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# DSSC HETEROJUNCTION PHOTOELECTRODE BASED ZnO-NANOROD/$TiO_2$; DEPENDENCY OF PHOTOELECTRODE MORPHOLOGY INVESTIGATED BY CALCULATING THE I-V CURVES

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**Abstract.** The simple diode model equation can be used to derive solar cell parameters based on current density-voltage measurement. This calculation has an objective to study the working of ZnO nanorod/$TiO_2$ as photoelectrode in dye-sensitized solar cell (DSSC). ZnO-Nr/$TiO_2$ bilayer heterojunction works as photoanode to collect and to transport the electron trough the cell. The equivalent circuit in real solar cell usually based on two diode models by considering the presence a large of recombination process inside the cell (non-ideal diode). We simplified the equivalent circuit with only one diode and one resistor ($R_{sh}$) in parallel with a series resistor ($R_s$) related to photovoltage occurs. The current loss due to back reaction and recombination process which is appeared at the interface area between photoanode/dye and electrolyte corresponds as parallel resistance ($R_p$). An ideality factor ($m$) due to non-linear $\beta$-recombination process which is occurred inside the cell is also derived using this model. The comparison between commonly photoanode (single type of $TiO_2$ mesoporous), multilayer ZnO nanorod/$TiO_2$, and planar heterojunction ZnO/$TiO_2$ is also observed in order to emphasize the interface quality of photoanode relate to solar cell parameters.

***Keywords*: DSSC, heterojunction photoanode, ZnO-nanorod, $TiO_2$,**

## 1. Introduction

Molecular photovoltaics (PV) such as polymer, hybrid, perovskite and dye-sensitized based solar cell offer a unique possibility to adjust distinctly the light-absorbing process and the charge-transporting phenomenon inside the cell [1]. This situation opens up the opportunities to develop and to focus the research only in one component of active material, namely photoanode. The electron transport layer or photoanode is commonly made from a nanostructures oxide layer which supports the chromophores molecules and accepts the photogenerated electron from dye excited state. Conventional oxides such as $SnO_2$, $Nb_2O_5$, $TiO_2$ and ZnO have been widely studied as electron transport layer in emerging PV including hybrid and dye-sensitized solar cells (DSSCs) [2,3]. In spite of many remarkable research efforts in other oxide including $BaSnO_3$ and $Zn_2SnO_4$ [4,5], ZnO and $TiO_2$ are still persisted as photoanode in molecular PV [6].

In Dye-Sensitized Solar Cells (DSSCs), photoanodes based ZnO with various nanostructured have been widely reported, including ZnO film, nanowire, nanoforest, nanocone, and nanorod [7]. Min Zi et.al reported that DSSC constructed with ZnO nanowire arrays as photoanode can absorb more dye, improve the photon utilization rate and provide rapid collection channel for the photoexcited carriers [8].

The primacy offers when using ZnO and $TiO_2$ based photoanode is the stability characteristics and the simply synthesis. ZnO and $TiO_2$ photoanode combination is performed due to sequence the advantages properties of both metal oxides. This combination can offer some advantages such as increment in transparency, charge carrier mobility, and dye loading [9]. The electrical characteristic of nanostructured ZnO and titanium dioxide nanoparticles ($TiO_2$) heterojuction will be ontained from calculating solar cell parameter based on I-V (current-voltage) curve. The resulted I-V curves will be extracted using diode model equation [10,11].

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In this work, the combination between microstuctrured ZnO, aluminium doped ZnO (ZnO:Al) and $TiO_2$ bilayer heterojunction as working electrode (photoanode) in DSSCs was studied. The microstructural of ZnO (planar and nanorod structured) with/without aluminum content was observed by investigating the absorption spectra of photoanode, surfaces morphology and measuring current density-voltage curve (*J-V*) of the cell. Some parameters including series resistance ($R_s$), parallel resistance ($R_p$), and recombination parameters (back reaction order – $\beta$) were also derived from J-V curve using diode model equation (equation 1). Figure 1 shows schematic structure of DSSC and simplified equivalent circuit of one diode model which is used in this work.

