Research Journal of Physical Sciences ISSN 2320–4796
Vol. **5(5),** 6-10, June **(2017)** *Res. J. Physical Sci.*

Synthesis and study of zinc oxide nanoparticles for dye sensitized solar cell

Sabita Sharma[1], Subash Chandra Bhandari[1], Shankar Prasad Shrestha[2] and Leela Pradhan Joshi[1*]
[1]Department of Physics, Amrit Campus, Tribhuvan University, Kathmandu, Nepal
[2]Department of Physics, Patan Multiple Campus, Tribhuvan University, Kathmandu, Nepal
leela.pradhan@gmail.com

Available online at: www.isca.in, www.isca.me
Received 15th April 2017, revised 21st May 2017, accepted 1st June 2017

Abstract

This article presents observation of structural, morphological, and optical properties of ZnO nanoparticles and its thin films. The Zinc Oxide nanoparticles were first synthesized by precipitation method from precursor solutions of zinc nitrate and sodium hydroxide. Thin films of ZnO were then prepared using the paste of ZnO with acetic-acid glacial, and Triton X-100 in ethanol on FTO substrates by doctor blade method. X-ray diffraction pattern of ZnO powder annealed at (500 ± 5) ^oC shows the hexagonal wurtzite structure with preferred orientation along (101) planes. Average grain size of ZnO using Williamson-Hall plot was found to be of 38 nm. Scanning Electron Microscope image of thin film of ZnO depicts the rod-like structures of ZnO. The optical direct band gap of the ZnO thin film was found to be of 3.18 eV. As-prepared ZnO nano structured thin films sensitized by dye extract of Callistemon citrinus were then used as photo anodes to fabricate the dye sensitized solar cells. The performance of assembled DSSC was tested by current-voltage characteristic curves under the sunlight illumination. The fill factor of DSSC assembled from ZnO loaded with dye at (60 ±5) ^oC was calculated to be of 0.47.

Keywords: Nanostructure, Dye sensitized solar cell, *Callistemon citrinus* dye, Precipitation method, W-H plot.

Introduction

Nanostructures of Zinc Oxide (ZnO), after titanium dioxide (TiO_2), have been considered as the potential future generation semiconductors for the fabrication of dye sensitized solar cells[1,2]. ZnO possesses exceptional properties such as wide direct band gap (3.37 eV), high electron mobility (100 $cm^2V^{-1}s^{-1}$), large exciton binding energy (60 meV), good transparency and strong room temperature luminescence and high chemical and thermal stability[3-5]. These properties facilitate ZnO to become a highly demanded semiconducting material in material science. It has been used in making nanoscale devices such as solar cells, varistors, gas sensors, thin film transistors, photodetectors, light-emitting diodes[6-7]. ZnO nanopoarticles can be synthesized employing a number of processes: mechanochemical, precipitation, hydrothermal, solvothermal, sol-gel, emulsion and microemulsion, vapour deposition, sonochemical[6-9]. One of the cost effective and efficient methods among mentioned above is a precipitation method. Thin films of ZnO are then prepared using nanoparticles of ZnO by doctor blade for dye-sensitized solar cell (DSSC). DSSC is consisted of a dye loaded nanocrystalline porous semiconductor photo anode, a redox liquid electrolyte for mediating electron transfer processes, and a counter electrode[10]. The performance of DSSC depends on the nature of dye used and its interaction with ZnO nano film layers, the study on interaction between dye and ZnO surface is vital. This article reports on the preparation of ZnO nanoparticles from the precursor solutions of zinc nitrate, and sodium hydroxide using a precipitation method and its utilization for *Callistemon citrinus* sensitized ZnO based dye-sensitized solar cell assembly for the first time.

