Calculation of DSSC parameters based on ZnO nanorod/TiO2 mesoporous photoanode

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Abstract. Photoanode of dye sensitized solar cell (DSSC) plays an important role as electron transport media to accept photogenerated electron from excited state of dye. There are several physical properties that are required from photoanode of DSSC. It should be highly transparent, have large surface area, has a conduction band lower than LUMO of dye molecule, has high charge carrier mobility and finally has a good stability in redox electrolyte process. In this work, DSSC with structure FTO/ZnO nanorod/TiO2 mesoporous/Ru-dye/gel electrolyte/Pt/FTO has been fabricated. In order to modified the structures of photoanode, ZnO nanorod was grown on aluminium doped ZnO seed layer by variation concentration of Al (0 wt%, 0.5 wt% and 1.0 wt%). Zinc nitrate hexahydrate and hexamethylenetetramine used as raw materials for ZnO nanorod growth solution and deposited by self-assembly methods on FTO/Al doped ZnO seed layer. It is then followed by deposition of titania (TiO2) paste by screen printing methods. DSSC parameters i.e. ideally factor ($n$), series resistance ($R_s$), and shunt resistance ($R_{sh}$) was derived from current density-voltage (I-V) curve using the simplify equation of ideal diode model. The influences of ZnO photoanode structures to the solar cell performance will be completely discussed.

1. Introduction
The increasing demand of energy supply has triggered many researchers to find an alternate of renewable energy resources. An interesting technology to develop is photovoltaic technology that could directly convert sunlight into electricity energy. Silicon-based semi-conductor dominated in photovoltaic applications for decades, however, the market is restricted due to their high production and environmental costs [1]. Recently, Dye-sensitized solar cells (DSSC), a low-cost photovoltaic device, have received attention to be investigated although it is required further research to enhance its efficiencies. DSSC was initiated in 1991 by O'Regan and Grätzel [2] and their devices showed efficiency as high as 12% [3]. Some advantages of DSSC are their low-cost and simple manufacturing processes, lightweight, flexible and low toxic [4].

DSSC consists of five components, a conductive substrate, a semiconductor layer, a sensitizer, a redox couple (electrolyte), and a counter electrode [5]. A thick semiconductor layer (e.g. TiO2, ZnO and SnO2) acted as a photoanode is coated or grown on a conductive substrate, a sensitizer (i.e. dye; e.g. N719, N3 or organic dyes or quantum dots (e.g. CdS, CdSe and PbS), an electrolyte (e.g. I3-/I- and Pt/FTO has been fabricated. In order to modified the structures of photoanode, ZnO nanorod was grown on aluminium doped ZnO seed layer by variation concentration of Al (0 wt%, 0.5 wt% and 1.0 wt%). Zinc nitrate hexahydrate and hexamethylenetetramine used as raw materials for ZnO nanorod growth solution and deposited by self-assembly methods on FTO/Al doped ZnO seed layer. It is then followed by deposition of titania (TiO2) paste by screen printing methods. DSSC parameters i.e. ideally factor ($n$), series resistance ($R_s$), and shunt resistance ($R_{sh}$) was derived from current density-voltage (I-V) curve using the simplify equation of ideal diode model. The influences of ZnO photoanode structures to the solar cell performance will be completely discussed.
Co$^{2+}$/Co$^{3+}$ redox couples) injected between the sensitizer and counter electrode, and a counter electrode (e.g. Pt and carbon materials) deposited on another conductive substrate [6, 7].

One of factors that play an important role in DSSC is photoanode. Photoanode is used to collect regenerated electrons from photoexcitation of dye molecules and transfer it to external circuit through transparent electrode. On the other hand, the positive charges would be collected as cations in electrolyte side, contributed in redox cycle with incoming electrons from the external circuit to produce electrical energy [8]. Differences between TiO$_2$ and ZnO coated on conductive polymer as photoanode has been investigated [9]. Anatase TiO$_2$ nanoparticles can be produced with low cost synthetic preparation method in both academic laboratory and industry and the crystalline structure and size of TiO$_2$ crystals give a contribution to the efficiency of DSSC based on TiO$_2$ photoanodes [9,10]. Moreover, TiO$_2$ mesoporous as photoanode in DSSC has been reach 12% efficiency as reported by Yella et.al. [3].

