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# A Review of Zinc Oxide Photo Anode Films for Dye-Sensitized Solar Cells based on Zinc Oxide Nanostructures

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**ABSTRACT**

ZnO is introduced as an alternative to $TiO_2$ in dye sensitized solar cells (DSSCs) due to its band gap similar to $TiO_2$, higher electron mobility, and flexible procedures of preparations. Several samples of ZnO films are prepared with the hydrothermal synthesis method and the sol-gel technique, respectively. These ZnO films were assembled as photo anodes in DSSCs using $N_3$ dye as the sensitizer. The performance of dye sensitized solar cells is mainly based on the dye as a sensitizer. Natural dyes have become a viable alternative to expensive and rare organic sensitizers because of its low cost, easy attainability, abundance in supply of raw materials and no environment threat. The nature of these pigments together with other parameters has resulted in varying performance. This review briefly discusses the emergence, operation and components of dye explained solar cells together with the work done on natural dye based dye sensitized solar cells over the years.



## Introduction

The increasing demand for fossil fuels and the environmental impact of their use are continuing to exert pressure on an already-stretched world energy infrastructure. Significant progress has been made in the development of renewable-energy technologies, such as solar cells, fuel cells and biofuels. However, although these alternative energy sources have been marginalized in the past, it is expected that new technology could make them more practical and price competitive with fossil fuels, thus enabling an eventual transition away from fossil fuels as our primary energy sources. Solar energy is considered to be the ultimate solution to the energy and environmental challenge as a carbon-neutral energy source. The conversion from solar energy to electricity is fulfilled by solar-cell devices based on the photovoltaic effect. Many photovoltaic devices have already been developed over the past five decades (Liu *et al.*, 2008; Goetz Berger and Hebling, 2000; Goetz Berger *et al.*, 2003). However, wide-spread use is still limited by two significant challenges, namely conversion efficiency and cost (Bagnall and Boreland, 2008; Green, 2004; Oliver and Jackson, 1999).

One of the traditional photo voltaic devices is the single-crystalline silicon solar cell, which was invented more than 50 years ago and currently makes up 94% of the market (Chapin *et al.*, 1954). Single-crystalline silicon solar cells operate on the principle of p–n junctions formed by joining p-type and n-type semiconductors. The electrons and holes are photo-generated at the interface of p–n junctions, separated by the electrical field across the p–n junction, and collected through external circuits. In principle, the single crystalline silicon semiconductor can reach 92% of the theoretical attainable energy conversion, with 20% conversion efficiency in commercial designs. However, because of the considerably high material costs, thin-film solar cells have been developed to address the product costs (Chopra *et al.*, 2004; Bergmann, 1999; Shah *et al.*,1999).

ZnO is another promising but less explored wide band gap semiconductor oxide used for DSSC. It has similar energy levels to $TiO_2$. More importantly, its much higher carrier mobility is more favourable for the collection of photo induced electrons (Zhang *et al.*, 2009; Seow *et al.*, 2009). DSSC built from ZnO nanoparticles shows the second-highest efficiency after $TiO_2$ (Zhang *et al.*, 2008; Rao and Dutta, 2008; Weintraub *et al.*, 2009; Bacsa *et al.*, 2009). Until recently, single-crystal ZnO nanotube arrays were fabricated on transparent conductive substrates by a two-step electrochemical deposition/chemical etching approach (She *et al.*, 2008; Elias *et al.*, 2008). The electrochemical deposition endows low temperature growth, precise control of the morphology and, more importantly, good electrical contact between nanotube arrays and conductive substrates.

Recently, self-powered systems have attracted more and more attention, for such systems could harvest energy from ambient sources and drive electrical devices without external power (Wang and seng, 2006). Our group has recently demonstrated the harvesting of mechanical energy from ambient sources using piezoelectric ZnO nanowires, which can be applied to power pH and UV sensors without the need for batteries (Xu *et al.*, 2010). In the present study, aligned ZnO nanotube arrays were fabricated by electrochemical deposition of ZnO nano rods followed by chemical etching of the centre part of the nano rods. The morphology of the nanotubes can be readily controlled by electro deposition parameters. By employing the 5.1 $\mu$m length nanotubes as photo anodes for DSSC, an overall light to electricity conversion efficiency of 1.18% was achieved. In addition, the DSSC can serve as a power source to drive a humidity sensor in a self-powered system. Therefore, this work provides a novel strategy of using solar cells for powering nano devices.

