Proceedings of the
International Conference on Mechanical Engineering and Renewable Energy 2011
(ICMERE2011) 22- 24 December 2011, Chittagong, Bangladesh

ICMERE2011-PI-099

Fabrication of hexagonal ZnO nanorods for the application of solar cells

M. F. Hossain[1,*], and **T. Takahashi**[2]

[1]Department of Electrical and Electronic Engineering, Rajshahi University of Engineering & Technology (RUET), Rajshahi-6204, Bangladesh.
[2]AGraduate School of Science and Engineering for Reseach, Gofuku 3190, Toyama 930-8555, Japan.
*faruk94_ruet@yahoo.com

Abstract- *The aim of this work is to fabricate nanostructured ZnO photoelectrode for improving the dye-sensitized solar cells performance. The nanostructured ZnO photoelectrode has been fabricated via hydrothermal method at 85℃, including the ZnO seed layer prepared on SnO_2:F (FTO) glass substrate by facing-target sputtering technique. Nanorods structured ZnO films have confirmed by using field emission electron and transmission electron microscopes. Ruthenium based dye and carbon counter electrode were used to fabricate the dye-sensitized solar cells (DSCs). Incident photon-to-current efficiency spectrum shows two peaks at 408 and 545 nm, which are closed to dye absorbance. The photoelectric conversion efficiency (1.41%) of the DSC is discussed with the surface morphology of ZnO nanorods photoelectrode and the corresponding dye-incorporations.*

Keywords: Dye-sensitized solar cells, Zinc oxide, Nanorods, surface morphology.

1. INTRODUCTION

Dye-sensitized solar cells (DSCs) are considered attractive for energy conversion applications because of their relatively low cost and high efficiency (11%) [1]. TiO_2 is playing an important role in science and technology for its unique optical, electrical, and chemical properties. It has been widely used in the area of solar energy conversion, surface modification of semiconductors, nanoelectronics, etc. [2, 3]. The high efficiency of DSCs is achieved only when the nanoporous TiO_2 electrodes are introduced [4]. However, ZnO is comparable to TiO2 [5]: 1) similar band gap, 2) higher electron mobility, 3) simpler tailoring and 4) easier surface modification. Considering the efficient charge transfer, Yang and Aydil introduced ZnO nanowire (ZW) electrode to DSC and achieved the conversion efficiency of 1.54% [6, 7], which was much higher than ZnO nanoparticle (ZP) electrode to DSSC (0.44%) [8]. Electron transport in film electrode is proposed to occur by hopping mechanism, which exhibits slownon-exponential current and charge recombination thus limiting efficient charge transfer [9]. Especially, the charge recombination occurs across the conducting substrate-electrolyte interface resulting in the poor cell performance.

Various methods available for fabricating one-dimensional ZnO nanostructures have been employed, such as catalytic growth [10], electrophoretical deposition [11] and metal organic chemical vapor deposition [12]. However, these are expensive and energy consuming processes. The low-temperature solution growth for preparing ZW may be developed to make a high efficient DSSC commercially competitive [13,14].

ZnO nanorods (NRs) have a large surface area and a long conduction pathway that lead straight to the electrode for efficient and fast electron transport [15]. It is reported that electron transport is tens to hundreds of times faster in nanorod array electrodes than in nanocrystalline particulate electrodes in dye-sensitized ZnO solar cells [16].

In this study, crystalline ZnO nanorods were synthesized through aqueous solution method at low temperature (~85°C) under ambient pressure. The ZnO seed layer was prepared by facing target sputtering (FTS) method. The crystal growth and surface morphology as well as photovoltaic performance of the ZnO nanorods were investigated and discussed.

