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Dye-sensitized solar cells sensitized with natural dye extracted from Indian Jamun

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Abstract

Dye sensitized solar cell (DSSC) is a device which absorbs light from the sun with a layer of dye molecules and directly converts into electric energy. DSSCs based on ZnO have drawn attention worldwide due to their low cost and easy preparation techniques compared to conventional silicon based photovoltaic devices. Silicon based solar cells were the most popular before the emerging of dye-sensitized solar cells. These silicon based solar cells devices have dominated photovoltaic industry until now.

The objectives of this study is to make DSSC using ZnO on ITO coated glass substrate as anode and characterize the DSSC properties such as conversion efficiency, short current density, open circuit voltage, and fill factor. ZnO thin films have been prepared on Indium tin oxide (ITO) glass substrate. These films were used to construct ITO/ZnO/Natural Dye/C/ITO, DSSCs with natural anthocyanin sensitizer extracted from wild Jamun fruits. The cells show open circuit voltage (V_{oc}) of 0.58V, short-circuit current (I_{sc}) of 1.66 mA and 0.58 fill factor (FF) with an conversion efficiency (η) of 1.23 %.

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Keywords: Dye Sensitized Solar Cells; ZnO; Jamun natural dyes; Electrolyte.

1. Introduction

Dye sensitized solar cell (DSSC) is third generation and environmental friendly dye based solar cell. It is the most suitable candidate for the next generation of building integrate photovoltaics [1]. Although a light-to-energy conversion exceeding 12% has been achieved with a liquid electrolyte [2], several practical factors such as the leakage or volatilization of the liquid solvent are still limiting their long term stability and industrial application [3]. It is a device which absorbs light from the sun with a layer of dye molecules and directly converts into electric energy. Gratzel and O'Regan found dye-sensitized solar cells (DSSC), which are regarded as the latest technology in solar cells, in 1991 [4]. For this reason, such cell is called Gratzel cell. The interest in the DSSC has increased with this development. The vision is to produce DSSC from cheap materials in low-cost processes, thus resulting in low-cost electricity production from solar radiation [5].

DSSCs are generally considered much more environmentally benign to produce than conventional silicon-based solar cells because they use relatively non-toxic materials that require little energy to manufacture. Silicon is the primary material comprising today's solar cells. In the manufacturing of most solar cells, silica (SiO_2) must be heavily heated to separate the silicon from oxygen, so that it can be

further processed into a solar cell. Processing silica to produce silicon is an energy-intensive process. At current efficiencies, it takes years for a conventional solar cell to generate as much energy as was used to make the silicon it contains.

Recently, some research groups have achieved conversion efficiencies of 11-12 %, for TiO₂ based dye-sensitized solar cells with inorganic dyes [6-7]. However, these cells still suffer from a high recombination rate between the injected electrons and the oxidized dye or ions in solution. The high recombination rate in DSSCs is attributed to the small size of the particles, which cannot establish significant band banding [8-12]. That is, an electric field that spatially separates the injected electrons from the holes in the dye or solution is not formed at the electrode-electrolyte interface [10]. Until now, the major part of the photoanode DSSC research has mainly focused on TiO₂ nanostructures. However, ZnO semiconductor can be a good alternative as it can exhibit several advantages in comparison with TiO₂ semiconductor, such as a direct band gap (3.37 eV), higher exciton binding energy (60 meV) compared to TiO₂ (4 meV), and higher electron mobility (200 cm² V⁻¹ s⁻¹) over TiO₂ (30 cm² V⁻¹ s⁻¹) for similar band gap energy levels [13-14]. In case of natural dye and ZnO thin film based DSSC solar cell, researchers have achieved efficiencies of less than 2% till date [15-16]. Recently we successfully [17] demonstrated ZnO nanorod based DSSCs with various dyes.

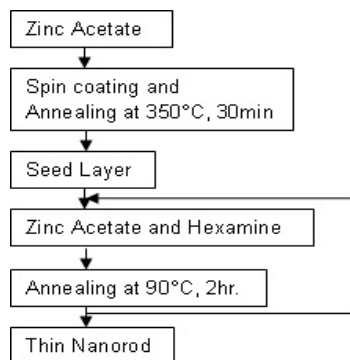
The purpose of this study is to identify the significant *I-V* curve parameters aspects of the nanocrystalline ZnO based DSSC using natural dyes. The knowledge of the significant *I-V* curve parameters aspects will be used as input in further research to increase the efficiency of DSSC and support the development of solar cells as a sustainable alternative for generating electric energy. In this work, we report significant *I-V* curve parameters and efficiency aspects of the nanocrystalline ZnO based DSSC using natural dye Jamun. The coated nanoporous electrode was examined by means of current voltage dependence (*I-V*) of the DSSC solar cell when illuminated and in the dark.