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**Dye- sensitized nano crystalline solar cell (DSC)**

The dye sensitized solar cell consists of an electrode with wide band gap semiconductor such as $TiO_2$ or ZnO sensitized using a suitable dye, a redox electrolyte and a counter electrode. In recent years dye-sensitized solar cells have attracted much attention because of their advantages like low cost, less toxic nature, transparency and flexibility (Regan and Gratzel, 1991). When the light is incident on the working electrode the incident light is absorbed by the dye anchored to the semiconductor, the resulting photoelectron being transferred from the excited level of the dye into the conduction band of semiconductor, and through the electrode into the external circuit. The electrolyte facilitates the transport of the electron and the regeneration of the sensitizer, through reduction of the tri-iodide ion at the counter electrode, followed by oxidation of the iodide ion at the dye (Gratzel, 2001). The electron transport and power conversion efficiency of the device depends upon various factors among them surface morphology of the working electrode and the dye used are important (Kim *et al*., 2012; Jiang *et al*., 2007; Baxter and Aydil, 2005). Compared with nano crystalline semiconductors, hierarchical patterns like nano rod and flower like structure based dye-sensitized solar cells represent a promising alternate for the large scale conversion of solar energy into electricity (Ko *et al*., 2011).

Dye-sensitized solar cells (DSSC) have been studied extensively as a potential alternative to conventional inorganic solid solar cells, by using nano-crystalline $TiO_2$ sensitized with ruthenium poly-pyridine complexes or metal-free organic dyes as photo-electrodes (Regan and Gratzel, 1991; Chen *et al*., 2007; Freitas *et al*., 2009). Solar cells based on $TiO_2$ nanoparticles with a size of 10–30 nm have been used as photo-anodes with a demonstrated 11% photovoltaic conversion efficiency (Nazeeruddin *et al*., 2005). In general, slow electron percolation through the interconnected nanoparticles and the charge recombination between injected electrons and electron acceptors (e.g. I− 3 ions) in the electrolyte hinder the DSSC performance (Katoh *et al*., 2007). Considerable efforts have been devoted to the development of more efficient photo-anode materials including ordered meso-structured materials (Chen *et al*., 2009), one-dimensionally structured materials (nano-rod, nanowire, nanotube) (Mor *et al*., 2005), etc. Highly ordered $TiO_2$ nanotube arrays are particularly attractive, which have demonstrated enhanced power conversion efficiency (Kang *et al*., 2009; Varghese *et al*., 2009; Jennings *et al.*, 2008).

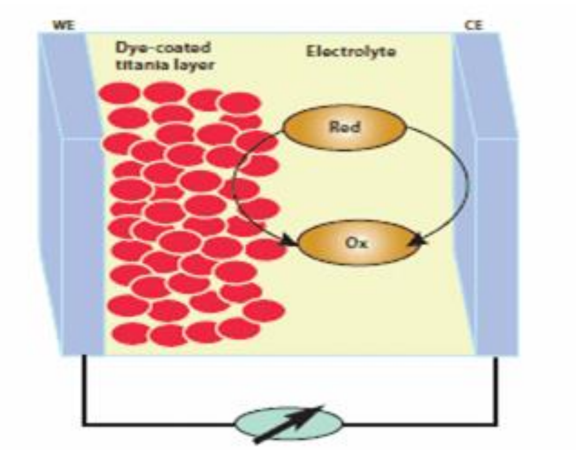


**Figure 1. Schematic representation of a dye-sensitized thin layer solar cell.**

**Structure of dye sensitized solar cell**

The main parts of single junction dye sensitized solar cell are illustrated. The cell is composed of four elements, namely, the transparent conducting and counter conducting electrodes, the nanostructured wide band gap semiconducting layer, the dye molecules (sensitizer) and the electrolyte. The transparent conducting electrode and counter-electrode are coated with a thin conductive and transparent film such as fluorine doped tin dioxide ($SnO_2$).

**Transparent substrate for both the conducting electrode and counter electrode**

Clear glass substrates are commonly used as substrate because of their relative low cost, availability and high optical transparency in the visible and near infrared regions of the electromagnetic spectrum. Conductive coating (film) in the form of thin transparent conductive oxide (TCO) is deposited on one side of the substrate. The conductive film ensures a very low electric resistance per square. Typical value of such resistance is 10-20 $\Omega$ per square at room temperature. The nanostructured wide band gap oxide semiconductor (electron acceptor) is applied, printed or grown on the conductive side. Before assembling the cell the counter electrode must be coated with a catalysing layer such as graphite layer to facilitates electron donation mechanism to the electrolyte (electron donor) as well be discussed later. One must bear in mind that the transparency levels of the transparent conducting electrode after being coated with the conductive film is not 100% over the entire visible and near infrared (NIR) part of the solar spectrum. In fact, the deposition of nanostructured material reduces transparency of the electrode.

