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Effect of the Thickness of Quasi One-Dimensional Zinc Oxide Nanorods Synthesized via Multiple Growth Process under Ammonia Assisted Hydrolysis Technique on the Performance of Dye-Sensitized Solar Cell

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Vertical array quasi ZnO nanorods is synthesized on FTO coated glass substrate via a one-dimensional crystal growth of attached-nanoseeds in an aqueous solution containing zinc acetate and ammonia at room-temperature. The growth processes are carried out at five different cycle growth process (one to five times) in order to obtain quasi one-dimensional ZnO nanorods with various morphologies in terms of diameter and length of the nanorod. These quasi ZnO nanorods are coated with cis-bis (isothiocyanato)bis (2,20-bipyridyl-4, 40-dicarboxylato)-ruthenium (II) bis-tetrabutylammonium dye (N719) and are then used as photovoltaic material of dye-sensitized solar cell (DSSC). FESEM results show the diameter and length of ZnO nanorod increase with the number of growth cycle. The UV absorption spectra show that the optical absorption increases with the length of ZnO nanorods coated with the dye. The J_{sc} of the cell is increased by increasing the length of the nanorods up to the optimum length of 180 nm. The highest J_{sc} and V_{oc} of 0.72 mAcm^{-2} and 0.6 V under illumination of 100 mWcm^{-2} light were obtained for the cell with the ZnO nanorods synthesized with 3rd growth cycle.

Keywords: ammonia, dye-sensitized solar cell, hydrolysis process, vertical array quasi zinc oxide nanorod

1. INTRODUCTION

Dye-sensitized solar cell (DSSC) invented by Gratzel and his co-workers receives a large attention of many researchers since a photoelectrochemical cell utilizing TiO_2 nanocrystaline and zinc

porphyrin (YD2-*o*-C8) dye achieved world record efficiency as high as 12.3% [1]. DSSC becomes a research of choice in the field of solar cells in recent years owing to its advantages of low cost, easy fabrication and flexibility over other types of solar cells such as silicon and thin film solar cells [2]. DSSC is normally based on the photo-excitation of dye molecules adsorbed on the surface of sintered TiO_2 nanoparticles [3]. The dye harvests the incident light and generates electrons, which crosses about 10^3-10^6 nanoparticle to reach the collection electrode [3]. Some works on nanowires or nanorods provide direct conduction path for electrons from the valence band of metal oxide semiconductor to the collection electrode, thereby eliminating the grain boundaries between nanoparticles [3-4]. It is beneficial for electrons injection by replacing TiO_2 nanoparticles by nanorods (nanotubes or nanowires) [5-6] to improve the solar cell performance.

Recently, ZnO has widely been utilized as alternative material to TiO_2 in DSSC due to its unique properties with similar band gap (3.20 eV) and large exciton binding energy of 60 MeV at room temperature. There are special reasons of ZnO to become a photovoltaic material of choice due to close band gap and energetic position of the maximum valence band and the minimum conduction band compared with TiO_2. Wurtzite hexagonal structure of ZnO promotes the generation of well-aligned ZnO nanostructure and it also present superior electrons transport comparedwith TiO_2 [7-8]. ZnO with nanorods morphology is among the shape that becomes the focus of attention of many researchers to be utilized in DSSC. So far, DSSC utilizing ZnO nanorod with reasonably high performance, such as prepared by: a one-step catalyst-free chemical-vapor deposition (CVD) method has demonstrated the power conversion efficiency as high as 1.82% [9].

ZnO nanorod based DSSC that was prepared using another method, such as hydrothermal technique, has also been reported to obtain the efficiency as high as 1.69% [10-12]. Meanwhile, the DSSC utilizing ZnO nanorod prepared with a nucleation–dissolution–recrystallization growth technique has been reported to demonstrate the efficiency as high as 1.32% [13]. Some efforts were also put on the enhancement of surface area for ZnO nanorod [14-15] for the utilization in DSSC. ZnO nanoflower is one of ZnO nanostructure that was synthesized via hydrothermal technique, producing the efficiency as high as 1.9%, which highlights the advantage of large surface area of nanoflower over nanorods [19]. DSSC ZnO nanobelt that was prepared by electrodeposition technique demonstrated the efficiency as high as 2.6% [15], while ZnO hierarchical based nanorods synthesized via a two-step route of aqueous solution demonstrated the efficiency as high as 1.51% [16]. ZnO nanotube that was reported in [17] possessed 1.18% conversion efficiency. However, tetrapod like ZnO nanorods as photoelectrode for DSSC, prepared by dc thermal synthesis technique possessed 4.78% energy conversion efficiency [18]. As well known, ZnO nanorods prepared using the technique reported in [9] and other techniques [10-18], possessed the dimension of several micron in length and diameter. Also, the distribution of the nanorods on the substrate surface are not closely packed that exhibits high rod to rod separation. Owing to the unique properties of ZnO nanorod, the use of highly compact and high surface area of quasi ZnO nanorods in DSSC that have been synthesized by our facile new technique should theoretically improve the performance of the device in term of photocurrent.

