

Self-Assembly of ZnO-Nanorods and Its Performance in Quasi Solid Dye Sensitized Solar Cells

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Abstract. Zinc oxide (ZnO) nanorods (NRs) were successfully prepared by self-assembly methods using zinc nitrate hexahydrate and hexamethylenetetramine as raw materials. ZnO-NRs were grown on FTO/ZnO seed layer and to enhance dye adsorption it was continued by deposition of titania (TiO₂) paste by screen printing method. Deposition time of ZnO-NRs were varied, for 120, 150 and 180 minutes and subsequently stacked with one layer of TiO₂ mesoporous. The resulting heterojunction layers of FTO/ZnO-NRs/TiO₂ was then applied as a photoanode in quasi-solid dye sensitized solar cell (QS- DSSC) with polymer gel electrolyte (PGE) as a hole conductor. UV-Vis spectrometer was used to investigate the changes of dye adsorption in photoanode with/without inserting titania mesoporous. Characterizations of scanning electron microscopy (SEM) and X-ray diffraction was carried out and the results shows that increasing the deposition time produces a smaller average grain size, diameter and denser layer of ZnO-nanorods. From current-voltage measurement, higher efficiency ($\eta = 2.53\%$) was obtained for 120 min ZnO nanorods with short circuit current density (J_{sc}) of 2.84 mA/cm² and open circuit voltage (V_{oc}) of 0.7 V. The combination of TiO₂ and ZnO-NRs shows a better performance in solar cells characteristics due to increases of dye adsorption on photoanode and high photogenerated electron transport rate. This work emphasizes an optimum condition of ZnO-NRs in combination with TiO₂ mesoporous as an alternative photoanode in QS- DSSC.

1. Introduction

Many researchers have been investigated the use of metal oxides such as zinc oxide and titanium dioxide as working electrode in many types emerging photovoltaic devices [1]. As semiconducting material with high energy exciton binding (~ 60 meV), direct wide band gap (~ 3.34 eV), and high electron mobility ($200 - 300$ cm² V/s), ZnO is attractively to use as an active electrode in hybrid/organic solar cells [2], meanwhile titanium dioxide (TiO₂) commonly use in dye sensitized solar cell (DSSC) systems [3]. A. K. Chandiran et.al. have been investigated the differences between ZnO and TiO₂ as working electrode in DSSC and their self-advantages. TiO₂ based photoanode generally introduce a high external quantum efficiency (EQE) due to high energy internal surface area, making a large contact with dye particles, while ZnO photoanode with high electron mobility will also



produce a high recombination process on interface between ZnO and dye particle [4]. In order to utilizing the unique properties of ZnO in dye sensitized solar cells, many researchers have tried to modify the micro/nanostructures ZnO surface become nanocone, nanowire, nanorod or even nanoforest to produce a large surface area (in consequences with a better contact and high loading of dye particles) [5,6].

In dye sensitized solar cell (DSSC) systems, photoanode plays an important role in order to collect the regenerated electrons from photoexcitation of dye molecules and transfer it to external circuit through the transparent electrode, meanwhile the positive charges would be collected as cations in electrolyte side, contributed in redox cycle with incoming electrons from the external circuit thus electrical works were performed [7]. Besides that, there were several physical properties requirement as a photoanode layers in DSSC -systems such as highly transparent at visible area (400-750 nm), large surface area leading to high loading of dye particles, has a level conduction band lower than LUMO (lowest unoccupied molecular orbital) of sensitizer (dye) in order to compensate the generated charge injection at opposite side, high charge carrier mobility or even produces an efficient charge transport, and also has a good stability on redox electrolyte processes [8].

Almost physical properties of semiconductor metal oxides as photoanode correlated with its nano-crystalline morphology contribute to the efficient operation of the device. On a flat surface, only a few amount of light can absorb and used in photoexcitation in active layer (dye molecule) because of smaller cross section/interfacing area between dye molecule and photoanode. To enhance the incoming light absorption in active layer, one of methods is by surface micro/nanostructures engineering of photoanodes. Fine structures photoanode could be enhance the interfacing surface between metal oxide and dye molecules. According to this, we try to combine ZnO nanorod with titania mesoporous as working electrode in dye sensitized solar cell using polymer gel electrolyte based on polyethylene glycol and ionic liquid (mosalyte). It was already reported, the uses of this kind gel electrolyte in DSSC system shows a relatively stable photovoltaic performance [9, 10]. Figure.1 shows the energy band diagrams and schematic structure of the device during this research. Combination between zinc oxide nanorods and titania mesoporous were expected to enhance device performance due to the advantages properties of each metal oxides.

