IOP Conference Series: Materials Science and Engineering

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To cite this article: Nandang Mufti *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **515** 012023

View the article online for updates and enhancements.

This content was downloaded from IP address 222.190.110.170 on 13/10/2019 at 12:21

IOP Conf. Series: Materials Science and Engineering **515** (2019) 012023 doi:10.1088/1757-899X/515/1/012023

Photoelectrochemical Performance of ZnO Nanorods Grown on Stainless Steel Substrate

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Abstract: Solar energy can be converted into hydrogen fuel using photoelectrochemical (PEC) cell through split water molecules. Among semiconductor metal oxide materials, ZnO material has shown promising potential as PEC cells due to the large band gap value (3.37 eV), high excitation energy (60 meV), abundant material, and non-toxic. ZnO in the form of nanorods (NRs) can increase the conversion efficiency of the PEC performance because of the large surface area. In this research, we investigated the influence of zinc nitrate concentrations on the morphology of ZnO NRs on the stainless steel substrate and its PEC performance. Stainless steel was chosen as a substrate because of high conductivity, excellent corrosion resistance, and inexpensive. ZnO NRs are synthesized by the hydrothermal method. The structure and morphology of ZnO NRs were characterized by XRD and SEM. While PEC performances were studied using two probe method. The graph of current versus times was fitted by an exponential equation to determine time response and time decay of ZnO NRs. We found that ZnO NRs has good photoresponse but the current value is low.

Keywords: ZnO, NRs, stainless steel, photoelectrochemical performance

1. Introduction

Solar energy resource is the most abundant and clean energy [1–3]. Solar energy can be converted and utilize in a much technological application such as pollutant degradation, hydrogen generation, solar cell, photoelectrochemical [2–5]. Photoelectrochemical (PEC) is a process that converts solar energy into electrical energy or hydrogen through the electrochemical process under light irradiation [5]. Some semiconductor materials that are widely used for PEC cells are Fe_2O_3, TiO_2, ZnO, and Cu_2O [6].

ZnO is one of semiconductor materilas that has attracted attention due to its unique properties [6–8]. Moreover, ZnO has been widely used in photocatalysts [9], solar cells [10], gas sensor[11], light emitting diodes [12], spintronic device [1], ultraviolet (UV) lasers, [13]. ZnO has a band gap energy and excitonic binding energy around 3.3 eV and 60 meV respectively. ZnO is stable at room temperature with a wurtzite Crystal structure (No. 186, $P6_3mc$) and parameters lattice a,b = 3.248 Å and c = 5.205 Å [14]. This structure is a noncentrosymmetric structure with high polarization [15]. Therefore, ZnO is a

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good candidate for PEC cells due to the large band gap, can be grown in any substrate, non-toxic, and cheap [2,7]. Liu *et al.* have reported that ZnO in nanorods array can improve photoelectrochemical water splitting [16]. Composite ZnO nanorods/Cu_2O also enhanced the photoelectrochemical properties and self-powered biosensing[17]. However, the fabrication of PEC with high efficiency, stability, and cost-effectiveness, remains a challenge[6]. In order to solve these problems, we use a stainless steel substrate because it widely used materials and has many advantages such as corrosion resistance, mechanical strength, and electrical conductivity. In this study, we report performance of ZnO nanorods grown on stainless steel by hydrothermal method with a variation of zinc nitrate tetrahydrate concentration.

2. Methods

The ZnO nanorods (NRs) was synthesized in two steps by coating ZnO seed layer on Stainless steel substrate (SS) using spin-coating method and growing ZnO nanorods by hydrothermal method as reported in previous work[18] on ITO substrate. The ZnO seed layer synthesized by mixing zinc acetate dehydrate and MEA at 1:1 molar ratio. Then the solution was coated on SS by a spin coating method at the rate of 3000 rpm for 20 seconds and followed by preheating annealing at 90 ^{O}C for 10 minutes and 550 ^{O}C and two hours, respectively. The ZnO NRs were grown by a hydrothermal method in ZnO seed layer.