Materials and methods

Nanoparticles of zinc oxide were synthesized by precipitation method using zinc nitrate hexahydrate [$Zn\ (NO_3)_2.6H_2O$], sodium hydroxide (NaOH) and ethanol[11]. First of all, 0.5 M zinc nitrate solution was prepared in ethanol with continuous stirring for an hour. Simultaneously, 0.9 M ethanolic solution of sodium hydroxide was prepared with a continuous stirring for two hours in another beaker. The later solution was added to $Zn\ (NO_3)_2$ solutions drop wise, with vigorous stirring resulting to produce white precipitate. After complete addition, the mixture was allowed to settle for 24 hours. The precipitate formed here was centrifuged four times at rpm 850, with ten minutes each time for removal of supernatant liquid. The final precipitate was washed three times with distilled water, and finally with ethanol and dried at (500 ± 5) °C for 14 hours.

The reactions involved in the experiment can be described as follows[9,11]:

$$Zn(NO_3)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaNO_3 + 6H_2O$$
$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

To prepare thin film of ZnO in a doctor blade method firstly, we have grinded 0.5 gm of ZnO powder in a mortar with acetic acid glacial and Triton X-100. Then, 2.5 ml of ethanol was added, and the paste was sonicated for half an hour to form very smooth paste[12]. Thin films of this paste were then deposited on clean FTO substrates which were then heated at (150 ± 5) ℃ for 15 minutes and (400 ± 5) ℃ for an hour. The structural study of as synthesized ZnO powder was performed by X-ray diffraction (XRD) technique. A Bruker D2 phaser diffractometer, operating at the voltage 30 KV and current 10 mA, available at Nepal Academy of Science and Technology (NAST), Khumaltar, Nepal, was employed for that purpose. An incident beam of CuK_{α} (λ=1.5418Å) was used and the scanning angle for 2θ ranged from 0° to 80°. The surface morphology of thin film of ZnO was then studied using scanning electron microscope at the University of Warsaw, Poland. Band gap of ZnO was calculated using the Tauc plot from the captured transmission data using, UV-visible spectrophotometer (Ocean Optics, USB 2000, Singapore (Figure-3) using the equation 1[13]:

$$\alpha h\nu = B(h\nu - E_g)^{\frac{1}{2}} \quad (1)$$

Where: E_g is the direct band gap, h is Planck's constant and B is an energy independent constant[14]. The dye extract solution from bottle brush flower was prepared to sensitize the ZnO film for dye sensitized solar cell fabrication. The work was first attempt to study the interaction between dye molecules and ZnO. Locally available *Callistemon citrinus* locally named bottle brush flowers were collected and washed multiple times with distilled water. They were dried in ambient temperature for a week, and dried at (50 ± 5)℃ for another week. Finally, 1 gm of crushed powder was dissolved in 30 ml of ethanol with continuously stirring the mixture for half an hour and leaving it overnight at room temperature of 24℃. The final solution was then decanted using a clean strainer[15]. Above prepared ZnO samples were then soaked into dye solution at room temperature 24℃ and (60 ± 5)℃ for an hour. Ultimately, these dye loaded samples were rinsed with ethanol to remove excess dyes, and dried off in air at room temperature. An electrolyte of iodine-triiodide redox couple was prepared by mixing 0.5 M potassium iodide and 0.05 M iodine in ethylene glycol for DSSC assembly[16]. Solar cells were fabricated, using dye sensitized ZnO photo anodes, graphite coated FTOs as counter electrodes and potassium iodide-iodine liquid electrolyte. The DSSC performance was measured with the help of Digital Fluke multimeters in presence and absence of sunlight. I-V measurements were taken for both solar cells in presence of sunlight of intensity (870 ± 10) W/m^2. Also, I-V measurement was taken in dark light having intensity (80 ± 5) W/m^2 for the solar cell in which dye was loaded at. (60 ± 5)℃, to ensure the power has indeed been generated from the solar cell.

Results and discussion

Figure-1a shows the XRD pattern of the as-synthesized ZnO powder. An intense peak is observed at 2θ = 36.5573° that corresponds to (101) plane (JCPDS card no. 36-1451) of wurtzite crystal structure of ZnO. Other peaks observed at 2θ = 32.0855°, 34.7322°, 47.8682°, 56.8764°, 63.1458°, 66.7067°, 68.2255°, 69.3465°, 72.8421° and 77.2236° show orientation along (100), (002), (102), (110), (103), (200), (112), (201), (004) and (202) planes respectively. The grain size of the ZnO was calculated by Williamson-Hall plot shown in Figure-1b where: λ is wavelength of X-ray, β is full width at half maximum (FWHM) of the peak and θ is Bragg's angle[17]. The average grain size was calculated using the equation 2. Table-1 shows the d-spacing and FWHM of each ZnO peaks of XRD profile.

