

Fabrication and Analysis of ZnO Based Dye-Sensitized Solar Cell Using Natural Dye

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Abstract: This paper is focused on the fabrication and study of photoelectric parameters of dye-sensitized solar cells (DSSCs) based on ZnO nano-particles, ZnO particle are coated on substrate using spin coating method. Set of naturally extracted dyes were selected and used for sensitizing ZnO based DSSC. All natural sensitizers were extracted by water and these natural sensitizers are used as Dye's. The short circuit current density (I_{sc}) and V_{oc} were measured and fill factor are obtained for all the above sensitizers the data we get from ZnO based DSSCs are measured and analysed then the photo-electrochemical performance were compared to find out which dye has given good efficiency.

Keywords: DSSC, ZnO (Zinc Oxide), Short circuit current (I_{sc}), Open circuit voltage (V_{oc}), Efficiency (η)

1. Introduction

Dye-sensitized solar cell (DSSC) is the third generation of solar cell which has been developed by O'Regan and Gratzel in 1991 [1]. This simple assemble of solar cell (also known as photovoltaic device) works by converting inexpensive photon from solar energy to electrical energy, based on sensitization of wide bandgap semiconductor, dyes and electrolyte [2,3]. The advantages of DSSC are that it can be engineered into flexible sheets, low cost of sensitization material production, ease of fabrication and low process temperature. Due to the low cost of the overall production of DSSC, it has been expected that the DSSC type of solar cell will give a higher return of investment (ROI) when compared to Silicon based solar cell (Si-SC). The performance of the DSSC is highly dependent on the sensitizer dye and wide bandgap material such as TiO₂, ZnO and Nb₂O₅ [3]. Material TiO₂ is highly preferable due its ability of the surface, to resist the continuous transfer of electron under illumination solar photon (ultra-violet range).

One of most efficient sensitizer is produced from heavy transition metal coordination compound, which is ruthenium polypyridyl complex [6]. This complex is used widely due to its intense charge-transfer (CT) absorption in Visible light spectrum; good absorption, long excited lifetime and highly efficient metal-toligand charge transfer (MLCT). However, the ruthenium based complex is very expensive and hard to prepare. Thus, an alternative organic dye such as natural dyes is suggested with similar characteristic with high absorption coefficients [7-13]. The good side of natural dyes is includes their availability, environmental friendly and low in cost.

The backbone of a DSSCs is a mesoporous layer of semiconductor oxide nano-particles, which are sintered together to establish a good electric contact between the particles. The nano-particle film is deposited on a ITO coated glass substrate, which allows light to enter into the cell. Attached to the surface of the ZnO there is a monolayer of dye molecules, which are responsible for harvesting the light. The sensitized film is surrounded by an electrolyte solution

of high ionic strength, usually composed of an organic solvent containing a redox pair.

The most successful combination of materials is still the one reported in the pioneering work by the Gratzel group [8], which opened the research field of Dye Sensitized Solar Cells. In this configuration the main components are a layer of nano-particles sensitized by a natural dye with Iodine redox couple in an organic solvent, which acts as the redox mediator. Gratzel and O'Regan found a successful combination of a nano-structured semiconductor electrode with an efficient and stable dye.

Dye Sensitized Solar Cells (DSSC) has attracted intense scientific and technological attention for more than a decade because of their unique hybrid architecture, relatively low cost and application for use in diffuse light harvesting conditions (Oregan and Gratzel, 1991; Hagfeldt et al., 2010; Gratzel, 2001; Gratzel, 2005). As a result, emphasis has been given on TiO₂ based DSSC exhibiting an overall conversion efficiency of 11% (Gratzel, 2001, 2005). Of late, ZnO has been considered as a promising alternate Photo anode material in DSSC, due to its comparable band gap energy (3.43 eV), electron affinity, high electron mobility (205–1000 $cm^2V^{-1}S^{-1}$), and stability against photo corrosion (Gratzel, 2001, 2005; Zhang et al., 2009; Xu and Sun, 2011; Mende and Driscoll, 2007). The values of reported efficiencies for various ZnO structures are very wide and range from as low as 0.02% to as high as 7% (Zhang et al., 2009; Anta et al., 2012; Baskoutas and Bester, 2010; He et al., 2010; Shi et al., 2013).