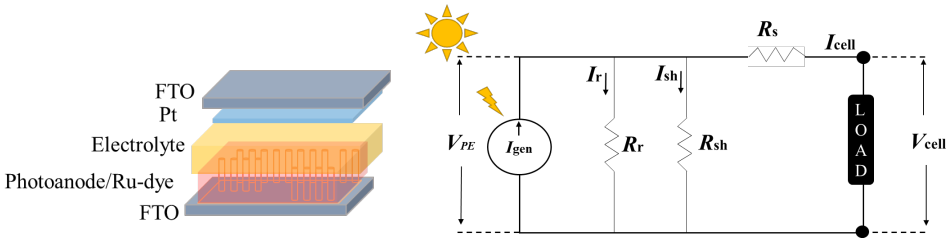



**Figure 1**. (a) Representative schematic structure of dye-sensitized solar cell (DSSC) (b) Equivalent circuit of one diode model [12]

In a single diode model, cell current ($I_{cell}$) and cell voltage ($V_{cell}$) are expressed in equation 1 related to equivalent circuit which is shown in figure 1b, where $m$ is ideality factor, $k_B$ is Boltzmann constant and T is temperature at 298 K ($\frac{k_B T}{q} \cong 25.85\ mV$),

$$I_{cell} = I_{ph} - I_0.\left[exp\left(\frac{V_{cell}+I_{cell}R_s}{m\frac{k_B T}{q}}\right) - 1\right] - \left[\frac{V_{cell}+I_{cell}R_s}{R_p}\right] \quad (1)$$

$$I_{cell} = I_{gen} - I_{rec} \quad (2)$$

Photogenerated current ($I_{gen}$) is produced from the sum of generated current ($I_{ph}$) of an illuminated solar cell and dark saturation current ($I_0$). $I_{rec}$ is the sum of current through $R_r$ and shunt resistance ($R_{sh}$) which is relates to $\beta$- recombination process inside the cell ( $I_{rec} = I_r + I_{sh}$). The series resistance ($R_s$) and parallel resistance ($R_p$) can be obtained by fitting I-V curve using equation 1, $R_p$ is the sum of $R_r$ and $R_{sh}$ in parallel configuration. In practice, the fill factor (FF) value is influenced by $R_s$, $R_{sh}$ and additional recombination occurring inside the cell ($R_r$). $R_{sh}$ or $R_p$ is correlated to leakage current across the cell edge, and the presence of impurities in the junction between dye and photoanode system [11]. Resistances characteristics of solar cell are representation of active cell heterojunction quality. The ideality factor ($m$) is related to solar cell quality and recombination process. The $m$ value can be estimated from fitting I-V curve using diode model equation (1). According to $\beta$-recombination model, the recombination relates to the back-reaction current at the photoanode/dye/electrolyte interface. The ideality factor ($m$) is also recognized as the inverse order of back reaction while the dark saturation ($I_0$) is found proportional to the back reaction in the dark [12].

## 2. Experimental

### *2.1. Materials*

All chemicals used in this study were analytical grade without any further purification. Zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) and zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) were purchased from Merck and used as raw materials. 2-Methoxyethanol and diethanolamine (Merck)

were used as solvent and stabilizer for ZnO thin film (seed layer) preparation. Deionized water (local brand) and Hexametylenetetramine (HMTA) purchased from Sigma-Aldrich were used as solvent and complexing agent of ZnO nanorod growth solution. Aluminum chloride ($AlCl_3$) purchased from Sigma-Aldrich was used as aluminum dopant source material. The preparation procedure of aluminum doped ZnO film (planar) and nanorod were followed our previous works [9,11]. Titania mesoporous (Ti-Nanoxide T/SP), Titania microchannel (Ti-Nanoxide MC-SP), Chenodeoxycolic Acid and Ruthenizer 535-bis TBA (dye molecules,) were purchased from Solaronix. Fluorine doped tin oxide (FTO) 7 ohm/square with low iron 2.2 mm thick glass substrate coating one side with and without platinum layer was used as a cathode and anode.