Combination between ZnO and TiO$_2$ as photoanode is one of alternative to develop photoanode system based on metal oxide material. Mozaffari et.al reported that incorporated of ZnO nanoparticles could enhance Jsc value due to supressing of recombination reaction, which occur in TiO$_2$ region [11]. In this case, ZnO nanoparticles act as carrier trapping to capture charge photogenerated from TiO$_2$/dye to reduce recombination process inside DSSC cell. In order to enhance performance of photoanode, combination between ZnO and TiO$_2$ based on advantages of each metal oxide. ZnO has high electron mobility (200 – 300 cm$^2$V/s), on the other hand TiO$_2$ has high energy internal surface area which could increase dye loading on photoanode system.

ZnO properties can be easily changed by engineering modification of its structure, particularly for nanorod structure. One of the ways modifications is adjusting ZnO seed layer to effect nanorod growth. The effect of seed layer condition to ZnO nanorod growth using chemical solution preparation has been investigated [12-13]. From the previous result [14], ZnO doped with a small amount of Al could enhance electrical and optical properties. Differences of Al doping concentration provide an influence on the grain growth leading to produce different surface morphology of ZnO layer. In this paper, we study the effect of Al doping concentration of ZnO seed layer (Al:ZnO) to ZnO nanorod (ZnO-Nr) growth. We also combine Al:ZnO/ZnO-Nr layer with TiO$_2$ mesoporous as photoanode system in quasi-solid DSSC.

The performance of DSSC can be evaluated based on sunlight-electric power conversion energy ($\eta$):

$$\eta = \frac{V_{oc}J_{sc}FF}{P_{in}} \times 100\%$$  \hspace{1cm} (1)

where $V_{oc}$ is the open-circuit voltage (V), $J_{sc}$ the short-circuit current density (mA cm$^{-2}$), $FF$ the fill factor, and $P_{in}$ the power of the incident light.

The mechanism of DSSC can be analysed through equivalent circuits, which can be useful to improve cell performance. Figure 1 shows the equivalent circuit of the single diode model which is widely used for the analysis of silicon solar cells and also DSSC [1]. The relation between external current and voltage is expressed in Equation 2.

$$I = I_{ph} - I_0 \left( e^{\frac{q(V-IR_S)}{n k_B T}} - 1 \right) + \frac{V-IR_S}{R_{sh}}$$  \hspace{1cm} (2)

Figure 1. An equivalent circuit of single diode model
where $I_{ph}$ is photogenerated current, $I_0$ is dark saturation current, $n$ is ideality factor, $R_S$ is series resistance, $R_{sh}$ is shunt resistance, $k_B$ is Boltzmann's constant, $q$ is elementary charge, and $T$ is absolute temperature. The ideality factor $n$ was quantitatively recognized as the inverse of the transfer factor $\beta$, and approaches to unity at high Fermi level [15].

2. Experimental

2.1. Photoanode preparation

Zinc acetate dehydrate (Zn(CH$_3$COO)$_2$.2H$_2$O) and zinc nitrate hexahydrate(Zn(NO$_3$)$_2$.6H$_2$O) purchased from Merck used as raw materials for ZnO seed layer preparation and ZnO nanorods growth solution respectively. 2 methoxyethanol and diethanolamine (Sigma Aldrich) use as solvent and stabilizer on ZnO seed layer preparation. Meanwhile, aluminium chloride (Sigma Aldrich) was used as Al doping source. Deionized water and hexamethylenetetramine (HMTA) use as solvent and complexing agents on ZnO-Nr preparation.

