



Conference Paper

Effect of Concentration Ratio of Precursor-Surfactant Solution on The Performance of Boron-doped ZnO Nanotubes Dye Sensitized Solar Cells

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Abstract Boron doped zinc oxide (ZnO) nanotubes have successfully been grown using seed-mediated hydrothermal method at various concentrations of precursor-surfactant solution. The growth of ZnO nanotubes was carried out at a temperature of 90°C for 8 hours and a drop in temperature to 50°C for 16 hours. In this study, the effect of concentration ratio of precursor-surfactant was evaluated. Samples were characterized using UV-Vis Spectroscopy, X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray (EDX). UV-Vis spectra of the samples showed that the ZnO nanotubes were grown on the Fluorine Tin Oxide (FTO) and the strong absorption occurred in the wavelength range of 300-400 nm, which is typical spectrum for hexagonal-nanostructure. XRD patterns showed five diffraction peaks at $2\theta = 32.05^\circ, 34.5^\circ, 36.35^\circ, 47.75^\circ$ and 56.9° . The analysis of EVA Diffrac Plus confirmed the peaks were represented to the lattice of (100), (002), (101), (102), and (110) respectively. FESEM images of the samples showed the hexagonal-shaped ZnO nanotubes with an average diameter of 50-340 nm and an average thickness of 1.2 - 4.4 μm observed for all samples. Uniformity the size and shape of ZnO nanotubes become higher as concentrations of ZNH decreased. The EDX spectra of the samples showed the percentage of weight of Zn, O, and B was 69.35%, 21.60% and 4.76% respectively, while the percentage of their atoms was 33, 06%, 42.08% and 13.71% respectively. The B-doped ZnO nanotubes solar cells were fabricated by arranging a sandwich structure, consisting of the FTO, ZnO nanotubes, dye, electrolyte and platinum thin film. I-V characteristics of cell were carried out under irradiation of 100 mWcm^{-2} halogen lamp. The I-V curves produced the highest efficiency from the cells utilizing the B-doped ZnO nanotubes with their concentration ratio of precursor-surfactant of 0.1 M : 0.04 M as the active material, which was 0.352%. This value is much higher than that of pure ZnO nanotube based DSSC of 0.05%.

Keywords: Boron, Dye Sensitized Solar Cells, Zinc-Oxide (ZnO) Nanorods, Hydrothermal method

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Received: 1 August 2016

Accepted: 18 August 2016

Published: 6 September 2016

Publishing services provided
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Selection and Peer-review under the responsibility of the ICoSE Conference Committee.



1. Introduction

In the last decade, one-dimensional nanostructured materials have attracted considerable attention. *Zinc Oxide* (ZnO) among oxide systems has been chosen as one of short wavelength device materials. ZnO has wide-direct band gap energy of 3.3 eV [1,2] comparable to that of TiO_2 3.2 eV [3]. The interesting optical and electronic properties, such as transparent, high transmittance, easy to deposit on many substrates and low cost materials, make nanostructured ZnO as one of most potential active materials for solar cells [4]. Furthermore, some nanostructured ZnO have successfully been produced in diverse groups of growth morphologies, such as ZnO nanowires [5], nanotubes, nanobelts and tetrapods, [6] and nanosheets [7]. Some physical parameters need to be controlled in order to apply ZnO nanostructures for many applications, such as geometrical shape, crystal morphology and orientation [8]. Some efforts have been performed in order to improve the properties of ZnO nanostructures by doping various elements, such as In [9], Al [10], Ga [11] and B [12]. Among them, B-doped ZnO nanotubes are capable of reaching high conductivity, electric mobility and low resistivity [13].

Although some techniques have produced metal-doped ZnO nanorods, such as thermal evaporation and vapor-liquid-solid, but these methods need sophisticated equipment and high temperatures. On the other hand, wet chemical methods, including seed-mediated hydrothermal growth method provides more promising route in producing well-aligned doped ZnO nanostructures, including B-doped ZnO nanotubes. The method allows the synthesis of ZnO nanostructures at lower temperature, more effective and convenient for use with simple and low cost equipments, which can improve the performance of metal-doped (including B-doped) ZnO nanostructures based Dye Sensitized Solar Cells (DSSCs).

