Enhancement of Energy Conversion Efficiency for Dye Sensitized Solar Cell Using Zinc Oxide Photoanode

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Abstract. Dye sensitized solar cell (DSSC) is a third generation solar cell that is well known for its low cost, simple fabrication process and promised reasonable energy conversion efficiency. Basic structure of DSSC is composed of photoanode, dye sensitizer, electrolyte that is sandwiched together in between two transparent conductive oxide (TCO) glasses. Each of the components in the DSSC contributes important role that affect the energy conversion efficiency. In this research, the commonly used titanium dioxide (TiO$_2$) photoanode has previously reported to have high recombination rate and low electron mobility which caused efficiency loss had been compared with the zinc oxide (ZnO) photoanode with high electron mobility (155 cm$^2$V$^{-1}$s$^{-1}$). Both of these photoanodes had been deposited through doctor blade technique. The electrical performance of the laboratory based DSSCs were tested using solar cell simulator and demonstrated that ZnO is a better photoanode compared to TiO$_2$ with the energy conversion efficiency of 0.34% and 0.29% respectively. Nanorods shape morphology was observed in ZnO photoanode with average particle size of 41.60 nm and average crystallite size of 19.13 nm. This research proved that the energy conversion efficiency of conventional TiO$_2$ based photoanode can be improved using ZnO material.

1. Introduction
Photovoltaic technology had shown rapid growth in the past two decades [1]. It is known that this type of technology supports the use of renewable energy source from sun to produce electricity. There are many types of photovoltaic cell such as gallium arsenide (GaAs) based solar cell [2], silicon (Si) based solar cell [3] and dye sensitized solar cell (DSSC) [4]. Each type of solar cell has their own speciality with difference energy conversion efficiency. Based on research that had been done, GaAs based solar cell has remarked the energy conversion efficiency of 30% [5], Si solar cell with 25% [6] and 12.3% for DSSC [7]. Even though GaAs and Si based solar cell have recorded higher energy conversion efficiency compared to DSSC, these type of solar cells required complicated fabrication process and high manufacturing cost [8,9].Thus, DSSC is suggested as an alternative renewable energy supply as it promised low cost, simple fabrication process and reasonable energy conversion efficiency for low power appliances [10, 11].
DSSC is a third generation solar cell that is first introduced by O’Regan and Gratzel in 1991 which inspired by the photosynthesis process to absorb solar energy or also known as photon and convert it into electrical energy [12, 13]. Basic structure of DSSC is composed of semiconductor photoanode layer, dye sensitizer, electrolyte which is sandwiched together in between two transparent conductive oxide (TCO) glasses that will work as working electrode and counter electrode as shown in Figure 1 [14, 15]. Each of the components in the DSSC contributes an important role that affect the energy conversion efficiency. When DSSC is exposed to the photon, dye molecules that are mounted on the surface of semiconductor photoanode layer will absorb the incoming photon. The photoexcitation of the dye will cause an injection of electrons into semiconductor photoanode layer. The injected electrons will disperse through the semiconductor photoanode structure and emits through the working electrode, external load and proceed to the counter electrode. Next, electrolyte that contains iodide–triiodide (I–/I3–) will act as the mediator to fetch the electrons which arrived at the counter electrode and regenerate the oxidized electrons in the dye molecules. The cycle will continue repeated with the presence of photon in the environment.

![Figure 1. Basic structure and operating principle of DSSC.](image)

The process of photon converted into electrical energy was mainly happen in semiconductor photoanode layer. Semiconductor photoanode layer is the agent that will provide the pathways for electrons to move through and also provide the surface for the dye to be attached. Thus, the selection of the semiconductor photoanode material for the DSSC needs to be taken seriously so that the DSSC will work efficiently. The most commonly used semiconductor photoanode material in DSSC is titanium dioxide (TiO2) [16, 17]. However, TiO2 have the drawback of low electron mobility (0.1 – 4 cm²V⁻¹s⁻¹) [18] that causing it to have high recombination rate [19, 20] which leads to energy conversion efficiency loss [21]. Thus, in this research, the performance of the DSSC with commonly used TiO₂ photoanode had been compared with the zinc oxide (ZnO) photoanode that had been reported to have high electron mobility (155 cm²V⁻¹s⁻¹) [22].

