

EFFECT OF BIAS ON THE SOLAR CELL CHARACTERISTICS

Pratik Debnath, Suman Chatterjee

Department of Physics, University of North Bengal, Siliguri-734013, India

Keywords: Dye-sensitized solar cells, Zinc Oxide Nanorods, Photovoltaic properties, Sol-gel method.

Considerable attention was created over the past decade on Dye-sensitized solar cells (DSSCs) as a viable alternate technology for renewable energy. Much attention was attracted due to their high efficiencies and potentially low production costs. In this paper, Dye-sensitized solar cells with natural dyes were successfully synthesized using ZnO nanostructures. ZnO nanorods were grown on an ITO coated glass using sol-gel method and used to fabricate DSSCs using natural dyes and liquid Potassium Iodide electrolyte. Different natural dye were analyzed for its suitability to be used in DSSC and subsequently used to fabricate the cell. Finally the photovoltaic properties of the ZnO based DSSC samples were systematically analyzed. Roles of new sensitizer dye were investigated and the results were compared. The ZnO nanorods grown by the sol-gel method have more uniform thickness. The DSSC structure with Carbon counter electrode yields an open circuit voltage markedly higher from DSSC on an ITO glass and has energy conversion efficiency less than 2%.

1. Introduction

In recent years, great attention has been paid to Dye-sensitized solar cells (DSSCs) due to their low fabrication cost as a viable alternate technology for renewable energy. It has attracted much attention due to their high efficiencies and their potentially low production costs. In this work we grew ZnO nanorods on a ZnO film using sol-gel technique. ZnO has shown a great deal of research interest in DSSCs due to some of its fascinating properties. Compared to other semiconductors, ZnO has unique properties such as large exciton binding energy, wide band gap, high breakdown strength, cohesion and exciton stability.

DSSCs are a promising low cost, green energy source [1,2]. A power conversion efficiency of 11.18% has been achieved in 2005 [3]. DSSC is a device for the conversion of

visible light into electricity, based on the sensitization of wide bandgap semiconductors (e.g, TiO₂, ZnO) [4]. The performance of the cell mainly depends on a dye used as sensitizer. The absorption spectrum of the dye and the anchorage of the dye to the surface of ZnO are important parameters determining the efficiency of the cell [5]. Generally, transition metal coordination compounds (ruthenium polypyridyl complexes) are used as the effective sensitizers, due to their intense charge-transfer absorption in the whole visible range and highly efficient metal-to ligand charge transfer [6]. However, ruthenium polypyridyl complexes contain a heavy metal, which is undesirable from point of view of the environmental aspects [7].

Moreover, the process to synthesize the complexes is complicated and costly. Alternatively, natural dyes can be used for the same purpose with an acceptable efficiency [8,9,10,11,12]. The advantages of natural dyes include their availability and low cost [9]. The sensitization of wide bandgap semiconductors using natural pigments is usually ascribed to anthocyanins. The anthocyanins belong to the group of natural dyes responsible for several colors in the red–blue range, found in fruits, i.e. Rose Bengal. Chlorinyl and hydroxyl groups present in the anthocyanin molecule can be bound to the surface of a porous ZnO film. This makes electron transfer from the anthocyanin molecule to the conduction band of ZnO [6]. As reported [8,9], anthocyanins from various plants gave different sensitizing performances. However, there is no acceptable explanation behind these results, so far.

In this study, DSSCs were prepared using natural dyes Rose Bengal, Bedana and Sea buckthorn as photo sensitizers, as these dye is abundant in tropical countries [11,13,14]. Rose Bengal, Indian origin dye is one of the best photo sensitizer for ZnO photoanode to date and is much cheaper than Ru-complex dyes [11,15,16]. It is in xanthene class which absorbs wide spectrum of solar energy [11,17] and energetically matches the ZnO and usual KI-I₂ redox couple [18,19,20] for DSSCs applications. The absorption spectra of dyes were recorded using a UV–VIS spectrophotometer and the efficiency of the DSSC solar cells related to dye structures is discussed. This would be useful information for selecting xanthene class dyes and also lead to the synthesis of dyes for DSSCs. The performance of DSSCs using the mixed Rose Bengal - Bedana dyes was also investigated [15,21]. Our hypothesis

was that two xanthene having different absorption characteristics would give even more synergistic effect compared to the mixed xanthene–chlorophyll dye reported by B. Pradhan et al. [11]. This is because xanthene has advantages over chlorophyll as DSSC sensitizer [9]