Our previous work of ZnO nanorods that was synthesized from the current technique possesses photovoltaic effect in a photoelectrochemical cell with the highest short-circuit current density, J_{sc} of 0.22 $mAcm^{-2}$, open circuit voltage, V_{oc} of 0.44 V, fill factor, *FF* of 30% and the conversion efficiency

of 0.03% [19]. In this work, we fabricated a dye-sensitized solar cell of FTO/ZnO/LiI-I_2/platinum utilizing quasi one-dimensional highly compact ZnO nanorods synthesized by a novel technique, namely, ammonia assisted rapid hydrolysis at room-temperature [20]. The objective of the work is to highlight the synthesis of highly compact quasi one-dimensional ZnO nanorod by the present technique, to investigate the effect of the number of growth cycle on the morphology and optical absorption of ZnO nanorods. The effect of ZnO nanorods morphology in term of the length was then correlated with the performance of the DSSC in term of J_{sc} and V_{oc}.

2. EXPERIMENTAL DETAILS

2.1. Materials

All chemicals were used without further purification as follows: Fluorine doped Tin Oxide (FTO) substrates with sheet resistance 15-20 ohm were purchased from solaronix. They were cleaned by standard procedures before use. Ethanol with purity of 99.5% was purchased from Fluka. Zinc acetate dehydrate (Zn $(CH_3COO)_2$ $2H_2O$) with purity 99% was purchased from Across. Ammonia solution (NH_3) with 30% concentration in water and electrolyte composition of tetrabutyl ammonium iodide were purchased from Aldrich. Lithium iodide, iodine and 4-tertbutylpyridine in 3-methoxy-propionitrile (Aldrich) were purchased from Aldrich. Cis-bis (isothiocyanato) bis (2,20-bipyridyl-4, 40-dicarboxylato)-ruthenium (II) bis-tetrabutylammonium (N719) dye and platinum-paste platinum-catalyst were purchased from Solaronix. All the aqueous solutions were prepared using double distilled and ion-exchange water.

2.2. Synthesis and characterization of quasi ZnO nanorods

Highly compact vertical array quasi ZnO nanorods were synthesized using our new simple technique under rapid hydrolysis process of zinc salts in the presence of ammonia at room temperature as reported previously [20]. Transparent FTO conducting substrate underwent routine cleaning by acetone, iso-propanol and ethanol for 15 minutes, respectively and dried under nitrogen flow. ZnO nanoseeds on FTO surface were prepared via alcohothermal seeding method adopting our previous approach in preparing CuO nanowires and quasi ZnO nanorods on the substrate surface [19-21]. The seeding process was started with the deposition of ethanoloic solution of 0.01 M zinc acetate dihydrate on clean FTO surface by spin-coater at 3000 rpm. The sample was then dried up at 100 ^oC on hot plate for 15 minutes. The process of seed coating the solution on FTO was repeated three times and annealed in air at 350 ^oC for 1 hour for the last treatment. The room temperature growth process of quasi ZnO nanorods from the nanoseeds was carried out by immersing the nanoseeds-attached FTO into a 0.01 M aqueous solution containing zinc acetate dihydrate. 100 μL of 30% ammonia solution was added into the reaction, corresponding with 360 mM concentration, while being stirred with magnetic stirrer. The sample was then taken out and washed several times using pure water to remove any precipitate on the surface and dried using a flow of nitrogen gas.