In this paper, the ZnO based DSSC is prepared using natural fruit dye extracted from *Garcinia indica*, *Pomegranate*, *Syzygium cumini* which are used as sensitizer. These fruit based dye has been selected due to its widely available in local area and low in conservation cost. The ZnO electrical properties and DSSC efficiency is then investigated.

a. Principle Of Operation Of DSSC

Figure 1 shows the components of DSSC, complete structure of our DSSC. Under illumination of sun light energy, photon will strike through conductive layer glass; Indium-doped Tin Oxide (ITO) towards dye molecules which mount on the surface of ZnO particles. The photon excitation of dye will cause an injection of an electron into conduction band of the ZnO layer. These electrons will circulate the external loop through the load. Meanwhile, dye molecule which had lost electron will be restored by electron donation from redox electrolyte (contain iodide/triiodide), which in this experiment; a mixture of Potassium Iodide (KI) and Iodine (I₂) [3]. This process occurs very fast avoiding any recombination of electrons rejected earlier. Under illumination, voltage is generated through potential difference between Fermi level of ZnO layer and redox electrolyte.

2. Experimental Section

a. Preparation of ZnO Nanoparticles.

Zinc acetate (B DH), sodium hydroxide pellets (Scharlau), and polyethylene glycol (Applied Science) were used as received. All the materials were first cleaned and rinse with distilled water and dried. All the chemicals were weighed with analytical balance and mixed in cleaned round bottom flask.

For the sol-gel method we used, 2.7 (g) of zinc acetate dehydrate and 0.5 (g) of polyethylene glycol (PEG) were taken and dissolved in 250 (ml) of distilled water. 2 (g) of sodium hydroxide was dissolved in 500 (ml) of distilled water with vigorous stirring. The sodium hydroxide solution was added to the zinc acetate solution drop wise and the mixture was refluxed for 8 hrs at 120°C.

The obtained ZnO solution was centrifuged to solid matter and solution. The solid matter was washed first by distilled water repeatedly, finally dried in Furnace to obtain ZnO. After preparing the colloidal nanoparticles optical absorption was done using Gensys-2 PC spectrometer to determine the size of colloidal nanoparticles. About 5 ml of the colloid were taken for measurement. Here for measurement the colloid nanoparticles were taken as soon as they reach the final temperature. We record the UV-visible absorption spectra between 20nm and 50 nm. The solvent was used as a blank solution.

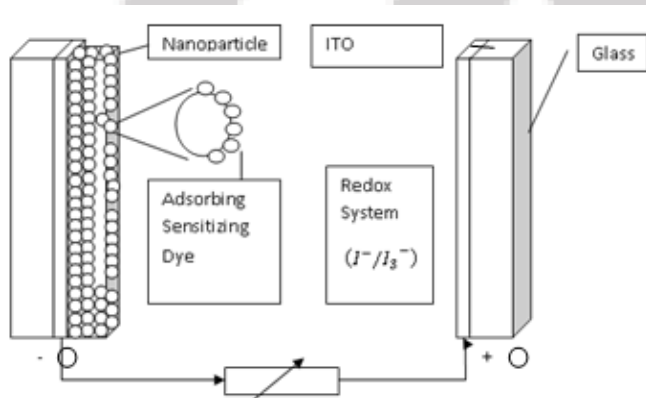


Figure 1: Components of DSSCs

b. Natural Dyes Extraction

1. *Garcinia indica*: four fruits are taken and cut into half pieces and then pieces of pulp are dipped into 200(ml) of water for overnight then in the morning the pulps are removed and obtained Dye is filtered using cotton cloth and this prepared dye is kept in air tight bottle.
2. *Syzygium cumini*: 250gm of *Syzygium cumini* fruits are taken and dried into direct sunlight for 7 days then the pulp of the fruits are taken and grinded using grinder the powder obtained is mixed with 200 ml of water and kept for 4 hours then the solution is filtered using a piece of cotton cloth and dye is preserved in air tight bottle.
3. Pomegranate: A fresh pomegranate arils with pink pulp are taken by breaking the fruit open then soak the stuff in 300ml water for 6 days then boil the extract for 30 min, and simmer for at least an hour thus obtained dye is stored in air tight container.