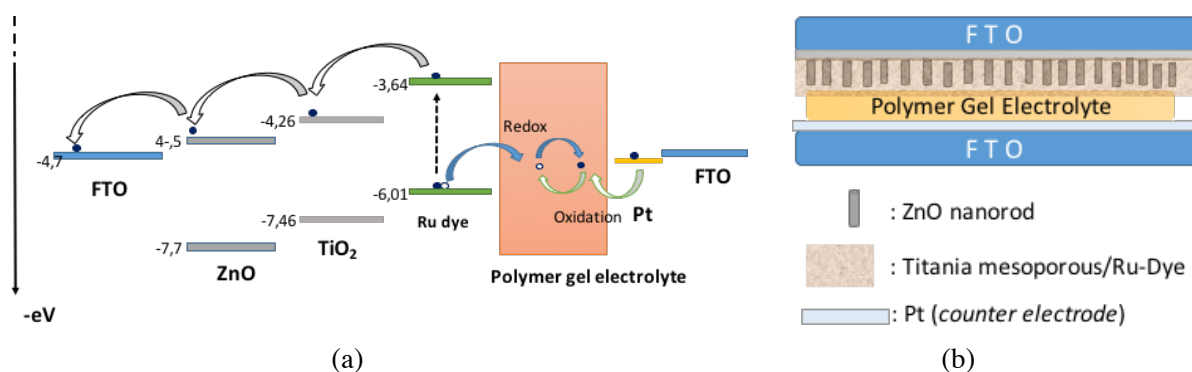


Figure 1. (a) Energy band diagrams and (b) Schematic representation of FTO/ZnO-Nrs/TiO₂/Ru-dye/Pt/FTO device structure.

2. Experimental Methods

All chemicals used in this study were analytical grade without further purifications. Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were purchased from Merck and used as raw materials for ZnO seed layer preparation and ZnO nanorods growth solution respectively. Titania mesoporous (Ti-Nanooxide T/SP) and dye molecules (Ruthenizer 535-bis TBA) purchased from Solaronix S.A. (Switzerland). Low iron 2.2 mm thick glass substrate, with a 7 ohm/square (FTO) fluorine doped tin oxide coating one side with and without platinum layer used as a cathode and anode (Solaronix S.A).

2.1. Photoanode preparation

Two layers of ZnO seed layer was deposited on FTO substrate using spin coating technique at 1500 rpm. Before used, FTO substrate were cleaned in ethanol and acetone by ultrasonic cleaner equipment. ZnO seed layer precursor made from 0.5mM zinc acetate dehydrate in 2-methoxyethanol anhydrous (Sigma-Aldrich) and diethanolamine (Sigma Aldrich) as a solvent and stabilizer respectively. A transparent precursor solution was achieved and continued with deposits it onto cleaned FTO substrate. Two step annealing treatment at 250 °C and 500 °C was followed to form the ZnO particle as seed layer. These all methods following the procedure from our previous research [11].

ZnO nanorods (ZnO-Nrs) were grown by self-assembly methods in isolated weighting bottle, with FTO/ZnO seed layer side was facing down at 45 °. The solution for growing ZnO nanorods was prepared by dissolving equimolar zinc nitrate hexahydrate and hexametylenetetramine (HMTA) in deionized water. Temperature of growth was fixed at 100 °C for 120 min, 150 min and 180 min inside the regularly laboratory oven. After that, ZnO nanorods was washed in ethanol and deionized water several times and then annealed at 500 °C for 30 min on isolated hotplate. For combination with titania mesoporous, one layer of Ti-Nanooxide T/SP was deposited by screen printing methods and gradually annealed until 500 °C for 30 minutes on hot plate.

