

Dye-Sensitized Solar Cell Utilizing Quasi One-Dimensional of Highly Compact Vertical Array ZnO Nanorod

A.A. Umar^{1,*}, M.Y.A. Rahman^{2,*}, R. Taslim², M.M. Salleh¹

¹ Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia

² College of Engineering, Universiti Tenaga Nasional, 43009, Kajang, Selangor, Malaysia

*E-mail: akrajas@ukm.my, yusri@uniten.edu.my

Received: 9 May 2012 / Accepted: 12 June 2012 / Published: 1 August 2012

Highly compact quasi one-dimensional ZnO nanorods was synthesized for dye-sensitized solar cell of FTO/ZnO/electrolyte/platinum. ZnO nanorods were grown on FTO substrate at room temperature via ammonia assisted rapid hydrolysis process technique. The sample was grown throughout the substrate by multi-growth process for about 5-30 minutes. ZnO nanorods were characterized by FESEM with vertical array oriented with the average diameter and length of 48 nm and 220 nm, respectively. The (*cis*-bis(isothiocyanato)bis(2,2'-dicarboxylato)-ruthenium(II) bis-tertbutylammonium) (N719) dye was coated on the samples and utilized in the cell to improve its performance. The cell performance was tested in dark and under illumination of 100 mWcm⁻² light. The cell exhibits photovoltaic effect with the J_{sc} of 0.45 mAcm⁻², V_{oc} of 0.56 V and FF of 24%.

Keywords: 1-D ZnO nanorod, Dye-Sensitized solar cell, N719 dye

1. INTRODUCTION

Researches on solar cell demonstrates a significant development since Gratzel introduced dye-sensitized TiO₂ solar cell with the efficiency as high as 11% [1]. Since then, dye sensitized solar cell (DSSC) had a huge attention of many researchers to further improve the performance of the device. One of such options is by replacing TiO₂ nanoparticle by nanorod, nanotube or nanowire [2-3], thereby eliminating the grain boundaries between nanoparticles [4].

Recently, ZnO has widely been used as alternative material to TiO₂ [5] in DSSC due to its unique property with comparable band gap structure. ZnO with nanorods morphology is among the shape that becomes the focus of attention of many researchers to be utilized in DSSC. So far, DSSC

utilizing ZnO nanorod with reasonably high performance, such as prepared by a one-step catalyst-free chemical-vapor deposition (CVD) method has demonstrated the conversion efficiency as high as 1.82% [6]. ZnO nanorod-based DSSC was prepared using another method, such as hydrothermal technique, has also been reported to produce the efficiency as high as 1.0%-1.69% [6-9]. Meanwhile, the DSSC utilizing ZnO nanorods prepared with a nucleation–dissolution–recrystallization growth technique has been reported to produce the efficiency as high as 1.32% [11]. The ZnO nanorods prepared using the technique as reported in [6] and other techniques [7-11] produced a dimension of several micron in length and diameter. The arrangement of the nanorod on the surface are relatively rare that exhibits high rod to rod separation. In other words, the number of nanorod over certain surface area is relatively low. Owing to the unique properties of ZnO nanorods in DSSC, the use of highly compact ZnO nanorods in the DSSC should presumably improve the performance of the cell.

Our previous work on ZnO nanorods that was grown from the current technique possesses good response in photoelectrochemical cell with the highest short-circuit current density, J_{sc} of 0.22 mAcm^{-2} , the open circuit voltage, V_{oc} of 0.44 V and the fill factor, FF of 30% [12]. In this work, we demonstrate the dye sensitized solar cell of FTO/ZnO-dye/LiI-I₂/platinum utilizing quasi one-dimensional highly compact ZnO nanorods prepared by a novel technique, namely, ammonia assisted rapid hydrolysis process at room-temperature [14]. The N719 dye (*cis*-bis(isothiocyanato)bis(2,2'-dicarboxylato)-ruthenium(II) bis-tertbutylammonium) was chosen to be coated on the ZnO nanorods since the TiO₂ solar cell with this dye posses the conversion efficiency, η of 5.36% [15]. This paper describes the preparation of highly compact quasi one-dimensional ZnO nanorods by the above-mentioned technique. It also highlights the fabrication and performance study of the DSSC utilizing the ZnO samples prepared via this technique.