### *2.2. Photoanodes based ZnO preparations*

For planar heterojunction, ZnO films are prepared from 0.5mM zinc acetate dehydrate in 2-methoxyethanol anhydrous and diethanolamine is used as a solvent and stabilizer respectively. Two layers of ZnO film were deposited on FTO substrate using spin coater at 1500 rpm. FTO substrates were cleaned in ethanol and acetone by ultrasonic cleaner equipment. Two steps heating treatment subsequently required at 250 °C and 500 °C to forming ZnO thin film. The obtained ZnO thin film was used in planar heterojunction as ZnO/$TiO_2$ photoanodes and also as seed layer for nanorod growth. These all methods were followed the procedure from our previous works [9,11].

The ZnO film was also used as ZnO seed layer for ZnO nanorods (ZnO-Nrs). Nanorods structure was grown by self-assembly method in isolated weighting bottle, with FTO/ZnO seed layer side was facing down at 45°. The growth solution was prepared by dissolving equimolar zinc nitrate hexahydrate and hexametylenetetramine (HMTA) in deionized water. Al doped ZnO nanorod was prepared by adding $AlCl_3$ 1.0 weight % with respect to the ZnO nanorod growth precursor. Growing temperature was fixed at 100 °C for 150 min inside the regularly laboratory oven. After that, Al doped ZnO nanorods was washed in ethanol and deionized water several times and annealed up to 500°C for 30 min on an isolated hotplate. Single layer of Ti-Nanoxide T/SP was deposited by screen printing method and gradually annealed at 500°C for 30 minutes, for combination with titania mesoporous [9].

### *2.3. Fabrication of dye-sensitized solar cells*

The FTO with ZnO film/$TiO_2$ and Al doped ZnO-Nrs/$TiO_2$ on top are ready to use as working electrode (photoanode) of DSSC with structure FTO/photoanode/Ru-dye/Pt/FTO. Single type of $TiO_2$-mesoporous is also used as a reference, and prepared by two layer of Ti-Nanooxide T/SP and one layer Ti-Nanoxide macrochannel (MC/SP). The photoanodes was immersed on dye solutions (Ruthenium) containing of 535-bisTBA and chenodeoxolycacid (1:10) overnight. The FTO/photoanode/Ru-dye was washed by acetonitrile and ethanol several times to remove the residues of dye molecules. Drilled platinum coated FTO substrate (Pt/FTO) was used as counter electrode and was sandwiched with working electrode (FTO/ photoanode /Ru-dye) separated by hot melt surylin film (thickness 25 μm). Finnally, electrolyte with triiodide/iodide redox coupled (Mosalyte TDE-250) was injected to the hole at Pt/FTO side, and sealed with transparent tape to avoid a leaking.

### *2.4. Measurements*

The Scanning Electron Microscopy (JEOL JSM-6510A) was used to identify the surface morphology of ZnO-Nanorods and photoanode heterojuction morphology. Ultra-Violet Visible spectroscopy (T70+ PG Instrument) was carried out to ensure Ru-dye molecules attached on photoanode surfaces. Current density voltage (*J-V*) characteristic was measured by Yokogawa GS 200 DC voltage-current source and Yokogawa digital multimeter 7555 under 36.5 mW/$cm^2$ light

irradiation. The obtained data from J-V curved was fitted using diode model equation to calculate the solar cell parameters.

