Zinc Oxide/TiO$_2$ Bilayer Heterojunction as a Working Electrode in Quasi Solid Dye Sensitized Solar Cells

A Aprilia[1*], L Safriani[1], Wa Ode S Arsyad[2], N Syakir[1], T Susilawati[1], C Mulyana[1] Fitrilawati[1], R Hidayat[3]

[1] Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, JL. Raya Jatinangor KM 21. Kabupaten Sumedang, 45363, West Java, Indonesia.
[2] Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Halu Oleo, Anduonohu 93232, Kendari, Sulawesi Tenggara, Indonesia.
[3] Department of Physics, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, West Java, Indonesia.

*a.aprilia@phys.unpad.ac.id

Abstract. Bilayer heterojunction of aluminium doped zinc oxide (AZO) and titanium dioxide (TiO$_2$) mesoporous has been successfully deposited on fluorine tin oxide (FTO) substrate as working electrode in dye sensitized solar cell. This layer was used as working electrode in quasi solid dye sensitized solar cell. The solar cell structure is FTO/ZnO/TiO$_2$/PGE/Pt/FTO using polymer gel electrolyte (PGE). In polymer gel electrolyte system, hybrid copolymer based on poly-TMSPMA (3-methoxysilyl propyl methacrylate) was used as a matrix to trap ionic liquid. An addition of aluminum as atom dopant also studied to observe the physical properties changes of photoanode related to solar cell performance. AlCl$_3$ was used as dopant material with the concentrations at 0.5 weight % and 1.0 weight% of zinc acetate dehydrate as raw material. Based on our previous result, the existence of Al dopant would decrease the surface roughness of ZnO layer, reduce the grain size of ZnO particles, transmittance at visible light increase and also change the charge carrier density. Nevertheless, the highest efficiency was achieved for undoped ZnO/TiO$_2$ photoanode (η=0.67%). Based on current-voltage measurement data analysis (using diode model equation) the ideality factor (n) of device using undoped ZnO was smaller (n=2.96) than AZO 0.5 wt% and 1.0 wt% (n=~4), indicate better quality of undoped ZnO/TiO$_2$ interfaces rather than AZO/TiO$_2$.

1. Introduction

Zinc oxide is a II-IV semiconductor material which is widely used in variety of optoelectronics devices, including ultraviolet photodetector, gas sensing, field effect transistor, Schottky diodes, light emitting device arrays and also in emerging photovoltaic (PV) devices [1, 2]. This type metal oxide has a high energy exciton binding ($\sim$ 60 meV), direct wide band gap ($\sim$ 3.34 eV), exhibit near UV emission, high electron mobility (250 cm^2 V/s), and also shows a transparent conductivity and piezoelectricity [2,3]. Many researchers have been studied the effect of ZnO morphologies correlated with some applications, particularly in solar cell devices [4, 5]. One of the type emerging PV device which is used this kind of metal oxide is dye sensitized solar cell (dssc). Many morphology of ZnO structures have been developed for dssc application, for the examples are nanosphere, nanowire, nanorod, nanobelt, and nanocone, in order to enhance device performance [6,7].

In dye sensitized solar cell (dssc) system, photoanode plays an important role as an electron transport material to accept the photogenerated electrons from the excited state of the dye. Considering the role of photoanode, several requirements need to be possessed by metal oxides (as photoanodes on dssc) i.e. highly transparent, possess high surface area to maximize adsorption of dye molecules, has high electron mobility for efficient electron transport and be inert to the redox electrolyte to reduce electron recombination rate [8]. Zinc oxide (ZnO) and titanium dioxide (TiO$_2$) are commonly - used as photoanode materials in solar cell devices. S.A Mozaffari et.al. have been investigated the use both of ZnO nanoparticles and TiO$_2$ as entity of photoanode system. ZnO nanostructure could be acted as carrier trap and suppress the recombination process of the injected photoelectrons that produced by space charge on individual TiO$_2$ nanoparticle [9]. The main factor of reducing the solar cell performance by utilizing the TiO$_2$ particle as individual photoanodes, is charge recombination of photogenerated excitons. Therefore an addition of ZnO nanostructures was expected could be anticipate charge recombination process due to ZnO high electron mobility. Besides that, employing ZnO nanostructure as photoanode generally produce high short circuit current (I_{sc}) regards to an efficiently in charge transport [10].