2. EXPERIMENTAL SECTION

At first, the FTO substrates were cleaned by ultrasonic system in ethanol, then distilled water, and then dried in pure N_2 steam flow. A thin ZnO seed-layer was deposited on FTO (8 Ω/□, Solaronix) substrate by FTS technique (shown in Fig. 1) [17, 18]. In the FTS system, the distance between the target-to-target, and the center of the targets' to the substrate were 100 mm and 50 mm, respectively. Zn rectangular plates (having 115 x 75 mm, thickness of 3 mm and purity of 99.95 %) were used as targets. The chamber was evacuated to a vacuum level of 7×10^{-4} Pa. ZnO seed-layer was deposited reactively at DC input power of 100 W with sputtering pressure of 0.1 Pa and a fixed Ar to O_2 gas ratio (G_R) of 6:4. The thickness of the ZnO seed-layer was around 100-120 nm measured by an ACCRETECH SURFCOM 1500

surface-profiler.

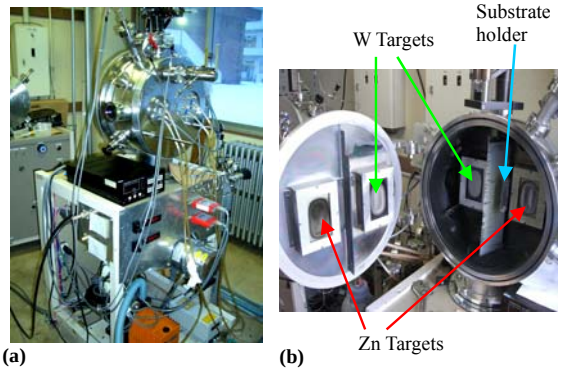

Fig. 1. Facing Target Sputtering system in our laboratory.

The well-aligned ZnO nanorods arrays were fabricated by simple hydrothermal method at 85° C. For the synthesis of the ZnO nanorods arrays, analytical grade zinc nitrate hexahydrate [$Zn(NO_3)_2$. $6H_2O$, Wako, Japan], and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$, Wako, Japan) were used as reagents without further purification. In a typical reaction procedure, a 50 mM of zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] was dissolved in 50 ml of deionized water (Millipore Milli-Q Plus purification system, 18.2MOcm) water, and then 50 mM of HMTA was dripped under constant stirring at room temperature to ensure well dispersion of the reactant. The mixed solution was transferred into a glass beaker. The glass beaker was heated at constant temperature of 85° C for 3 hrs by well controlled temperature-controller without shaking and stirring. An electric-fan was used to cool up-side of the glass beaker. At the end of the growth period, the glass beaker had been cooled to room temperature naturally. The film thickness is approximately 2.5~3μm. The crystal structures of the nanostructured ZnO films were investigated by grazing incidence X-ray diffraction (GIXRD) analysis (SHIMADZU XRD-6000) with Cu-Kα line. The optical properties of the films were measured with JASCO V-550 UV/VIS spectrophotometer at room temperature. The surface morphologies were studied using field emission scanning electron microscope (FE-SEM, JEOL, JSM 6700F) and transmission electron microscope (TEM).

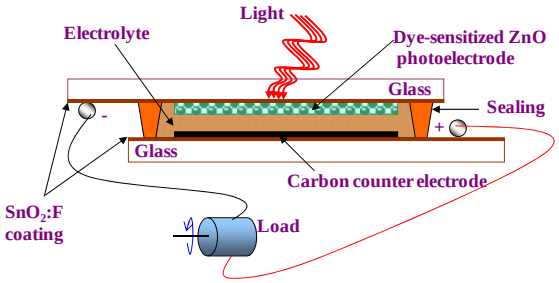

Fig. 2. A schematic representation of DSC.

The nanostructured ZnO films were sensitized in dye [cis-di (thiocyanate) bis (2,2′-bipyridyl-4,4′-di- carbo--xylate) ruthenium (II)] for 24 hour at room temperature. The DSCs were fabricated according to Fig. 2 by clamping the dye-sensitized ZnO electrode against carbon counter electrode [19] and filling the inter-electrode space by the electrolyte of 0.5M KI/0.05M I_2 /0.05 M 4-*tert* butylpridine by the capillary force. The active cell area was 0.25 cm^2. The intensity of light was 100 mW/cm^2. The photovoltaic performances of DSCs were measured using a Keithley Model-2400 source measure unit, and a monochromator (SG-80, Yokogawa).