The growth process was then repeated for the next sample and changed the growth solution until five times for every 5 minutes to produce ZnO nanorods with different length and thickness. The other ZnO nanorods samples were synthesized by varying by the number of growth step. The samples were then dried using a flow of nitrogen gas. Since thermal treatment can tune the morphology of ZnO nanorod [20] and the best morphology can optimize the performance the DSSC [10], the samples were dried in air and sintered at 350 °C for 30 min in air for DSSC fabrication.

The morphology of quasi ZnO nanorods was studied using a field emission scanning electron microscope (FESEM) machine model ZEISS SUPRA 55VP operating at an acceleration voltage of 3 kV. The average diameter of the nanorods was measured by taking diameter of ten nanorods. The optical absorption of quasi ZnO nanorods was characterized using a double beam UV/VIS/NIR spectrophotometer model Lambda 900 Perkin Elmer. Difference thickness of quasi ZnO nanorods produced from this technique was monitored by recording the UV-Vis spectra of the film immediately after the sample remove from furnace for annealing process.

2.3. Dye-sensitized solar cell fabrication and its performance study

All ZnO nanorods films on the FTO prepared by five growth cycles were firstly immersed in a 5 mM solution containing di-tetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (N719 dye) at room temperature for 4 hours. Platinized ITO counter electrode, prepared by spin coater was assembled with two clips. The cell was filled with an electrolyte containing 0.6 M tetrabutyl ammonium iodide, 0.1 Li, 0.05 iodine, and 0.5M 4-tertbutylpyridine in 3-methoxy- propionitrile. The cell was masked with 1 cm^2 holed- rubber band as an illuminated area of the cell.

The current–voltage, *J-V* characteristic in dark and under illumination at room temperature were obtained using a 237 Keithley high voltage source interfaced with personal computer. The *J-V* under illumination was performed to investigate the photovoltaic effect in the device. The intensity was controlled by radiometer. The photovoltaic parameters such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (*FF*) and efficiency (η) were analyzed from the *J-V* curve under illumination.

3. RESULTS AND DISCUSSION

Vertically oriented quasi one-dimensional ZnO nanostructures from nanoseed particles on the FTO substrate have been successfully grown via a simple and quick growth process, namely, one-dimensional crystal growth of nanoseeds via an ammonia-assisted rapid hydrolysis process. The particular process of the growth ZnO nanorods took only approximately 4 to 5 min to form spherical nanoseeds into vertically oriented one-dimensional nanostructures for single growth process. Fig. 1 shows the surface morphology of quasi ZnO nanorods by FESEM images prepared via seed-mediated method and ammonia assisted controlled multiple growth process, namely: ZnO 1^{st}, 2^{nd}, 3^{rd}, 4^{th}, and 5^{th}

growth process. From Fig. 1A, ZnO nanorod was grown on the FTO substrate that is initially covered with ZnO nanoseeds via alcoholthermal method [20].

