Growth Mechanism, Crystalline State and Photoelectrochemical Properties of ZnO Nanostructure for DSSC Application

Moe Moe Aye , Than Than Win, Yin Maung Maung & Ko Ko Kyaw Soe

Abstract— ZnO nanostructure film was fabricated by wet chemical deposition method in this research.. The effects of Zn2+ concentration on structural and morphology of ZnO films were firstly investigated in detail by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). After that ZnO nanorod films were studied to assess their suitability as photoelectrodes in dye-sensitized solar cells (DSSCs). Eucalyptus bark extract solution was used as natural dye sensitizer. The maximum photoelectric conversion efficiency 0.308% of DSSC was found to be 0.04M Zn2+ concentration. By investigation on growth characteristics of ZnO with different molarities, these kinds of structure were useful in solar cell application.

Keywords— CBD method, conversion efficiency, natural dye-sensitizer, ZnO Nanostructure, XRD

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1 Introduction

Dye-sensitized solar cells (DSSCs) with advantages of low manufacturing cost and comparable light-to-electricity conversion efficiency to conventional silicon-based photovoltaic cells have been considered as the next generation clean energy source[1-7]. Nanostructure metal oxides are one of the key factors in determining the power conversion efficiency of DSSCs, because the nanostructured networks provide a huge surface area to accommodate a large quantity of dye molecules that relate to the light harvesting of photoelectrode in DSSCs. Zinc oxide (ZnO) is one of the most versatile materials on account of its various remarkable properties such as a wide band gap of 3.37eV at room temperature, large exciton binding energy of 60meV, excellent chemical and thermal stability, transparency, biocompatibility, and wide electrical conductivity range, ZnO materials are global interest currently and has a variety of applications in an emerging area of nanotechnology. Quanfu Yang et al.(2011) reported that the efficiency of ZnO DSSC using eosin Y sensitizer was 0.138%[8-15]. In this research, the wet CBD method was employed to fabricate ZnO nanorod films with special attention paid to the effect of Zn^{2+} concentration on the structure, morphology and photoelectro- chemical properties of ZnO nanorod films.

2 Experimental Procedure

2.1 ZnO Nanorod Film Fabrication

To investigate the effect of Zn2+ concentration on the properties of ZnO nanostructure, a sequence of experiments were performed for different molarities of zinc nitrate. All aqueous solutions were prepared using deionized water. Before ZnO nanorod films deposition, commercial glass (2cm×2cm) were thoroughly cleaned. For CBD growth process, the aqueous solutions of zinc acetate dihydrate [Zn $(NO_3)_2.6H_2O$, 99.9% purity] and hexamethyltetramine (HMT) ($C_6H_{12}N_4$, 99.9% purity) were used as precursor source for the growth of ZnO nanorods. Different molarities such as 0.02M, 0.04M, 0.06M of zinc nitrate and hexamethyltetramine (HMT) were mixed together with deionized water and stirred with magnetic stirrer, aqueous solution was formed. In this experiment, the synthesis process of ZnO nanorods contained seed layer formation and nanorod growth. In the first step, the glass substrates were immersed into the aqueous solution for 1h at a required temperature 80°C to form seed layer. In the second step, seed layer coated glass was tilted against the wall of the aqueous solution in beaker. Then the beaker was heat treated for 4h at a constant temperature 80°C. After growth, the substrate was removed from the solution, rinsed with deionized water and dried at room temperature. The sample was annealed at 500°C for 1h, ZnO nanorod film was obtained. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM, JSM-5610) were used to characterize the crystalline state and morphology of nanorod films.

2.2 Assembling Cells and Performance Test for DSSC

Eucalyptus bark extract solution was used as natural dye sensitizer. It was adsorbed in to the ZnO film by immersing in natural dye sensitizer for 3h. And then it was heated at 80°C for 30 min, ZnO film based DSSC was obtained and served as photoelectrode. The counter electrode was made by TCO glass coated with carbon layer. The photoelectrode and counter electrode were sandwiched together using an alligator clamp in which an electrolyte solution was infiltrated using iodine. Photoelectrochemical cell (PEC) measurement was performed using Na-lamp, Fluke Scopemeter and the dye-sensitized area of photoelectrode of the cell was $0.25cm^2$.

