

## Growth of Zinc Oxide Nanowire with Natural Dye Extract for Dye Sensitized Solar Cell Application

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### Abstract

This research focused on the synthesis of ZnO nanowires for its application in DSSC devices using the natural bark dye sensitizer. Zinc oxide nanowires grown from hexamethylenetetramine ( $C_6H_{12}N_4$ ) and zinc nitrate ( $Zn(NO_3)_2 \cdot 6H_2O$ ) were used as photoelectrodes for dye-sensitized solar cells. Firstly, ZnO seed layer film was coated by using spin coating technique. ZnO nanowires were grown by using chemical bath deposition (CBD). The concentration of the hexamethylenetetramine in chemical bath deposition (CBD) significantly affected the growth rate of the nanowires. Structural, diameter in size and morphology of ZnO nanowire films were investigated in detail by X-ray diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM). The optical properties of ZnO nanowire films were studied by UV-Vis spectroscopy. The nanowires structure was sensitized with natural bark dye and assembled into a DSSC. High performance carbon electrode was prepared onto ITO substrate and used as counter electrode. I-V characteristic was measured and conversion efficiency ( $\eta_{con}$ ) and fill factor (FF) were determined. It was found that OH<sup>-</sup> ion concentration played a key role during the process of regulating the growth rate and forming the ZnO nanowires by chemical bath deposition (CBD). The conversion efficiency of DSSC at growing time 14 h (4.257%) was investigated to be larger than that of the cell at 7 h (2.795%). According to the experimental results, ZnO nanowires might be promising, credible and applicable for photoelectrode of dye-sensitized solar cell (DSSC) architecture.

**Keywords:** chemical bath deposition; ZnO nanowire; photoelectrode, natural bark dye sensitizer; counter electrode

### I. Introduction

Dye-sensitized solar cells (DSCs) have attracted great interest because of their potential application as a cost-effective alternative to the p-n junction solar cells [Pradhan, B., et al., 2007]. Dye-sensitized solar cells (DSCs) based on semiconductor electrodes have been investigated since 1960 [Imoto, K., et al., 2003]. DSCs are unique compared with almost all other kinds of solar cells in that electron transport and light absorption are each handled by different materials in the cells. The sensitizing dye in a DSC is anchored to a wide-band gap semiconductor such as ZnO [Imoto, K., et al., 2012, Chen, T. Y., et al., 2009, Kakuta, N., et al., 2012, Sreekala C. O., et al., 2012]. A dye-sensitized solar cell (DSSC) is a low-cost solar cell belonging to the group of thin film solar cells. In particular, dye-sensitized solar cells of the third generation of solar cells have become a very interesting and practical alternative for advances in solar cell technology [ó Regan, B. and Grätzel, M., 1999]. The working mechanism of the dye-sensitized solar cell is unique in that it does not follow the principles of the traditional p-n junction solar cell [Chen, C. Y., 2007]. The dye sensitizer absorbs the photons, while the role of the semiconductor film is to facilitate charge transport to the collecting transparent

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conductive oxide glass substrate. It is based on a semiconductor formed between a photo-sensitized anode and an electrolyte, a photoelectrochemical system. The DSSCs convert the energy in light absorbed by dyes or pigments into other forms of energy. The DSSCs realized the optical absorption and the charge separation process by the association of a sensitizer as light-absorbing material with a wide band gap semiconductor of nanocrystalline morphology [Freitas, J. N., 2009]. The major disadvantage to the DSSC design is the use of the liquid electrolyte, which has temperature stability problems [Zhang, Y., et al., 2012].

Zinc Oxide (ZnO) is an inorganic binary compound belonging to the II-VI semiconductor materials group. [Wang, Z. L., 2009]. One of the most attractive properties of this semiconductor is its wide band gap of  $\sim 3.37$  eV at room temperature. A semiconducting material with a wide band gap has the ability to be effective during processes at high temperature and power, and also with operations applying large electric fields [Ozgur, U., et al., 2005]. Other desirable characteristics of ZnO include its near UV emission, large exciton binding energy around 60 MeV that allows sufficient excitonic emission within the UV range at 298 K, visible light transparency, transparent conductivity and piezoelectricity, biocompatibility, structure and property controllability, and simplicity of synthesis process [Yi, G. C., et al., 2005]. Some of the many applications that utilize the distinctive properties of ZnO nanowires include sensors [Wan, Q., et al., 2004, Li, Q. H., et al., 2004], UV photodetectors [Harnack, O., et al., 2003, Keem, K., et al., 2004, Kind, H., et al., 2002, Ohta, H., et al., 2003, Ahn, S. E., et al., 2004], light-emitting device arrays [Park, W.I. and Yi, G. C., 2004], field-effect transistors [Arnold, M. S., et al.], p-n junction diodes [Liu, C. H., et al., 2003], Schottky diodes [Wang, Y. X., et al., 2008], optoelectronic nanocircuits [Johnson, J. C., et al., 2002], dye-sensitized solar cells [Weintraub, B., et al., 2009], biomedical sciences [Zhou, J., et al., 2006, Li, Z., et al., 2008].