The ZnO NRs were grown on ZnO seed layer substrate using a hydrothermal method. The concentration of precursors of zinc acetate dehydrate are 50 mM, 60 mM, and 70 mM and hexamethylenetetramine (50 mM). the solution was heated with growth temperatures of 90 °C for 6 hours. The Samples were cleaned by distilled water and dried at room temperature. Lastly, the ZnO NRs were annealed at 550 °C for 2 hours. The ZnO NRs samples were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM) to analyze crystal structural and surface morphology including ZnO NRs distribution and thickness.

3. Results and Discussion

The ZnO NRs samples were successfully synthesized and then characterized using x-ray diffractometer. This characterization aims to determine the crystal structure of ZnO NRs in variation of the Zinc Nitrate Tetrahydrate (ZNT) concentration as shown in Figure 1. Based on the diffraction in Figure 1.a shows that ZnO NRs has a single phase, and no impurities are observed. The crystal structure of the ZnO NRs is wurtzite-type hexagonal with space group *P63mc* (see Figure 1.b) in agreement with JCPDS standard (No.36-1451). The high-intensity peaks indicate that ZnO NRs has good crystallinity [18,19]. Increasing ZNT concentration increase (002) Bragg peak indicate that ZnO NRs grew along the *c*-axis.

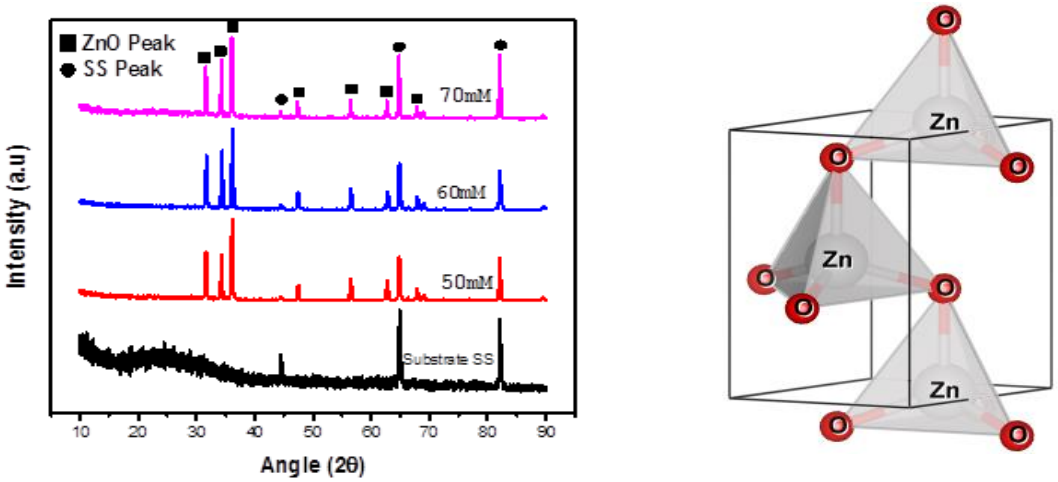


Figure 1. (a) The X-ray diffraction pattern of ZnO NRs in a variation of ZNT concentration (b) crystal structure ZnO NRs

Moreover, the XRD patterns of ZnO NRs analyzed by Rietveld refinement to determine structural propeties. The lattice parameter of ZnO NRs in a variation of ZNT concentration summarized in Table 1. The lattice parameters of ZnO NRs are *a,b* = 3.250 Å, and *c* = 5.205 Å in accordance with previously reported [14]. The c/a parameter is 1.6 indicating that ZnO NRs have hexagonal wurtzite structure [14,20]. The goodness of fit (*GoF*) of the refinements has a value between 1.3 and 1.53 that prove the quality of refinements are good.