Al:ZnO (undoped, 0.5 wt% and 1.0 wt% of Al) seed layer was deposited twice on FTO substrate using spin coater at 1500 rpm. Two step annealing treatment at 250°C and 500°C was followed to form ZnO seed layer. Self-assembly method was used to grow ZnO-Nr in isolated weighting bottle, with FTO/Al:ZnO seed layer side was facing down at 45°. Growth temperature was fixed at 100°C for 150 minutes. After that, ZnO nanorods was washed in ethanol, deionized water several times, and subsequently annealed at 500 °C for 30 min on furnisher. For photoanode system, one layer of Ti-nanooxide T/SP was deposited on FTO/Al:ZnO/ZnO-Nr by screen printing method and gradually annealed until 500°C for 30 minutes on hotplate.

2.2. DSSC assembly

FTO/Al:ZnO/ZnO-Nr/TiO$_2$ photoanode is ready to use as working electrode of quasi-solid DSSC. Photanode was then immersed on Ruthenium dye (535-bisTBA; purchased from Solaronix) and chenodeoxolydacid (1:10). After overnight, FTO/Al:ZnO/ZnO-Nr/TiO$_2$/Ru was rinsed by acetonitrile several times to remove residue of dye molecules. Drilled platinum coated FTO substrate was used as counter electrode and stack together with working electrode FTO/Al:ZnO/ZnO-Nr/TiO$_2$/Ru separated by hot melt surylin film (thickness 25 µm). Polymer gel electrolyte (PGE) was prepared using gel hybrid copolymer (TMSPMA:TEMS=3:1) dissolved in 0.2 ml propylene carbonate (PC) and mixed with 0.2 ml mosalyte as ionic liquid. Finally, PGE was injected to the hole of Pt/FTO side, and sealed with transparent tape to avoid leaking.

2.3. Characterizations

The scanning electron microscopy (JEOL JSM-6510A) was used to identify the surface morphology of ZnO-Nanorods. X-ray diffraction (X-pert Pro, PW3050/60 x-ray diffractometer) measurement was used to investigated ZnO-Nr structure and continued with data analysis to determine crystals lattice by Debye-Scherrer method. Current voltage (J-V) characteristics was measured using source lamp with power input 36.5 mW/cm$^2$ integrated with Yokogawa GS 200 DC voltage-current source and Yokogawa digital multimeter 7555.

3. Results and Discussions

The cross-sectional image of ZnO-Nr that was grown on ZnO seed layer array deposited on FTO substrate is presented in Figure 2. It is clearly shown that ZnO-Nr has already been formed and vertically aligned. SEM images of Al:ZnO/ZnO-Nr surface layer at different Al doping concentration is shown Figure 3. Diameter of ZnO-Nr is remarkably changed with the existence of Al doping in ZnO seed layer. For undoped seed layer, diameter average is around 350 nm, while for seed layer with Al doping concentration 0.5 wt% and 1.0 wt% is 120 nm and 190 nm, respectively. A small amount addition of Al doping could reduce ZnO seed layer grain size and produce more flat surface with less bulge structure due to $\text{Al}^{3+}$ ion fill the vacant Zn sites resulted smaller crystallite size [16, 17]. ZnO-Nr that was grown on Al:ZnO seed layer showed small diameter compared to undoped seed layer. It could be explained
that a nucleation sites process for nanorod growth depend on grain size of seed layer, therefore the small grain size of ZnO seed layer resulted a small diameter of nanorod [13].

Figure 2. SEM image of cross sectional ZnO-Nrs/ZnO seed layer

Figure 3. SEM images of Al:ZnO/ZnO-Nr with different Al doping concentration (a) 0wt% Al (b) 0.5wt% Al (c) 1.0wt% Al.