## 3. Results and Discussion

Our previous results showed that the existence of $TiO_2$ layer can improved the dye loading significantly which is shown in absorbance spectrum increments of ZnO-Nr/$TiO_2$/Ru-dye [10]. Figure 2 shows the Ultra-Violet Visible (UV-Vis) absorbance spectra of photoanodes based ZnO layer and ZnO nanorod/$TiO_2$ heterojunction. Aluminum doped ZnO nanorod (Al:ZnO-NR) relatively has low absorbance in visible region due to higher transparency in comparison with ZnO-NR. The aluminium dopan can reduce the ZnO particle size due to smaller atomic radius of Al atoms that occupy Zn sites [11, 14]. Besides that, many researchers have already reported that the aluminium dopan atoms in ZnO film can increase the film transparency due to reducing particle size [15]. The absorbance peak is appeared at visible range caused by ruthenium dye both for Al:ZnO/$TiO_2$/Ru and ZnO-NR/$TiO_2$/Ru samples. A higher absorbance peak is observed for ZnO-NR/$TiO_2$/Ru related to higher dye loading in comparison with Al:ZnO-NR. In order to study the ZnO nanorod structure and $TiO_2$ nanoparticle junction quality, SEM image of Al:ZnO-NR/$TiO_2$ photoanode was carried out (figure 3 (a)). The $TiO_2$ nanoparticle seems cannot diffuse appropriately between rods and is estimated act as a trap site. Figure 2 (b) is undoped ZnO-NR surface). By comparing figure 3 (a) and (b), the structure of Al:ZnO-NR relatively produces a higher self-attraction than undoped ZnO-NR. Figure 3 (b) shows morphology of ZnO-NR/$TiO_2$ and it is clearly shown that the particle size of $TiO_2$ approximately about >30 nm. Ideally, the space between rods can be filled by $TiO_2$ nanoparticle which contributes in enhancement interface area between both metal oxides and dye loading. Schematically, our device heterojunctions are illustrated in figure 4.

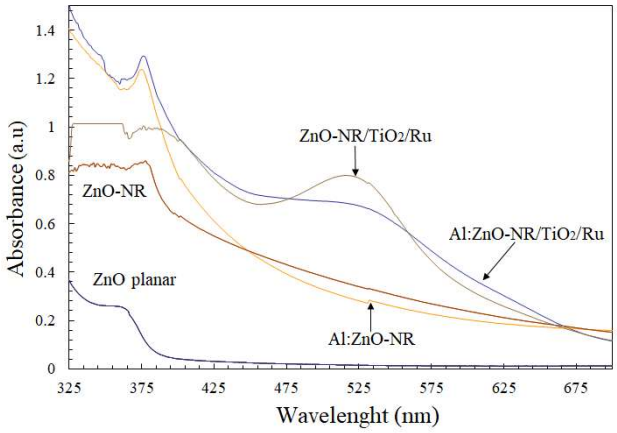
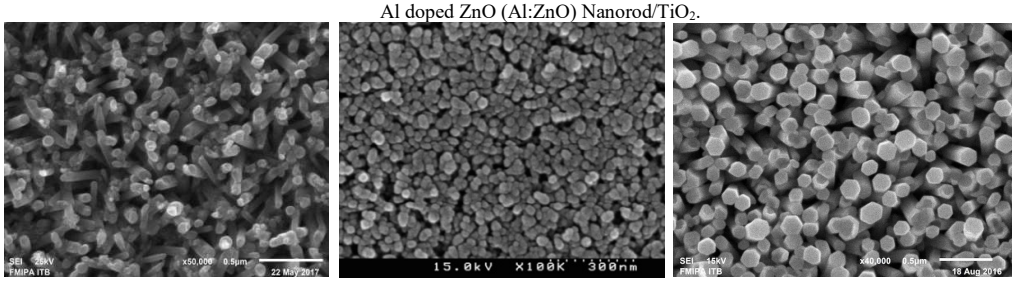
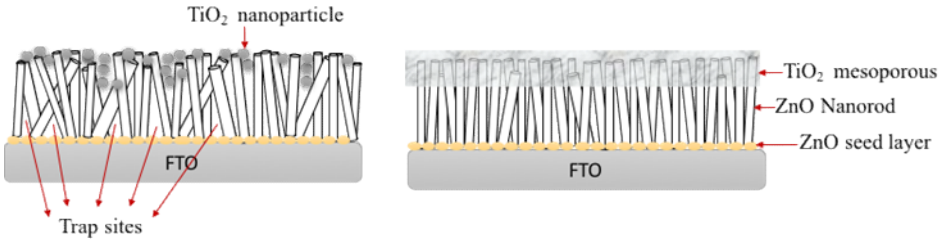



**Figure 2.** Ultra-Violet Visible (UV-Vis) absorbance for ZnO thin film, ZnO nanorod/$TiO_2$ and Al doped ZnO (Al:ZnO) Nanorod/$TiO_2$.