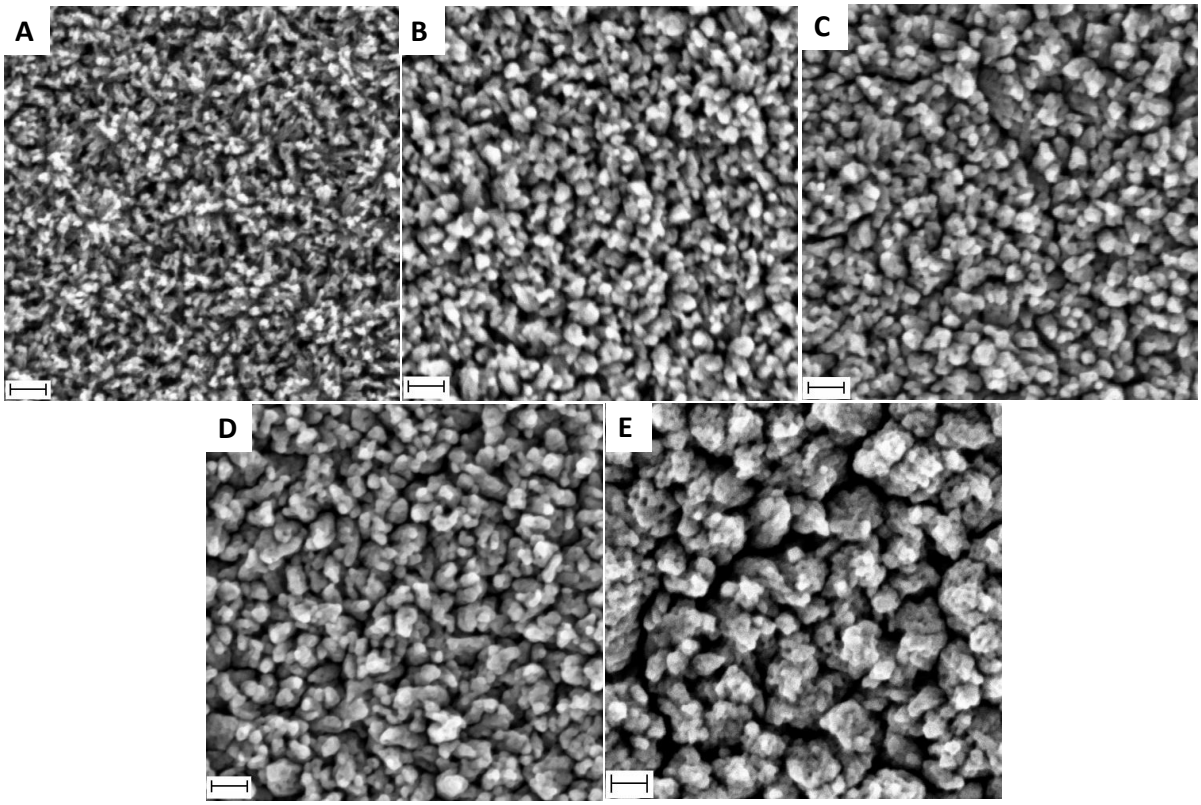

Figure 1. FESEM surface micrograph of ZnO nanorod prepared by seed mediated method via multiple growth steps, A) 1× growth step, B) 2× growth steps, C) 3× growth steps, D) 4× growth steps and E) 5× growth steps. Scala bar 100 nm

Zinc metal initially reacts with hydroxide ions to make zincate ion ($Zn(OH)_2^{2-}$) soluble. Ammonium hydroxide will be produced when ammonia is dissolved in H_2O.

$$NH_3\,(aq) + H_2O(l) \longrightarrow NH_4^+\,(aq) + OH^-(aq) \qquad \ldots(1)$$

Zinc hydroxide is formed by adding ammonium hydroxide solution (limited reactant) to zinc salt solution;

$$2Zn + 2OH^- \longrightarrow Zn(OH)_2^{2-} \qquad \ldots(2)$$

The full equation is:

$$Zn\,(CH_3COO)_2.2H_2O + 2NH_4OH \longrightarrow 2CH_3COONH_{4\,(V)} + Zn\,(OH)_2 \qquad \ldots(3)$$

If excess ammonium hydroxide is added, the precipitation of zinc hydroxide will be dissolved to form a colorless solution of zincate ions:

$$Zn(OH)_2 + 2OH^- \longrightarrow Zn(OH)_4^{2-} \quad ..(4)$$

There are two reactions that occur with zinc salts and ammonium hydroxide. After heat treatment under oxygen atmosphere, $Zn(OH)_2$ will form ZnO. This agrees well with the literature that reported the formation of N-doped ZnO film assisted ammonia [22].

$$2Zn(OH)_2O_2 \longrightarrow 2ZnO + 2H_2O$$

The average diameter of quasi ZnO nanorods is 16 nm for single growth step. ZnO nanorods were further grown when the sample was immersed once again in the growth solution as shown in the SEM micrographs presented in Fig.1B-1E. The diameter of nanorods increased nearly two times to 26 nm in average. The diameter of the ZnO nanorod increases with the number of growth-step and this behavior is depicted in Fig. 3 (b).