2. Experimental methods

2.1. Fabrication of DSSC

The fabrication process started with cleaning the transparent conductive oxide glass (TCO, 25 mm x 25 mm, ±15 Ω/cm²) in ultrasonic bath using ethanol, acetone and deionized water for 10 minutes sequentially. Next, the glasses were dried using air blower. There are two types of photoanode paste prepared in this research. First, TiO₂ photoanode paste was prepared by mixing 1 g of TiO₂ powder (99% anatase) with 1.5 ml of 0.1M nitric acid solution in a mortar. The solution was stirred using pestle until a soupy solution was formed. Next, ZnO photoanode paste was prepared by mixing 1 g of ZnO powder (98% wurzite) with 6 ml of ethanol mixed with deionized water (7:3) and 0.5 ml of 0.1M nitric acid.
nitric acid solution. Same as the preparation of TiO₂ photoanode paste, the ZnO solution also need to be stirred using pestle until a fine and soupy solution was formed. Before applying the photoanode paste on the TCO glass, the sheet resistance of the TCO was tested using multimeter to determine which side of the glass is conductive. Then, the conductive surface of the TCO glass was placed faced up and covered the edges of the glass using scotch tape leaving 1.0 x 1.5 cm² as the active area as shown in Figure 2. After that, the photoanode paste was deposited on the conductive surface of the TCO glass using doctor blade technique. Then, the samples were annealed at 450 °C in the furnace for 1 hour.

Figure 2. Deposition photoanode paste using doctor blade technique.

After the annealing process of the photoanodes, the substrates were soaked in 0.3 mM ruthenium (Ru N719) dye that had been synthesized using 25 ml ethanol solution for 24 hours. In order to control the environment effect, the samples were stored in a closed space without the presence of light. Figure 3 shows the image of photoanode substrate after the dye soaking. Meanwhile, the counter electrode was prepared by applying the soot of the candle on the conductive surface of the ITO glass as shown in Figure 4. Then, the complete DSSC structure was done by sandwiching the working electrode and counter electrode together using a binder spacer. Next, a drop of iodine solution was dropped in between the two glasses as a mediator for the redox process.

2.2. Characterization
In order to analyze the performance and efficiency of the fabricated DSSC, characterization process was done. Scanning Electron Microscope (SEM-EDX, JOEL JSM-6010LV, Oxford Instrument) was used to observe the surface morphology of each type of synthesized photoanode and the average particle size was measured using ImageJ software. The crystallite size and structure of the photoanode was observed through x-ray crystallography technique using X-Ray Diffraction instrument (D2 Phaser, Bruker). Meanwhile, the absorption ability of the Ru N719 dye was analyzed using UV-Visible Spectroscopy (Lambda 950, Perkin Elmer). Lastly, for the electrical characteristics and energy
conversion efficiency of the fabricated DSSC was investigated using Solar Simulator (SMU 2450, Keithley). During the electrical testing process, the DSSC was exposed under 1000 W/m² light supplied by Xenon Lamp Power Supply (XPS-1600, Solar Light) imitating the real solar energy. From the current-voltage (IV) characteristics, the energy conversion efficiency can be calculated.

3. Results and discussions

3.1. Surface morphology

The surface morphology observed for TiO₂ and ZnO photoanode were shown in Figure 5. Observed in surface morphology of TiO₂ photoanode is the spherical agglomeration of the nanostructure with the average particle size of 19.0 nm. As for the ZnO photoanode, the surface morphology observed is in nanorods shape with the average particle size of 41.6 nm that is bigger than TiO₂ photoanode. The bigger particle size of the photoanode nanostructure will offer bigger surface for the dye attached and thus more light can be absorbed and harvested [23]. In addition, the nanorods structure of ZnO photoanode can provide direct pathways for the electrons to move through the cell and thus increase the energy conversion rate that is in good agreement with the past research [24, 25].