(a) (b) (c)

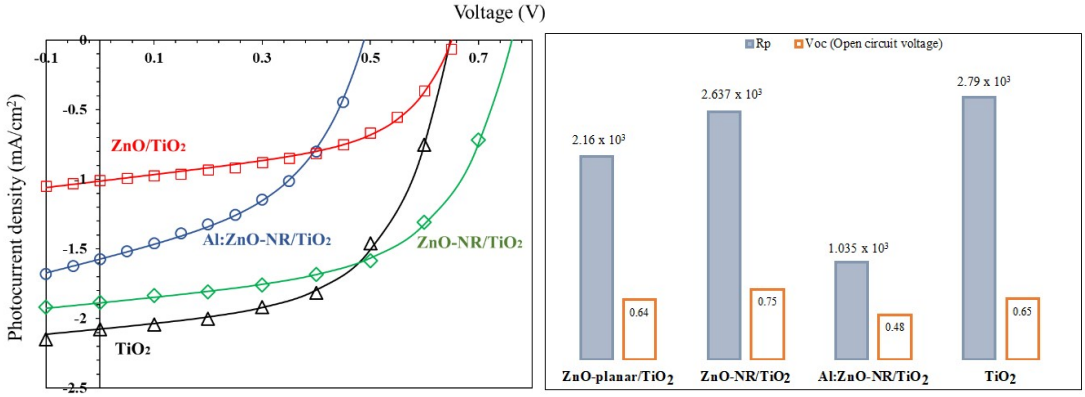
**Figure 3.** SEM images of surface morphology for (b)Al:ZnO-NR/$TiO_2$ photoanode (one time $TiO_2$ coating) (c) ZnO-NR Undoped (reprint from [9]) (d) ZnO-NR undoped/$TiO_2$ photoanode.




(a) (b)

**Figure 4**. Schematic illustrations of (a) Al:ZnO-NR/$TiO_2$ and (b) Undoped ZnO-NR/$TiO_2$ photoanode

Figure 4 (a) illustrates Al:ZnO-NR/$TiO_2$ heterojunction and shows that $TiO_2$ nanoparticle cannot diffuse properly on Al:ZnO-NR surfaces because of disordered nanorod alignment. Undoped ZnO-NR relatively well-ordered hence the infiltration $TiO_2$ was more efficient. This heterojunction condition will be connected with solar cell performance via current-voltage (I-V) characteristic for further explanations.




(a) (b)

**Figure 5**. Current density-voltage curve (J-V), symbols are experimental data and the solid line is curve derived from fitting results.

Current density-voltage (J-V) curve from all devices both using ZnO and $TiO_2$ based photoanodes are shown in figure 5 (a). The simplified diode model (eq.1) was used in fitting process and some parameters are derived from this calculation. Current density-voltage curves fit very well to the experimental J-V curves. All parameters derived and observed (from J-V curve experiment and fitted) are shown in table 1. A highest efficiency of $\eta$ = 2.17% is achieved by ZnO-NR/$TiO_2$, which is in good agreement with our previous work using the same photoanodes ($\eta$ = 2.31% for quasi solid-DSSC) [9]. From all devices, low performance are observed both for ZnO/$TiO_2$ and Al:ZnO-NR/$TiO_2$ photoanode. These results are associated with heterojunction quality between ZnO and $TiO_2$ as represent in figure 4 (a). The quality of photoanode heterojunction is related to open circuit voltage ($V_{oc}$) and parallel resistance ($R_p$) value. Figure 5 (b) shows the values of $R_p$ and $V_{oc}$ have the same trend pattern. Moreover, $R_p$ also affects fill factor (FF) since its correlate with the leakage current in forward bias condition [16]. A lower $R_p$ increases an ideality factor ($m$) corresponds to recombination process inside the cell. In table 1, a low $R_p$ is obtained by Al:ZnO-NR/$TiO_2$ based photoanodes which has a low values of $J_{ph}$, $V_{oc}$ and FF respectively, and agree with $TiO_2$ junction quality as represent in figure 3 based on SEM image (figure 3 (a)).

