

Fabrication and Electrical Properties of Dye Sensitized Solar Cells Using Henna, Beetroot and Amla Dyes

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Abstract: *Dye sensitized solar cells were fabricated using natural dyes extracted from beetroot, henna and Amla. The ZnO nanorod working electrode has been prepared by simple hydrothermal method. The crystallinity and morphology of the prepared electrode has been studied using X-ray diffraction and scanning electron microscopy techniques. The effect of natural dye extract temperature, pH of the dye and the solvent used for dye preparation on the solar cell characteristics have been studied. The efficiency of henna extract sensitized ZnO nanorod solar cells are found to be better than the other solar cells sensitized using beetroot and Amla extracts.*

Keywords: Henna, ZnO Nanorods, Natural dyes, Dye Sensitized solar cells.

1. Introduction

The DSSC is an attractive and promising device for solar cell applications that have been intensively investigated worldwide, and its PV mechanism is well understood [9–18]. Recently, commercial applications of the DSSC have been under intensive investigation. The cost of commercially fabricating DSSCs is expected to be relatively low because the cells are made of low-cost materials and assembly is simple and easy. Dye-sensitized solar cells (DSSC) have attracted much attention in relation to photovoltaic cells and the search for cheap and effective sources of renewable energy [1]. The overall efficiency of power conversion of a DSSC is controlled by the primary processes electron injection, charge recombination, dye regeneration and electron collection at the electrode [2]. Charge separation occurs initially in the dye upon irradiation; electrons subsequently proceed to the interface between the dye and TiO₂ through a bridge or link. Careful design of the structure of the dye with appropriate links can thus minimize the rate of charge recombination; to improve the cell performance [3]. The design of various links that spatially separate the dye chromospheres and TiO₂ provides a model system for fundamental investigation. For flexible links, the insertion of saturated –CH₂– groups into the dye significantly diminished the coupling of electrons between the dye and TiO₂, leading to a markedly decreased rate of electron injection [4-8]. The dye-sensitized solar cell consists of an electrode with wide band gap semiconductor such as TiO₂ or ZnO sensitized using a suitable dye, a redox electrolyte and a counter electrode. 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 [9]. 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 [10-12].

In a dye sensitized solar cell, ruthenium based complex sensitized solar cells have exhibited maximum efficiency of 12% and they are the preferred materials for dye sensitization [13]. However, ruthenium based synthetic dyes are relatively expensive for large-scale applications in solar cells and also involve complex synthetic procedures [14]. In order to replace the expensive ruthenium compounds, many kinds of natural dyes have been investigated and tested as low-cost materials and environmentally friendly alternatives to artificial sensitizers for dye sensitized solar cells [15-16].

In this work, ZnO nanorod like structures have been prepared by simple sol-gel hydrothermal method and used as a working electrode for dye sensitized solar cells. Natural dyes extracted from beetroot, henna and Amla have been used to sensitize the working electrode and solar cells have been fabricated and the characteristics of these dye sensitized solar cells have been studied [17].

2. Experimental

2.1. Deposition of Indium Doped Tin Oxide Thin Films (ITO)

100 cc of 2 M stannic chloride solution was prepared in doubled distilled water and 14.285 gm of Indium chloride was dissolved in it, to obtain the 20% doping concentration of Indium. A few drops of oxalic acid were added in it for removal of whitish precipitate from the above mixture, 10 cc solution was taken as a precursor solution and 10 cc of propane 2-ol was added in it which gives the 20 cc spraying solution. The final solution was sprayed through the specially designed glass nozzle at the spray rate of 5 cc per minute. The substrate temperature was maintained at 475°C. It is found that, the conducting glasses have 10-20 C/cm² sheet resistance and about 90% transparency.