c. Preparation of Conductive ITO Glass

Conductive ITO coated glass was purchased from Farnell. Initially, a multimeter measurement of the ITO glass shows resistance of 19Ω/cm. Then, two piece of conductive glass were taken and washed with soapy water and then cleaned with distilled water then they are taken and merged separately into two identical beaker containing 10 ml of 95wt % methanol solution. Both of the beakers undergoes ultrasonic bath for 30 minutes at 50°C, then ozone cleaning of substrates is been carried out for 30min obtained substrates are taken and cleaned with hot air drier.

d. Preparations of Electrodes

A piece of conductive glass is selected and placed on a metal sheet. A Scotch tape at four sides was used as masking material on the conductive layer to restrict the thickness and area of the paste. Thin layer of ZnO nano particles is obtained by spin coating on area of 1 cm x 1 cm hole. Then this slide is baked into oven at 180°C so that solvent vaporize and only ZnO remains on the surface. The coated glass is immersed into natural dye solution and left for 12 hours. For the other electrode the ITO substrate is used.

e. Full Assembly of DSSC and Analysis

First, the ZnO film coated glass was immersed into the dye for about 24 hours. Then, the electrolyte solution is prepared using technique published in reference [21], the electrolyte solution (0.5 (M) Potassium Iodide and 0.05(M) of Iodine) is prepared. The electrolyte liquid is inserted between the electrodes by capillary action. Binder clips are used to hold the electrodes together.

Solar energy conversion efficiency consist of photocurrent-voltage ($I - V$) characterization curve been obtain using modified computerized digital Keithley multi meters under illumination of 50W halogen lamp (Osram.). From the resultant ($I - V$) graph, the fill factor of the DSSC can be calculated as shown in equation 1 [6, 21].

$$(FF) = (I_{max}) * \frac{(V_{max})}{(I_{sc})} * (V_{oc}) \quad (1)$$

Where I_{max} and V_{max} referred to maximum photo-current and photo-voltage at maximum power output P_{max} . While the I_{sc} referred to short-circuit photocurrent and V_{oc} is referred to open-circuit photo-voltage. Then, the efficiency of the solar cell is defined as equation 2,

$$\eta = (P_{max})/(P_{in}) \quad (2)$$

Where P_{in} is the illumination input power at surface of the DSSC.

3. Results and Discussion

a. Efficiency of DSSC

From the fully assembled DSSC, it is interesting to evaluate the solar energy conversion efficiency. Under irradiation of halogen lamp in a black box, The $I - V$ characteristic of all sensitizers were measured and plotted for analysis and comparison as shown below from figure 3.1(a, b), figure 3.2, figure 3.3, shows reading for a DSSC with a Dye *Garcinia indica*, *Syzygium cumini*, *Pomegranate* respectively, with halogen illumination.

Properties of solar cell can be determined when it is under homemade 7.7 mW/cm^2 halogen illumination. The $I - V$ curve will have a phase shift to lower y-axis during the halogen illumination. Higher efficiency of DSSC is expected to show higher y-axis shift as in the figure 3.1(a). To calculate the efficiency, value that undergoes 4th quadrant will be taken under consideration with inverted photocurrent value to positive range. The resultant graph taken from the 4th quadrant of I-V curve in figure 3.1(a) is shown in figure 3.1(b).

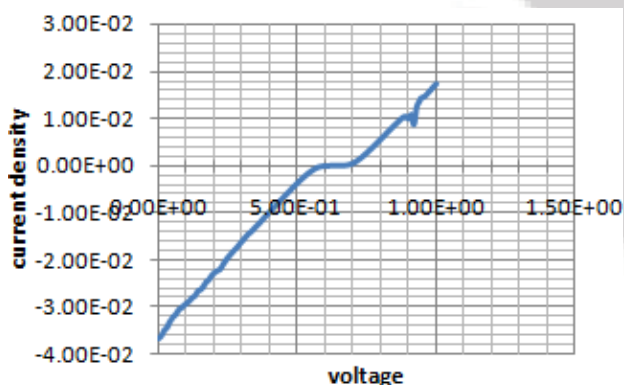


Figure 3.1(a): The DSSC conversion efficiency test for *Garcinia indica* sample of with halogen illumination.

In the fig. 3.1(b), the result of halogen present test result shows almost a straight line cutting through $0.6V$.