Table 1. The crystal structure of ZnO NRs based on Rietveld refinement at different ZNT concentration

ZNT (mM)	50 mM	60 mM	70 mM	Model
$a = b$ (Å)	3.250	3.251	3.250	3.2494
c (Å)	5.205	5.209	5.205	5.203
V (Å^3)	47.62	47.71	47.63	47.58
c/a	1.60	1.60	1.60	1.60
GoF (%)	1.3	1.45	1.53	-
Bragg *R*-Factor	5.3	9.7	6.7	-

Figure 2. displays the morphology of ZnO NRs from SEM at different ZNT concentration. The ZnO NRs have a form of hexagonal with different size distribution and align along c-axis. The diameters of the rods were measured using *ImageJ*. The average diameter of ZnO nanorods increases from about 224 nm to 264 nm and 315 nm when the ZNT varies from 50 mM to 60 mM and 70 mM respectively. This phenomenon due to increased Zn^{2+} ions from ZNT enhance the amount of zinc hydroxide produced, which rises the growth rate ZnO NRs [21].

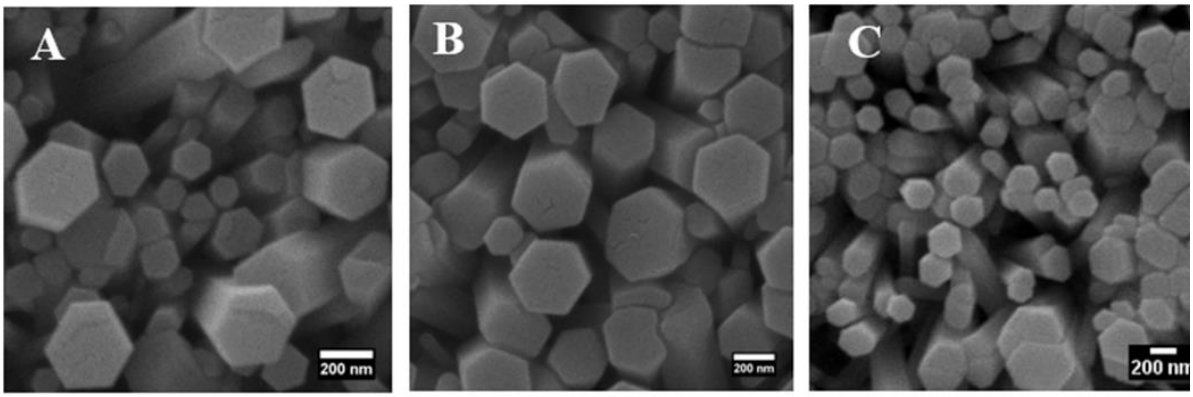


Figure 2. SEM images of ZnO NRs with concentration of ZNT of (a) 50 mM (b) 60 mM and (c) 70 mM

The schematic photoresponse measurement and is shown in Figure 3.a. This measurement was performed using the two probes method where ZnO nanorods are placed as a photoactive or working electrode (WE) and platinum as a counter electrode (CE). The electrolyte solution is 1M NaOH. The photoresponse measurement was carried out at ZnO NRs with 70 mM ZNT concentration with 3 cm^2 x 3 cm^2 dimension and a lighting power value of 7.3 mW/cm^2. The measurement was done under on/off light irradiation cycle at the particular interval as shown in Figure 3.b.