The series resistance characteristic on dye sensitized solar cell was attributed by many factors such as transport resistance (R_t), ohmic series resistance (R_{OS}), diffusion resistance (R_d), and charge transfer resistances (R_{ct}). R_{os} is correspond to the resistance of FTO sheet and redox electrolyte solution. R_d is the resistance related to electrolyte properties and R_{ct} is the resistance that induced from interfacing between photoanode and electrolyte [11]. The series resistance can be simply calculated using diode model equation for solar cell as shown in equation (1) [12]:

$$I_{cell} = I_{ph} - I_0 \cdot \left[exp \left(\frac{V + I_{cell}R_s}{nV_t} \right) - 1 \right] - \left[\frac{V + I_{cell}R_s}{R_{sh}} \right] \tag{1}$$

where I_{ph} is photogenerated current, I_0 is dark saturation current, n is ideality factor and V_t is voltage of Boltzmann factor at 298 K ($V_t = \frac{k_B T}{q} \cong 25.85 \, mV$). R_{sh} is shunt resistance correlated to leakage current across the cell edge, and the presence or the impurities in the junction between dye and photoanode system. The ideality factor (n) can be estimated from the diode model equation (1) for open circuit condition ($V = V_{oc}$ and $I_{cell} = 0$),

$$V_{oc} = nV_t \ln \left(\frac{I_{ph} + I_0}{I_0} \right) \cong nV_t \ln \left(\frac{I_{ph}}{I_0} \right) \tag{2}$$

using $I_{ph} + I_0 \approx I_{ph}$ because of $I_0 \ll I_{ph}$.

In this work, combination between ZnO (with/without aluminum doped) and TiO$_2$ bilayer heterojunction was used as working electrode (photoanode) in quasi solid dssc. Poly-TMSPMA (3-methoxysilyl propyl methacrylate) was used as gel matrix for ionic liquid as polymer gel electrolyte system (PGE). The influence of different aluminum content was studied by investigating the absorption spectra of photoanode, surfaces morphology and measuring current density-voltage curve (J-V) of the cell. An ideality factor (n), series resistance (R_s) and shunt resistance (R_{sh}) also derived from J-V curve using diode model equation (equation 2).

2. Experimental Methods

2.1. Photoanode preparation and DSSC assembly
In this work, ZnO layer was prepared by sol-gel method with zinc acetate dehydrate (Zn(CH$_3$COO)$_2$.2H$_2$O) (Merck) as raw material. 2-methoxyethanol anhydrous, aluminum chloride (AlCl$_3$) and diethanolamine were used as solvent, dopant material and stabilizer respectively. All materials were purchased from Sigma-Aldrich without further purifications. The aluminum doped ZnO (AZO layer) preparation procedure was followed our previous research [13]. AlCl$_3$ (0.5 weight % and 1.0 weight % respect to the 0.5 M of ZnO precursor) was added into precursor solution and stirred until clear solution was achieved. The precursor solution was spin coated onto transparent conductive

oxide substrate (FTO ~ 7 Ohm/square). The sample was subsequently subjected to heat treatment up to 500°C using a hotplate. Afterward, one layer of TiO$_2$ mesoporous (Ti-Nanoxide T/SP; with anatase particle size about 15-20 nm purchased from Solaronix-SA) was deposited by screen printing technique and gradually annealed until 500°C for 30 minutes on hotplate. The photoanodes was immersed in dye solution containing of 535-bisTBA (Solaronix-SA) and chenodeoxolydacid (1:10) overnight. Before used, the FTO/AZO/TiO$_2$/Ru-dye was washed several times by acetonitrile and ethanol to remove the residual of dye molecules.

The dye sensitized solar cell was built by employing the FTO/AZO/TiO$_2$/Ru-dye as active layer and drilled platinum coated FTO substrate as counter electrode (CE). The CE was sandwiched with FTO/AZO/TiO$_2$/Ru-dye separated by hot melt surylin film (thickness of 25 μm). The polymer gel electrolyte (PGE) was prepared from Poly-TMSPMA gel mixed with 0.2 ml of Mosalyte. The PGE was injected to the hole of Pt/FTO side, and sealed with transparent tape to avoid leaking. The device with AZO/TiO$_2$ photoanode of 0.5 wt% and 1 wt% aluminum dopant are assigned as AZO 0.5 and AZO 1.0, respectively.