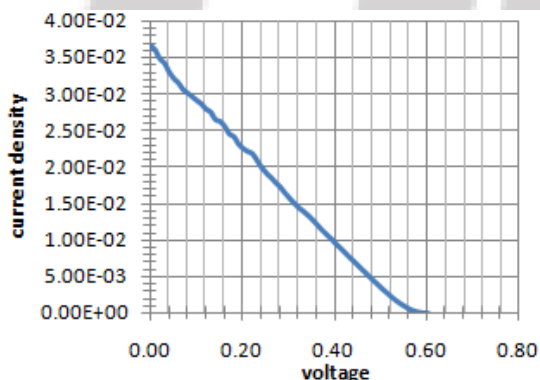


Figure 3.1(b): The 4th quadrant region result of tested halogen illumination of DSSC with *Garcinia indica* Dye result

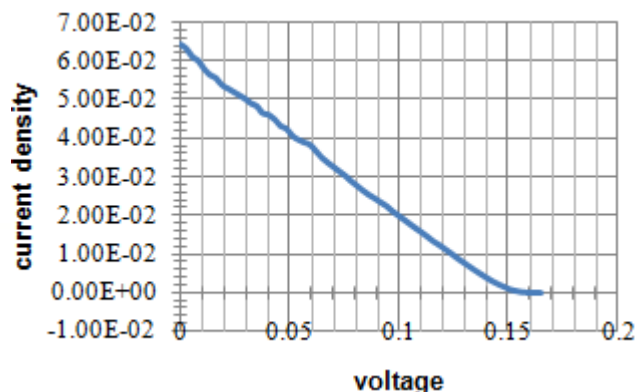


Figure 3.2: The 4th quadrant region result of tested halogen illumination of DSSC with *Syzygium cumini* Dye result.

In the fig. 3.2 the result of halogen present test result shows almost a straight line cutting through $0.16V$.

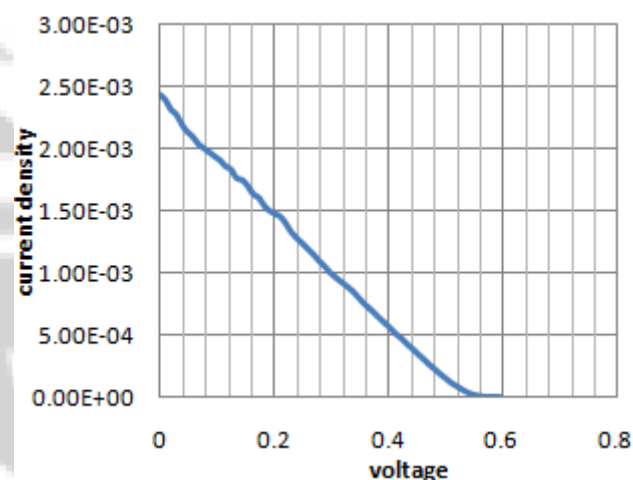


Figure 3.3: The 4th quadrant region result of tested halogen illumination of DSSC with *Pomegranate* Dye expected result.

In the fig. 3.3 the result of halogen present test result shows almost a straight line cutting through $0.57V$. The efficiency (η) and fill factor (FF) of fabricated cell has been calculated using equation (1) and (2).

Table 3.1: Photo-electrochemical parameter of DSSC for all the sensitizers were tabulated

Natural dye	V_{oc} (V)	I_{sc} (mA) / cm^2	P_{max} (mW) / cm^2	V_{mp} (V)	I_{mp} (mA) / cm^2	(FF)	$\eta\%$
Syzygium cumini	0.16	64.5	3.821	0.099	38.6	0.37	0.5
Pomegranate	0.57	2.43	0.31	0.269	1.15	0.224	0.04
Garcinia indica	0.6	36.7	4.89	0.263	18.6	0.22	0.63

Table 3.1 Summarized the performance of the DSSCs in terms of short-circuit photo current (I_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and energy conversion efficiency η compared to those of other extracts. The efficiency of cell sensitized by the *Garcinia indica* was the best among the others. This is due to broader absorption range of the sensitizers, higher interaction between ZnO nano crystalline film and the pigment extracted from *Garcinia indica* which leads to a better charge transfer. The current density and open circuit voltage are 2.43mA and $6V$ respectively. it has higher value of efficiency (0.63%) than the

others But the fill factor of *Syzygium cumini* extracted Dye based DSSC shows best value of 37%

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