**Table 1.** The solar cell parameters that collected from J-V characterization and calculated using simplified diode model equation

| Photoanodes | $J_0$ (mA/cm$^2$) | $J_{ph}$ (mA/cm$^2$) | $V_{oc}$ (volt) | FF (%) | η (%) | m | $R_p$ (Ω.cm$^2$) | $R_s$ (Ω.cm$^2$) | 1/m (β) |
|---|---|---|---|---|---|---|---|---|---|
| **ZnO/$TiO_2$** | 0.05 x $10^{-6}$ | -1.01 | 0.64 | 52 | 0.92 | 2.8 | 2160 | 12 | 0.36 |
| **ZnO-Nr/$TiO_2$** | 3.33 x $10^{-6}$ | -1.88 | 0.78 | 56 | 2.17 | 3.8 | 2637 | 6 | 0.26 |
| **Al:ZnO-Nr/$TiO_2$** | 4.44 x $10^{-3}$ | -1.57 | 0.48 | 47 | 0.97 | 3.1 | 1035 | 0.009 | 0.32 |
| **$TiO_2$** | 7.33 x $10^{-4}$ | -2.08 | 0.65 | 54 | 2 | 3.3 | 2790 | 0.12 | 0.3 |

The series resistance ($R_s$) is related to the ohmic contact of DSSC's. It shows that the $R_s$ value is the same order of magnitude for all devices. Lower $R_s$ is observed for Al:ZnO-NR/$TiO_2$ photoanode, which is probably correlated to electrical properties of Al:doped ZnO [14]. In fact, $R_s$ represents the various ohmic losses that occur within the cell. $R_s$ is corresponds to cell solder bonds, cell-interconnect busbars, cell metallization and resistances within the emitter base region [13]. Meanwhile, dark current density/saturation current density ($J_0$) is related to the backreaction process during applied forward bias without any external photogenerating current. At dark condition, current flow inside the cell is influenced by both of series resistance ($R_s$) and parallel resistance ($R_p$). Based on diode model equation, a large $J_0$ will produce a low FF on I-V curve, directly in decreasing of open circuit voltage ($V_{oc}$). The quality of solar cell is also represented in FF value. According to table 1, all samples show relatively small FF (< 60%), therefore improvement in fabrication process is necessary (academic/laboratory scale). Comparison with single type $TiO_2$ photoanodes, the thickness of heterojunction of ZnO nanostructures/$TiO_2$ must be increased. A higher photocurrent that produced by single type $TiO_2$ DSSC's is related to higher dye loading attached. Nevertheless, this work shows that the simple calculation (using single diode model equation) can give an insight of photonode heterojunction quality simultaneously with solar cell performance.

## 4. Conclusions

Single-diode model is a simple equation to calculate solar cell parameters and easy to be implemented. The correlation between DSSC parameter (extracted from I-V curve) and heterojunction quality (photoanodes morphology) is explained in this work. From fitting results using single diode model equation, a beter surface morphology and inter-connection of photoanode will induce a higher parallel resistance, relatively smaller dark current, higher open circuit voltage and photogenerated current. The cell resistance directly influences to device wuality revealed from FF value. The low values of $R_s$ and high $R_p$ are highly required to obtain high performance solar cells.

## 5. Acknowledgement

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