2.2. Preparation of Working Electrode

In our experiment, indium doped tin oxide (ITO) glass substrate was used as Substrate. All the chemicals used in the experiment were purchased from Aldrich. Initially, the ITO glass substrates were ultrasonically soaked in acetone and ethanol, and then dried at 100 °C in an oven. To synthesize ZnO nanorods, two step chemical methods have been used. In the first step, ZnO seed layer has been prepared by simple sol-gel method. The detail for the preparation of seed layer is as described in one of our earlier works [18, 19]

To prepare ZnO seed layer, 0.3 M of zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was dissolved in a mixture of 10 mL ethanol and 0.25 mL water. ITO coated glass substrates were dipped in the prepared solution and this resulted in the formation of seed layer, these seed layer films are annealed at 300 °C for 30 minutes. In the second step, ZnO nanorods have been prepared by hydrothermal method. To prepare ZnO nanorods, an aqueous precursor solution was prepared by dissolving 0.02 M zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.2M hexamethylenetetramine ($(\text{CH}_2)_6\text{N}_4$) in 20 mL deionized water. The solution was transformed into teflon stainless steel autoclave and the seed layer coated substrate was vertically dipped in the aqueous solution and it was maintained at a bath temperature of 85 °C for 4 hrs. After the growth period, the substrates were removed from the solution and were thoroughly washed with deionized water to remove the residual salt from the surface of the film. Now the prepared film was annealed at 450 °C for 30 minutes and this resulted in the formation of ZnO nanorods [17-20].

2.3. Preparation of Natural Dye Sensitizer

For henna extract preparation fresh henna leaves were put into 100 mL of ethanol. Solid dregs in the solution were filtered by filter paper to obtain a pure natural dye solution. For beetroot and amla extract preparation, the cleaned vegetable and fruits were cut into small pieces and put into two different beakers. Chopped vegetable and fruits were soaked in 200 ml of ethanol at different temperatures. Then the residual parts were removed by filtration and the filtrate was washed with hexane several times to remove any oil or chlorophyll present in the extract. This was directly used as dye solution for sensitizing ZnO nanorod electrodes. The henna extract was extracted from the ethanol solvent at different temperatures such as room temperature, 50 °C, 75 °C and 100 °C. To study the effect of pH on the performance of solar cell, the pH of the henna extract solution was changed by adding dilute HCl and dye solution with three different pH values 1.0, 2.0 and 3.0 have been used as sensitizer. To study the effect of extracting solvent on the performance of solar cell, the henna extract was also extracted by using methanol. By using methanol the natural dye was extracted at a temperature of 75 °C [17].

2.4. Assembling the Solar Cell

To assemble the natural dye sensitized ZnO nanorod based solar cell, the prepared ZnO nanorod electrode were immersed in the synthesized dye solution at room temperature for 24 h, after that period the film was rinsed in anhydrous ethanol and then dried (Fig.1). A carbon-coated ITO electrode was then placed over the dye-adsorbed ZnO

nanorod electrode. A redox electrolyte was prepared using 0.5 mol KI, 0.05 mol I_2 , and 0.5 mol 4-tert-butylpyridine and a drop of electrolyte solution was injected into the into the cell. The photocurrent-voltage (J-V) characteristics of the devices were measured using white light from a xenon lamp (max.150 W) using a sun 2000 solar simulator (MHRD & IIT-BOMBAY). Light intensity was adjusted using a Si solar cell to ~AM-1.5. Incident light intensity and active cell area were 100 mWcm^{-2} (one sun illumination) and 0.4 cm^2 ($0.5 \times 0.8\text{cm}$), respectively.

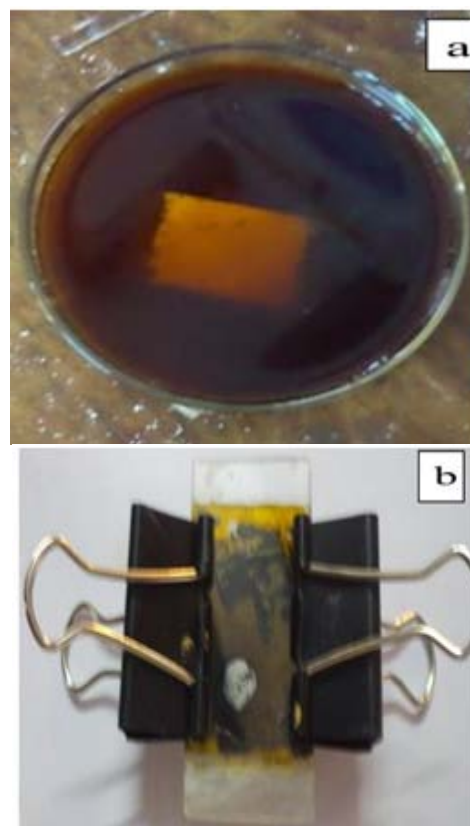


Figure 1: (a) prepared ZnO nanorod electrode were immersed in the Synthesized dye solution (b) Assembly of the Solar Cell Structure

3. Results and Discussion

Figure.2 (a, b, c) shows the photocurrent density-voltage (J-V) characteristics of natural dyes (prepared at room temperature) sensitized ZnO nanorod based solar cells.