To increase the conversion efficiency of ZnO nanorod-based DSSCs, it would be desirable to eliminate the interface between ITO and the ZnO nanorods. Replacing the ITO layer with a ZnO film could eliminate the heterogeneous interface. Further more, since ZnO is transparent to the whole visible spectrum, it is a good TCO material. Chen et al. have recently carried out this concept by growing ZnO nanorods on a ZnO film using a two-step method [22]. In this work we grew ZnO nanorods on a ZnO film using sol-gel technique. ZnO has shown a great deal of research interest in DSSCs due to some of its fascinating properties.

2. Experimental

2.1. Preparation of ZnO nanorod and counter electrode

Spin-coating is a simple method for preparing ZnO nanoseed from Zinc acetate solution. In this process, we prepared 5mm solution of Zinc acetate dehydrate, $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$, (98% Merck) with distilled methanol. The mixture was well mixed using an ultrasonic bath for 1 h and then the resultant paste was dropped over a conductive indium tin oxide (ITO) coated glass plate having $350 \Omega\text{-cm}$ (Hartford Glass Co., Inc.) and the solution spun at 1000 rpm for 30s using a spin coater. Thus the Zinc acetate solution is spread on a rotating substrate [8,9]. The coated 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 [23]. After evaporation of solvent, a thin ZnO film was formed whose thickness can be controlled by repeating the above process. Concentration of the solution in the spin coater and spinning rate of the substrate are also play important roles in adjusting the thickness of the formed seed layer. Vertical ZnO nanowire arrays on the aligned nanocrystalline seeds were grown by dipping the substrate in the mixture of 5mM soln. $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$, (98% Merck) and 5mm soln. of hexamethyl tetramine, $(\text{CH}_2)_6\text{N}_4$ at 90°C for 1.5hr. The substrates were

removed from the solution, rinsed in deionized water, and dried in room temperature. This method yields one electrode (photoanode).

The counter electrode (cathode) is prepared by deposition of carbon dust (Solaronix, SA) on another conductive ITO coated glass. The molecular structure of used dye is given below **Fig.1(a)**.

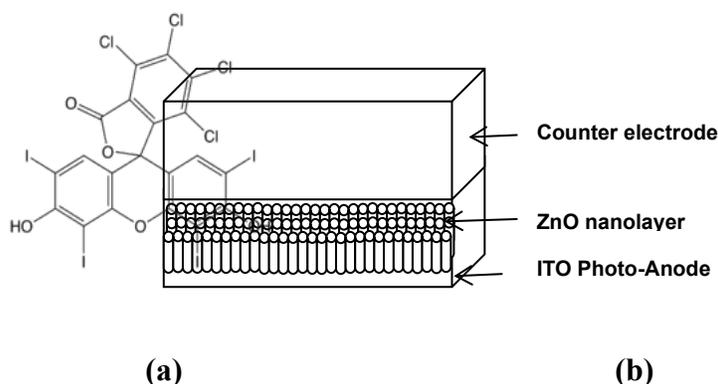


Fig.1 Molecular structure of Rose Bengal (4,5,6,7-tetrachloro-2',4',5',7'-tetraiodofluorescein) and its formula $C_{20}H_4Cl_4I_4O_5$ and molar mass $973.69 \text{ g mol}^{-1}$.

2.2 Dye Deposition.

The device was then immersed in a solution of sensitized dye Rose Bengal for 24 hours to allow the dye molecules to bond covalently to the surface of the ZnO. The sample were then rinsed with ethanol to remove excess dye on the surface and air-dried at room temperature.

2.3. DSSC assembling

DSSCs were assembled following the procedure described in the literature [10], the carbon dust 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 was drawn into the space between the electrodes by capillary action. Two binder clips were used to hold the electrodes together **Fig.1(b)**.

3. CHARACTERIZATION AND MEASUREMENT

3.1. Experimental Setup for I-V Characterization

An Oriel Xenon-lamp (450 Watt) (projector light) was used as the light source, and a digital source pico-ammeter (Keithley 2400) was used to measure the dark-light and illuminated I-V curves of the DSSC during the experiments for efficiency measurement. The position of the light source was adjusted such that the light intensity is 100 mW/cm^2 (the equivalent of one sun at Air Mass of 1.5) is delivered to the surface of the measured DSSC solar cell. The current-voltage characteristics of DSSCs under various light intensities were obtained.