2. EXPERIMENTAL

ZnO nanoseeds on FTO surface were prepared by using an alcohol thermal seeding method adopting our previous method in preparing CuO nanowires and highly compact ZnO nanorod on FTO surface [13,14]. Briefly, the process is as follows: a thin layer of 0.01 M ethanolic solution of zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Across) on a clean FTO surface was firstly prepared by spin-coating process and annealed in air at 350°C for 1 hour. The room temperature growth process of ZnO nanorods from the nanoseeds was carried out by immersing the nanoseeds-attached FTO into a 0.01 M aqueous solution of zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Aldrich). 100 μL of 30% Ammonia solution (NH_3 , Aldrich) was added into the reaction while being stirred with magnetic stirrer for 5 to 30 minutes, changing the growth solution every 5-6 minutes, and then the sample was annealed in air at 350 °C for 30 hours.

The resulting ZnO nanorods film on the FTO with the average thickness of 220 nm was then immersed in N719 dye for 4 hours and assembled with a platinum counter electrode that was prepared by sputter coater on ITO surface and filled with an electrolyte (0.6 M tetrabutyl ammonium iodide, 0.1 LiI, 0.05 M iodine, and 0.5M 4-tertbutylpyridine in 3-methoxy- propionitrile) containing redox couple I/I_3^- . The cell was illuminated with 100 mWcm^{-2} light from xenon lamp as light source. A rubber band

was placed on top and bottom of the clamped cell in order to avoid the cell from breaking. A 1.00 cm² hole was made at the top of rubber band as an area of illumination. The structure of the cell is shown in Fig. 1.

The morphology of ZnO nanorods was characterized by a field emission scanning electron microscope (FESEM) model ZEISS SUPRA 55VP that was operated at an acceleration voltage of 3 kV. The optical property of ZnO nanorods on FTO surface was characterized using a double beam UV/VIS/NIR spectrophotometer model Lambda 900 Perkin Elmer. Photoluminescence (PL) was studied at room temperature with Perkin Elmer LS55 Luminescence Spectrometer. *J-V* curves in dark and under illumination were recorded by a Keithley high voltage source model 237.