2. Materials and Method

Experimental Section

2.1. Synthesis of ZnO nanorods thin film and counter electrode

ZnO nanorods were synthesized using sol-gel spin coating technique. In this process, we prepared 5 mM solution of Zinc acetate dehydrate, (CH₃COO)₂Zn, 2H₂O, (98% Merck) with methanol. The solution was spun on indium tin oxide (ITO) coated glass substrate at 1000 rpm for 30s. The Zinc acetate solution is spread on a rotating substrate according to [18-19]. The substrates were heated to 350°C in conventional oven for 30 min to yield layers of ZnO islands with their (100) plane parallel to the substrate surface. After evaporation of solvent, a thin ZnO film was formed as shown in flow chart in figure 1. The process was repeated for five to seven times to control the thickness of the film. Concentration of the solution and spinning speed of the substrate also play important roles in adjusting the thickness of the fabricated film.



The counter electrode (cathode) is prepared on another ITO coated glass by using amorphous carbon dust.

2.2. DSSC assembling

DSSCs were assembled following the procedure described in the literature [19]. The amorphous carbon coated counter electrode was placed on the top so that the conductive side of the counter electrode faces the ZnO film. The iodide based solution as the liquid electrolyte (0.5M potassium iodide mixed with 0.05M iodine in water-free ethylene glycol) was placed at the edges of the plates. The liquid electrolyte was drawn into the space between the electrodes by capillary action. Two binder clips were used to hold the electrodes together as shown in figure 2(a) & 2(b).

Figure 1: Flow Chart - Preparation of ZnO nanorod



Figure 2 : (a) ZnO nanorods based DSSCs with natural dyes (b) Liquid Electrolyte KI_3 .

3. Results and Discussion

The morphology of the ZnO samples was observed using a scanning electron microscope (SEM) with a field emission gun operating at 200 kV. Figure 3 displays ZnO nanorod seeds and grow arrays in a wide surface area. The nanorods have an average length of 600 nm diameter ranging from 100 to 200nm and they are mostly vertically aligned with the substrate having hexagonal shapes. The thickness of ZnO film was around $\sim 50 \mu m$.

The solar conversion efficiency (η) of a DSSC can be estimated using the conversion efficiency formula:

$$\eta = \frac{P_{max}}{P_{in}} \quad (1)$$

where P_{max} and P_{in} denote the maximum output power and the input power respectively.

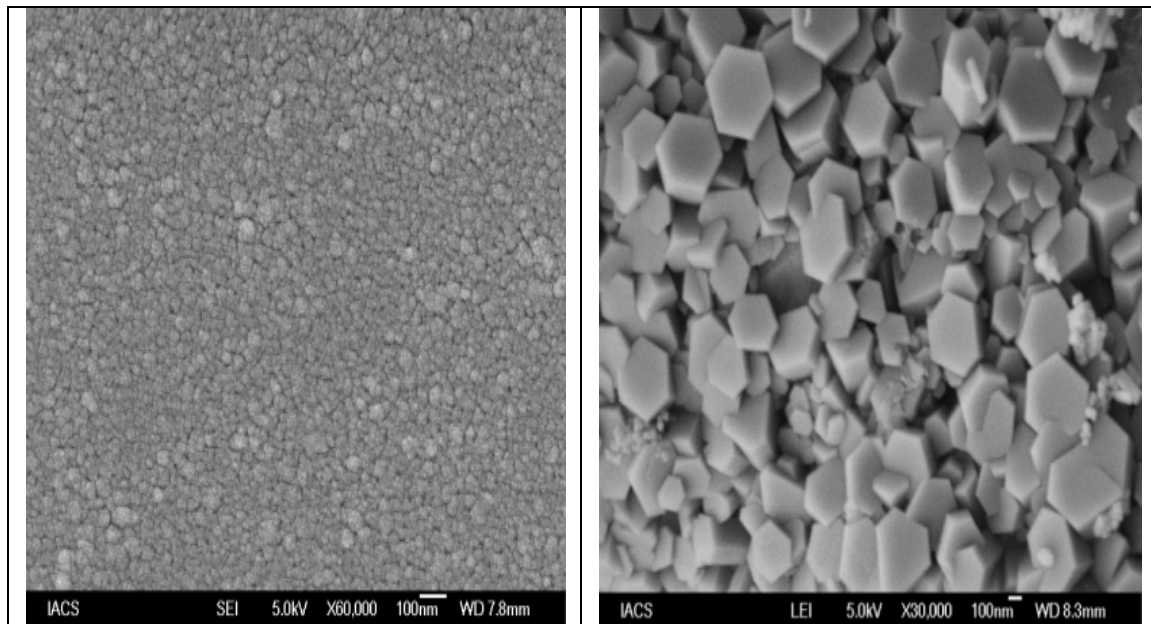


Figure 3: SEM images of seed ZnO and seed grow ZnO.