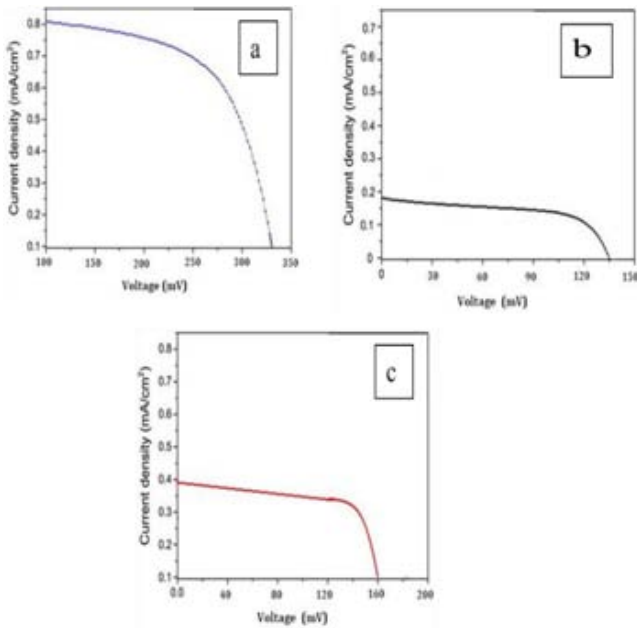


Figure 2: (a, b, c). (J-V) characteristics of natural dyes (Henna, Amla, Beetroot)

The conversion efficiency (η) of the Henna extract sensitized ZnO nanorod based solar cell is 0.65% with short circuit current density of 0.84 mA/cm², open circuit voltage of 324 mV and fill factor of 0.24, while the conversion efficiency (η) of the beetroot extract sensitized solar cell is 0.1% with a short circuit current density of 0.39 mA/cm², open circuit voltage of 160 mV and fill factor of 0.26. The conversion efficiency (η) of the Amla extract sensitized solar cell is 0.07% with a short circuit current density of 0.18 mA/cm², open circuit voltage of 127 mV and fill factor of 0.31 (Table.1).

Table 1: Solar cell parameters of the ZnO nanorod based solar cells Sensitized with different natural dyes.

Natural Dyes	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF	Cell Efficiency η %
Amla	127	0.18	0.31	0.07
Henna	324	0.84	0.24	0.65
Beetroot	160	0.39	0.26	0.16

The pH of the dye extract has an important effect on the performance of henna natural dye sensitized solar cells and it is shown in Table 2. The solar cells fabricated using ZnO nanorod sensitized using dye extract with pH values 1, 2 and 3 show efficiency values of 0.60%, 0.66%, 0.64 % respectively(Fig.3).

Table 2: Solar cell parameters of the cells sensitized with Henna dye extracted with different pH values

pH	Voc (V)	Jsc (mA/cm ²)	FF	Cell Efficiency η %
1	312	0.31	0.62	0.60
2	397	0.47	0.36	0.66
3	361	0.39	0.46	0.64

The dyes synthesized at pH = 2 shows good interaction with the working electrode, the reason is at pH = 2, the hennotannic acid existed as lawsone ion, which is stable form of lawsonia; an increasing pH hydrated this ion to quinonoidal bases. However, the cell deterioration by acid leaching is expected as the pH goes lower (pH = 1), which results in a lower efficiency.

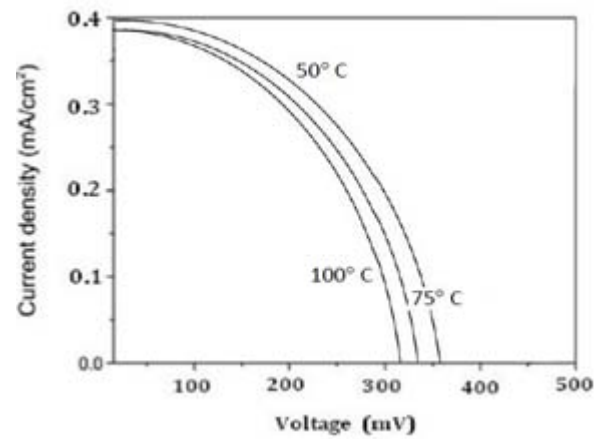


Figure 3: J-V characteristics of Henna extract sensitized solar cells extracted at different pH values

