

INVESTIGATION OF ELECTRODEPOSITED NANO ZNO PHOTO ANODE FOR DYE-SENSITIZED SOLAR CELL (DSSC)

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Abstract

This paper reports on the deposition and characterization of nano porous zinc oxide (ZnO) by using simple and low-cost electrodeposition. SEM, XRD and UV-VIS were used to studying structural, morphology, and optical properties of thin films ZnO. It was found that ZnO have nano sheet-like structure with about 1 μm in size. Optical energy band gap is shift from 3.44 eV to 3.46 eV after dyeing process. Organic dye of *Clitoria ternatea* was extracted and used as synthesizer. Anthocyanin peak was observed in absorption spectrum. The Zinc oxide films is employed as photoanode on the dye sensitized solar cells (DSSC). The I-V characteristic curve parameters show PCE 0.02% and fill factor 31.7%.

Keywords: ZnO nanosheets, organic dye, electrodeposition, DSSC

Introduction

Nanostructured Zinc Oxide (ZnO) have been widely investigated, including their application in photo anode of dye-sensitized solar cell. Many method are used to deposit ZnO nanostructures, such as vapor deposition, hydrothermal, spray pyrolysis. The electro deposition methods have advantages over these method because of its fast, simplicity, low cost, and low process temperature (Vasekar and Dhakal, 2013). In addition, this method can be used to control morphology of the grown ZnO nanostructures (Jiangfeng *et al.*, 2010). In previous work, porous nano sheets ZnO have been achieved by adding various additive such as KNO_3 , KBr , K_2SO_4 , KCl into the electrolyte bath (Hou *et al.*, 2012a; 2012b). However, few studies on these

topics have been reported on abortion of dye on nano porous ZnO films.

In this research we focused on prepared and characterized nano porous ZnO including their application as photo anode in organic dye-sensitized solar cell. The efficiency of dye sensitized solar cells aspect to be revealed.

Experimental

Preparation of ZnO

ZnO films was deposited using the following procedures. commercially available fluorine-dope tin oxide (FTO) coated glass (8 ohm/square) was cut

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3.7×2.0 cm² in size and was cleaned with soap and then ultrasonication in acetone solution for 10 min. A high purity zinc sheet was cut in the same dimension and well-polished. This sheet is used as counter electrode. Zinc nitrate hexahydrate 0.1 M (Zn(NO₃)₂·6H₂O) was used as a source of zinc ions. This precursor was added in to 100 ml of deionized water (DI). Potassium Bromine (KBr) 0.01M, and Potassium Nitrate (KNO₃) 0.01M are used as additive. Deposition was carried out with laboratory DC power supply in constant current mode at current density -1.0 mA/cm² for 20 min based on modified of literature method (Zhang, 2011). The electrolyte bath was kept constant temperature at 65°C for all deposition period. After deposition the samples were rinse in deionized water dried in air and annealing under atmosphere at 250°C for 30 min.

Preparation of Electrolyte

Redox electrolyte solution was prepared by dissolving quantity of 0.5 M Potassium iodine (KI) and 0.05 M of iodine (I₂) in 20 ml of ethanol solution (Shelke *et al.*, 2013).

Organic Dye Extraction

Dye extraction was using the following procedures. A 5 g of Clitoria ternatea were washed and crushed within 5 ml deionized water in the plastic bag and then was filtered with filter paper to get homogeneous aqueous solution (Ludin *et al.*, 2018).

DSSC Fabrication

In brief, zinc oxide on FTO coated glasses was immersed in organic dye solution for 12 h and dried at room temperature. Graphite counter electrodes were coated by pencil on FTO coated glasses. A drop of electrolyte solution was put on one surface of the films then sandwiched without using any spacer and fixed with metal clip as showed in Figure 1. Over all cell dimension is 2.0×3.7 cm² and active area for light exposure is 1.0×1.0 cm².