2.2. Sample characterizations
The atomic force spectroscopy (AFM) was used to identify the surface morphology of ZnO with different Al content. Ultra-violet visible spectroscopy (T70+ PG Instrument) was carried out for each layer which is built the photoanode system. Current density voltage (J-V) characteristic was investigated using halogen lamp (power input 30 mW/cm^2) integrated with Yokogawa GS 200 DC voltage-current source and Yokogawa digital multimeter 7555.

3. Results and Discussions
The effect of aluminum doped into ZnO morphology was observed by atomic force microscopy (AFM). Undoped ZnO layer (without aluminum dopant) shows a smallest surface roughness compared to others. Undoped ZnO layer morphology has a mountain like surface structure with approximate height about 13.9 nm (figure 1(a)). An addition of Al dopant increases the surface roughness that attributed to the increment of average particle height (28.78 nm for AZO 0.5 and 24.79 nm for AZO 1.0). The average of particle size also reduce as appeared in figure 1. It was already reported, that aluminum as dopant atom could be reduced the ZnO grain size due to the grain packing density behavior [13, 14].

Figure 2 shows the absorbance spectra of each layer that used as photoanode and also for the heterojunction active layer (AZO/TiO$_2$/Ru-dye). There is no significant difference in absorbance spectra between ZnO and AZO 0.5. The blue shift on absorbance peak (368 nm to 345 nm) is related to the small change on energy gap ~3.23 eV to ~3.19 eV (determined by Tauc plot). When titanium dioxide was coated onto AZO layer, the absorbance spectra was increased at ultra-violet region attributed to TiO$_2$ absorbances. The active layer of AZO/TiO$_2$/Ru-dye absorb at visible light region due to the existence of ruthenium particle (as sensitizer). It was already reported that TiO$_2$ has large surface area and can enhance dye loading inside the cell [8].
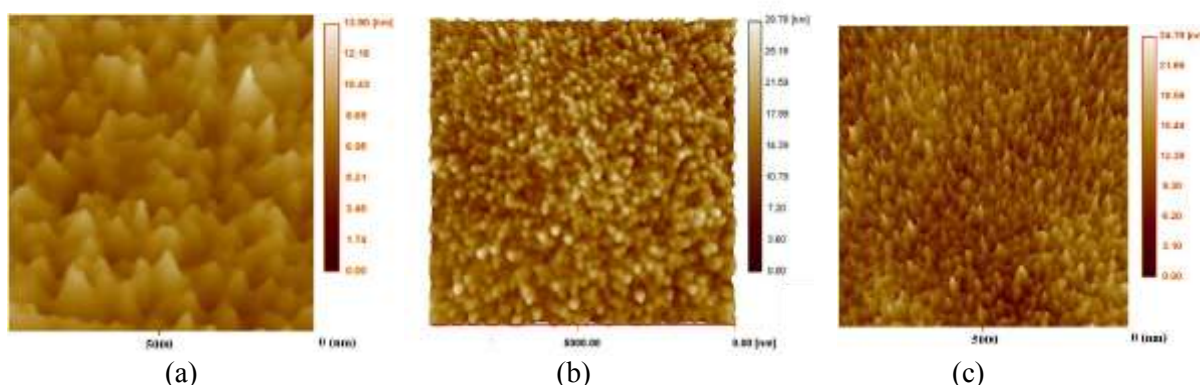

| (a) | (b) | (c) |

Figure 1. Atomic force microscopy images of ZnO layer deposited on glass substrate (a) undoped ZnO, (b) 0.5 wt% AZO and (c) 1.0 wt% AZO.
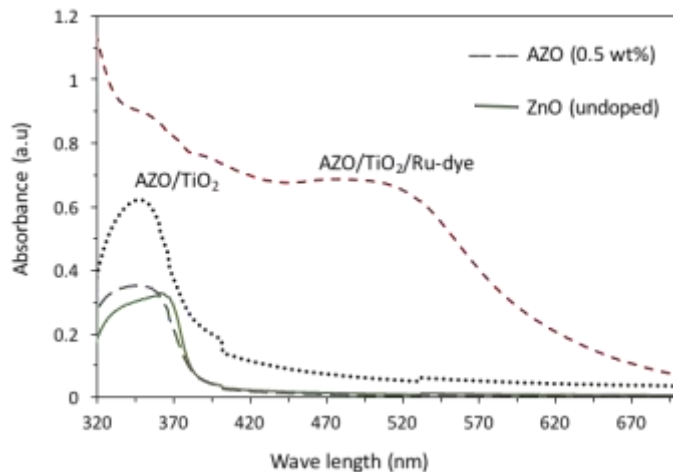
Figure 2. UV-Vis spectra of each layers; thin layer of aluminum doped ZnO (AZO-0.5 wt%) and ZnO, thin film AZO/TiO$_2$ photoanode before and after immersed in Ru-dye solution.