The effect of dye ex-tracting temperature on the performance of dye sensitized solar cells is shown in Table 3. Solar cell sensitized using dye extracted at 50 °C shows a power conversion efficiency of 0.92%, with V_{oc} of 345 mV, J_{sc} of 0.42 mA/cm² and FF of 0.64. Solar cell sensitized using the dye extracted at 75 °C shows power conversion efficiency of 1.08%, with V_{oc} of 336 mV, J_{sc} of 0.38 mA/cm² and FF of 0.85. Solar cell sensitized using dye extracted at 100 °C shows a conversion efficiency of 0.94% with V_{oc} of 329 mV, J_{sc} of 0.39 mA/cm² and FF of 0.74(Fig.4).

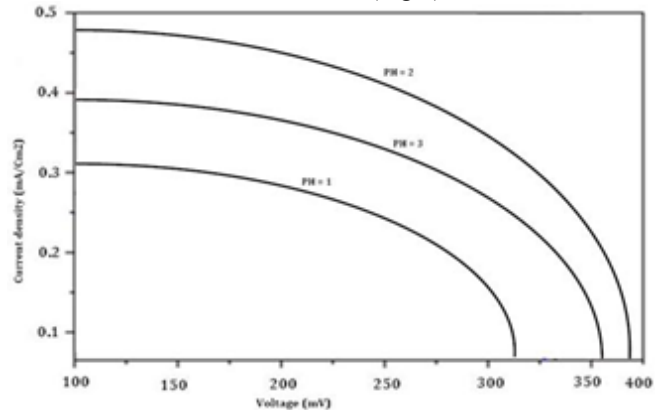


Figure 4: J-V characteristics of Henna extract sensitized Solar cells e at different temperatures

Table 3. Solar cell parameters of the cells sensitized with Henna dye extracted with different temperatures.

Temperature (°C)	Voc (V)	Jsc (mA/cm ²)	FF	Cell Efficiency η %
Room temp	370	0.36	0.49	0.65
50 °C	345	0.42	0.64	0.92
75 °C	336	0.38	0.85	1.08
100 °C	329	0.39	0.74	0.94

Table 4. Solar cell parameters of the cells sensitized with Henna dye extracted with different solvents

Solvent	Voc (V)	Jsc (mA/cm ²)	FF	Cell Efficiency η %
Ethanol	332	0.37	0.86	1.05
Methanol	339	0.42	0.68	0.96

Figure 5.shows the photocurrent density-voltage (J-V) characteristics of natural dye (extracted using different solvent) Sensitized ZnO nanorod based solar cells. As shown in Table 4, the solar cells prepared using natural dye

extracted in ethanol shows a higher efficiency than that of solar cells prepared using natural dye extracted in methanol.

The Figure (5) clearly shows that the dye extracted using methanol absorbs less light compared to that of the dye extracted using ethanol.

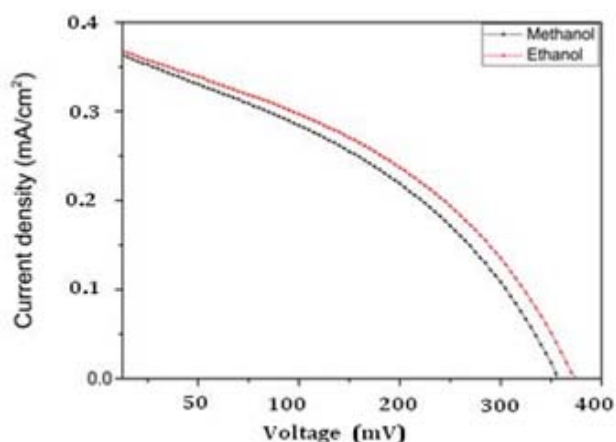


Figure 5. J-V characteristics of natural dye (extracted using different solvent)

Finally, DSSCs as promising alternatives to the conventional silicon based solar cells require specific modifications and inspired connections before they can be applied to a production line. The electrolyte thickness, the efficient current collection, and effective isolation of the cells to the module are of the main issues to be solved before.