ZnO is also biocompatible and biosafe for environmental applications. ZnO crystallines are into two main forms, hexagonal wurtzite and cubic zinc blende. Under general conditions, ZnO exhibits a hexagonal wurtzite structure [Diaz V. E., et al., 2012]. The ratio of  $c/a$  of about 1.60 is close to the ideal value for a hexagonal cell. ZnO nanostructures can be easily prepared by using physical, chemical or electrochemical methods owing to easy growth along the  $c$ -axis of the wurtzite hexagonal structure. Among these methods, ZnO nanowires are grown by chemical bath deposition (CBD) using chemical reactions. The chemical bath deposition method (CBD) has lots of advantages since it does not require high temperature or vacuum. However, the time required for the synthesis takes several hours. Microwave heating has been used for rapid synthesis of ZnO nanowires [Hemant, C., et al., 2006].

## II. Experimental Procedure

### Preparation of ZnO nanoparticles

In this experiment, 0.1M of zinc acetate [ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ] and 0.16M of sodium hydroxide [NaOH] were used as starting materials. Firstly,  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and NaOH were weighed with digital balance.  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and NaOH were mixed with desired molar ratio and stirred vigorously with magnetic stirrer for 2 h. At the same time, precipitation process was performed and the solution was annealed at constant temperature of  $80^\circ\text{C}$  for several time intervals to deposit ZnO nanoparticles. After that,

ZnO nanoparticles were collected and annealed at 500°C. X-ray diffraction (XRD) analysis was performed to examine the phase identification and crystal structure of hydrothermal synthesized ZnO powder.

### Preparation of ZnO layer

Firstly, the indium doped tin oxide (ITO) glass substrates were cleaned in a solution of acetone and isopropanol for 10 min. Then, they were cleaned in deionized water (DIW). The substrates were then annealed at 80 °C for 60 s previous to each spin coating in order to enhance adhesion. Besides, ZnO nanoparticles solution was prepared by mixing ZnO nanoparticle grown from 0.1M of zinc acetate [ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ] and 0.16 M of sodium hydroxide [NaOH] with isopropanol as solvent to form viscous paste. It was then coated onto indium doped tin oxide (ITO)/glass substrate at 2000 rpm for 30 s by spin coating technique. Thus, coating layer was formed on the substrate and it was annealed at 500 °C for 1 h for diffusion film. The structure of ZnO nanofilm was observed by X-ray diffraction method.

### Growth of ZnO nanowires

In order to grow ZnO nanowires, the seed film was subsequently dipped in a mixture solution of 0.016M of  $\text{Zn}(\text{NO}_3)_2$  and 0.050 M of hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ ) solution with DIW by using chemical bath deposition method (CBD) and annealed at 80°C for 7h and 14h respectively. During the reaction, heterogeneous growth of nanowires was limited by homogeneous nucleation of ZnO particles. Finally, the substrates were taken out of the growth solution and rinsed with deionized water and annealed at 500°C for 1 h. The morphological, structural and optical characterizations were also observed by field emission scanning electron microscopy (FESEM), X-ray diffraction, UV-vis analysis. As a result, it was obvious that ZnO nanowire was significantly formed on ZnO seed layer film at different deposition time intervals.

### Preparation of natural bark dye-sensitizer

Tayok-magyi, Kala-magyi [*Pithecellobium dulce* (Roxb.), Benth], was used as a dye in this work. Firstly, Tayok-magyi, Kala-magyi's bark, was dried at room temperature. Then, it was crumbled and grinded with blender into small pieces. Secondly, the pieces of bark were soaked in ethanol solvent and annealed at 80 °C for 30 min. The dye solution was extracted and filtered to get pure dye solution. After cooling, the pH of dye solution was measured to be 6. The optical properties of natural dye-sensitizer were examined by UV-vis spectroscopy.