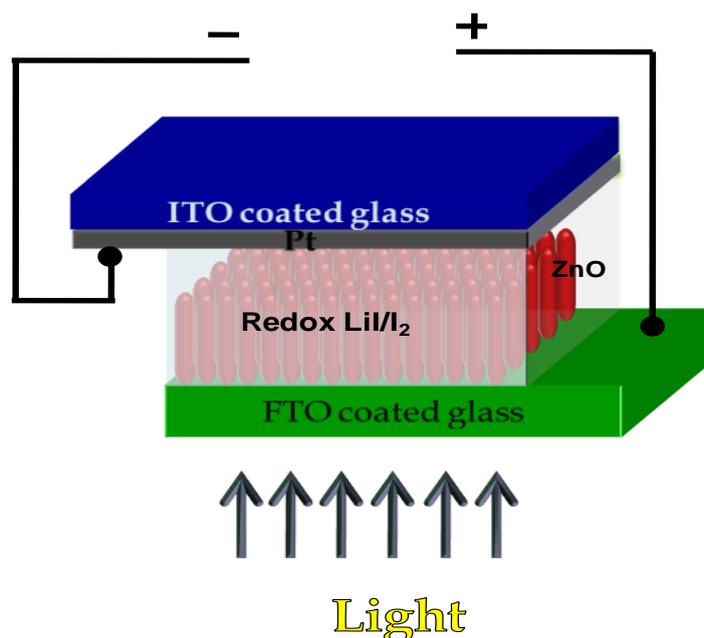


Figure 1. Structure of the cell

3. RESULTS AND DISCUSSION

Quasi 1-D ZnO nanorods have been synthesized from nanoseeds particles on the FTO substrate via a simple and quick growth process in the presence of ammonia. The growth process took only for about 3 to 5 minutes to change from spherical nanoseeds to vertical oriented nanorods for each cycle growth step. Figure 2 shows FESEM image of ZnO nanorods grown on FTO surface prepared via ammonia assisted seed-mediated method. ZnO nanorod was grown on the FTO substrate that was initially coated with ZnO nanoseeds via alcohol thermal method. The ZnO nanorod was grown by four cycle growth process taking about 5-30 minutes growth time. It was clearly seen that ZnO nanorod was grown free standing vertically. It was also observed from the micrograph that nanorod was grown highly compact compared to ZnO nanorod that was prepared via hydrothermal method [11]. The average diameter and length of ZnO nanorods are 48 nm and 220 nm, respectively.

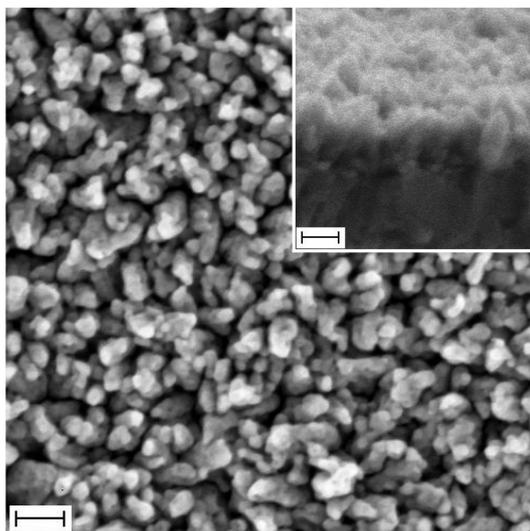


Figure 2. FESEM image of ZnO nanorods that was prepared via multiple growth-steps. Inset is the cross section of ZnO nanorod. Scale bar 100 nm

We measured room temperature PL properties of ZnO nanorods that was grown by this technique to study the typical spectra of ZnO crystal, which usually exhibits two strong emission peaks, near band edge (NBE) at 370-390 nm and green band at 510-550 nm, respectively. The ZnO nanorods was excited at 325 nm and an NBE peak at 380 nm and little peak around 500 nm were observed. The UV peak at room temperature is attributed to an NBE free exciton transition, namely, the recombination of a free exciton through an exciton–exciton collision. It has been suggested that high crystallinity is due to decrease of impurity and structural defects such as oxygen vacancy and dislocations. The green peak of ZnO is due to radiative recombination of a photo-generated hole with an electron attributed to an oxygen vacancy [15]. The amount of oxygen on the surface is expected to drastically change the green-band peak. The slight green emission that remained may have resulted from the surface defect as single ionized oxygen vacancy. It is generally agreed that the surface states play a crucial role in PL spectra of nanomaterials [17-18].

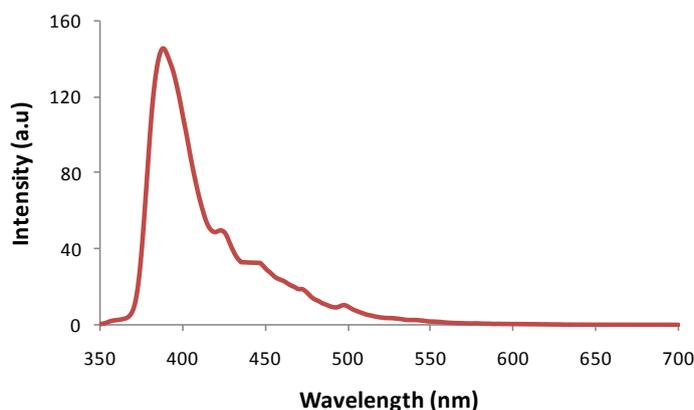


Figure 3. Room temperature PL spectrum of ZnO nanorods produced via ammonia assisted hydrolysis process