Figure 3 shows the current density-voltage (*J-V*) characteristic under irradiation by halogen lamp (30 mW/cm^2). The J-V characteristic confirm that utilizing AZO in photoanode system (particularly for 0.5 and 1.0 wt % of Al content) do not show a better result compared with undoped ZnO. The efficiency (η) of the device with AZO 0.5 and AZO 1.0 is 0.38% and 0.47% respectively, while undoped ZnO is 0.68%. Actually, this result was not expected before, considering from our previous research that an addition of small aluminum concentration as doping agent can enhance device efficiency [13]. We assume that lower efficiency when using AZO layer is correlated by AZO/TiO$_2$ interface quality. Figure 4 represent the illustration of heterojunction between ZnO and TiO$_2$ based on AFM images.
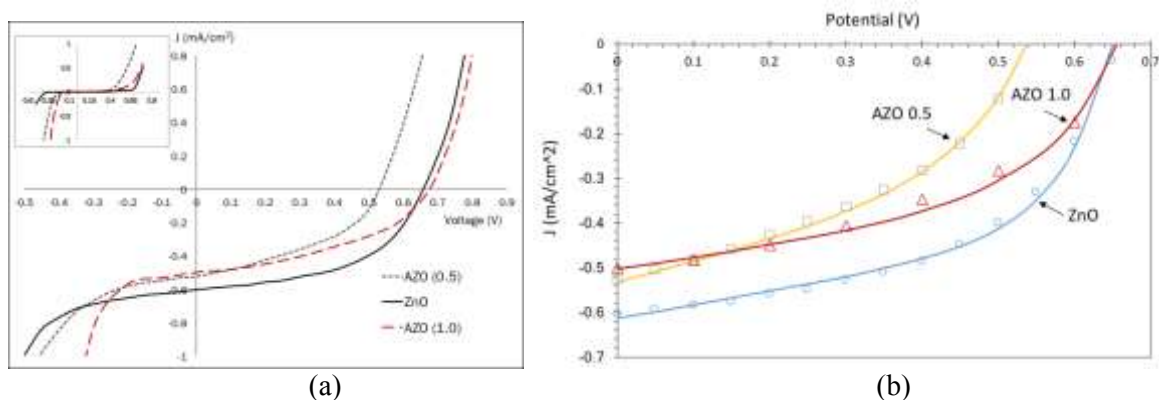

(a)   (b)

Figure 3. (a) Current density-voltage (*J-V*) characteristics of FTO/ZnO/TiO$_2$/PGE/Pt/FTO dye sensitized solar cell. The inset picture is *J-V* curve at dark condition. (b) *J-V* curve of experimental data (marked) and fitted by diode model equation (solid line).
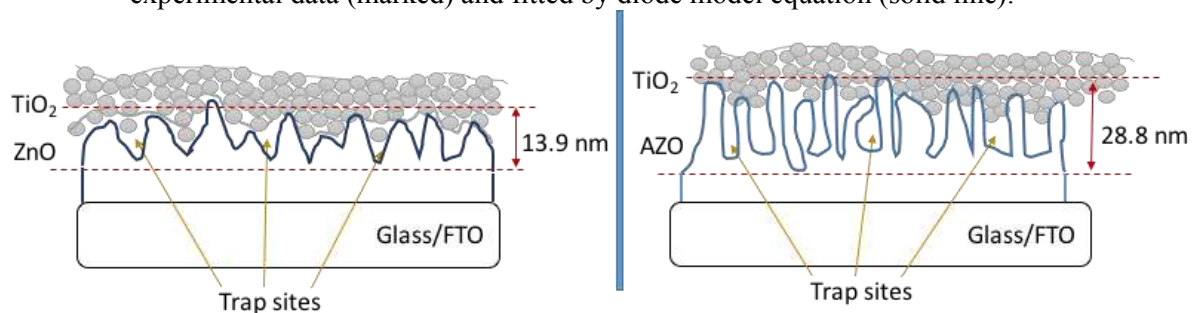

Figure 4. Illustration of ZnO and AZO/TiO$_2$ heterojunction in photoanode system in this work. AZO layer has relatively small grain size with high altitude (mountain like surface) produces more trap sites at interface area with TiO$_2$.