Figure 4 shows x-ray diffraction pattern of Al:ZnO/ZnO-Nr deposited on FTO substrate. It is clear apparently shown that peak (2θ) located between 34.3° and 34.7° corresponds with (002) plane and all samples possess pure hexagonal wurtzite structure with c-axis orientation. This result also consistent with the standard card Joint Committee on Powder Diffraction Standard (JCPDS) 36-1451. The average grain size of the ZnO-Nr was calculated using Scherrer’s formula as presented in Table 1. Sample with Al concentration 1wt% has a smallest average grain size than others. The smallest peak intensity is resulted from ZnO-Nr grown on Al:ZnO seed layer with 0.5 wt% Al doping related to self-attraction between nanorod as depicted in Figure 3(b).

Table 1. X-ray Diffraction parameter on Al:ZnO/ZnO-Nr with different Al doping concentration.

| Al doping concentration (wt%) | (2θ) | Crystallite grain size of ZnO-Nr (nm) | Crystal lattice c (Å) |
|-----------------------------|------|------------------------------------|----------------------|
| 0                           | 34.49| 25.58                              | 5.20                 |
| 0.5                         | 34.65| 21.14                              | 5.17                 |
| 1.0                         | 34.39| 15.35                              | 5.21                 |
Fig. 4. XRD patterns of Al:ZnO/ZnO seed layer with variation of Al concentration.

Fig. 5 shows the characteristic J-V curves for the DSSC with Al:ZnO/ZnO-Nr layer and TiO₂ mesoporous layer as photoanode. The measurement was done under illumination of 36.5 mW/cm² intense light. The photovoltaic parameters, which were measured, are presented in Table 2. The highest efficiency $\eta=2.46\%$ was obtained from device with photoanode made of Al:ZnO/ZnO-Nr with Al doping concentration 1.0 wt%, which is due to highest short current density at 3.4 mA/cm². A high current density indicated a higher photogenerated electron transport rate and a better interfacing between ZnO-Nr and TiO₂ mesoporous compared to other samples. As shown in SEM images (Figure 3), ZnO-Nr with Al doping concentration 1.0 wt% has more dense morphology and homogeneous therefore it gives large surface contact area with TiO₂ mesoporous and also dye particle.

Figure 5. J-V curve of Al:ZnO/ZnO-Nr at different Al doping concentration.

Series resistance ($R_s$), shunt resistance ($R_{sh}$) and ideality factor ($n$) were determined using Equation 2. A raw (marked points) and fitted (solid line) data using all parameters, which obtained from Equation 2 is shown in Figure 5. The series resistance value correlated with bulk resistance of semiconductor
material, metallic contact, TCO electrode, electrolyte and interconnections, and the contact resistance between the metallic contact and the semiconductor [18]. The smallest \( R_S \) was resulted from device with Al:ZnO seed layer (1.0 wt% Al doping) which lead to highest photocurrent density. A large photocurrent density also related to low recombination process inside the cell, which indicated with a small ideality factor value (\( n \)). The higher value of \( n \) could be contributed by potential drop at interfacial layer and the recombination current between metal/insulator layer [18]. In this case, employing 1.0 wt% Al doping of ZnO seed layer for ZnO-Nr growth shows smallest \( n \) value which related to low recombination process thus produce a high photogenerated current. \( R_{SH} \) inside the cell is mainly caused by leakage across the cell edge and the presence of crystal defect and/or impurities in the dye/photoanode interfacing region [18]. A high \( R_{SH} \) value indirectly could represent by high FF as seen on Table 2 and J-V curve (Figure 5). A deep investigation on charge transport and recombination mechanism is need to understand and explain device parameters inside the cell.