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3 Results and Discussion

3.1 Effect of Zn^{2+} Concentration on Structure Character of ZnO Films

Figure 1(a-c) showed the XRD profile of ZnO films with different Zn^{2+} concentrations. Three major different peaks of (100), (002) and (101) were observed in these XRD spectra. It was reported that ZnO exhibited hexagonal structure indexed to the standard of JCPDS file. At low Zn^{2+} concentration, (100) diffraction pattern was more intense than that of (002) and without (101) peak. As the Zn^{2+} concentration was high, (002) diffraction peak in XRD patterns was dominant which revealed the preferentially oriented growth in c-axis direction. Another view from diffracted intensity, the intensity of the peak (002) was stronger with an increase in Zn^{2+} concentration. Lattice constant, hexagonality and average crystallite size of ZnO nanostructure were calculated and listed in Table 1.

Table 1 Lattice parameters, hexagonality and crystallite size of ZnO nanorod films

Sample	*ZnO-1*	*ZnO-2*	*ZnO-3*
Zn^{2+} Concentration(M)	0.02	0.04	0.06
a(Å)	3.1792	3.2266	3.2365
c(Å)	5.1681	5.1688	5.1718
c/a	1.6256	1.6019	1.5979
Crystallite size(nm)	18.88	26.77	27.23

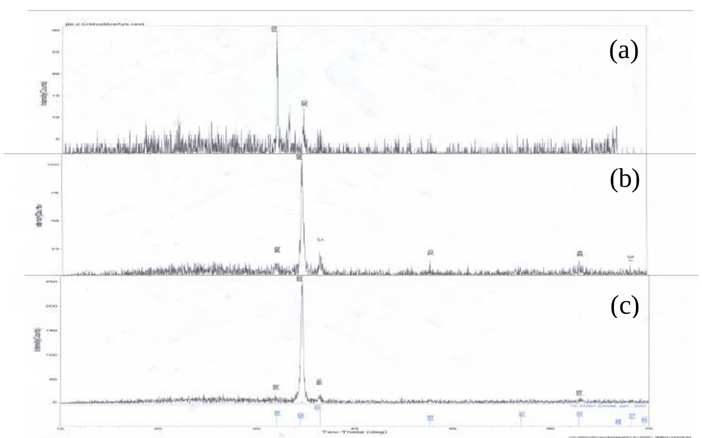

Fig. 1. XRD spectrum of (a)0.02M (b) 0.04M (c) 0.06M ZnO nanorod films

3.2 Surface Morphology

Figure 2(a-c) showed the evolution of the ZnO nanostructure as a function of Zn^{2+} concentration, and kept the other constant experimental conditions. As can be seen from these figures, network flake like structure were observed. Many flake like products exhibited nanoflower(oleander) on glass substrate. In the lower concentration of Zn^{2+} that nanoflower were widely distributed. As the Zn^{2+} concentration was increased the composite morphology of oleander and rod like structure were uniformly observed. The diameter and the length of ZnO nanorods were in the range of (130-300 nm) and (2-5 μm). The ZnO nanorods were disorderly, and had a wide size distribution. It was convinced that some defects were formed on ZnO nanorods due to disengaged growth on the solution. Polycrystalline glass not provided the nucleation of ZnO and influence nanorods growth, which leads to disordered growth of nanorods. The result of SEM observation showed that the diameter and length increased with Zn2+ concentration decreasing.