2.2. DSSC assembly

The FTO with ZnO-Nrs and titania mesoporous on top is ready to use as working electrode (photoanode) of gel state (quasi solid) DSSC with structure FTO/ZnO-Nrs/TiO₂/Ru-dye/Pt/FTO. The photoanodes was immersed on dye solutions (Ruthenium) containing of 535-bisTBA (Solaronix SA) and chenodeoxylydic acid (1:10) overnight. Before use, the FTO/ZnO-Nrs/TiO₂/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 it was sandwiched with working electrode (FTO/ZnO-Nrs/TiO₂/Ru-dye) separated by hot melt surylin film (thickness 25 µm). Polymer gel electrolyte (PGE) was prepared by dissolves a polyethylene glycol (0.25 M) in polycarbonate and mixed with 0.2 ml of mosalyte. After that, PGE was injected to the hole at Pt/FTO side, and sealed with transparent tape to avoid a leaking.

2.3 Characterizations

The scanning electron microscopy (JEOL JSM-6510A) was used to identify the surface morphology of different time of growth ZnO-Nanorods. In order to study an addition of titania mesoporous on photoanode system, ultra-violet visible spectroscopy (T70+ PG Instrument) was carried out for each layers includes Ru-dye loaded on photoanode surfaces. To confirm the nanorod structure on each samples, X-ray diffraction measurement was used (X-pert Pro, PW3050/60 x-ray diffractometer) and continued with data analysis to determine crystals lattice of ZnO-Nrs by Debye-Scherrer method. Current voltage (J-V) characteristics was investigated using halogen lamp (power input 36.5 mW/cm²) integrated with Yokogawa GS 200 DC voltage-current source and Yokogawa digital multimeter 7555.

3. Results and Discussions

The SEM images of ZnO-Nrs on FTO substrate was observed as shown in figure 2. The images show that a pore size (space between each ZnO-Nrs) was decreased as time of growth increased. A sample with 180 min time of growth denser than the others, with pore size approximately 50-150 nm. The 120 min pore size was bigger than other samples (200-500 nm). This results imply, when the deposition time increase, the space between nanorod would be reduced. From SEM images it is ensured that TiO₂ with particle size about 15-20 nm could be diffused easily and fill the ZnO-Nrs pores.

Figure 3 shows x-ray diffraction pattern of ZnO-Nrs on FTO substrate. All peaks of ZnO-Nrs were observed as hexagonal wurtzite zinc oxide structure consistent with the standard card Joint Committee

on Powder Diffraction Standard (JCPDS) 36-1451. In order to investigate the influences of growing process, Debye –Scherrer formula was employed to determine the crystal lattice of each sample [12]. The result showed that the ZnO-Nrs samples prepared through self-assembly methods have strong peak located (20) between 34.1° and 34.5° corresponds with (002) plane and possessed pure hexagonal wurtzite structure with high c -axis orientation. The sharp peaks on XRD pattern indicate that the ZnO-Nrs possessed an excellent crystal quality. The average grain size of the ZnO-Nrs was estimated using Scherrer's formula that already reported elsewhere [11,12], and the sample with 180 min time of growth has a smallest average grain size than the others.