![Figure 4](image)

**Figure 4.** (a) Preparation of counter electrode (b) Carbon coated layer.

![Figure 5](image)

**Figure 5.** Surface morphology of (a) TiO₂ (b) ZnO photoanode X-ray diffraction analysis.

Figure 6 presents the XRD pattern of the TiO₂ and ZnO deposited on the glass substrate. For the TiO₂ photoanode, all of the peaks were indexed with the anatase phase (JCPDS card no 00-021-1272). Meanwhile, the ZnO photoanode were indexed in hexagonal ZnO (JCPDS card no 00-036-1451)
indicating that the nanorods structure were crystallize in wurzite structure. The crystallite size of the 
TiO$_2$ and ZnO photoanode were calculated by XRD line broadening measurement using the Scherrer’s 
equation:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

The XRD data were recorded by using Cu Kα radiation ($\lambda = 1.5406$ Å) over the 2θ range of 20° – 
80°. The calculated average crystallite size for the TiO$_2$ and ZnO photanode is 18.76 nm and 19.13 nm 
respectively.

Figure 6. XRD pattern for TiO$_2$ and ZnO photoanode.

3.2. Optical performance
The ability of a DSSC to absorb sunlight is depending on the dye sensitizer. Thus, it is important to 
measure the absorption capability of the dye viaoptical characterization. In this research, the 0.3 mM 
Ru N719 dye had been tested under 200 – 800 nm light spectrum. Figure 7 shows the absorption 
spectrum of 0.3 mM Ru N719 dye. The absorption peak ($\lambda_1$, $\lambda_2$, $\lambda_3$ and $\lambda_4$) was observed at 211 nm followed 
by $\lambda_5$ at 312 nm, $\lambda_6$ at 393 nm and $\lambda_7$ at 536 nm. Thus, it can be conclude that the absorption spectrum of 
the 0.3 mM Ru N719is broad to absorb the visible part of the solar spectrum.
3.3. Electrical performance

Table 1 listed the comparative performance between TiO$_2$ and ZnO photoanode based DSSC in terms of short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF) and energy conversion efficiency ($\eta$). The I-V curve of the TiO$_2$ and ZnO photoanode based DSSC were also shown in Figure 8. According to the electrical characterization, the highest energy conversion efficiency recorded is 0.34% is obtained from ZnO photoanode based DSSC. By default, the ZnO photoanode had shown better performance as the photoanode compared to TiO$_2$ (0.29%).

| Types of photoanode | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF | $\eta$ (%) |
|---------------------|----------------------|-------------|----|------------|
| TiO$_2$             | 2.42                 | 0.46        | 0.26 | 0.29       |
| ZnO                 | 2.85                 | 0.43        | 0.28 | 0.34       |

4. Conclusions

The enhancement of energy conversion efficiency for DSSC using ZnO had been done in this research. The highest energy conversion efficiency was achieved by ZnO photoanode with the energy conversion efficiency of 0.39% compared to 0.29% by TiO$_2$ photoanode. The nanorods structure obtained in the surface morphology shows that bigger particle of photoanode nanostructure can help to provide bigger surface area for the dye attached and thus more light can be absorbed and harvested. The ZnO nanorods structure also helps to provide the direct pathways for the electrons to move through the cell that can increase the energy conversion rate. The high energy conversion efficiency achieved by the ZnO photoanode is also supported by the chemical properties of ZnO itself where it
has the high electron mobility (155 cm$^2$/V·s) and large free excitation binding energy (60 meV). This research proved that the energy conversion efficiency of the ZnO based DSSC can be further boosted in future and it is a suitable candidate for the photoanode in DSSC.