In this present paper, we deal with the synthesis of B-doped ZnO nanotube arrays grown by a simple seed-mediated hydrothermal technique on FTO with ZnO seed-layer. The main goal of this work is to establish the effect of the boron-doped solution and concentration ratio of precursor-surfactant solution on the optical and structural properties of the grown ZnO nanotubes and on the performance of B-doped ZnO nanotubes based DSSCs.

2. Experiments

In order to grow ZnO nanotube arrays on the FTO substrate, the seed-mediated hydrothermal growth method was performed. This method principally contains of two steps, namely seeding and growing processes. The seeding process was carried out in order to ZnO seed layer by depositing zinc acetate dihydrate (ZAD) on the substrate. Meanwhile, the growing process took a place in aqueous solution containing Trimethyl borate, zinc nitrate hexahydrate (ZNH) and hexa-methylene-tetramine (HMT).

In this seeding process, ZnO nanoseeds were coated on the FTO by using a method of alcohol-thermal seeding. This technique was firstly begun by forming a thin layer of ethanolic solution of 10 mM zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) on a FTO by

using spin-coating technique at 3000 rpm for 30 seconds. This process was carried out in order to make sure the solution was evenly distributed on the substrate and to get the sufficient thickness of the seed growth on the substrate. The sample was then dried at 100 °C on a hot-plate for 15 minutes and then cooled down to 60°C. These procedures were repeated three times in order to get appropriate thickness of ZnO nanoseeds. The sample was finally annealed at 350°C for 1 hour in a furnace. Growth process was started by immersing the ZnO nanoseed coated FTO in the growth solution. The growth solution was prepared by varying concentration of precursor-surfactant (ZNH-HMT) solutions: 0.04 M : 0.06 M; 0.04 M : 0.08 M; 0.04 M : 0.1 M; 0.04 M : 0.14 M; 0.06 M : 0.04 M; 0.08 M : 0.04 M; 0.1 M : 0.04 M; 0.14 M : 0.04 M. Boron doping was preparing by mixing 0.055 mL *Trymetil borate* in 5 mL *DI water* (0.4 mM solution). The sample was put in the oven for 8 hours at 90°C. The temperature was then decreased to 50°C in 16 hours. Finally, the sample was annealed in the furnace at 250°C for 30 minutes. XRD method performed in order to examine the structure and phase structure of the ZnO nanostructures by using diffractometer model Bruker D8 Advance. The morphology of the samples was observed using field-emission scanning electron microscopy (FESEM) analysis (Zeiss Supra 55VP FESEM) with the magnification of 10000x and 50000x. The thickness of the ZnO nanostructures was estimated from the cross-sectional image of the FESEM. The elemental analysis was carried by using energy dispersive x-ray (EDX) spectrometer. Optical spectrophotometer UV-Vis Lambda 900 Perkin Elmer was employed to study the optical absorption of the ZnO samples. The absorbance of the samples was measured in the wavelength ranging from 300 to 800 nm.

Before fabrication the DSSC, the gallium doped ZnO nanostructures were immersed into 0.3 mM N719 dye solution for 2 hours. The samples were then taken out, rinsed gently with ethanol and then dried under a flow of nitrogen gas. Platinum film as a catalyst coated on counter electrode was prepared by spin coating platinum pellets at 1000 rpm for 30 seconds on the FTO substrate. The samples were then dried at 100 °C on a hot-plate for 5 minutes and then cooled down to 60°C. The platinum film coating process was repeated three times in order to get appropriate thickness of Pt films. The sample was finally annealed at 400°C for 30 minutes in a furnace. A standard electrolyte namely iodolyte was used. A DSSC was fabricated by arranging the sandwich structure of the parafilm between the ZnO nanostructures and the platinum counter electrode. The electrolyte was injected into the cell and filled via a capillary. The performance study of the DSSC was carried out by observing the current-voltage characteristics in the dark and under illumination using an AM 1.5 simulated halogen light with an intensity of 100 mW cm⁻². The illuminated area of the cell was 0.23 cm². The current-voltage curves in the dark and under illumination were recorded by a Gamry 1000 interfaced with a personal computer.