Table 2. Performance parameters of DSSC with Al:ZnO/ZnO-Nr at different Al doping concentration and TiO\(_2\) mesoporous layer as photoanode.

| Al doping concentration (wt%) | \( R_S \) (Ohm) | \( R_{SH} \) (Ohm) | \( n \) | \( J_{SC} \) (mA/cm\(^2\)) | \( V_{OC} \) (Volt) | FF (%) | \( \eta \) (%) |
|-----------------------------|-----------------|-------------------|------|-----------------|----------------|--------|-----------|
| 0                           | 100             | 7000              | 3.2  | 1.00            | 0.60           | 46     | 0.76      |
| 0.5                         | 150             | 14000             | 3.4  | 0.85            | 0.58           | 50     | 0.67      |
| 1.0                         | 65              | 4500              | 2.9  | 3.40            | 0.60           | 44     | 2.46      |

4. Conclusions
ZnO-Nr has been successfully grown on ZnO seed layer doped with Al (0 wt%, 0.5 wt% and 1.0 wt%) deposited on FTO substrate using self-assembly method combined with TiO2 mesoporous layer as photoanode in DSSC. Based on SEM image and XRD measurement, a better structure and morphology of ZnO-Nr was obtained by Al:ZnO seed layer (1.0 wt% Al doping). From J-V curve, device with photoanode FTO/Al:ZnO (1.0 wt% of Al)/ZnO-Nr/TiO\(_2\) mesoporous has efficiency 2.46% which is attributed by high photocurrent density (3.4 mA/cm\(^2\)). This work emphasizes that combination between a proper ZnO-Nr structure and TiO\(_2\) mesoporous could enhance device performance.

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References
[1] Gonga J, K. Sumathya, Qiao Q and Zhou Z 2017 Renewable Sustainable Energy Rev. 68 243
[2] O’Regan B and Gratzel M 1991 Nature \textbf{353} 737
[3] Yella A, Lee H W, Tsao H N, Yi C, Chandiran A K, Nazeeruddin M K, Diau E W G, Yeh C Y, Zakeeruddin S M and Gratzel M 2011 Science \textbf{334} 629
[4] Gratzel M 2006, \textit{Prog. Photovolt: Res. Appl.} \textbf{14} 429
[5] Obotowo I N, Obot I B and Ekpe U J 2016 \textit{J. Mol. Struct.} \textbf{1122} 80
[6] Ye M, Wen X, Wang M, Iocozzia J, Zhang N, Lin C and Lin Z 2015 \textit{Mater. Today} \textbf{18} 155
[7] Hagfeldt A, Boschloo G, Sun L, Kloo L and Pettersson H 2010 \textit{Chem. Rev.} \textbf{110}, 6595
[8] Basheer B, Mathew D, Benny K. George B K and Reghunadhan Nair C P 2014 \textit{Sol. Energy Mater. Sol. Cells} \textbf{108} 479
[9] Aravind Kumar C, Mojtaba A-J, Mohammad K N and Michael G 2014 ACS Nano \textbf{8} 2261-2268
[10] Hegazy A, Kinadjian N, Sadeghimakki B, Sivoththaman S, Allam N K and Prouzet E 2016 \textit{Sol. Energy Mater. Sol. Cells} \textbf{153} 108
[11] Mozaffari S A, Ranjbar M, Kouhestanian E, Salar Amoli H and Armanmehr M H 2015 \textit{Mater.
Sci. in Semiconducting Processing \textbf{40} 285

[12] Kim K H, Utashiro K, Abe Y and Kawamura M 2014 \textit{Materials} \textbf{7} 2522
[13] Lee H, Shin J H, Chae J, Kim J B, Kim T H and Park K B 2013 \textit{Electron. Mater. Lett.} \textbf{9} 357
[14] Aprilia A, Wulandari P, Suendo V, Herman, Hidayat R, Fujii A and Ozaki M 2013 \textit{Sol. Energy Mater. Sol. Cells} \textbf{111} 181
[15] Bisquert J and Mora-Sero I 2010 \textit{J Phys Chem Lett} \textbf{1} 450
[16] Lee J H and Park B O 2003 \textit{Thin Solid Films} \textbf{426} 94
[17] Imai Y and Watanabe A 2004 \textit{J. Mater. Sci.: Materials in electronics} \textbf{15} 743
[18] Hafez H S, Yahia I S, Sakr G B, Abdel-Mottaleb M S A and Yakuphanoglu F 2012 \textit{Adv. Mater. Corros.} \textbf{1} 8