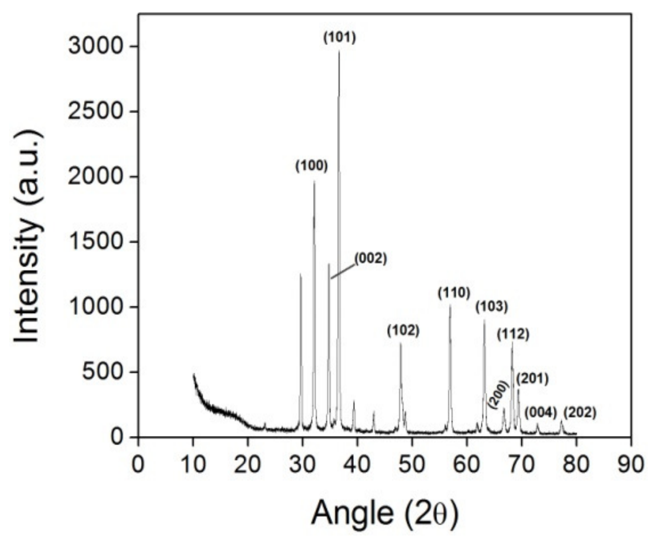

Figure-1a: XRD of ZnO powder prepared by precipitation method.

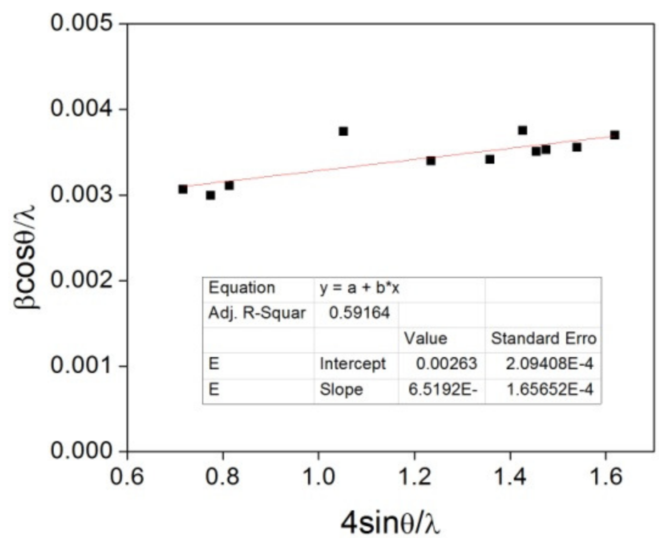

Figure-1b: Williamson-Hall plot corresponding to above XRD peaks.

$$\frac{\beta cos\theta}{\lambda} = \frac{1}{D} + \varepsilon\frac{4sin\theta}{\lambda} \quad (2)$$

Linear fit of $\beta\cos\theta/\lambda$ versus $4\sin\theta/\lambda$ plot was performed, and the reciprocal of the y-intercept gives the crystallite size of 38 nm.

Table-1: 2θ, FWHM and d -spacing corresponding to observed XRD peaks of ZnO.