The absorption spectra of dye solution were recorded using an UV-VIS spectrophotometer (Perkin Elmer Lamda-35 model UV-VIS). **Fig.2** shows the light absorption spectra of Rose Bengal dye solution. The absorption spectrum in the visible light scope ranges from 400nm to 800 nm, having peak at 549nm.

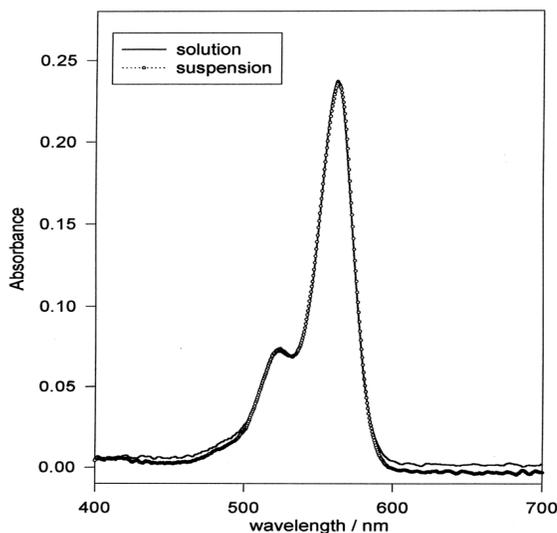


Fig. 2 Light absorption spectra of Rose Bengal dye solution.

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

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

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

$$\text{FF} = P_{\max} / J_{\text{sc}} \times V_{\text{oc}} \quad (2)$$

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

$$\eta = J_{\text{sc}} \times V_{\text{oc}} \times \text{FF} / P_{\text{in}} \quad (3)$$

where P_{in} is the power of incident light.

3.2. Structure Characterization

Fig. 3 shows top view and SEM image of ZnO nanorods. The morphology of the samples was observed using a Field emission scanning electron microscope (FESEM) (Philips XL30FEG) with a field emission gun operating at 200 kV. The nanorods have an average length of 100 nm, diameter ranging from 10 to 20nm and they are mostly vertically aligned with the substrate. A ZnO film of thickness $\sim 2 \mu\text{m}$ can be clearly seen.

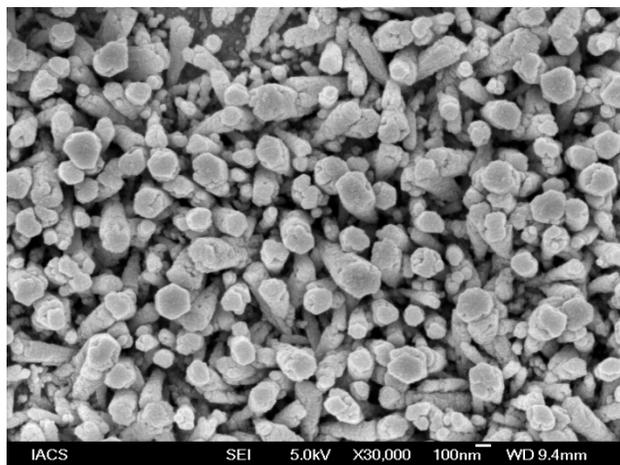


Fig. 3 Scanning electron microscope (SEM) picture of ZnO nano tubes film grown on ITO coated glass plate used in the dye-sensitized solar cell

4 . Results and Discussion

4.1. Photovoltaic Properties

The Power vs. Load resistance is plotted in **Fig.4**. The plot shows the internal resistance of the DSSC cell to be in the order of 2k Ω .