3. RESULTS AND DISCUSSIONS

Figure 3 shows the GIXRD pattern of ZnO seed layer, NRs structures. The ZnO seed-layer shows two clear and sharp diffraction peaks of (002) and (103), which indicates that the deposited ZnO seed layer has the high quality wurtzite structure [19]. The nanostructured ZnO photoelectrode show very high crystallinity. The crystallite size [using peak (101)] of ZnO seed layer, and NRs, are 14.2, and 23.5 nm, respectively.

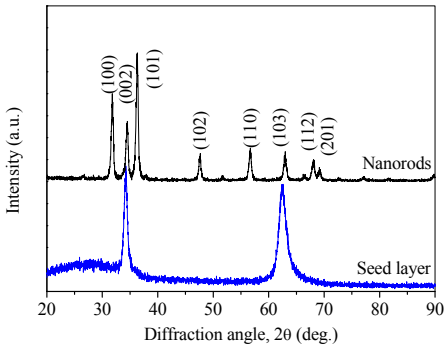

Fig. 3. The GIXRD patterns of ZnO seed-layer and NRs structures.

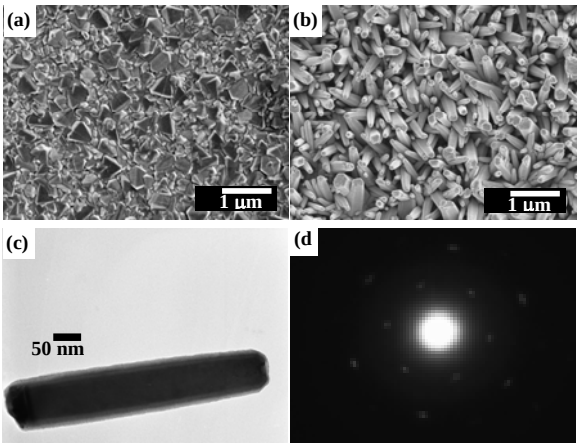

Fig. 4. The FE-SEM images of (a) ZnO seed-layer, and (b) ZnO NRs, (c) TEM images of single ZnO NRs, and (d) SAED pattern of ZnO NRs.

Figure 4 shows the FESEM images of sputter-deposited ZnO seed layer and ZnO NRs prepared with 85°C deposition temperature. It is cleared from Figure 4(a) that the ZnO seed-layer shows a high compact surface with some grain clusters. The average grain cluster size is around 114 nm [19]. Figure 4(b) shows the well aligned ZnO NRs with uniform surface.

Figure 4(c) displays the single ZnO nanorod with an average diameter of 120-150nm. The electron diffraction experiments of single crystal conventionally involve the bright, dark field and selected-area electron diffraction (SAED) pattern. Figure 4(d) is showed the results of the SAED analysis, which reveal that the single ZnO NR is polycrystalline in nature.

Figure 5 shows the difference of absorbance spectra of ZnO NRs prepared with deposition temperature of 85°C. It shows the highest ΔA value in whole the wavelength region, which means that this sample is more photoactive. The ΔA spectrum of the ZnO films is similar to the absorption peak of ruthenium based (N3) dye.

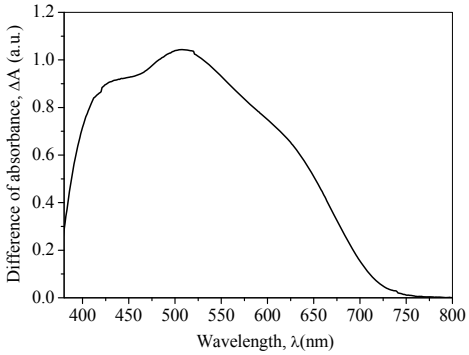

Figure 5. The difference of absorbance spectra of nanorods (NRs) ZnO photoelectrode

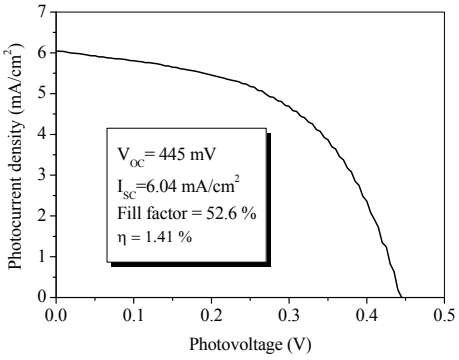

Fig. 6. I-V characteristics curve for DSC.