Since a DSSC usually contains a series resistance, R_s and a shunt resistance, R_{sh} , the fill factor (FF) is introduced to count both effects.

$$FF = \frac{P_{max}}{I_{sc} \times V_{oc}} \quad (2)$$

where V_{oc} is the open-circuit voltage and I_{sc} is the short-circuit current. The solar conversion efficiency of a DSSC can be calculated by,

$$\eta = \frac{I_{sc} \times V_{oc} \times FF}{P_{in}} \quad (3)$$

3.1. The Equivalent Circuit Model of DSSC

A solar cell is generally characterized using the equivalent circuit of the single diode model as shown in figure 4 and the relation between the current I and the voltage V is given by

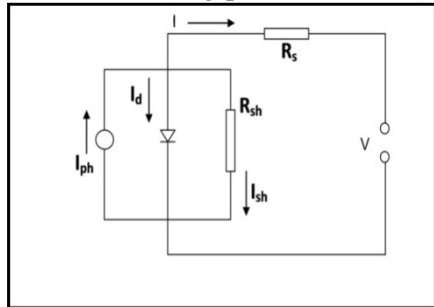
$$I = I_{ph} - I_s \left[\exp \left\{ \frac{q(V + R_s I)}{A k_B T} \right\} - 1 \right] - \frac{V + R_s I}{R_{sh}} \quad (4)$$

where I_{ph} , I_s , R_s , R_{sh} , q , A , k_B , and T are the photocurrent, the saturation current of the diode, the series resistance, the shunt resistance, the electron charge, the ideality factor, the Boltzmann constant, and absolute temperature, respectively. Using equation (4) and fitting I-V curve, physical parameters of DSSC with Jamun dye have found and presented in table 1.

3.2. Performance of the DSSC

We have recorded I - V characteristics of ZnO nanorods based DSSCs using natural dye Jamun with varied external resistances under illumination. Figure 5 shows the current voltage curve with fitting of dye based on DSSC solar cell. The physical parameters open-circuit voltage (V_{oc}), short circuit current (I_{sc}), maximum voltage (V_{max}), maximum current (I_{max}), values of DSSC cell with natural dye were calculated from figure 5 and fitted with the Eq. 4 for one diode equivalent circuit model (Fig. 4) by Newton-Raphson's method. As shown in Fig. 5, very good curve fitting, $R^2 = 0.99$ and $\text{Chi}^2 = 0.003$ were obtained in voltage range 0 - 0.55 V Results of curve fitting are given in Table-1.

The parasitic resistances (series and shunt) of DSSCs are important parameters that affect on efficiency of cell. The resulting parasitic resistances, series (R_s) and shunt resistance (R_{sh}) were evaluated from fitting



I - V curve results. The fill factor (FF) for this cell using natural dye was also evaluated from the I - V characteristics using equation (2) and finally the energy conversion efficiency (η) were calculated using equation (3). All these results are presented in Table-1.

The cell parameters like Ideality factor (A), Fill factor (FF) and energy conversion efficiency (η) of ZnO nanorod based DSSCs with natural dye were calculated and presented in Table-1, where values were calculated from current voltage curve of DSSC cell fabricated with natural Jamun dye.

Figure 4: Equivalent Circuit Diagram of DSSC.

Ideality factor indicates perfectness of the solar cell in the equivalent circuit, and it is 1.0 for a perfect cell. In our observation, an improvement in ideality factor (A) was observed 4.8 for Jamun dye based DSSC.

Table 1. The physical parameters open-circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF) and energy conversion efficiency (η) values calculated from current voltage curve of natural dye DSSC cell.

DSSC/Dye	V_{oc} (V)	I_{sc} (mA)	I_0 (μ A)	FF	R_s (Ω)	R_{sh} (k Ω)	Ideality Factor, A	η (%)
Jamun	0.58	1.56	21	0.58	62	3.25	4.8	1.23

After absorbing photon energy from the illuminated white light, the dye molecules in the DSSC become excited and inject electrons to the left side of ZnO nanorods as shown in figure 6. Due to favorable energy

difference, electron transfer occurs between the lowest unoccupied molecular orbital (LUMO) of the dye and the conduction band of ZnO. The photogenerated electrons percolate rapidly through the ZnO nanorods and are collected by the conducting glass support. The highest occupied molecular orbital (HOMO) of the dye is energetically lower than the redox potential, E_{redox} of the iodide/triiodide couple. The energy difference provides the driving force for hole injection into the electrolyte.