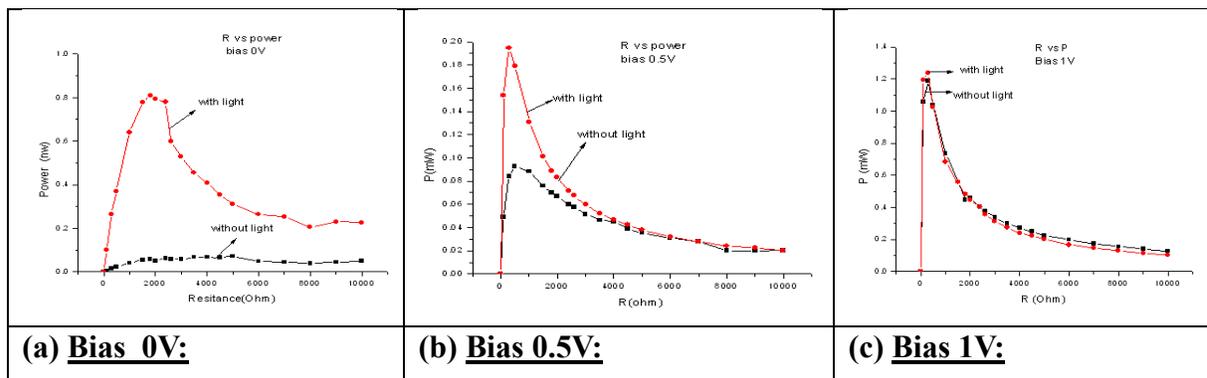


Fig. 4 Power vs. Load resistance characteristics of the fabricated dye-sensitized solar cell
We have recorded I-V characteristics of ZnO nanorods based DSSCs using Rose Bengal dye.

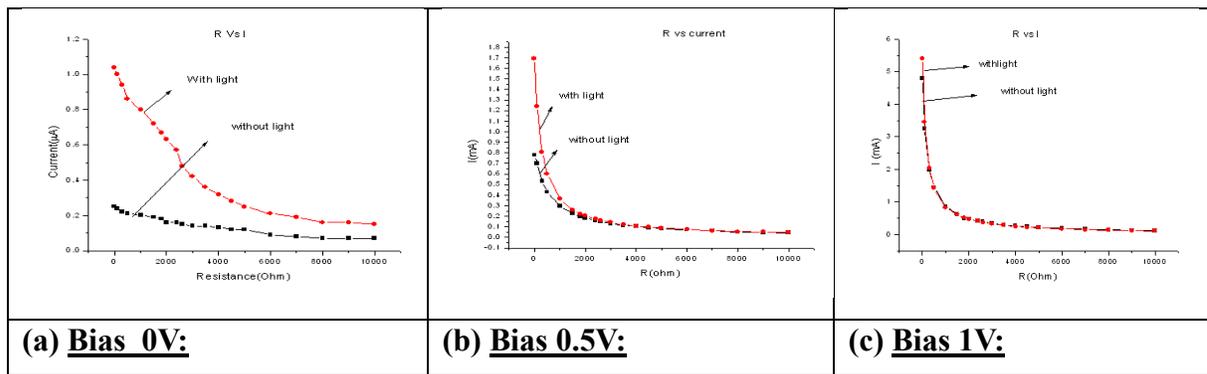


Fig. 5 Photocurrent - Resistance characteristics for ZnO-nanorod DSSC

Fig. 5 shows the photocurrent - resistance characteristics for ZnO-nanorod DSSC at two different biasing condition (0.5V and 1V) with and without light. The DSSC solar cell has an open circuit voltage V_{oc} of 0.35 V and short-circuit current density of $J_{sc} = 1.96 \text{ mA/cm}^2$.

The DSSC has an energy conversion efficiency less than 2% (i.e. $\eta = 1.73\%$). In general, the energy conversion efficiency of ZnO DSSCs is lower than that of TiO₂ DSSCs. Note that the efficiency of ZnO-nanorod-based DSSCs with natural dyes is typically 1% -2% [21]. The parasitic resistances R_s and R_{sh} in DSSCs are major role play in improving efficiency. We also studied the series resistance R_s and shunt resistance R_{sh} of the DSSC from I-V curve using the equivalent circuit one-diode model.

Table 1 The caption of a table.

Description 1*	Description 2	Description 3
Row 1, Col 1	Row 1, Col 2	Row 1, Col 3
Row 2, Col 1	Row 2, Col 2	Row 2, Col 3
Row 3, Col 1	Row 3, Col 2	Row 3, Col 3

* The legend of a table

From the above figures we can say that there is an effect of external bias on the DSSC. First, when the biasing voltage is 0V i.e. there is no bias, without light the DSSC can be taken as a diode. The open circuit voltage of the DSSC creates a depletion region. Hence there is no current flowing. Subsequently, the power is also zero. The experimental results also verify this where the current and power is close to zero without light at zero bias.

Now, in the presence of light, there is current in the cell even when the biasing voltage is zero as the depletion layer gets decreased in the presence of light.