## III. Results and Discussion

### Structural characterization by X-ray Diffraction Method

To examine the crystal structure and phase formation of Zinc Oxide nanoparticles, seed layer film, and nanowires films, it was performed using monochromatic  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) operated at 40 kV (tube voltage) and 30 mA (tube current). Sample was scanned from 10° to 70° in diffraction angle,  $2\theta$  with a step-size of 0.01°. Figure 1(a) and 1(b) showed the XRD spectra of Zinc Oxide nanoparticles, seed layer nanofilm with zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) and sodium hydroxide (NaOH).

Figure 2(a) and 2(b) showed the XRD profile of ZnO nanowire films with different growing time with  $Zn^{2+}$  concentrations. After growing time for 7 h, eight diffracted peaks in observed spectrum were matched with those of standard zinc oxide. After growing time for 14 h, there were nine diffracted on XRD profile. All diffracted peaks of observed spectrum well matched with those of standard zinc oxide. Figure 2(a) and 2(b) showed the XRD patterns of the ZnO nanowires growth on ITO glass seed layer substrate by using chemical bath deposition method. In Figure 2(a), a dominant diffraction peak for (002) plane indicates a high degree of orientation with the c-axis vertical to the substrate surface. In the other hand, (100) plane in Figure 2(b) is a dominant diffraction peak. X-ray diffraction (XRD) demonstrated the hexagonal wurtzite structure of the ZnO nanowires. Lattice constant, hexagonality and average crystallite size of ZnO nanoparticles, ZnO seed layer, and ZnO nanowire films were calculated and listed in Table 1.

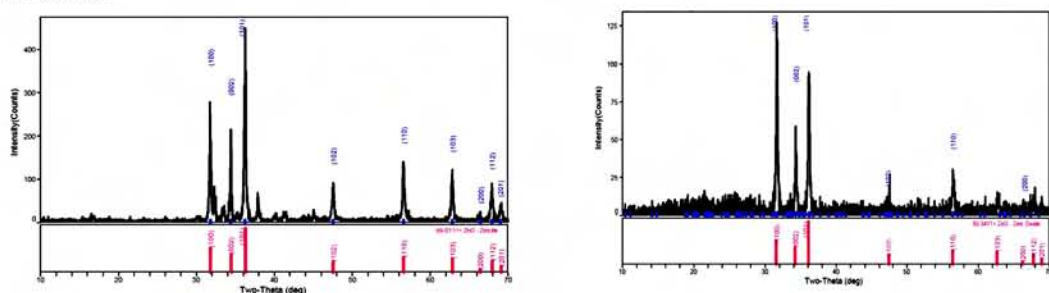


Figure 1. XRD spectra of (a) ZnO nanoparticles and (b) ZnO nanofilm

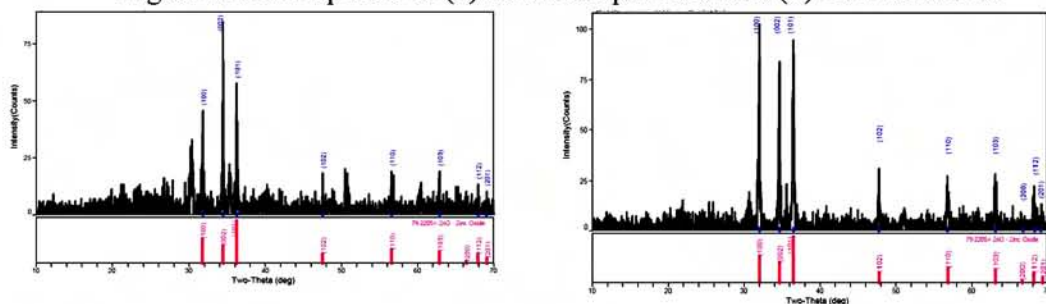


Figure 2. XRD spectra of ZnO nanowire at growing time (a) 7 h and (b) 14 h

Table 1. Lattice parameters, hexagonality and crystallite size of ZnO nanoparticles, ZnO Seed Layer, and ZnO nanowire films

Sample (ZnO)	Lattice parameter (Å)		Hexagonality (c/a)	Crystallite size (nm)
	a	c		
Nanoparticles	3.2490	5.2067	1.6025	31.47
Nanofilm	3.2580	5.2070	1.5980	28.45
Nanowires(7h)	3.2481	5.2177	1.6064	39.35
Nanowires (14h)	3.2279	5.2106	1.6142	29.18