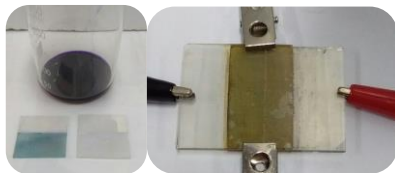


Figure 1. ZnO DSSC device fabrication

I-V Characteristic

Laboratory made Potentiostat (Dstat) (Dryden and Wheeler, 2015) is used to evaluated

I-V Characteristic curves in linear sweep mode at scan rate 100mV/s under illumination. High-pressure mercury bulb are used as light source. Illumination intensity was calibrated by solar power meter (SM206) at 100 mW/cm². The energy conversion efficiency is defined as $\eta = (FF \times I_{sc} \times V_{oc}) / P_{in}$ where P_{in} is the power of the incident light. The fill factor (FF) is defined as $FF = (P_{max}) / (I_{sc} \times V_{oc})$ where P_{max} is Power maximum of device.

Characterization and measurements

XRD Analysis

The X-ray diffraction pattern of ZnO films on FTO substrate is showed in Figure 5. It can be seen that all the peaks of 31.7°, 34.4°, 36.2°, 62.8°, 66.3°, 76.9°, 47.5°, and 56.6° which is corresponding to the ZnO wurtzite structure (ICCD PDF#01-080-0075). In addition, the crystallite size (D) was estimated by applying Debye-Scherrer's equation (Saji *et al.*, 2010),

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where, K is the particle shape factor its value is 0.827 for hexagonal ZnO, β is the full width at half maximum (FWHM) diffraction peak corresponding to (100) plan, and θ is the Bragg's angle obtained from 2θ value corresponding to the same plane. λ is the wave length of Cu-K α radiation (0.15 nm). The average crystallite size of ZnO is estimated to be 118 nm.

SEM Analysis

Figure 3(a) showed a cross section of ZnO films. Films thickness is around 12 microns.

The surface of films in Figure 2(b) and Figure 2(d) is relatively smooth and uniform while that

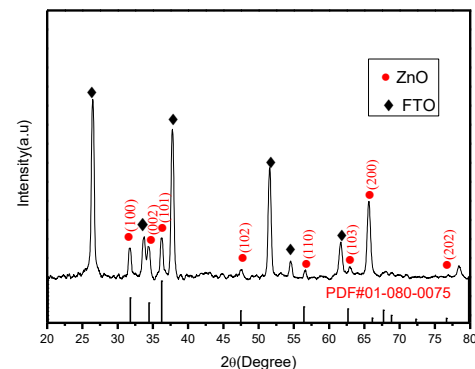


Figure 2. XRD patterns of the ZnO

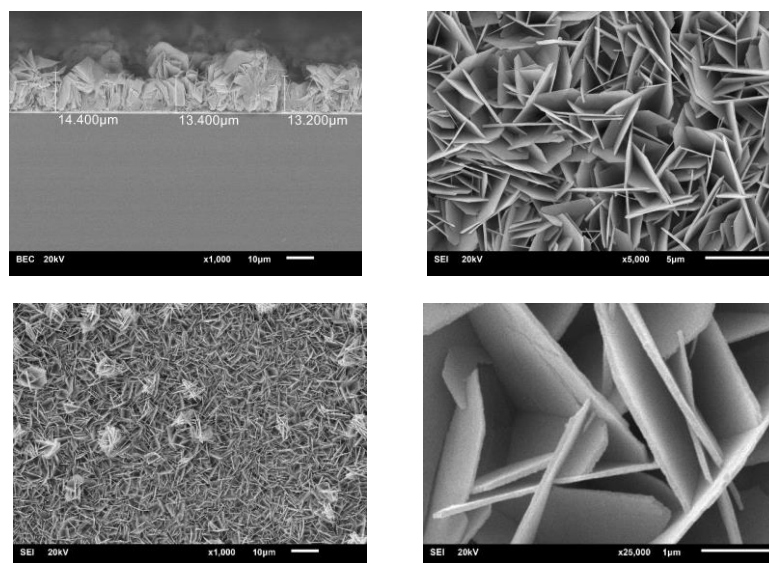


Figure 3. SEM image of ZnO films electrodeposition at -1.0 mA/Cm^2 (a) Cross section, (b) Surface $\times 5000$ (c) Surface $\times 1000$ and (d) surface $\times 25000$