3. Results and Discussion

Fig. 1 (A) showed UV-Vis spectra of 4 samples with different concentrations of precursor (ZNH) of 0.06 M, 0.08 M, 0.1 M and 0.14 M, with constant concentration of

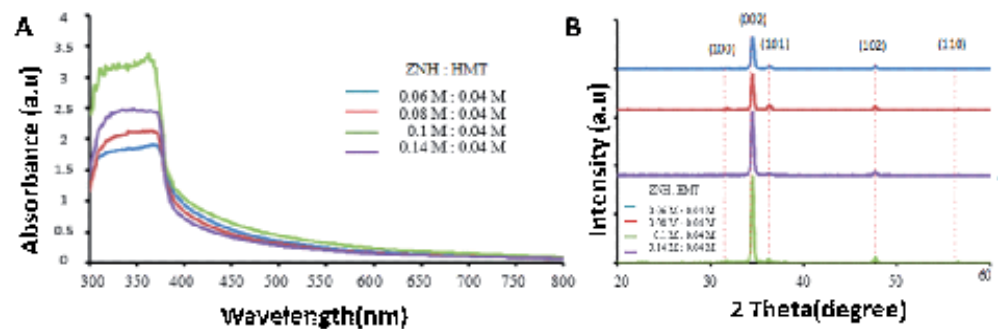


Figure 1: (A) UV-Vis spectra of samples containing Boron-doped ZnO nanotubes with different ZNH concentration and (B) XRD patterns of boron-doped ZnO nanotubes with various ZNH concentrations.

HMT surfactant of 0.04 M. The figure showed the strong absorption observed at the wavelength range 300–400 nm. The absorption peak occurred at a wavelength of 370 nm for all samples. There was sharp cross point at about 370 nm, which represented good structural quality of ZnO nanostructures [14]. The XRD pattern of the samples of Boron-doped ZnO nanotubes with various ZNH concentrations was shown in Fig. 1(B). At the figure, it was shown 5 diffraction peaks at $2\theta = 32.05^\circ$, 34.50° , 36.35° , 47.75° and 56.55° . EVA diffract plus analysis confirmed the 5 diffraction peaks represented to crystal orientation of (100), (002), (101), (102), and (110). The strongest diffraction peak at $2\theta = 34.50^\circ$ which represented to (002) crystal orientation was preferred orientation, that represented to hexagonal structure of ZnO [15].

FESEM images of the samples with different ZNH concentration of 0.06M, 0.08 M, 0.1M and 0.14M with concentration of HMT of 0.04 M, as shown in Fig. 2. From the images, it can be seen that ZnO nanotubes were grown onto FTO for all samples with its cross-section of hexagonal shape with various diameter size. Homogeneity in size and shape of ZnO nanotubes increased with decreasing ZNH concentration. The diameter of ZnO nanotubes was in the range of 50–340 nm and the thickness of about 1.2 – 4.4 μm for all samples. The diameter of 0.06 M ZNH sample was 100–125 nm, while the diameter of 0.08 M and 0.1 M samples was 125–210 nm and the diameter of 0.14 M ZNH sample was 190–340 nm, with geometrical shape of nanosheet was observed. The cross-section images showed the thickness of ZnO nanotubes increased with increasing ZNH concentration until 0.1 M and decreased as the concentration of ZNH higher than 0.14 M. The thickness of samples was 1.2 μm , 3.5 μm , 4.2 μm and 4.1 μm , respectively. Fig. 3 illustrated EDX spectra of the samples and showed the peaks of Zn and O clearly at 1 keV and 0.58 keV, respectively. At the figure, it was also observed other peaks, which represented to C and B.

Fig. 4(A) illustrates the I-V characteristics in dark condition of the DSSCs utilizing the samples prepared at various precursor concentrations. The I-V curves are the typical characteristics of diode-like. It can clearly be seen that the cells do not show rectification property since the dark current in the reverse bias is not significantly different than that in the forward bias. Thus, the device does not allow the current to be dominant in one direction either in forward or reverse bias. For both biases, the different in the current for all cells is also small indicating that the concentration of