Now we increase the bias voltage to 0.5V. When there is no light, the applied bias voltage reduces the depletion region created by the built-in voltage of DSSC. So, quite a few electrons can go to the conduction band from the valence band. Hence, we get a small current. In the presence of light, the effect of photons and the biasing voltage combined, the number of electrons in the conduction band gets increased and the current is also increased. If the biasing voltage gets increased more (1V in this case), the current also gets increased for both with and without light. From the **Fig 5** we can observe that for 1V bias the value of current for with and without light are very high compared to the previous biasing voltages.

5 . Conclusion

In conclusion, we have demonstrated a new DSSC structure with an ITO coated glass substrate. A ZnO nanorod grown by the sol-gel method. The ZnO nanorods grown by the sol-gel method have more uniform thickness. The DSSC solar cell has found an open circuit voltage V_{oc} of 0.35 V and short-circuit current density of $J_{sc} = 1.96 \text{ mA/cm}^2$. The DSSC has an energy conversion efficiency less than 2% (i.e. $\eta = 1.73\%$). The DSSC structure yields an open circuit voltage markedly higher from DSSC on an ITO glass. We find that the efficiency of ZnO nanostructures based DSSCs is related to the various natural dyes.

Higher electrical conductance in the ZnO film and appropriate dyes are needed to improve the DSSC efficiency. We are confident that these types of fabrication at low cost can also improve efficiency performance of DSSC solar cell by using liquid electrolyte KI3.

Acknowledgements: The authors would like to address their thanks to North Bengal University, Siliguri, India, for financial, infrastructural and technical support of this work.

References

1. B. O'Regan and M. Grätzel, Nature, vol. 353, no. 6346, pp. 737–740, (1991).
2. M. Grätzel, Progress in Photovoltaics, vol. 8, no. 1, pp. 171–185, (2000).
3. M. K. Nazeeruddin, F. de Angelis, S. Fantacci, et al., Journal of the American Chemical Society, vol. 127, no. 48, pp. 16835–16847, (2005).
4. M. Gratzel, J. Photochem. Photobiol. C 4(2003) 145
5. K. Tennakone, G.R.R.R.A. Kumara, A.R. Kumarasinghe, P.M.Sirimanne, K.G.U. Wijayantha, J. Photochem. Photobiol. A 94(1996) 217.
6. S. Hao, J. Wu, Y. Huang, J. Lin, Sol. Energy 80 (2006) 209.
7. Y. Amao, T. Komori, Biosensors Bioelectron. 19 (2004) 843.

8. A.S. Polo, N.Y. Iha, Sol. Energy Mater. Sol. Cells 90 (2006) 1936.
9. C.G. Garcia, A.S. Polo, N.Y. Iha, J. Photochem. Photobiol. A 160 (2003) 87.
10. G.P. Smestad, Sol. Energy Mater. Sol. Cells 55 (1998) 157.
11. Basudev Pradhan, Sudip K. Batabyal, Amal J. Pal, Sol. Energy Mater. Sol. Cells 91 (2007) 769-773.
12. N.J. Cherepy, G.P. Smestad, M. Graetzel, J.Z. Zang, J. Phys. Chem. B 101 (1997) 9342.
13. T. Frank, J. Clin. Pharmacol. 45 (2005) 203.
14. N. Terahara, N. Saito, T. Honda, K. Tokis, Y. Osajima, Phytochemistry 29 (1990) 949.
15. B. Pradhan, A. Bandyopadhyay, A. J. Pal, Appl Phys. Lett. 85 (2004) 663.
16. S. Bandhopadhyay and A. J. Pal, J. Phys. Chem. B (2003), 107, 2531-2536.
17. H. Tsubomura, M. Matsumura, Y. Nomura, T. Amamiya, Nature 261 (1976) 402
18. N.W. Duffy, L.M. Peter, R.M.G. Rajapakse, K.G.U. Wijayantha, J.Phys.chem. B 104 (2000) 8916.
19. M. Graetzel, Nature, (2001), 114, 338-344.
20. M. Law, Lori E. Greene, Justin C. Johnson, Richard Aykally and Peidong Yang. Nat. Mat. (2005),4,455-9.
21. H. Tsubomura, M. Matsumura, Y. Nomura, T. Amamiya, Nature 261 (1976) 402
22. H. Chen, A. Du Pasquier, G. Saraf, J. Zhong, and Y. Lu, Semiconductor Science and Technology, vol. 23, no. 4, Article ID 045004, (2008).