Figure 6 shows the photocurrent-photovoltage characteristics curve of DSC based on ZnO NRs. Inset of Fig. 6 shows the η, *FF*, V_{OC}, and J_{SC} values of the DSCs corresponding to Fig. 6. The DSC of ZnO NRs prepared with 85 °C has been showed the efficiency of 1.41%, which is higher than the ZnO photoelectrode prepared on sol-gel based ZnO seed layer [20], may be due to the ZnO NRs formed on highly crystalline ZnO seed layer. The fill factor of the DSC has reasonable value.

Figure 7 shows the IPCE curve of DSC with ZnO NRs as a function of wavelength. The IPCE value at around 545 nm has contributed by the dye absorption, corresponding to the visible $t_2 \rightarrow \pi^*$ metal-to-ligand charge transfer (MLCT). The DSC shows reasonably high IPCE value. The IPCE spectrum shows two peaks at 408 and 545nm, which are close to ruthenium based dye (N3-dye) absorbance. The improvement in the IPCE suggested that the high energy conversion efficiency results predominantly from sufficient dye-loading by ZnO NRs arrays, which enlarges internal surface area within the photoelectrode [20].

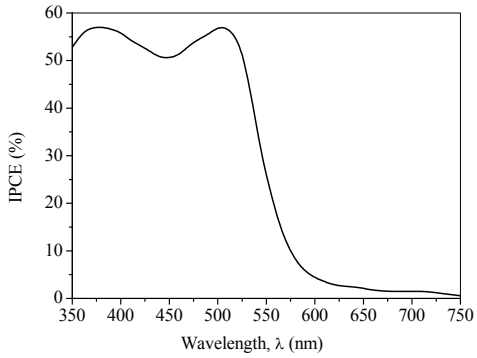

Fig. 7. IPCE spectrum for DSC with ZnO nanorods

4. CONCLUSION

The hexagonal ZnO NRs were successfully prepared ZnO coated FTO substrate by open-hydrothermal technique with 85°C, where ZnO seed layer was deposited on FTO by FTS method. The ZnO seed and upper layers both have high crystalline structure. The ZnO NRs were confirmed by FESEM and TEM images. The average size of NRs is 120-150 nm. The DSC with ZnO NRs has showed the 1.41% photoelectric conversion efficiency and 65.4% IPCE value.

6. ACKOWLEDGEMENT

The authors would like to thank the University of Toyama, for measurement of GIXRD, UV-VIS, FE-SEM, AFM and photovoltaic performance.

.

7. REFERENCES

[1] M. Grätzel, "Photoelectrochemical cells", *Nature*, Vol. 414, pp. 338-344, **2001.**

[2] A. Hagfeldt, M. Grätzel, "Molecular Photovoltaics", *Accounts Chemical Research,* Vol. 33, No. 5, pp.269-277, 2000.

[3] J. Nanda, K. S. Narayan, B. A. Kuruvilla, G. L. Murthy, D. D. Sarma, Sizable photocurrent and emission from solid state devices based on CdS nanoparticles, *Applied Physics Letter,* Vol. 72, No. 11, pp. 1335-1337, **1998**.

[4] K. Kalyanasundaram, M. Grätzel, "Applications of functionalized transition metal complexes in photonic and optoelectronic devices", *Coordination Chemistry Reeview,* Vol. 177, pp. 347-414, **1998**.

[5] T. P. Chou, Q. F. Zhang, G.E. Fryxell, G.Z. Cao, "Hierarchically Structured ZnO Film for Dye-Sensitized Solar Cells with Enhanced Energy Conversion Efficiency", *Advanced Materials*, Vol. 19, No. 18, pp. 2588-2592, 2007.