**Nanostructured photo electrode**

In the old generations of photo electro chemical solar cells (PSC) photo electrodes were made from bulky semiconductor materials such as Si, GaAs or CdS. However, these kinds of photo electrodes when exposed to light they undergo photo corrosion that results in poor stability of the photo electro-chemical cell. The use of sensitized wide band gap semiconductors such as $TiO_2$, or $ZnO_2$ resulted in high chemical stability of the cell due to their resistance to photo corrosion. The problem with bulky single or poly-crystalline wide band gap is the low light to current conversion efficiency mainly due to inadequate adsorption of sensitizer because of limited surface area of the electrode. One approach to enhance light-harvesting efficiency (LHE) and hence the light to current conversion efficiency is to increase surface area (the roughness factor) of the sensitized photo electrode. Due to the remarkable changes in mechanical, electrical, magnetic, optical and chemical properties of nanostructured materials compared to its phase in bulk structures, it received considerable attention (Gleiter, 1989).

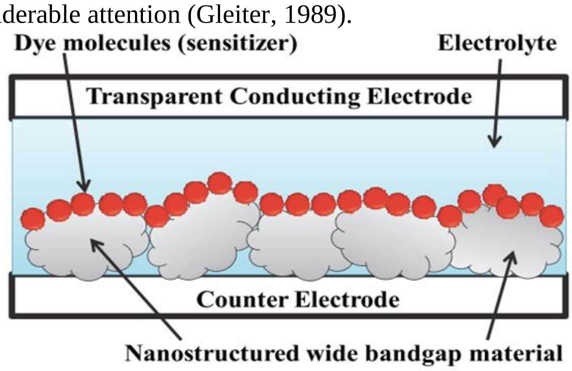


**Figure 2. Schematic of the structure of the dye sensitized solar cell.**

Moreover, because the area occupied by one dye molecule is much larger than its optical cross section for light capture, the absorption of light by a monolayer of dye is insubstantial. It has been confirmed that high photovoltaic efficiency cannot be achieved with the use of a flat layer of semiconductor or wide band gap semiconductor oxide surface but rather by use of nanostructured layer of very high roughness factor (surface area). Therefore, Gratzel and his co-workers replaced the bulky layer of titanium dioxide ($TiO_2$) with nonporous $TiO_2$ layer as a photo-electrode. Also, they have developed efficient photosensitizers (new Ru complex) that are capable of absorbing wide range of visible and near infrared portion of the solar spectrum and achieved remarkable photovoltaic cell performance (Nazerruddin *et al.*, 1993; O' Regan and Gratzel, 1991; Smestad and Gratzel, 1998). Nano-porosity of the $TiO_2$ paste (or colloidal solution) is achievable by sintering (annealing) of the deposited $TiO_2$ layer at approximately 450 ◦C in a well- ventilated zone for about 15 minutes.

The high porosity (>50%) of the nanostructured $TiO_2$ layer allows facile diffusion of redox mediators within the layer to react with surface-bound sensitizers. Lindstrom *et al.*, 2001 reported "A method for manufacturing a nanostructured porous layer of a semiconductor material at room temperature. The porous layer is pressed on a conducting glass or plastic substrate for use in a dye-sensitized nano-crystalline solar cell." (Lindstrom *et al.*, 2001).

**Photo electrochemical Cell Components**

The sensitization principle has been known in photo electrochemistry for over a century (Moser, 1887) and has been applied in photography to secure wide-spectrum response, at first in panchromatic black-and-white emulsions, and more recently with spectrally selective dyes in colour photography (West, 1974). The work of Gerischer and Tributsch, 1968; Tributsch, 1968, on ZnO, definitively established the mechanism of dye sensitization and indicated its significance for photo electrochemistry by finally rendering compatible effective wideband visible spectral absorption with the stability of an semiconductor substrate, otherwise sensitive only to ultraviolet. It is now evident that the process involves the excitation of the dye from its charge-neutral ground state to an excited state by the absorption of the energy of a photon, followed by relaxation through electron loss to the semiconductor substrate. The dye is left as a surface-adsorbed cation. This process is associated with neutralisation of the dye cation by reaction with a redox species in the contacting electrolyte, which in turn recovers an electron from a counter electrode, there by constituting a closed regenerative cycle for the conversion of incident light into an electric current.