2θ (Deg)	FWHM (Deg)	Obs. (d/ Å)	JCPDS (d / Å) (hkl)
32.0855	0.2818	2.7863	2.8143 (100)
34.7322	0.2773	2.5798	2.6033 (002)
36.5573	0.2892	2.4550	2.4759 (101)
47.8682	0.3617	1.8980	1.9111 (102)
56.8764	0.3413	1.6169	1.6247 (110)
63.1458	0.3542	1.4706	1.4771 (103)
66.7067	0.3971	1.4005	1.4071 (200)
68.2255	0.3740	1.3730	1.3781 (112)
69.3465	0.3789	1.3535	1.3582 (201)
72.8421	0.3906	1.2969	1.3017 (004)
77.2236	0.4182	1.2339	1.2380 (202)

Figure-2 shows the scanning electron microscope (SEM) image of ZnO film prepared by doctor blade method with 200nm of resolution. The picture clearly depicts the development of rod-like structures along with a number of voids. The average diameter of the unit structure with respect to the scale bar provided at the bottom of figure was found to be 57 nm. This is bigger than the crystallite size calculated from XRD because of agglomeration formed during film preparation from ZnO paste. The XRD generally gives the lower limit. The band gap of ZnO was calculated using the transmittance versus wavelength data captured by UV-visible spectrophotometer, USB 2000. The corresponding plot of $(\alpha h\nu)^2$ versus hν plot is shown in Figure-3. Extraction of linear portion of this plot along hν axis gives the direct band gap of ZnO, 3.18 eV which is consistent with the reported value[3-4].

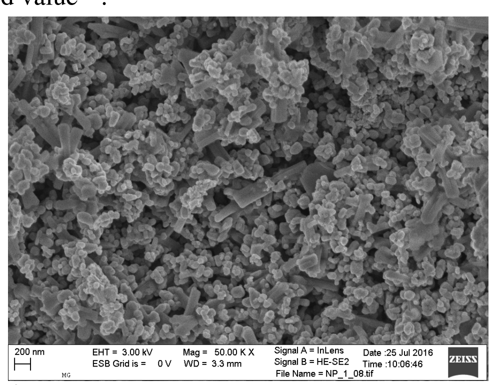

Figure-2: SEM image of ZnO film prepared by doctor blade method.

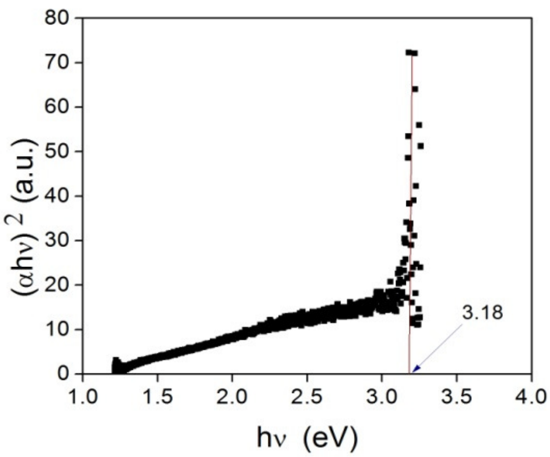

Figure-3: Measurement of band gap of ZnO.

The absorbance of the extracted dye of *Callistemon citrinus* diluted in ethanol was measured by UV-visible spectrophotometer is shown in Figure-4. It shows wide absorbance in the visible range with two maximum absorbances at 410 nm and 540 nm respectively[18]. The absorbance of ZnO films deposited on FTO substrate before and after dye loading is shown in Figure-5.

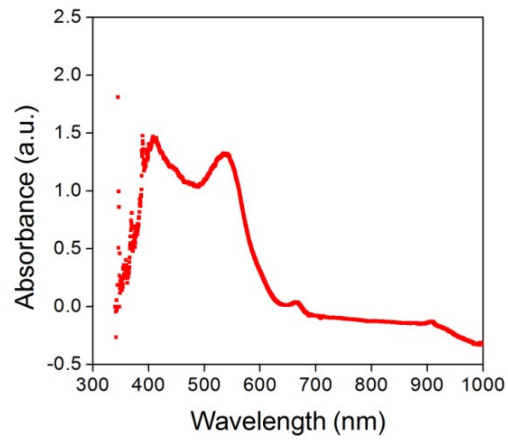

Figure-4: Absorbance of dye extract of Callistemon citrinus.