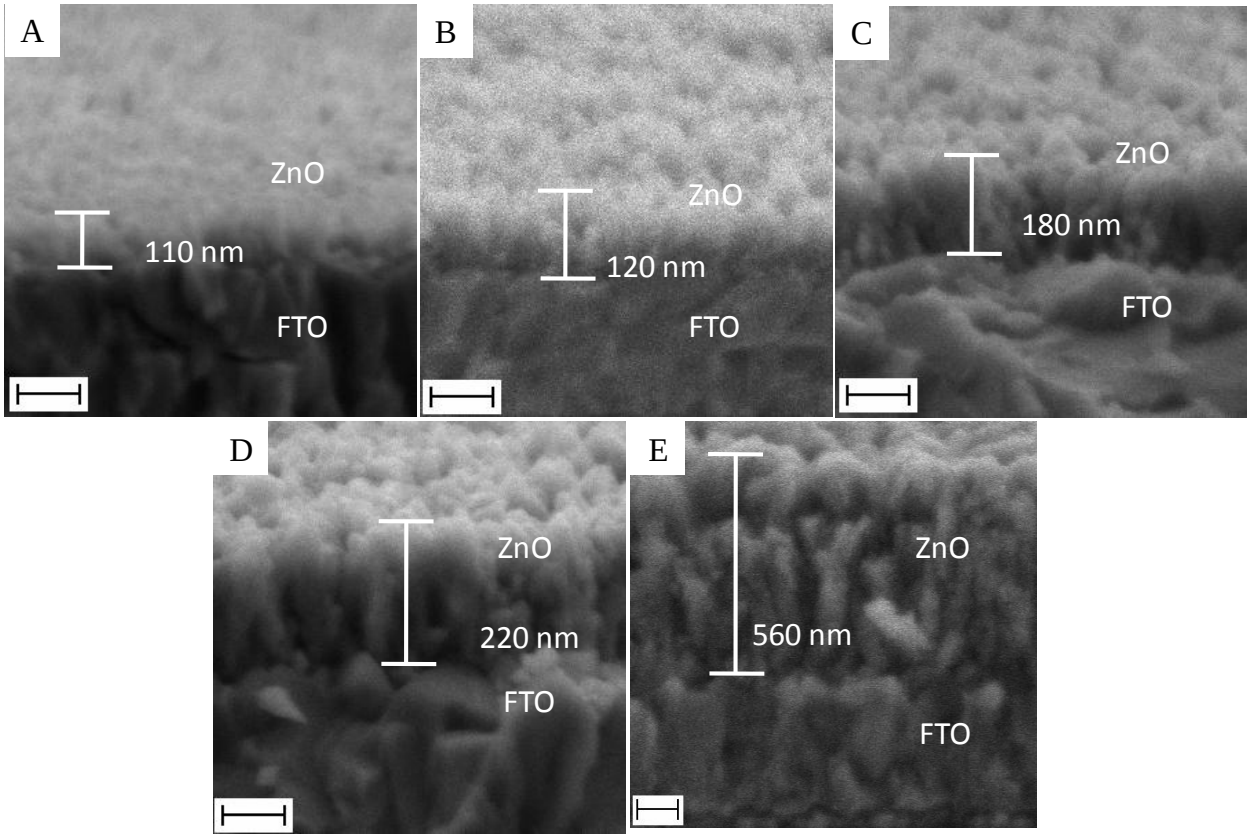

Figure 2. Cross sectional FESEM micrograph of ZnO nanorod via multiple growth step: A) 1× growth step, B) 2× growth steps, C) 3× growth steps, D) 4× growth steps and E) 5× growth steps. Scale bar 100 nm

In an ideal case, the nanorods should further grow until the entire precursors of zinc complexes are consumed and promote long nanorod formation on the substrate surface. However, active hydrolysis of zinc salt drove the formation of the precursors in the solution and aggregated on each other. Therefore, the quasi-nanorods growth was stopped earlier and their length was less developed [20]. Multiple growth process is an alternative process to the quasi nanorods length become longer and this is proven through cross-sectional view of FESEM micrograph for 1st to 5th cycle growth-step. By using a standard growth solution containing 10 mM of zinc salt and 360 mM of ammonia, the length of the quasi-nanorods could be effectively increased from approximately 110 nm (one cycle growth) to 220 nm (4th cycle growth time) and surprisingly for 5th cycle growth process, the length of ZnO nanorods increased twice longer than that for 4th cycle growth process as illustrated in Fig. 2. The variation of the length of ZnO nanorods with number of growth step is presented in Fig. 3 (a).