### Surface morphology

Figure 3(a) and 3(b) showed the FESEM images of the ZnO nanowire arrays grown at 80°C for 7 h and 14 h onto indium doped tin oxide (ITO) glass substrates. It could be seen that the ZnO nanowires grown aligned on the substrates. As can be seen

from these images, different structural and morphological changes were observed. The diameter and the length distributions between the ZnO nanowires for different growth time intervals exhibited a significant difference which shows dense nanowires with diameters between 250 nm and 400 nm and lengths between 3.57  $\mu\text{m}$  and 6.93  $\mu\text{m}$ . The ZnO nanowires were disorderly, and had a wide size distribution. In this study, ZnO nanowires are observed to be wurtzite hexagonal structure. The growth time is the key parameter to dominate the diameter ZnO nanowires. By increasing the growing time, both the length and diameter of ZnO nanowires are increased.

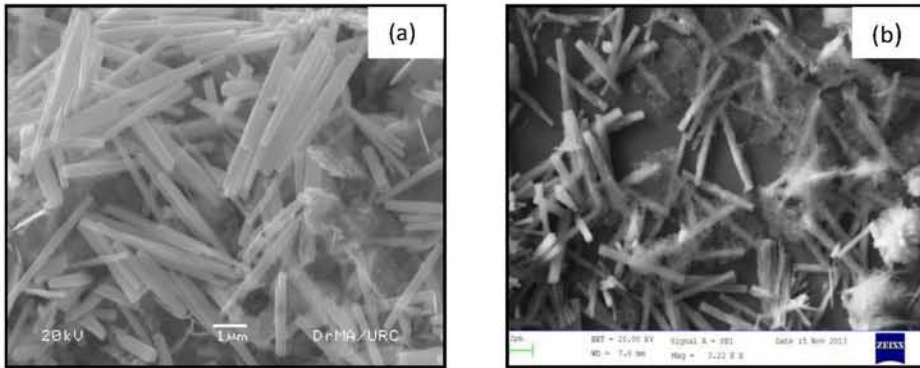


Figure 3. FESEM images of as-prepared ZnO nanowires with growing time of (a) 7 h and (b) 14 h at 80°C grown on ITO substrate

### Optical characterization

Figure 4(a) and 4(b) showed the optical absorption spectra of ZnO nanowires in the range of 300 nm-1100 nm for all samples. From these spectra, it can be seen that the absorption edge is around 371-390 nm. It can also be seen that the absorption edge of Tayok-magyi, Kala-magyi bark solution is around 400 nm-600 nm. The energy band gap ( $E_g$ ) of both samples and Tayok-magyi, Kala-magyi bark solution could be calculated from the absorption spectra and described in Table 2.

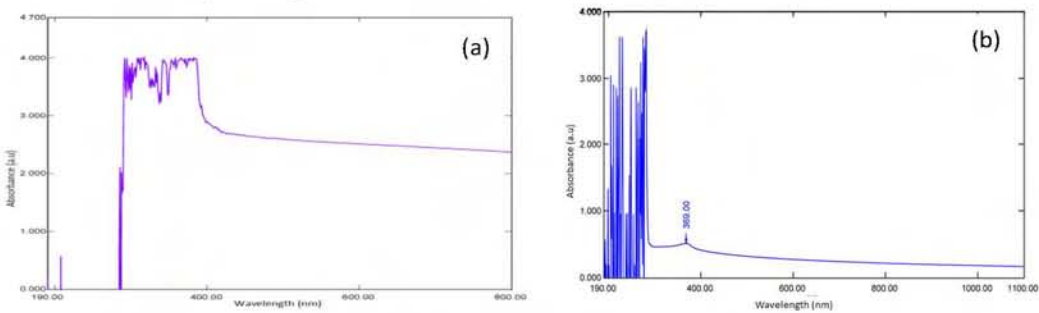


Figure 4. Optical absorption spectra of (a) ZnO (growing time, 7 h) and (b) ZnO (growing time, 14 h)

