887. Sensitization originated in panchromatic black-and-white emulsions and was initially used in photography to obtain a wide spectrum response. Spectral selective dyes were subsequently used in color photography, as noted by West in 1974.

A pivotal advancement occurred with the research conducted by Gerischer and Tribustsch in 1968, followed by Tribustsch's subsequent work in the same year. This research, focusing on  $\text{ZnO}$ , provided a definitive elucidation of the mechanism of dye sensitization. Their results demonstrated the importance of dye sensitization in photo electrochemistry by allowing for the durability of a semiconductor substrate that was otherwise only responsive to ultraviolet light while attaining efficient wideband visible spectrum absorption. It is now generally known that there are multiple important processes involved in sensitization. By absorbing photon energy, the dye is first excited from its charge-neutral ground state to an excited state. Subsequently, the dye undergoes relaxation by releasing electrons to the semiconductor substrate, leaving behind a surface-absorbed cation. At the same time, a reaction with a redox species in the contacting electrolyte neutralizes the dye cation.

When the redox species regenerates by acquiring an electron from a counter electrode, a closed regeneration cycle is then finished. The dye sensitization process is essential for effective photo electrochemical reactions because this cycle makes it easier to transform the light that comes in into an electric current.

The typical redox system in this regenerative photo electrochemical device is the iodide/tri-iodide pair,  $\text{I}^-/\text{I}_3^-$ , which operates in a manner akin to that of a conventional solid-state photovoltaic cell. In the original sensitized devices, however, charge could only be transferred to the substrate by a



monomolecular absorbed coating of the sensitizing dye. This limitation led to low optical absorption and, thus, low photo voltaic efficiency.

To overcome this issue, researchers attempted to incorporate the dye with a nanostructure semiconductor. By doing this, they hoped to increase the active interface region's predicted geometrical surface area for charge transfer and light absorption. This enhancement allowed the device to compete with solid-state equivalent efficiency by providing it with the necessary opacity and light absorption. Continuous development efforts have driven dye-sensitized cells to attain a white-light conversion efficiency above 10% since its first introduction by Regan and Gratzel in 1991. This outstanding performance is mainly due to the ultra-fast electron injection kinetics from the excited dye into the solid, which is achieved with nanostructure semiconductor.

Furthermore, the majority carrier nature of the device where electrons enter an n-type material makes charge carrier separation possible, which effectively reduces charge carrier recombination losses. Only after passing a phase barrier and being recaptured by the dye cation or the redox electrolyte- a process that is intrinsically slower than electron injection -can electrons be lost in this configuration. This complex interaction of variables is what makes dye-sensitized cells so incredibly efficient.

### Setting Up Electrodes And Dye Solutions

According to Calogero et al. (2010), Red turnip had the best performance of all. Their research revealed a remarkable  $J_{sc}$  of 9.5%  $\text{mAcm}^{-2}$  and a high input photon to current conversion efficiency of 65% at 470 nm. Rich in beta lacin pigments, red turnip has ball-shaped red roots that grow wild in the Mediterranean region. It was first discovered growing in areas with chilly nights in the spring. Slices of red turnip were soaked in a 0.1 M HCl solution for an entire night to remove the color. Natural dye solutions that are acidic may be kept stable for more than a year by storing them properly, shielding them from the sun, and refrigerating them at a temperature of around +4 °C. To create titanium oxide nano-particles, the sol-gel method was applied

By using Calogero et al. (2010)'s methods the fourth-highest efficiency was attained. The DSSC based on wild Sicilian prickly pear had an efficiency of 1.19%. Utilizing pomegranate juice to sensitize the DSSC, Bazargan (2009) obtained the second-best efficiency of 1.50%. The tape casting process was used to deposit as red flavylum that forms strong connections with  $\text{Ti}^{4+}$  by releasing an  $\text{H}_2\text{O}$  molecule. The pigments from shiso leaves were used to get the third best performance. The leaf extract of the shiso plant, which is often consumed as a vegetable in Japan, is used as a coloring. Along with other pigments: malonyl shisonin and shisonin. The leaves were cooked in a solution of water and acetone that contained acetic acid after being gently crushed. Therefore, the efficiency reached 1,30% and the  $j_{sc}$  was [missing sentence continuation] 4.80  $\text{mAcm}^{-2}$  with a 0.53V  $V_{oc}$ . Additionally, Shisonin demonstrated a good 1.01% performance. Kumaraand associates (2006)