Fig. 4 shows typical room-temperature optical absorption spectra of uncoated ZnO nanorods and ZnO nanorods coated dye of N179. Two-separated excitonic character appears, namely, A- and B-excitonic, in both spectrums. This normally appear only if the nanocrystals contains low defect density, in other word, high-crystallinity [14, 16]. It is also observed that the ZnO nanorods film coated dye shows the highest absorption compared with uncoated ZnO nanorods film at 320 nm.

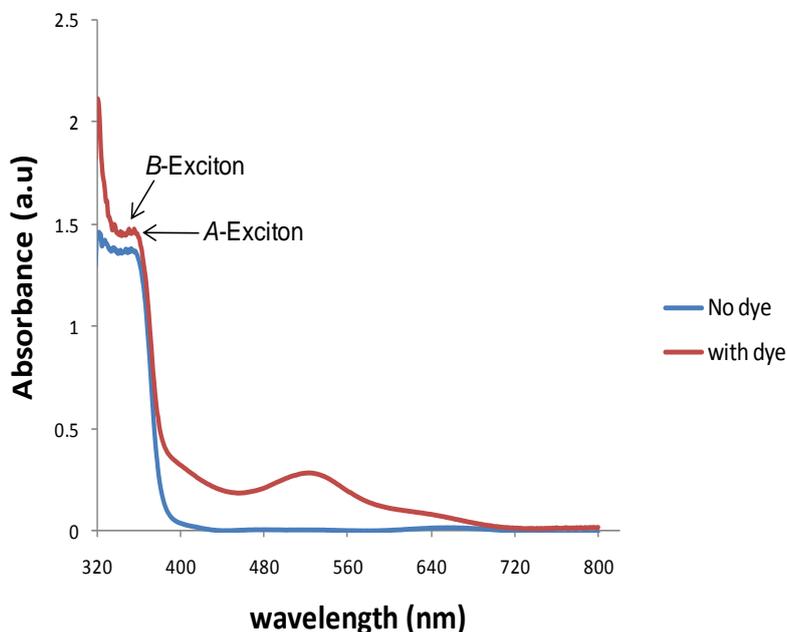


Figure 4. Typical UV-VIS optical absorption spectrum of ZnO nanorods and ZnO coated N179 dye

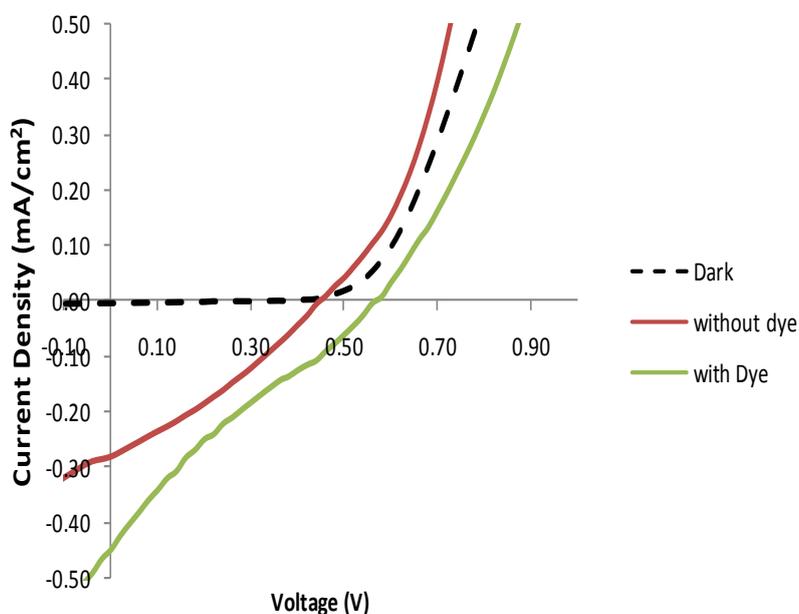


Figure 5. J-V curve of the solar cell of FTO/ZnO/electrolyte/platinum for uncoated ZnO nanorods and ZnO nanorods coated N719 dye