Recombination of charge carrier is also minimized in such devices since transport of only one type of carrier (electron, in general) is energetically possible from the dye to the semiconductor. The reaction mechanisms (5-10) inside the DSSC solar cell are as follows:

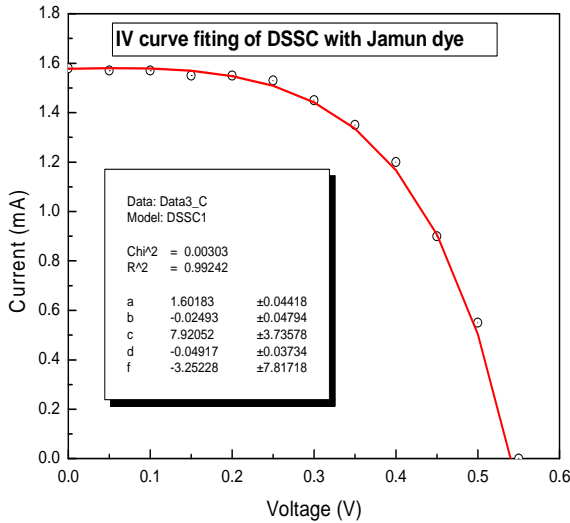
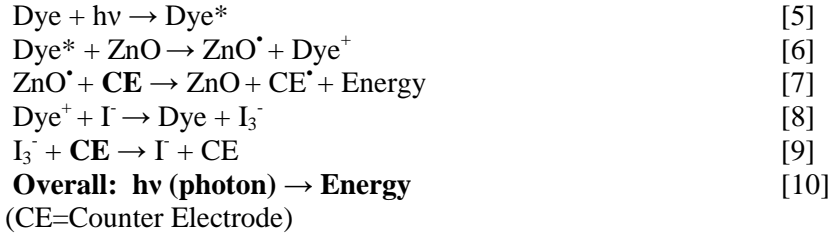


Figure 5: I-V curve fitting of DSSC with Jamun dye.

The incident photon to current efficiency (IPCE) of the ITO coated ZnO based DSSC can affect on the collection efficiency. The recombination process is wavelength dependent because the penetration length of the light increases with the decreases of the absorption coefficient of the dye. In other words, illumination at wavelengths in which the dye absorption coefficient is low leads to the photo injection of electrons a long way from the current collector. If such a distance is longer than the electron diffusion length, these electrons are lost in recombination processes.

A fit of a one-diode model curve to a measured $I-V$ curve is shown in figure 5. The ZnO nanorod based DSSC was prepared at the North Bengal University, Siliguri and is a 50 μm thick cell with only 1.23% efficiency.

The fit parameters are given in the table 1. The fit results give explanations of the low efficiency of

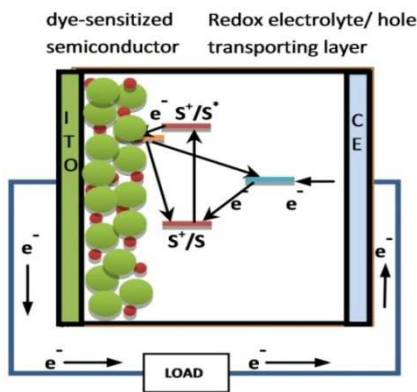


Figure 6: Working Principle of DSSC with dye.

the DSSC: First of all, the dye content of this cell is too low, probably due to a non-optimized ZnO electrode. Secondly, the electron mobility has a relatively low value, probably due to poor electric contacts between the ZnO colloids. The high series resistance R_s of 62 ohm resulting from the fit may be explained by a non-optimized cell design and the fact that there are also contact resistances, which are included in the series resistances of the model. In this case, R_{sh} is too high for this DSSC and limits its performance.

4. Conclusion

Dye-sensitized solar cells (DSSCs) were assembled using extracts from various dyes as sensitizers for nanocrystalline ZnO photoelectrodes. Based on our investigation, it was found that Jamun possesses the photosensitization effect among other extracts of natural dyes studied. Natural dyes as alternative sensitizers for DSSCs are expected to be promising because of many reasons such as the simple preparation technique and low cost. The physical parameters of solar cell: series resistance (R_s), ideality factor (n), saturation current (I_s), shunt resistance (R_{sh}) and photocurrent (I_{ph}) were measured from measured current-voltage characteristics. ZnO thin films have been prepared on Indium tin oxide (ITO) glass substrate. These films were used to construct ITO/ZnO/Natural Dye/C/ITO, DSSC with natural anthocyanin sensitizer extracted from wild Jamun fruits. The cell shows open circuit voltage (V_{oc}) of 0.58V, short-circuit current (I_{sc}) of 1.66 mA and 0.58 fill factor (FF) with an conversion efficiency (η) of 1.23 %. Our research work will help understand the physics of low cost ZnO based DSSCs, predict the efficiency, and facilitate the development of future structures of natural dye based DSSCs.

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