### Application for solar cells with dye sensitization (DSC)

Dye-sensitized solar cells offer a promising solution for renewable energy generation, leveraging inexpensive and eco-friendly materials. These cells, capable of producing various colors depending on the sensitizing dye used, find potential applications in building-integrated photovoltaic (BIPV), such as power windows and shingles. An Australian business called Sustainable Technologies International has successfully produced electric power-generating glass tiles for field testing on a big scale; a wall of these tiles is currently present in the first structure.. Lightweight and flexible dye-sensitized cells or modules present appealing prospects for powering calculators, gadgets, and mobile devices both indoors and outdoors. Additionally, these solar cells can serve as colorful decorative elements indoors. With an efficiency of 10%, dye-sensitized solar modules provide an alternative to traditional crystalline silicon-based modules due to their flexibility.

Sony revealed in 2010 that it could fabricate modules with an efficiency of about 10%, meaning that there is a chance for DSSC modules to be commercialized.



## Conclusion

This review has provided a comprehensive overview of dye-sensitized solar cells (DSSCs), delving into their development, operational principles, and constituent components. Additionally, it has explored the extensive research conducted in the realm of natural dye-based DSSCs, tracing the trajectory of advancements and innovations in this field over the years. In the field of photovoltaics, dye-sensitized solar cells are a potential development since they provide a more affordable and sustainable option than traditional silicon-based solar cells. The foundational principles of DSSCs lie in their utilization of sensitizing dyes, typically organic or inorganic compounds, to capture sunlight and convert it into electrical energy.

## References

1. Bazargan MH. Performance of nano structured dye-sensitized solar cell utilizing natural sensitizer operated with platinum and carbon coated counter electrodes digest. *Journal of Nonmaterial's and Biostructures* 2009;4 :723–7.
2. Calogero G, Marco GD, Cazzanti S, Caramori S, Argazzi R, Carlo AD, et al. Efficient dye-sensitized solar cells using red turnip and purple wild Sicilian prickly pear fruits. *International Journal of Molecular Sciences* 2010; 11: 254–67.
3. Kumara GRA, Kaneko S, Okuya M, Onwona-Ageyeman B, Konno A, Tennakone K. Shisole a pigments for dye-sensitized solid-state solar cell. *Solar Energy Materials and Solar Cells* 2006;90:1220–6.
4. Moser, J. (1887) Notiz Uber Verstärkung photoelektrischer Ströme durch optischer Sensibilisierung, *Monatsh. Chem.*, 8, pp.373.
5. West W. (1974) First hundred years of spectral sensitisation, *Photogr. Sci. Eng.*, 18, 35-48.
6. Gerischer, H. and Tributsch, H. (1968) Electro chemische Untersuchungen zur spectral unsensibilisierung von ZnO Einkristallen, *Ber. Bunsenges, Phys. Chem.*, 72, 437-445.
7. Tributsch, H. (1968) Ph.D. thesis, Techn. Hochschule München, Germany.
8. O. Regan, B. and Gratzel, M. (1991). A low-cost, high efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films, *Nature*, 353, 737–740.
9. Gratzel, M. *Nature* 2001, 414, 338.
10. Pagliaro, M.; Palmisano, G., and Ciriminna, R. (2008). Working principles of dye-sensitized solar cells and future applications, third print edition of Photo voltaics *International journal*, www.pv-tech.org.
11. Kim, Y.T.; Park, J.; Kim, S.; Park, D.W.; Choi, J. *Electrochimica Acta* 2012, 78, 417.
12. Jiang, C.Y.; Sun, X.W.; Lo, G.Q.; Kwong, D.L.; Wang, J.X. *Appl. Phys. Lett.* 2007, 90, 263501.
13. Baxter, J. B.; Aydil, E. S. *Appl. Phys. Lett.* 2005, 86, 53114. Ko, S.H.; Lee, D.; Kang, H.W.; Nam, K.H.; Yeo, J.Y.;
14. Hong, S.J. *Nano Letters* 2011, 11, 666.
15. Chen C-Y, Wu S-J, Li J-Y, Wu G, Chen J-G and Ho K-C 2007 *Adv. Mater.* 193888
16. Freitas J N, Nogueira A F and Paoli M-A D 2009 *J. Mater. Chem.* 195279
17. Nazeeruddin MK, Angelis FD, Fantacci S, Selloni A, Viscardi G, Liska P, Ito S, Takeru B and Grätzel M 2005. *J. Am. Chem. Soc.* 12716835
18. Katoh R, Furube A, Kasuya M, Fuke N, Koide N and Han L 2007 *J. Mater. Chem.* 173190
19. Chen D, Huang F, Cheng Y-B and Caruso R A 2009 *Adv. Mater.* 212206
20. Mor G K, Varghese O K, Paulose M and Grimes C A 2005. *Adv. Funct. Mater.* 151291
21. Kang T-S, Smith A P, Taylor B E and Durstock M F 2009. *Nano Lett.* 9601
22. Varghese O K, Paulose M and Grimes C A 2009. *Nat. Nanotechnol.* 4592
23. Jennings J R, Ghicov A, Peter L M, Schmuki P and Walker A B 2008 *J. Am. Chem. Soc.* 130 13364
24. Zhang Q, Dandeneau C S, Zhou X and Cao G 2009 *Adv. Mater.* 214087
25. Seow Z L S, Wong A S W, Thavasi V, Jose R, Ramakrishna and Ho G W 2009 *Nanotechnology* 20 045604