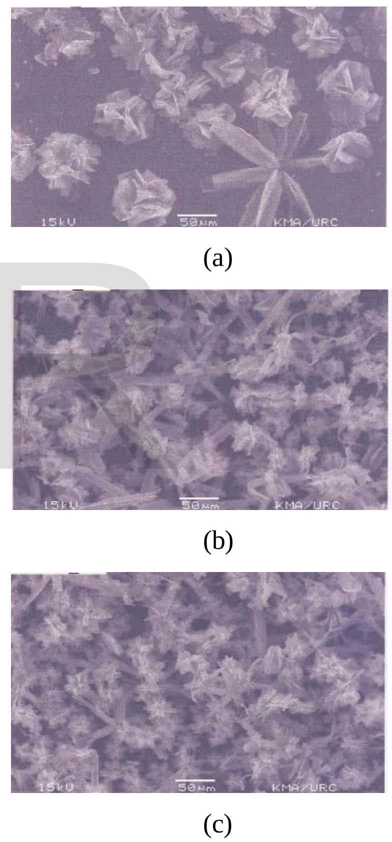

Fig. 2. SEM image of ZnO nanostructure grown on glass substrate with different solution concentration (a)0.02M (b) 0.04M (c) 0.06M

3.3 Photoelectrochemical Properties

The I-V performance of the DSSCs enhanced with ZnO nanorod film electrode were shown in figure 3(a-c). In these figures it was observed that the solar cell parameters depended on Zn^{2+} concentration. The DSSC containing 0.04M Zn^{2+} concentration exhibited maximum short circuit current, moderate open circuit voltage and an enhancement of conversion efficiency. Solar cell parameters of DSSC with ZnO nanorod film electrode were listed in Table 2.

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TABLE 2 PHOTOVOLTAIC CELL PARAMETER FOR DSSC WITH ZNO FILM ELECTRODE

DSSC	ZnO-1	ZnO-2	ZnO-3
Zn^{2+}	0.02	0.04	0.06
V_{oc}(V)	0.0375	0.1242	0.1278
I_{sc}(μA)	0.2539	5.6363	3.2080
V_m(V)	0.0298	0.1140	0.1076
I_m(μA)	0.2062	5.0366	2.6460
η(%)	0.043	0.308	0.153

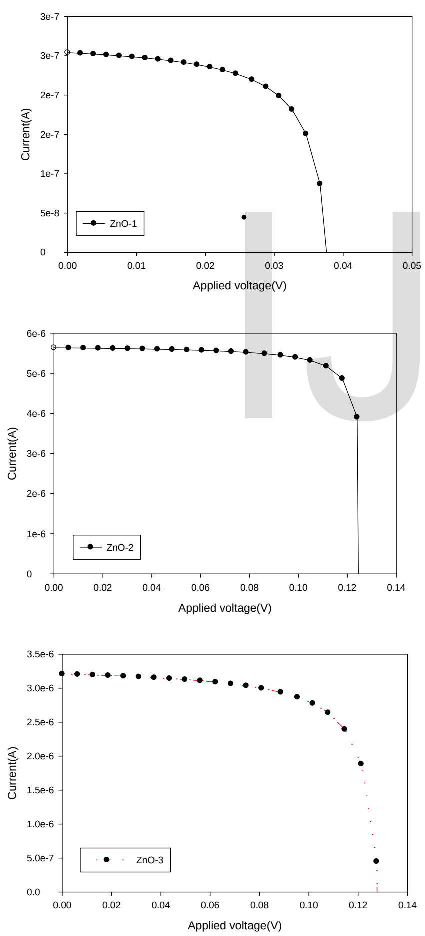

Fig. 3. I-V characteristic of ZnO DSSC curves

4 Conclusion

Uniformly distributed ZnO nanorods with submicron diameter have been successfully grown at low temperature by using chemical bath deposition. The mechanism of the nanorods growth on the different molarities was proposed. XRD results demonstrated that ZnO nanorod films with the hexagonal wurtzite structure growing along with (002) crystallographic orientation. The composite oleander and rod like morphology of ZnO nanostructure were observed after increasing in Zn^{2+} concentration. The photoelectrochemical measurement showed that the maximum photoelectric conversion efficiency was 0.308%. From the results, Zn^{2+} ion concentrations played a key role during the process of regulating the growth rate and forming the ZnO nanorods semiconductor films by CBD. Thus the present research allowed more economical coating, easily adoptable and technically simplicity thereby making products that were more compact. In conclusion, the ZnO nanorod films electroded DSSC with Eucalyptus dye sensitizer exhibited the potential to be a low-cost photovoltaic cell application.