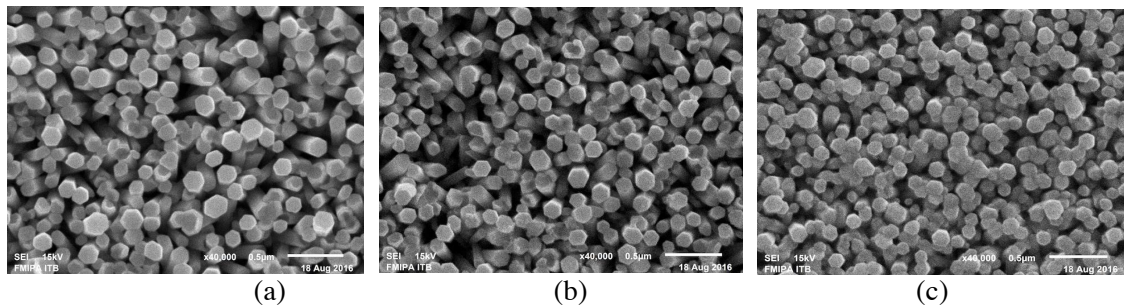


Figure 2. SEM images for ZnO Nanorods (a) 120 min (b) 150 min (c) 180 min

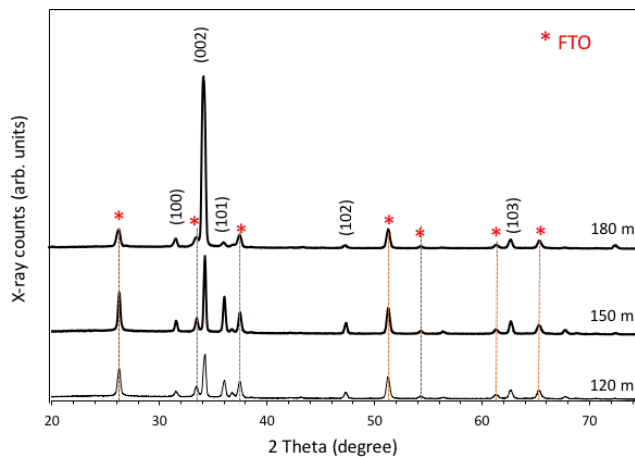


Figure 3. XRD patterns of ZnO-Nrs by variations of deposition time. Peaks marked by red star attributed to fluorine tin oxide film on glass substrate. In fact, there are several ZnO peaks that agreed with JCPDS data for hexagonal wurtzite zinc oxide structure. A dominant (002) preferred orientations was observed as time of growth increase, particularly for samples with 180 min time of growth. It indicates that increasing a deposition time the nanorods with smaller structure were formed.

Table 1. X-ray diffraction parameters of ZnO-Nrs. a and c were crystal lattice in wurtzite (hcp) structure, and D is grain size of ZnO-Nrs

ZnO-Nrs time of growth (minutes)	2 θ (100)	2 θ (002)	a (Å)	c (Å)	D (nm)
120	31.48	34.15	3.28	5.25	53.9
150	31.54	34.22	3.27	5.24	68.9
180	31.87	34.44	3.24	5.20	44.8
ZnO (JCPDS)	31.76	34.42	3.25	5.20	

Table 1. shows x-ray diffraction parameters of ZnO-Nrs and this results were supported by SEM images for 180 min time of growth that shows a smallest average diameter of ZnO-Nrs. These results

indicate that increases time of growth would reduce the grain size, diameters and producing a denser layer of ZnO-Nrs structures. Actually, this phenomenon come to an understanding with the size of nanorods strongly depend on $[Zn^{2+}]$ and $[OH^-]$ concentrations during the growth process. Thus a long time of growing process facilitates the supersaturation of ZnO leading to produce a smaller structure [13]. Lin et.al have been clarified that increasing temperature and time deposition on ZnO-nanorods growth by hydrothermal method, the aspect ratio (L/r) would be increased while the concentration of precursor keeps constants [14].

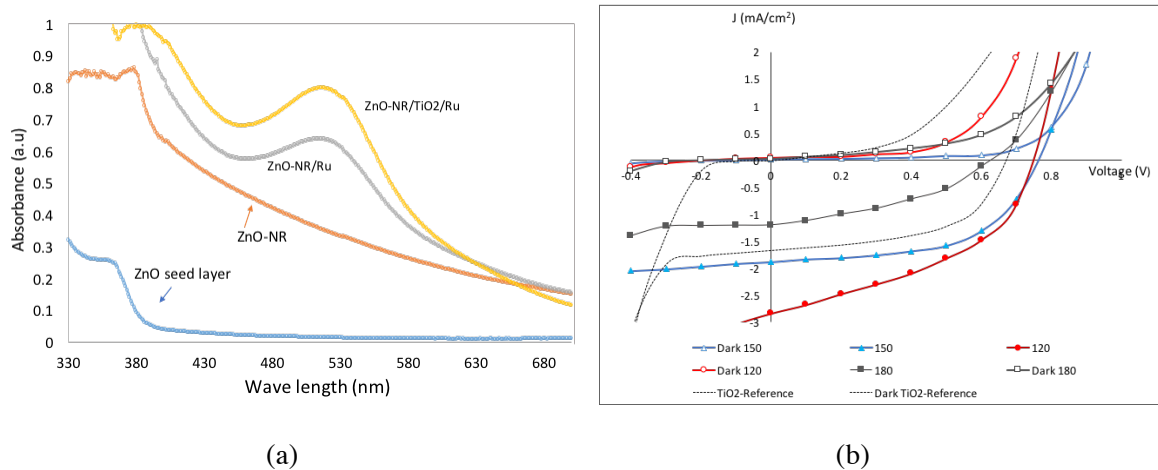


Figure 4. (a) Ultra-violet visible spectra of each layers that composed of ZnO-Nrs/TiO₂ photoanodes for 120 min time of growth nanorods structure (b) Current-voltage characteristics curve of gel state dye sensitized solar cell (quasi solid DSSC) measured under irradiation of 36.5 mW/cm² halogen lamp.