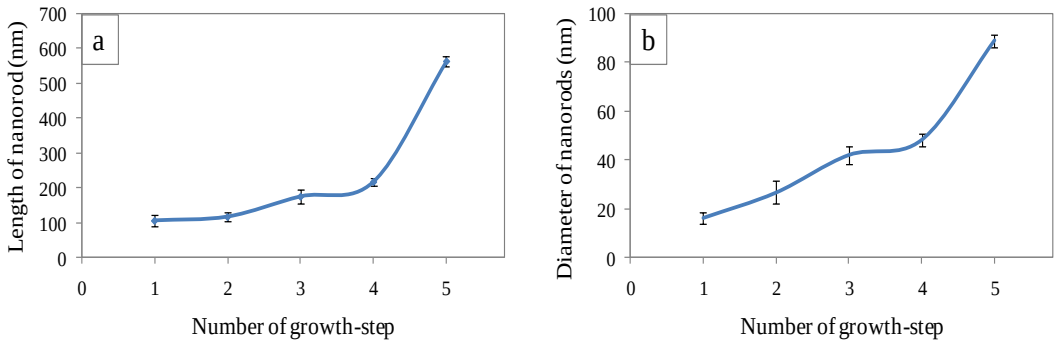

Figure 3. a) Variation of length and b) diameter of ZnO nanorods with number of growth steps

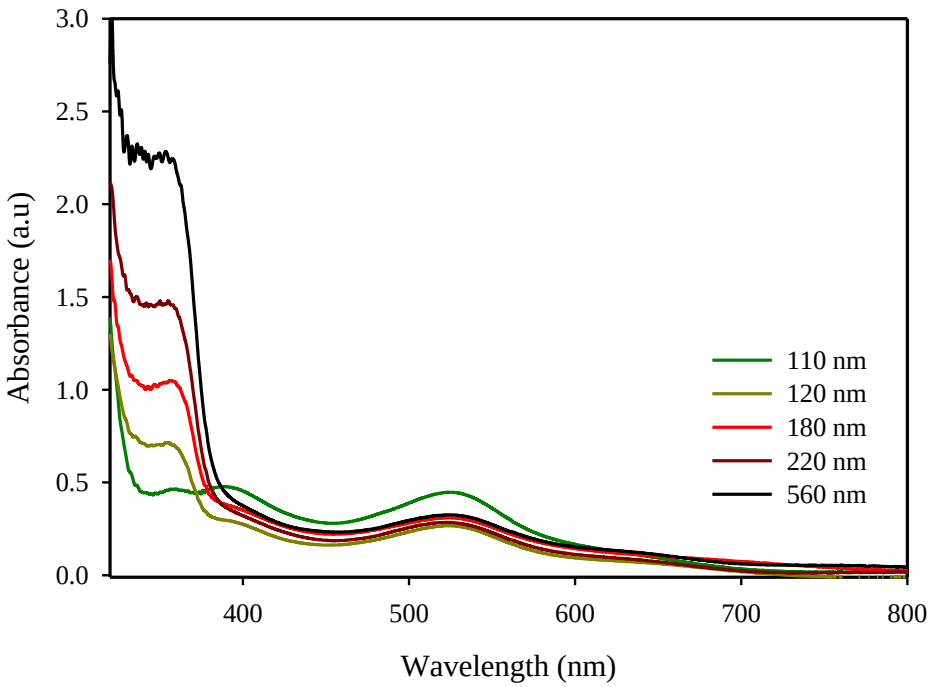

Figure 4. UV-VIS optical absorption spectra of quasi ZnO nanorods coated with N719 dye with various thicknesses