The absorption decreases with the increasing wavelength for all samples until the wavelength of 380 nm. In the visible region ($\lambda > 400$ nm), the absorption of ZnO nanorods coated dye increases until the wavelength of 520 nm and started to decrease until wavelength 700 nm instead of the absorption of uncoated ZnO nanorods. This result is in good agreement with that previously reported [19] on the optical behaviour of ZnO nanorods film and Cds quantum dot on ZnO nanorods prepared by wet chemical process assisted methods. From the figure, the absorption peak was not observed for uncoated ZnO nanorods film but the peak occurs for coated ZnO nanorod film occurs at the wavelength of 520 nm and it is expected to give the best performance when utilized in a photoelectrochemical cell.

Table 1. Photovoltaic parameters of the solar cell with and without dye

Cell	J_{sc} (mAcm ⁻²)	V_{oc} (V)	FF (%)
Uncoated ZnO	0.28	0.44	30
ZnO coated N719 dye	0.45	0.56	24

Fig. 5 shows the current density-voltage curve for the ZnO photoelectrochemical cell in dark and under illumination at room temperature. The device shows rectification property in which the current is dominant in one direction that is in forward bias [20]. Table 1 shows the photovoltaic parameter of the device utilizing ZnO nanorods that have been synthesized by the specified technique. There were two ZnO samples, namely, uncoated ZnO nanorod and ZnO coated N719 dye. It can be seen that the highest short-circuit current density, J_{sc} is 0.45 mAcm⁻² and open circuit voltage, V_{oc} is 0.56 V obtained from the cell utilizing ZnO nanorods coated dye and its J_{sc} was 60.7% higher than that of the cell utilizing uncoated ZnO nanorods. The better performance of ZnO nanorods DSSC was due to a better light harvesting of the ZnO nanorods which served as photovoltaic material of the cell. The result was supported by the UV-Vis absorption spectra of both ZnO samples presented in Fig. 4. As presented in Fig.4, ZnO sample coated with N719 dye shows better optical absorption at the operating wavelength of the cell, which is about at 380 nm. With the better light harvesting, more electron-hole pairs are generated from the valence band to conduction band of ZnO upon the illumination of light. Higher current was collected by FTO electrode and consequently by platinum electrode. This is in a good agreement with the cell utilizing ZnO nanoflower that was reported by C.Y. Jiang et al. 2007 [10]. Comparing with the other solar cell that was reported I. Gonzales-Valls et al (2011), ZnO nanorods was grown for 6 hours with 1.60 μ m height by hydrothermal method and 2 hours dye loading time has yielded J_{sc} of 2.26 mAcm⁻² and V_{oc} of 0.553 V, respectively. The power conversion efficiency of the DSSC was also reported for ZnO nanorods synthesized via hydrothermal method which was 0.56 % with FF 44% [6]. The power conversion efficiency of our DSSC was lower than those reported in [6-9,11] since ZnO nanorods as the photovoltaic material is 220 nm only in average thickness. Smaller number of electron-holes pair are generated compared with thicker ZnO layer upon

illumination. However, ZnO nanorod that was grown by the present technique is very promising technique since the preparation is simple, quick and economical.