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REFERENCES

[1] Y.Chul Yi et al., "ZnO nanorods: synthesis, characterization and applications," Semiconductor Science and Technology, vol. 20, pp. 22, 2005.

[2] J.Guozhi et al., "Growth mechanism of ZnO nano structure using chemical bath deposition," Journal of Ovomic Research, vol. 6, no. 6, pp. 303, 2010.

[3] Nanda Shakti, Sunita Kumari, P.S. Gupta, 'Structural, optical and electrical properties of ZnO nanorod array prepared by hydrothermal process', Journal of Ovonic Research , vol. 7, no. 3, pp. 51 – 59, 2011.

[4] P.Gowthaman et al., "Structural and optical properties of ZnO nanorods prepared by chemical bath deposition method, Australian Journal of Basic and Applied Sciences, vol. 5, no. 11, pp. 1379, 2011.

[5] Y.Gyu-Chul et al., "ZnO nanods: synthesis, characterization and application," Semicond. Sci. Technol., vol. 20, pp. 22, 2005.

[6] A. I. Inamdar et al., "The influences of complexing agents on growth of zinc oxide thin films from zinc acetate bath and associated kinetic parameters," Int. J. Electrochem. Sci., vol. 2, pp. 797, 2007.

[7] Sufeng Wei, Jianshe Lian, Hua Wu, "Annealing effect on the photoluminescence properties of ZnO nanorod array prepared by a PLD-assistant wet chemical method", Materials Characterization, vol. 61, no. 11, pp. 1239-1244, 2010.

[8] Michael Gratzel, "Dye sensitized solar cells," Journal of Photochemistry and Photobiology C: Photochemistry Reviews, vol. 4, pp. 145, 2003.

[9] Quanfu Yang et al., "Preparation and photoelectrochemical performance research of ZnO nanorods arrays," Proceedings of Shanghai International Nanotechnology Cooperation Symposium, pp. 105, 2011.

[10] S. Rajaram et al., "Nanocrystalline TiO2/ZnO thin films: Fabrication and application to Dye-sensitized solar cells, J. Phys. Chem.B, vol. 109, pp. 24254, 2005.

[11] S. Ying Lan et al., "Effects of substrate, morphology and optical properties of vertically aligned ZnO nanorod arrays grown by low temperature CBD method," Journal of Inorganic Materials, vol. 25, no. 10, pp. 24, 2010.

[12] P. Gowthaman, M. Saroja, M. Venkatachalam, J. Deenathayalan and T. S. Senthil, "Structural and optical properties of ZnO nanorods prepared by chemical bath deposition method" Australian Journal of Basic and Applied Sciences, vol. 5, no. 11, pp. 1379, 2011.

[13] Lihui Zhang, Heqing Yang and Li Li, "Synthesis and characterization of core/shell-type ZnO nanorod/ ZnTe nanoparticle composite by a one step hydrothermal route", Material chemistry and physics, vol. 120, pp. 526-531, (2010).

[14] Hui Tong, Miki Inada, Yumi Tanaka, Naoya Enomoto and Junichi Hojo, "Dye Sensitized Solar Cells Based on ZnO Nanorod/TiO2 Nanoparticle Composite Films", Materials Science Forum, vol. 724, pp. 397-403, 2012.

[15] Jae Young Park, Sang Sub Kim, "Growth of Nanograins in Electrospun ZnO Nanofibers" Journal of the American Ceramic Society, vol. 92, no. 8, pp. 1691 – 1694, 2009.