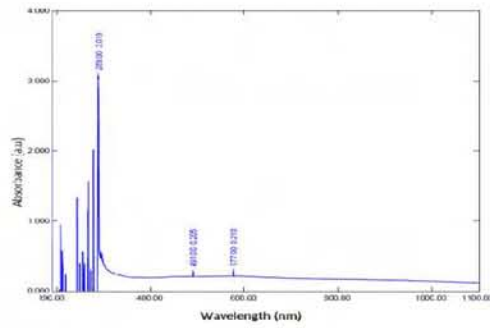


Figure 5. The optical absorption spectrum of Tayok-magyi's bark solution (Pithecellobium dulce (Roxb.), Benth)

Table 2. Energy band gap of the ZnO nanowires and Tayok-magyi bark solution

Sample	$E_g$ , Optical Band gap (eV)
ZnO (growing time, 7 h at 80°C)	3.283
ZnO (growing time, 14 h at 80°C)	3.328
Tayok-magyi's bark solution	2.327

**Photovoltaic properties**

Figure 6 (a) and (b) show the I-V curves of ZnO nanowire (photoelectrode DSSC cells) under 5086 lux illumination. The summarized photovoltaic parameters for the two DSSCs were listed in Table 3. It was found that the Photovoltaic behaviors of both DSSCs were quite acceptable, appropriate and suitable for cost effective DSSC with natural bark dye extract. Effect of annealing temperature on photovoltaic parameters of ZnO nanowire electrodes sensitized with bark dye were calculated and described in Table 3.

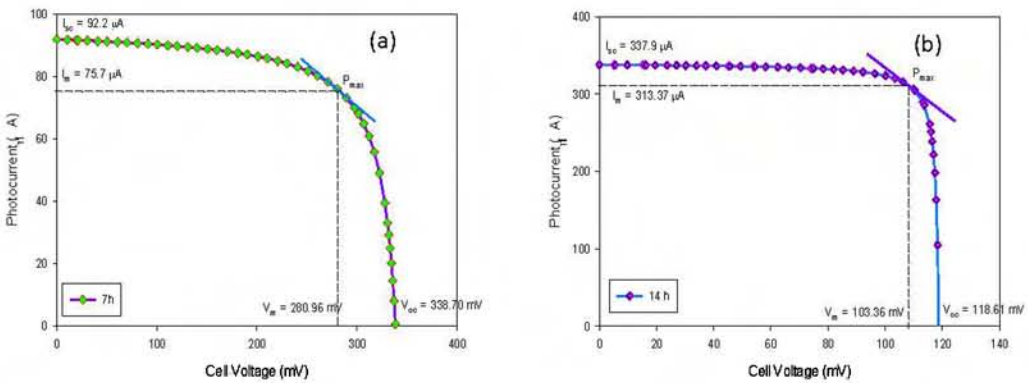


Figure 6. I-V curve of ZnO nanowire photoelectrode with natural dye sensitizer extract for growing time of (a) 7 h and (b) 14 h at 80°C

Table 3. Photovoltaic parameters of ZnO nanowire photoelectrode with dye sensitizer extract

Specimen	$I_{sc}(\mu A)$	$V_{oc} (mV)$	FF	Efficiency (%)
ZnO (7h)	92.2	338.7	0.68	2.795
ZnO (14 h)	338	118.6	0.81	4.257

#### IV. Conclusion

Dye-sensitized solar cells based on ZnO nanowire films were successfully fabricated and investigated on their structure, morphology, light absorption and photoelectric properties. ZnO nanowires were grown onto indium doped tin oxide (ITO) glass substrates by chemical bath deposition (CBD) method. XRD results demonstrated that ZnO nanowire films with the hexagonal wurtzite structure growing along with crystallographic orientation. As a result of UV-Vis spectrum, major peaks of ZnO nanowires were formed at 370-390 nm. The optical band gaps of ZnO nanowires film were evaluated to be 3.2832 eV and 3.3275 eV respectively. The experimental data resulted from this research gave that the ZnO nanowire was successfully favoured on ITO/glass even though the fabrication technique used in this study was not confused and complicated. From the results,  $Zn^{2+}$  ion and  $O^{2-}$  ion concentrations played a key role during the process of regulating the growth rate and forming the ZnO nanowires semiconductor films by chemical bath deposition (CBD). Therefore, the efficiency of ZnO nanowire solar cell for growing time (14 h at 80 °C) was examined to be greater than that of ZnO nanowire solar cell for growing time (7 h at 80 °C). The results showed that ZnO and bark natural dye exhibited a promising application in the preparation of dye sensitized solar cell. Thus the present research allowed more economical coating, easy adaptability and technical simplicity thereby making products that were more compact.

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