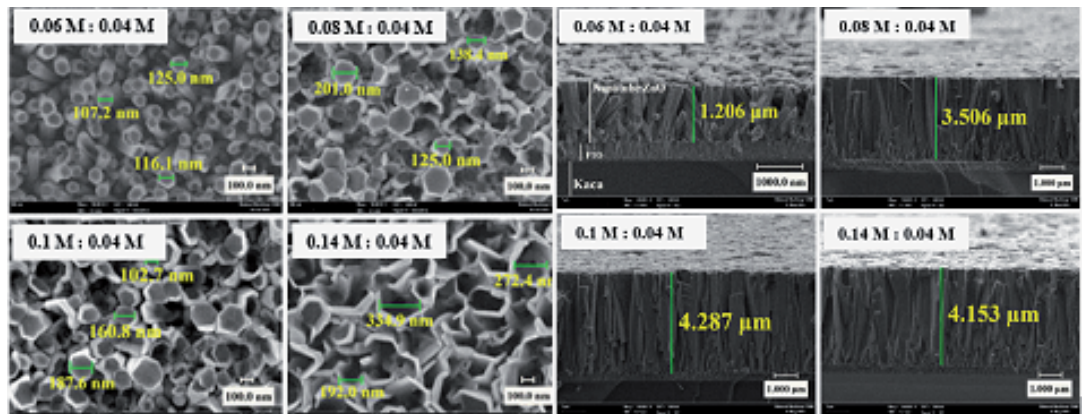


Figure 2: FESEM images of boron-doped ZnO nanotubes at magnification of 50,000X and cross-sectional images of boron-doped ZnO nanotubes at various ZNH concentration.

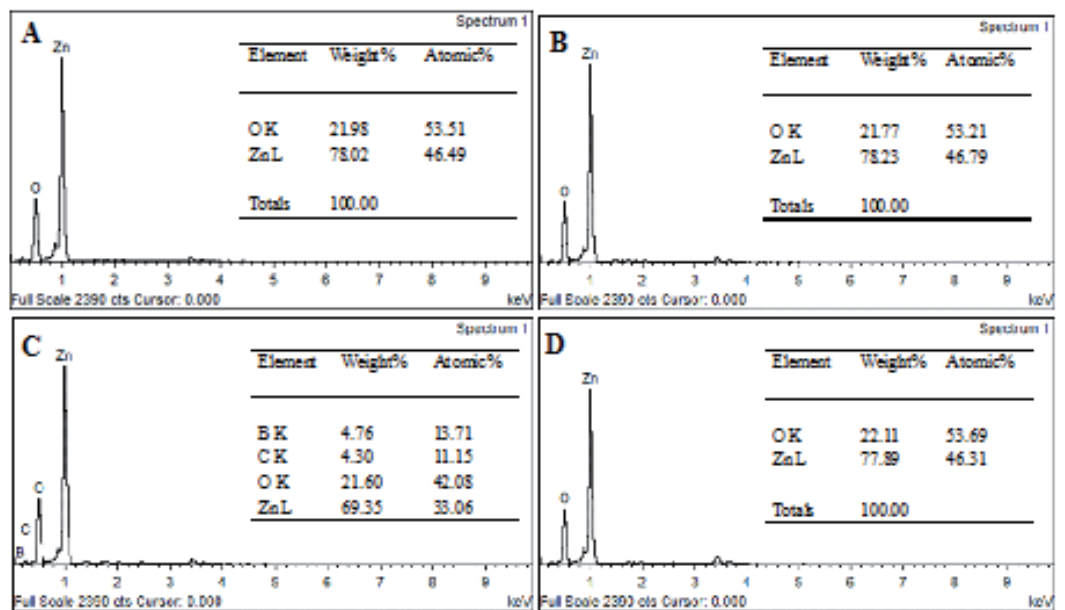


Figure 3: EDX spectra of B-doped ZnO nanostructures prepared at various precursor concentration.

precursor does not influence the dark current. However, the dark current in the device is quite high in both biases, which is in the mA range. This characteristic will result in high photocurrent and power conversion efficiency once the cells are illuminated with light. Fig. 7 shows the J-V curves of the DSSCs utilizing the ZnO nanostructures prepared at various ZNH concentrations under 100 mW cm^{-2} light illuminations. It is noticed that the cell with 0.1 M ZNH concentration generates the highest output power, whereas the device with 0.06 M ZNH concentration performs the lowest output power. The J-V curves do not follow the shape of that of silicon solar cell. The slope of J-V curves is quite high, indicating high internal resistance of the devices, leading to small fill factor (FF) illustrated in Table 1. The photovoltaic parameters are analyzed from Fig. 4(B) and described in Table 1. As can be clearly seen from the table, the cell utilizing ZnO nanostructures grown at 0.1 M concentration demonstrates the highest J_{SC} and η , while that utilizing the ZnO sample prepared at 0.06 M ZNH concentration performs the lowest J_{SC} and η . The increase in J_{SC} and η with the ZNH concentration