26. Zhang Q, Chou TP, Russo B, Jenekhe SA and Cao G 2008 *Angew. Chem. Int. Edn* 47 2402
27. Rao A R and Dutta V 2008 *Nanotechnology* 19 445712 Weintraub B, Wei Y and Wang Z L 2009 *Angew. Chem. Int. Edn* 48 8981
28. Bacsa R R, Dexpert-Ghys J, Verelst M, Falqui A, Machado B, Bacsa W S, Chen P, Zakeeruddin S M, Grätzel M and Serp P 2009 *Adv. Funct. Mater.* 19 875
29. She G-W, Zhang X-H, Shi W-S, Fan X, Chang J C, Lee C-S, Lee S-T and Liu C-H 2008 *Appl. Phys. Lett.* 92 053111
30. Elias J, Tena-Zaera R, Wang G-Y and L'evy-Clement C 2008 *Chem. Mater.* 20 6633
31. Wang Z L and Song J H 2006 *Science* 312 242
32. Xu S, Qin Y, Xu C, Wei Y, Yang R and Wang Z L 2010 *Nat. Nano technol.* 5 366.
33. J. Liu, G. Z. Cao, Z. Yang, D. Wang, D. Dubois, X. Zhou, G.
34. L. Graff, L. R. Pederson, J.-G. Zhang, *Chem. Sus. Chem.* 2008, 1, 22. Goetzberger and C. Hebling, 2000. *Sol. Energ. Mat. Sol. C* 62, 1.
35. Goetzberger, C. Hebling, H. Wand Schock, *Mater.* 2003. *Sci. Eng. R. Rep.* 40, 1.
36. D. M. Bagnall and M. Boreland, *Energ. Pol.* 2008, 36, 4390.
37. M. A. Green, *Sol. Energ.* 2004, 76, 3.
38. M. Oliver, T. and Jackson, *Energ. Pol.* 1999, 27, 371.
39. D. M. Chapin, C. S. Fuller, G. L. Pearson, *J. Appl. Phys.* 1954, 25, 676.
40. K. L. Chopra, P. D. Paulson, V. Dutta, *Prog. Photovoltaics* 2004, 12, 69.
41. R. B. Bergmann, *Appl. Phys. A* 1999, 69, 187.