Table 1. Parameters determined from current-voltage characteristics

Photoanode	J_0 (mA/cm^2)	J_{sc} (mA/cm^2)	V_{oc} (volt)	n	R_s (Ohm)	R_{sh} (Ohm)	FF (%)	Efficiency (%)
ZnO–Undoped (0%)	1.25×10^{-4}	0.61	0.65	2.96	120	8.5 K	51	0.67
AZO (0.5 %)	1.67×10^{-3}	0.53	0.53	4	130	19.5 K	41	0.38
AZO (1.0%)	8.3×10^{-2}	0.5	0.69	4.17	150	33.5 K	41	0.47

Device parameters were observed and calculated from *J-V* curves are shown in table 1. An ideality factor (*n*) which is represent the back transfer process (recombination) inside the cell was calculated using equation (2). The series resistance (R_s) and shunt resistance (R_{sh}) were estimated using equation (1). The relation of cell voltage (V_{PE}) under applied bias (*V*) is [11]

$$V_{PE} = V + I_{cell}.R_s \tag{3}$$

therefore, the equation (1) becomes

$$I_{cell} = I_{ph} - I_0.\left[exp\left(\frac{V_{PE}}{nV_t}\right) - 1\right] - \left[\frac{V_{PE}}{R_{sh}}\right]. \tag{4}$$

The device with undoped ZnO has an ideality factor of *n* = 2.96, while AZO 0.5 and AZO 1.0 has *n* = 4 and *n* = 4.17 respectively. The ideality factor value is representation of junction quality and recombination process inside the cell. In ideally junction, the recombination process represented by the recombination of minority carriers in the quasi-neutral regions, thus the *n* equal to 1. If the *n* has a value about 2, it means that other recombination mechanism was occur [11,12]. A high *n* value not only affect the *FF* (fill factor) but also produce a low V_{oc} in consequently with decreasing device efficiency. Besides that, the *FF* also influenced by incident light power density. However, in this work all samples show a relatively small *FF* perchance contributed by device quality and low irradiation incident light (30 mW/cm^2). H.S Hafez et.al. have reported the effect of illumination intensity to the device parameters (J_{sc}, V_{oc} and P_{max}). The change of P_{max} to the power incident light was practically linear, hence the value of internal resistance would not show a significant difference when using the low incident light compared with standard irradiation (100 mW/cm^2) [12]. The series resistance (R_s) for all samples in this work do not show a substantial variance. Nevertheless, the shunt resistance (R_{sh}) of ZnO photoanode has a smallest value than others. According to the diode model equation (equation 4), higher R_{sh} provide a lower leakage photogenerated current and can increase the *FF* value. R_{sh} value between ZnO and AZO seems cannot be comparable because ideality factor (*n*) between them is quite large. Device with AZO photoanode suspected has a more variety recombination process in comparison with undoped ZnO photoanode. This situation probably correlated with the junction quality in AZO/TiO$_2$ photoanode. More investigation are needed, in order to study the type recombination inside the cell.

4. Conclusions
Combination between ZnO and (AZO) with titanium dioxide (TiO$_2$) was investigated, particularly for 0.5 wt% and 1.0 wt% of aluminum respect to ZnO precursor. From AFM measurement, the ZnO and AZO layer have a mountain like surface structure. The existences of aluminum dopant would be decrease the ZnO grain size, meanwhile the height of mountain like structure was increased. UV-vis spectroscopy reveal a blue shift on AZO layer absorbance spectrum due to band gap change and particle size reduction. Moreover, the AZO/TiO$_2$ interfacing area produce more trap sites leading to

bad contact in consequences with high ideality factor (n) value and small efficiency. This work emphasizes that the small concentration of Al ($\leq$ 1 wt%) on ZnO layer (relative flat surface) is not proper to use as photoanode in dssc (in combination with TiO_2 mesoporous), however the large concentration (> 1 wt%) of Al dopant still needs to be investigated.

5. References

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