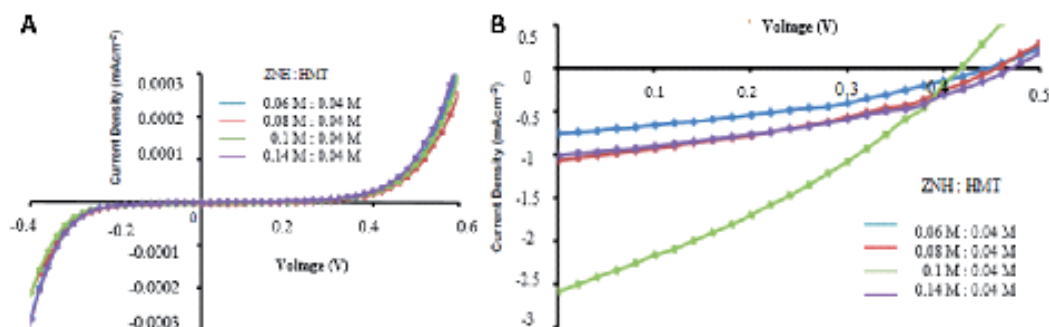


Figure 4: (A) I-V curve in dark condition of the DSSCs and (B) J-V curves of the DSSCs utilizing the ZnO nanostructures at various ZNH concentrations.

(ZNH : HMT)	V_{OC} (V)	J_{SC} (mAcm ⁻²)	V_{MPP} (V)	J_{MPP} (mAcm ⁻²)	FF (%)	η (%)
0.06 M : 0.04 M	0.46	0.75	0.28	0.592	0.503	0.166
0.08 M : 0.04 M	0.36	1.06	0.36	0.557	0.499	0.201
0.1 M : 0.04 M	0.42	2.57	0.24	1.47	0.342	0.352
0.14 M : 0.04 M	0.48	1.00	0.36	0.598	0.5375	0.215

TABLE 1: Physical and photovoltaic parameters of the DSSCs utilizing the ZnO nanostructures grown at various precursor concentrations.

could be explained by the UV-Vis absorption spectra as illustrated in Fig. 1(A). The B-doped ZnO nanostructures grown at 0.1 M possess the highest optical absorption. This sample absorbs the highest number of photon and consequently generates the highest number of electron-hole pairs, thus the J_{SC} and η are improved. From the table is also noticed that the J_{SC} and η decrease as the ZNH concentration increase. However, this trend is not seen for V_{OC} . Generally, the highest J_{SC} and η obtained from this work are still low. This might be due to the sensitization effect of the N719 dye loading into ZnO film in this work was still small. The small sensitization effect is due to small surface area for dye loading. The low in J_{SC} and η might also be caused by high power loss which is caused by high leakage current in this device as illustrated the I-V curves in dark condition shown in Fig. 4(A).

4. Conclusions

Boron-doped ZnO nanotubes have successfully been grown on the FTO at various concentration of ZNH. The UV-Vis spectra of the samples showed the strong absorption at the wavelength range 300-400 nm for all samples. The absorption peak was observed at 370 nm, which represented the good structural quality of ZnO nanostructures. XRD peak of ZnO nanotubes occurred at $2\theta = 34.50^\circ$ and other lower peaks. FESEM images showed the diameter of ZnO nanotubes in the range of 50-340 nm and the thickness of about 1.2 - 4.4 μm for all samples. The hexagonal geometrical shape was observed for all ZnO nanotubes. The homogeneity in size and geometrical shape increased with decreasing ZNH concentration. EDX spectra of the samples observed the weight percentage of compound of Zn, O, and B which was 69.35%, 21.60% and 4.76%, respectively and the atomic percentage of the samples was 33.06%, 42.08% and 13.71%,

respectively. The DSSC was fabricated by arranging the sandwich structure, containing ZnO nanotube coated FTO, dye, electrolyte and platinum coated FTO. Analyzing their I-V characteristics resulted the maximum efficiency of 0.352% from the DSSC based on ZnO nanotube with its precursor-surfactant concentration ratio of 0.1 M : 0.04 M.

5. Acknowledgements

This work was supported by The Ministry of Research, Technology and Higher Education of Indonesia under research grant International Research Collaboration and Scientific Publication of Dr. Iwantono, contract no. 550/UN.19.1/LPPM/2015.

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