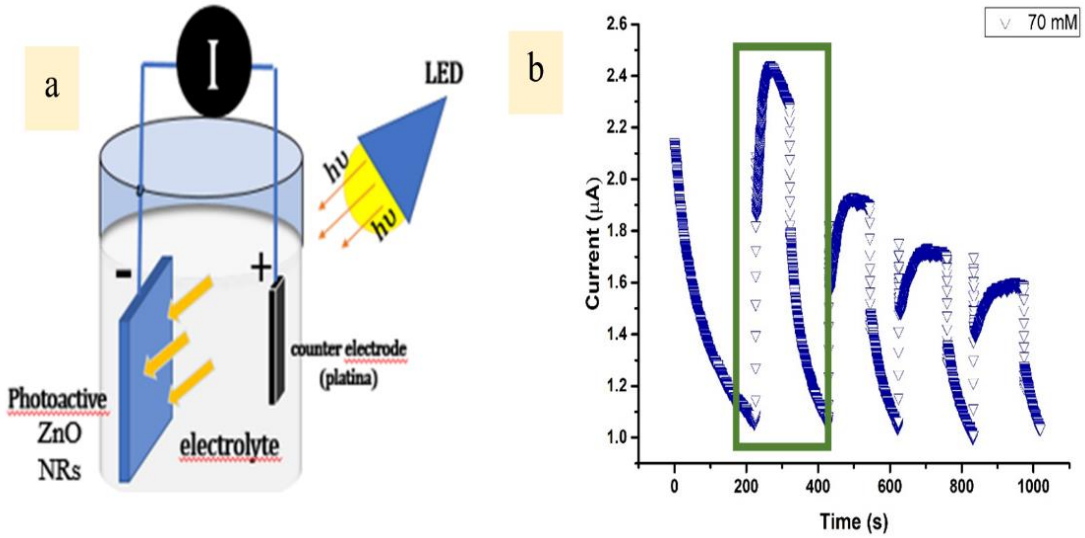


Figure 3. (a) schematic of photoresponse measurement (b) graph of current as a function of times under on/off light irradiation cycle.

Figure 3.b shows photoresponse of ZnO NRs under on/off light irradiation cycle. The sharp response current observed when the light illuminates ZnO NRs WE and then become saturated. The current decreases to the initial value when the light is turned off. This sharp peak of current due to photon can excite electrons from the valence band to the conduction band and pass the ZnO bandgap energy. The highest current change is 1.4 μA in the first cycle and its decreases by times. The graph between current and times in both on or off light irradiation can be fit using exponential as shown in Equation 1.

$$I = I_0 + A\exp(-(t - t_0)/\tau) \quad (1)$$

where I is current as a function of times, t is time, τ is time rise or decay, and A is amplitude.

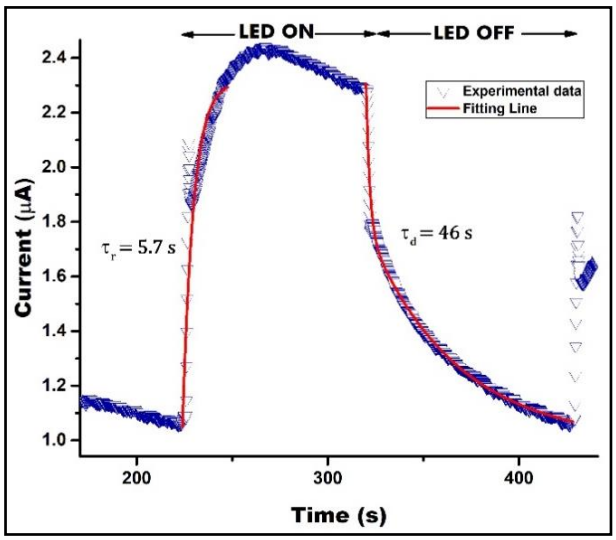


Figure 4. The Fitting of ZnO NRS photoresponse curve with 70 mM ZNT concentration at first cycle

In order to determine time rise (τ_r) and time decay (τ_d), the graph of ZnO NRs photoresponse with 70 mM ZNT concentration was fitted using equation 1 as shown in Figure 4. We found that the value of time rise is 5.7 s and time decay is 46 s. Time rise of ZnO NRs is shorter than time decay because the illumination of light in ZnO NRs produces electron-hole pairs $[h\upsilon \rightarrow e^- + h^+]$. Therefore, electrons more easily to excite from conduction band to valence band. at the same time, the hole will oxidize the oxygen ions on the surface $[O_2^- + h^+ \rightarrow O_2]$. When the light turns off, the hole that reacted with oxygen ions is difficult to release due to the oxidation process is also take times to oxidize [22]. Consequently, times decay is longer than time response.

4. Conclusion

The ZnO NRs has been successfully grown in stainless steel substrate. The diameter of ZnO NRs increases from 224 nm to 315 nm when ZNT varies from 50 mM to 70 mM respectively. Photoresponse measurement of ZnO NRs has time rise of 5.7 s and time decay of 46 s with current change 1.4 μA. The ZnO NRs on stainless steel substrate has good photoresponse for PEC application. However, the current value needs to be improved.

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Acknowledgments
This research was partially supported by PNBP of Universitas Negeri Malang 2018.