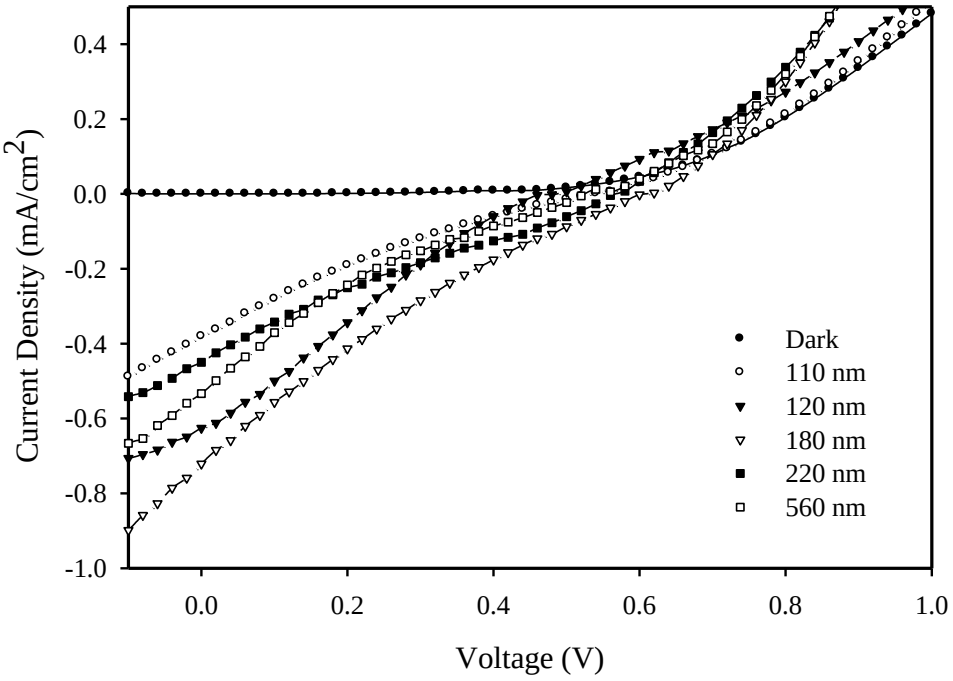

Figure 5. *J-V* curves of the dye sensitized solar cell of FTO/ZnO-dye/electrolyte/platinum

The UV-Vis absorption spectra of quasi ZnO nanorods coated with N719 dye for 1^{st}-5^{th} growth process are presented in Fig. 4. The absorbance of both samples in the spectral range of 300-400 nm increases steadily with the number of growth process that was also indicated by the length of nanorods of 110 nm to 560 nm for 1^{st} -5^{th} growth. It is believed that the number of growth process affects the UV absorption of the nanorods. Larger number of growth step, higher absorption. The absorption for quasi ZnO nanorods coated with dye occur in visible range (> 400 nm) indicated by prominent peak at range 523-526 nm as shown in Fig. 4. The highest peak at 500 nm occurs for single growth step of ZnO nanorods of 110 nm length, indicating that the dye fully adsorb the nanorods and resulted in more UV light could be absorbed at this wavelength [10].

Fig. 5 shows *J-V* characteristics of the dye-sensitized solar cell fabricated with quasi ZnO nanorods coated with N719 dye with various lengths in dark and under illumination at room temperature. The DSSC fabricated with quasi ZnO nanorods with 1^{st}, 2^{nd} and 3^{rd} growth cycle corresponding with 110 nm, 120 and 180 nm length perform the increasing trend in current-voltage and then drops at the ZnO length of 220 nm. The optimum J_{sc} and V_{oc} of 0.72 $mAcm^{-2}$ and 0.6 V, respectively were obtained at the ZnO length of 180 nm as illustrated in Table 1. This is due to the high surface area that make the dye could be absorbed by the nanorods [17]. The decrease in J_{sc} at the length of 220 nm might be caused by the distance between inter-rod become smaller with the larger diameter and more compact compared to ZnO grown with 1^{st} , 2^{nd} and 3^{rd}. It could make the dye only adsorb on the surface, resulting in a small amount of dye reaches the nanorods. The distance that electrons have to travel through is increased, thus the electrons-holes recombination rate decreases, thus decreases the photocurrent accordingly [18].

Table 1. Photovoltaic parameters of ZnO nanorods dye-sensitized solar cell with various lengths

ZnO length (nm)	J_{sc} (mAcm^{-2})	V_{oc} (V)	*FF*
110	0.42	0.54	0.20
120	0.63	0.48	0.23
180	0.72	0.60	0.20
220	0.55	0.50	0.18
560	0.60	0.42	0.22

4. CONCLUSIONS

We have successfully synthesized ZnO nanorods via ammonia assisted hydrolysis technique. The effect of the number of growth step on length and diameter of quasi ZnO nanorod has been investigated. The diameter and length of the nanorods increases with the number of growth step. The photoelectrochemical study shows that the J_{sc} increases with the length of nanorods. The DSSC with the ZnO nanorods coated with N719 dye possess the optimum performance in term of J_{sc} of 0.72 mAcm^{-2} at the 3× growth-step corresponding with 180 nm nanorods length. It suggests that high compact single crystal of ZnO nanorods lead to faster electrons transfer and improve the performance of the cell.

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