5. References

[1] Sharma S, Siwach B, Ghoshal S K and Mohan D 2017 **Renew. Sustain. Energy Rev.** 70 529

[2] Lee H J, Lee J W, Kim H J, Jung D-H, Lee K-S, Kim S H, Geum D, Kim C Z, Choi W J and Baik J M 2016 **Phys. Chem. Chem. Phys.** 18 2906

[3] Shanmugam V, Cunnusamy J, Khanna A, Boreland M B and Mueller T2013 **Energy Procedia** 33 64

[4] Hegazy A, Kinadjian N, Sadeghimakki B, Sivoththaman S, Allam N K and Prouzet E 2016 **Sol. Energy Mater. Sol. Cells** 153 108

[5] Norizan M N, Zahari S M, Mohamad I S, Osman R A M, Shahimin M M and Murad S A Z 2017 **IOP Conf. Ser. Mater. Sci. Eng.** 209 12029

[6] Blakers A, Zin N, McIntosh K R and Fong K 2013 **Energy Procedia** 33

[7] Akbar Z A, Oh J H, Hadmojo W T, Yang S J, Do Y R and Jang S-Y 2015 **Opt. Express** 23 A1280

[8] Shakeel Ahmad M, Pandey A K and Abd Rahim N 2017 **Renew. Sustain. Energy Rev.** 77 89.

[9] Abdin Z, Alim M A, Saidur R, Islam M R, Rashmi W, Mekhilef S and Wadi A 2013 **Renew. Sustain. Energy Rev.** 26 837

[10] Prabavathy N, Shalini S, Balasundararaprabhu R, Velauthapillai D, Prasanna S and Muthukumarasamy N 2017 **Int. J. Energy Res.** 41 1372

[11] Xie K, Guo M and Huang H 2015 **J. Mater. Chem. C** 3 10665

[12] Brian O and Gratzel M 1991 **Nature** 353 737

[13] Cavallo C, Di Pascasio F, Latini A, Bonomo M and Dini D 2017 **J. Nanomater.** 1

[14] Ye M, Wen X, Wang M, Iocozzia J, Zhang N, Lin C and Lin Z2015 **Mater. Today** 18 155

[15] Klein M, Pankiewicz R, Zalas M and Stampor W2016 **Sci. Rep.** 6 30077

[16] Nebi M and Peker D 2016 **J. Phys. Conf. Ser.** 766 120-26

[17] Liu J, Huo J, Zhang M and Dong X 2017 **Thin Solid Films** 623 25

[18] Chandiran A K, Abdi-Jalebi M, NazeruuddinM K and Grätzel M2014 **ACS Nano** 8 2261

[19] Zhang J, Zhou P, Liu J and Yu J2014 **Phys. Chem. Chem. Phys.** 16 20382

[20] Basu K, Benetti D, Zhao H, Jin L, Vetrone F, Vomiero A and Rosei F 2016 **Sci. Rep.** 6 23312

[21] M V, K P and M R G2018 **Appl. Surf. Sci.** 436 708

[22] Lai J, Jian D, Lin Y, Ku M and Jian W 2018 **Phys. B Condens. Matter** 532 135

[23] Mohamad I S, Ismail S S, Norizan M N, Murad S A Z and Abdullah M M A 2017 **IOP Conf. Ser. Mater. Sci. Eng.** 209 12028

[24] Nabialek M, Bloch K, Szota M and Sandu A V 2017 **Materiale Plastice** 54(3) 491-494

[25] Rouhi J, Mamat M H, Ooi C H R, Mahmud S and Mahmood M R2015 **PLoS One** 10 e0123433

Acknowledgments

The authors would like to thank School of Microelectronic Engineering, Centre of Excellence Geopolymer and Green Technology (CeGeoTech), Centre of Renewable Energy (CERE) and University Malaysia Perlis for providing the research facilities. Besides, the authors also would like to acknowledge the support from the Research Acculturation Grant Scheme (RAGS) under a grant number of RAGS/1/2015/SG0/UNIMAP/03/3 from the Ministry of Higher Education Malaysia.