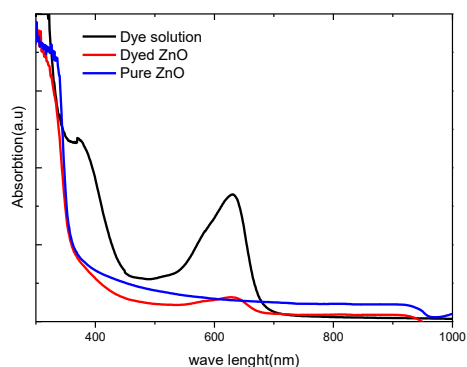


Figure 4. Absorbance spectrum of the deposited ZnO thin films before and after dyeing process

Figure 2(c) presented some small clusters randomly distributed on the films surface.

UV-vis Spectral Analysis

UV-vis spectroscopy used for study absorption of ZnO before and after dyeing process.

The optical absorption spectrum is shown in Figure 4 the absorption peak centred at 620 nm was confirmed a presence of Anthocyanin extracted from *Clitoria ternatea* flowers in dyed ZnO films. Absorption peaks of ZnO films after dyeing process have low intensity due to low bond between dye molecule and ZnO particle. Tauc's equation is used to estimate the optical band gap of the ZnO films (Ritala and Leskelä, 2001),

$$ahv = A(hv - E_g)\gamma \quad (1)$$

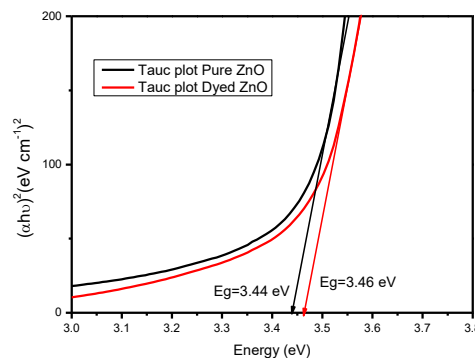


Figure 5. Tauc plot of the ZnO thin film deposited FTO substrate

where α is the absorption coefficient, h is the Planck's constant, ν is the frequency of light. The band energy gap of the ZnO film was calculated by extrapolating the straight portion of the graph on energy axis in the Tauc's plot based on the $(\alpha hv)^2$ vs. (hv) . The Optical band gap of ZnO was shifted from 3.4 eV to 3.6 eV after dyeing process, normally found in dye absorption of metal oxide films.

I-V Characteristic analysis

Figure 5 shows the photocurrent density-voltage (I-V) curves of ZnO/graphite DSSC. Table 1 showed performance parameters of photocurrent (I_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and efficiency (η) under the testing condition of 100 mW/cm^2 compare to literature. This results revealed that performance parameters of this work are in the same range of organic dye literature.

Table 1. List of literature of DSSCs with ZnO photoelectrode performance

Working electrode	Counter electrode	Dye	Voc(mV)	Isc(mA)	FF	$\eta\%$	Literature year
ZnO	Pt	Antocyanin	233.4	0.111	61.41	0.11%	Syukron (2014)
ZnO	Pt	Carica papaya	373.0	0.149	30.37	0.017%	Adedokun (2018)
ZnO	Pt	N719	645.0	10.40	0.56	3.75%	Marimuthu (2018)
Zno(nanosheet)	Pt	N719	0.66	0.68	0.52	0.23%	Moniruddin (2017)
ZnO	Graphite	Antocyanin	188.27	0.390	0.22	0.02%	This work

Conclusions

In conclusion, ZnO nanosheet was successful electrodeposited on FTO glassed by simple and low-cost two electrode electrodeposition at current density -1.0 mA/cm^2 by introduced KBr, KNO_3 as additive into the electrolytic bath. The analysis of XRD patterns indicates hexagonal wurtzite structure (ICCD PDF#01-080-0075), the crystallite size estimated by Scherrer equation is 118 nm. SEM study shows the surface of films is nanosheet-like structure, relatively smooth and uniform. *Absorption spectroscopy* analysis are confirmed a present of Anthocyanin organic dye extracted from Clitoria ternatea flowers. However, dyed ZnO have low peak intensity at peak centered of 620 nm due to low the present of bond between ZnO particle and dye molecule, which lead to a low conversion efficiency of DSSC device around 0.02%.

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