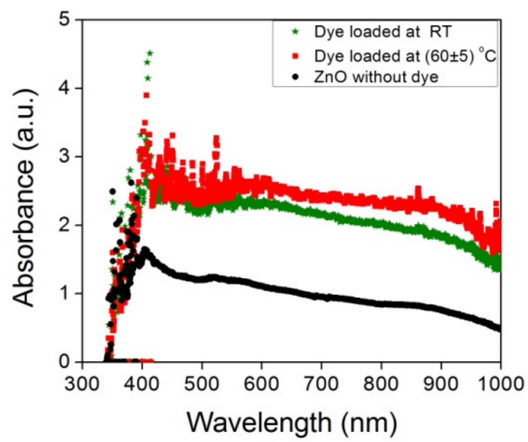

Figure-5: Comparison of absorbance of ZnO film before and after dye loading.

In this figure the red square and green star symbols represent the absorbance of ZnO after dye loading at (60 ± 5)℃ and at RT respectively. Whereas the bottom black circle symbol represents the absorbance of bare ZnO film. The absorbance of dye-loaded ZnO film at (60 ± 5)℃ was found to be greater than dye-loaded ZnO film at room temperature. It suggests that the heating effect enhances the dye-loading process.

Figure-6 shows the measured I-V curves of fabricated dye sensitized solar cells. In the figure, top two curves represent the IV of DSSCs, with dye loaded at (60 ± 5)^{o}C (black square) and RT (red circle), in presence of intensity of sunlight (870 ± 10) W/m^2 respectively. The bottom curve (blue triangle) represents the IV of DSSC at low intensity (dark light) of (80 ± 5) W/m^2. The short circuit current (I_{SC}) and open circuit voltage (V_{OC}) for the DSSC with dye loaded at (60 ± 5)^{o}C, were measured to be 53.2 µA and 289 mV respectively, and a fill factor of 0.47. The I_{SC} and V_{OC} for DSSC with dye loaded at RT were measured to be 49.6 µA and 271 mV respectively and fill factor of 0.43. The corresponding values at dark light were 17.9 µA and 206.5 mV respectively. In conclusion, increase in dye-loading temperature showed increase in absorbance of ZnO photo anode, which in turn enhanced the performance of the solar cell.

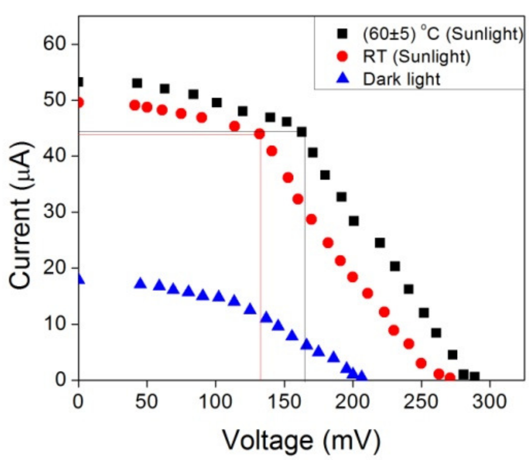

Figure-6: I-V characteristic curves of ZnO based DSSCs.

Conclusion

ZnO nanoparticles were successfully synthesized from the zinc nitrate and sodium hydroxide in ethanol solution using a precipitation method. The XRD investigation shows the crystallite size of ZnO of 38 nm. The surface morphology of thin film of ZnO shows the development of rod-like structure with number of voids. The optical measurement shows the band gap of ZnO was 3.18 eV. Dye sensitized solar cells fabricated with *Callistemon citrinus* sensitized ZnO photo anode shows maximum Isc and Voc were 53.2 µA and 289 mV respectively. The investigation on temperature effect on absorbance of dye loaded ZnO photo anodes showed slight increase in I-V curve for DSSC assembled with dye loaded (60 ± 5) ^{o}C than at room temperature.

Acknowledgement

The authors would like to thank Amrit Campus, and Nepal Academy of Science and Technology (NAST), Kathmandu, Nepal, and University of Warsaw, Poland, for their support to perform XRD and SEM experiments respectively.

References

1. Zhang Q., Dandeneau C.S., Zhou X. and Cao G. (2009). ZnO nanostructures for dye-sensitized solar cells. *Adv. Mater.*, 21(41), 4087-4108.