4. CONCLUSIONS

We have successfully prepared ZnO nanorod with a simple method of ammonia assisted rapid hydrolysis process technique and fabricated a solar cell of FTO/ZnO-dye/electrolyte/platinum. The performance has been tested in dark and under illumination of 100 mWcm⁻² light. The device shows rectification property and the photovoltaic effect under illumination, with the best J_{sc} of 0.45 mAcm⁻², V_{oc} of 0.56 V and FF of 24%. This result was 40% higher than the cell without dye as photosensitizer.

ACKNOWLEDGEMENTS

We acknowledge the support from the Universiti Tenaga Nasional and Ministry of Science and Technology and Innovation Malaysia under Science Fund 03-02-03-SF0196, TWAS COMSTECH No: 09-109RG/REN/AS.C_UNESCO FR: 32402J1214 and Universiti Kebangsaan Malaysia and Ministry of Higher Education of Malaysia under research grant UKM-GUP-NBT-08-25-086 and UKM-RRR1-07-FRGS0037-2009.

References

1. M. Gratzel, *Nature*, 414 (2001) 338.
2. M. Adachi, Y. Murata, I. Okada and S. Yoshikawa, *J. Electrochem. Soc.*, 150 (2003) G488.
3. D'urr, A. Schmid, M. Obermaier, S. Rosselli, A. Yasuda and G. Nelles, *Nature Mater.*, 4 (2005) 607.
4. N. Kopidakis, K.D. Benkstein, J. van dL and A.J. Frank, *J. Phys. Chem. B.*, 41 (2003) 11307.
5. L. Yang, Z. Zhang, S. Fang, X. Gao and M. Obata, *Solar Energy*, 81 (2006) 717.
6. M. H. Lai, M. W. Lee, Gou-Jen Wang and M. F. Tai, *Int. J. Electrochem. Sci.*, 6 (2011) 2122.
7. I. Gonzales-Valls, Y. Yu, B. Ballesteros, J. Oro and M. Lira-Cantu, *J. Power Sources*, 196 (2011) 6609.
8. P. Charoensirithavorn and S. Yoshikawa, in: Dye sensitized solar cell based on ZnO nano arrays, *The 2nd Joint International Conference on, "Sustainable Energy and Environment (SEE 2006)*, Bangkok, Thailand (2006).
9. M.F. Hossain, T. Takahashi and S. Biswas, *Electrochem. Comm.*, 11, (2009) 1756.
10. C. Y. Jiang, X. W. S., G. Q. Lo, D. L. Kwong and J. X. Wang, *App. Phys. Lett.*, 90 (2007) 263501.
11. Z. L. S. Seow, A. S. W. Wong, V. Thavasi, R. Jose, S. Ramakrishna and G. W. Ho, *Nanotechnology*, 20 (2009) 045604.
12. R. Taslim, M.Y.A. Rahman, A.A. Umar and M.M. Salleh, *Advanced Materials Research*, 364 (2012) 293.
13. A.A. Umar and M. Oyama, *Crystal & Growth Design*, 7 (2007) 2404.
14. A.A. Umar, M.Y.A. Rahman, R. Taslim and M.M. Salleh, *Nanoscale Research Letters*, (2011), 6: 1.
15. V. Kandavelu, H.-Sian Huang, J.-L. Jian, T.C.-K. Yang, K.-L. Wang and S.-T. Huang, *Solar Energy*, 83 (2009) 574.

16. G.H. Lee, *Solid State Comm.*, 128 (2003) 351.
17. K. Vanhusden C.H. Seager, W.L. Warren, D.R. Tallant and J.A. Voigt, *Appl. Phys. Lett.*, 68 (1995) 403.
18. J. Lee , J. Chung and S. Lim, *Physica E*, 42 (2010) 2143.
19. Lee W, Min S K, Dhas V, Ogale S B and Han S.-H, *Electrochem. Comm.*, 11 (2009) 103.
20. M.Y.A. Rahman, M.M. Salleh, I.A. Talib and M. Yahya, *Curr. Appl. Phys.*, 5 (2005) 599.