TiO₂ material is already known to has a large surface area; thus a dye particle efficiently adsorb prominent higher dye loading compared to ZnO [4]. Therefore, in this work we combine the titania mesoporous and ZnO-Nrs as photoanode of the devices. Figure 4 (a) shows UV-Vis spectra for all samples, it reveals that ZnO-Nrs/TiO₂/Ru-dye heterojunction layer has a higher absorbance at visible region (correlated with Ru-dye absorbance area) compared with ZnO-Nr/Ru-dye. This result implies that an addition of titania mesoporous is effective to enhance dye loading in photoanode.

Table 2. Device parameters determined from current-voltage characteristics.

ZnO-Nrs Time of growth (minutes)	J _{sc} (mA/cm ²)	V _{oc} (volt)	FF (%)	Efficiency (%)
120	2.84	0.74	44	2.53
150	1.88	0.75	60	2.31
180	1.3	0.62	40	0.88
TiO ₂ only	1.67	0.64	57	1.67

Current-voltage characteristics of all devices was carried out under irradiated by halogen lamp with 36.5 mW/cm² power input. The J-V (photocurrent density – voltage) curves are shown in figure. 4 (b). Short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and efficiency were observed and calculated as presented in table 2. Energy conversion efficiency obtained for quasi solid DSSC with 120 min, 150 min, 180 min time deposition of ZnO-Nrs are 2.53%, 2.31%, 0.88%

respectively. A lower efficiency for 180 min was induced by the low of short circuit current and the FF correlated with the ZnO nanostructures. ZnO-Nrs with 180 min time depositions has a smaller pores size thus the titania particles could not fill the pore efficiently and makes a self-layer on top of ZnO-Nrs. This situation produces an empty space between them (ZnO-Nrs/TiO₂) leading to a bad contact of photoanode systems consequently generating small current. By contrast, however the sample with 120 min time deposition of ZnO-Nrs has a large short circuit current density ($J_{sc} = 2.84 \text{ mA/cm}^2$) but shows a lower fill factor (FF) compared with 150 min. It was attributed by higher photogenerated electron transport rate and better interfacing between ZnO-Nrs and titania mesoporous, but it could be produce an unbalance of charge carrier mobility between cathode and anode leading to small FF. ZnO material has a fast electron transfer compared to TiO₂ but also has a high probability for recombination process, therefore the relative small FF was obtained. Interestingly in this case, the 150 min ZnO-Nrs shows a large FF compared to other samples even for TiO₂ only as photoanode, indicates a better junction inside DSSC system, predominantly between photoanode and electrolyte gel. These results assume that ZnO-Nrs/TiO₂ heterojunction; with an optimum condition of controllable ZnO nanostructures, can be used as an alternative photoanode in QS-DSSC.

4. Conclusion

ZnO nanorods with fine structure was successfully prepared using self-assembly method, with time of growth was varied by 120 min, 150 min and 180 min, at 100 °C. From SEM and XRD measurements, it concluded that increasing time of growth in deposition process produce a smaller average grain size, diameter and denser layer of ZnO-nanorods. From current-voltage measurement, higher efficiency was obtained using 120 min ZnO nanorods with short circuit current density (J_{sc}) of 2.84 mA/cm^2 and open circuit voltage (V_{oc}) of 0.7 volt. Furthermore, the combination of TiO₂ and ZnO-NRs shows a better performance in solar cells characteristics due to increases of dye adsorption in photoanode leading to high photogenerated electron transport rate. A better fill factor was achieved for device with 150 min ZnO-Nrs indicates an optimum condition of nanostructures and a balance of charge collections at each opposite electrodes.

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