2. Rani S., Suri P., Shishodia P.K. and Mehra R.M. (2008). Synthesis of nanocrystalline ZnO powder via sol-gel route for dye-sensitized solar cells. *Sol. Energ. Mater. Sol. Cells,* 92(12), 1639-1645.

3. Uthirakumar P., Lee Y.S., Suh E.K. and Hong C.H. (2008). Hybrid fluorescent polymer-zinc oxide nanoparticles: improved efficiency for luminescence conversion LED. *J. Lumin.,* 128(3), 287-296.

4. Madhu C., Kaur I. and Kaur N. (2017). Synthesis and investigation of photonic properties of surface modified ZnO nanoparticles with imine linked receptor as coupling agent-for application in LEDs. *J. Mater. Sci.: Mater. Electron.,* 28(9), 6388-6398.

5. Saleh S.M., Soliman A.M., Sharaf M.A., Kale V. and Gadgil B. (2017). Influence of solvent in the synthesis of nano-structured ZnO by hydrothermal method and their application in solar-still. *J. Environ. Chem. Eng.,* 5(1), 1219-1226.

6. Lanje A.S., Sharma S.J., Ningthoujam R.S., Ahn J.S. and Pode R.B. (2013). Low temperature dielectric studies of zinc oxide (ZnO) nanoparticles prepared by precipitation method. *Adv. Powder Technol.*, 24, 331-335.

7. Hong R., Pan T., Qian J. and Li H. (2006). Synthesis and surface modification of ZnO nanoparticles. *Chem. Eng. J.*, 119(2), 71-81.

8. Ao W., LI J., Yang H., Zeng X. and Ma X. (2006). Mechanochemical synthesis of zinc oxide nanocrystalline. *Powder Technol.*, 168(3), 148-151.

9. Kolodziejczak-Radzimska A. and Jesionowski T. (2014). Zinc Oxide - from synthesis to application: A Review. *Mater.*, 7(4), 2833-2881.

10. Narayan M.R. (2012). Review: Dye sensitized solar cells based on natural photosensitizers. *Renew. Sustain. Energ. Rev.*, 16(1), 208-215.

11. Oladiran A.A. and Olabisi I.A.M. (2013). Fabrication of dye sensitized solar cell (DSSC) using ZnO nanoparticles synthesized from zinc nitrate hexahydrate. *Can. J. Pure Appl. Sci.*, 7(3), 2635-2638.

12. Syukron A., Wahyuono R.A., Sawitri D. and Risanti D.D. (2014). The effect of paste preparation and annealing temperature of ZnO photoelectrode to dye-sensitized solar cells (DSSC) performance. *Adv. Mater. Res.*, 896, 183-186.

13. Bhandari S.C., Sharma S., Shrestha S.P. and Joshi L.P. (2017). Preparation of ZnO thin films by hydrothermal method using Zn acetate with ethylene glycol precursor materials for dye sensitized solar cell. *Imperial J. Interdisciplinary Res.*, 3(2), 920-924.

14. Ghobadi N. (2013). Band gap determination using absorption spectrum fitting procedure. *Int. Nano Lett*., 3, Article 2, 1-4.

15. Hao S., Wu J., Huang Y. and Lin J. (2006). Natural dyes as photosensitizers for dye-sensitized solar cell. *Sol. Energ.*, 80(2), 209-214.

16. Hemmatzadeh R. and Mohammadi A. (2013). Improving optical absorptivity of natural dyes for fabrication of efficient dye-sensitized solar cells. *J. Theorit. Appl. Phys.*, 7(1), 57-63.

17. Chaki S.H., Chaudhary M.D. and Deshpande M.P. (2016). SnS thin films deposited by chemical bath deposition, dip coating and SILAR techniques. *J. Semiconductors,* 37(5), 053001-053009.

18. Kushwaha R., Srivastava P. and Bahadur L. (2013). Natural pigments from plants used as sensitizers for TiO_2 based dye-sensitized solar cells. *J. Energ.,* Article ID 654953, 1-8.