4. Conclusion

The TiO₂ working electrodes have been prepared by simple hydrothermal method on ITO glass substrate. The ITO thin films have been prepared by spray-pyrolysis method. The prepared ZnO nanorod working electrode was sensitized with natural dyes extracted from Amla, Beetroot and Henna. The efficiency of Henna extracts sensitized solar cell shows better performance than the other dye sensitized solar cells. It was also found that the efficiency of the dye sensitized solar cells can be enhanced by changing the solvent used in the preparation of the dye, changing the dye extracting temperature and pH of the extract. Ethanol is found to be the suitable solvent for natural dye, the optimum dye extracting temperature is found to be 75 °C and the suitable value of pH is found to be 2. The main factors of limitation were found to be the current collector material and structure while the internal resistance of the cell depending on the ITO glass substrate and electrolyte do also affect the overall efficiency.

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References

[1] M. Grätzel, Nature, 2001, 414, 338;

- [2] T. W. Hamann, R. A. Jensen, A. B. F. Martinson, H. V. Ryswyk and J. T. Hupp, Energy Environ. Sci. 2008, 1, 66;
- [3] K. Kilsa, E. I. Mayo, D. Kuciauska, R. Villahermosa, N. S. Lewis, J. R. Winkler and H. B. Gray, J. Phys. Chem. A, 2003, 107, 3379;
- [4] J. R. Stromberg, A. Marton, H. L. Kee, C. Kirmaier, J. R. Diers, C. Muthiah, M. Taniguchi, J. S. Lindsey, D. F. Bocian, G. J. Meyer and D. Holten, J. Phys. Chem. C, 2007, 111, 15464;
- [5] J. Rochford, D. Chu, A. Hagfeldt and E. Galoppini, J. Am. Chem. Soc., 2007, 129, 4655;
- [6] N. R. de Tacconi, W. Chanmanee, K. Rajeshwar, J. Rochford and E. Galoppini, J. Phys. Chem. C, 2009, 113, 2996.
- [7] N. A. Anderson and T. Lian, Coord. Chem. Rev., 2004, 248, 1231;
- [8] M. Myahkostupov, P. Piotrowiak, D. Wang and E. Galoppini, J. Phys. Chem. C, 2007, 111, 2827
- [9] Kim, Y. T.; Park, J.; Kim, S.; Park, D. W.; Choi, J. Electrochemical Acta 2012, 78, 417.
- [10] Jiang, C. Y.; Sun, X. W.; Lo, G. Q.; Kwong, D. L.; Wang, J. X. Appl. Phys. Lett. 2007, 90, 263501
- [11] Baxter, J. B.; Aydil, E. S. Appl. Phys. Lett. 2005, 86, 053114
- [12] Ko, S. H.; Lee, D.; Kang, H. W.; Nam, K. H.; Yeo, J. Y.; Ong, S. J. Nano Letters 2011, 11, 666.
- [13] Yella, A.; Lee, H. W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W. G.; Yeh, C. Y.; Zakeeruddin, S. M.; Grätzel, M. Science 2011, 334, 629.
- [14] Zhu, H.; Zeng, H.; Subramanian, V.; Masarapu, C.; Hung, K. H.; Wei, B. Nanotechnology 2008, 19(46), 465204.
- [15] Chang, H.; Lo, Y. J. Sol. Energy 2010, 84, 1833.
- [16] Zhou, H.; Wu, L.; GAO, Y.; Ma, T. J. Photochem. Photobiol. A. Chem 2011, 219, 188.
- [17] ZnO Nanorods Based Dye Sensitized Solar Cells Bull. Korean Chem. Soc. 2014, Vol. 35, No. 4
- [18] Senthil, T. S.; Muthukumarasamy, N.; Kang, M. Mater. Lett 2013, 102-103, 26
- [19] Gomez-Ortiz, N. M.; Vazquez-Maldonado, I. A.; Perez-Espadas, A. R.; Mena-Rejon, G. J.; Azamar-Barrios, J. A.; Oskam, G. Sol. Energy Mater. Sol. Cells 2010, 94, 40.
- [20] Han, Z.; Liao, L.; Wu, Y.; Pan, H.; Shen, S.; Chen, J. J. Hazard. Mater. 2012, 217-218, 100.

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