The standard redox system is the iodide/tri-iodide couple, I- /I3-. This regenerative photo electrochemical device is evidently functionally equivalent to a conventional solid-state photovoltaic cell. However, as only a monomolecular adsorbed film of the sensitizing dye can transfer charge to the substrate, the original sensitized devices had low optical absorption, and therefore low photovoltaic efficiency. It remained therefore to associate the dye with a nanostructured semiconductor, so that the active interface area for light absorption and charge transfer greatly exceeded the projected geometrical area of the surface and gave the required opacity and light absorption, to provide a device capable of challenging the efficiency of its solid-state counterpart. Since the first presentation of this device (Regan and Gratzel, 1991), further development work has enabled these dye-sensitized cells to reach a white-light conversion efficiency exceeding 10%. That such a performance is attainable with a nanostructured semiconductor is due to the ultra-fast kinetics of electron injection from the excited dye into the solid. That separation of charge carriers, associated with the majority carrier nature of the device where the electrons enter an n-type material, strongly inhibits charge carrier recombination losses. Electrons can be lost only through recapture by the dye cation or by the redox electrolyte after crossing a phase boundary – an inherently slow process.

**Preparation of dye solutions and electrodes**

The best performance has been produced by Red turnip based on the work performed by Calogero *et al*., 2010. This work resulted in a remarkable Jsc of 9.5 mAcm−2 and a high incident photon to current conversion efficiency of 65% at 470 nm. Red turnip originally grew wild in the Mediterranean area, particularly in regions that have cold nights during the spring season. Its ball-shaped red roots contain a high concentration of betalain pigments. The red turnip extract was obtained by immersing its slices in 0.1 M HCl solution, overnight. If properly stored, protected from direct sunlight and refrigerated at about +4 ◦C, the acidic natural dye solutions are usually stable, with a deactivation half-time of more than 12 months. Sol–gel procedure was used for preparing titanium oxide nanoparticles.

The fourth highest efficiency also followed the work of Calogero *et al*., 2010. The same procedure was used for preparation of the dye. The efficiency of Wild Sicilian prickly pear based DSSC was found to be 1.19%. Work done by Bazargan, 2009 produced the second best efficiency. DSSC sensitized with pomegranate juice produced an efficiency of 1.50%. $TiO_2$ was deposited by tape casting technique. Pomegranate juice mainly contains cyanin derivatives and exists as flavyium at natural pH. Flavylium is red in colour and strongly bond with Ti4+ via emanating $H_2O$ molecule. The third best performance has been delivered by shiso leaf pigments. The shiso plant is well known in Japan as a vegetable and the leaf extract and is used as a food colorant. Leaves of this plant contain two anthocyanin pigments referred to as shisonin and malonylshisonin, as well as chlorophyll and other photosynthetic pigments. Shiso leaves were lightly crushed and boiled in water–acetone mixture containing acetic acid. An efficiency as high as 1.30%, Jsc of 4.80 mAcm−2 and Voc of 0.53V. Shisonin also produced a promising performance of 1.01% Kumara *et al*., 2006.

**Applications of Dye- sensitized solar cell (DSC)**

The physical nature of the dye sensitized solar cells, inexpensive, environment friendly materials, processing, and realization of various colours (kind of the used sensitizing dye); power window and shingles are prospective applications in building integrated photovoltaics BIPV. The Australian company Sustainable Technologies International has produced electric-power-producing glass tiles on a large scale for field testing and the first building has been equipped with a wall of this. The availability of light weight flexible dye sensitized cells or modules are attractive for applications in room or outdoor light powered calculators, gadgets and mobiles. Dye sensitized solar cell can be designed as indoor colourful decorative elements. Flexible dye sensitized solar modules opens opportunities for integrating them with many portable devices, baggage, gears, or outfits (Pagliaro *et al*., 2008). In power generation, dye sensitized modules with efficiency of 10% are attractive choice to replace the common crystalline Si-based modules.

In 2010 Sony announced fabrication of modules with efficiency close to 10% and hence opportunity of commercialization of DSSC modules is attainable.

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