[6] M. Law, L.E. Greene, J. Johnson, R. Saykally, P. D. Yang, "Nanowire dye-sensitized solar cells", *Nature Materials*, Vol. 49, pp. 455–459, 2005.

[7] J. B. Baxter, E. S. Aydil, "Nanowire-based dye-sensitized solar cells", *Applied Physics Letters*, Vol.

86, pp. 053114–053116, 2005.

[8] G. K. Mor, O. K. Varghese, M. Paulose, K. Shankar, C. A. Grimes, "A review on highly ordered, vertically oriented TiO_2 nanotube arrays: fabrication, material properties and solar energy applications", *Solar Energy Materials Solar Cells*, Vol. 90, pp. 2011-2075, 2006.

[9] K. D. Benkstein, N. Kopidakis, V. J. Lagemaat, A. J. Frank, "Influence of the Percolation Network Geometry on Electron Transport in Dye-Sensitized Titanium Dioxide Solar Cells", *Journal of Physical Chemistry B*, Vol. 107, pp. 759-7767, 2003.

[10] Y. Wu, P. Yang, "Direct Observation of Vapor−Liquid−Solid Nanowire Growth", *Journal American Chemical Society*, Vol. 123, pp. 3165-3166, 2001.

[11] Z. G. Chen, Y. W. Tang, L. S. Zhang, L. J. Luo. "Electrodeposited nanoporous ZnO films exhibiting enhanced performance in dye-sensitized solar cells", *Electrochimica Acta*, Vol. 51, pp. 5870-5875, 2006.

[12] J. B. Baxter, E. S. Aydil, "Dye-sensitized solar cells based on semiconductor morphologies with ZnO nanowires", *Solar Energy Materials Solar Cells*, Vol. 90, pp. 607-622, 2006.

[13] L. E. Greene, M. Law, J. Goldberger, F. Kim, J. C. Johnson, Y. F. Zhang, "Low-Temperature Wafer-Scale Production of ZnO Nanowire Arrays", *Angewadte Chemie*, Vol. 115, pp. 3139-3142, 2003.

[14] C. Pacholski, A. Kornowski, H. Weller, "Selbstorganisation von ZnO: von Nanopartikeln zu Nanostäbchen", *Angewadte Chemie International Edition*, Vol. 114, pp.1234-1237, 2002.

[15] S. M. Rajaram, J. L. Won, M. P. Habib, H. H. Sung, "Nanocrystalline TiO_2/ZnO Thin Films: Fabrication and Application to dye-sensitized solar Cells", *J. Physical Chemistry B*, Vol. 109, 24254-24259, **2005**.

[16] B. F. M. Alex, E. M. James, O. K. P. Mohammed, T. H. Joseph, "Dynamics of charge transport and recombination in ZnO nanorod array dye-sensitized solar cells", *Physical Chemistry Chemical Physics,* Vol. 8, pp. 4655-4659, **2006**.

[17] M. F. Hossain, S. Biswas, T. Takahashi, Y. Kubota, A. Fujishima, "Effect of substrate temperature on the facing target sputter deposited TiO photoelectrode of dye-sensitized solar cell", *Journal Vacuum Science Technology A*, Vol. 26, pp. 1012-1017, 2008.

[18] Z.H. Zhang, M.F. Hossain, T. Takahashi, "Facing-target sputtering deposition of ZnO films with Pt ultra-thin layers for gas-phase photocatalytic application", *Journal of Hazardous Materials*, Vol. 176, pp. 973-978, 2010.

[19] M. F. Hossain, T. Takahashi, "Microstructured ZnO photoelectrode grown on the sputter-deposited ZnO passivating-layer for improving the photovoltaic performances", *Materials Chemistry Physics*, Vol. 124 (2010) 940.

[20] M.F. Hossain, T. Takahashi, S. Biswas, "Nanorods and nanolipsticks structured ZnO photoelectrode for dye-sensitized solar cells", *Electrochemistry Communication*, Vol. 11, pp. 1756-1759, 2009.