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# Analysis of the electrodeposited ZnO as photo anode for solar cells

***Abstract***. *There are many methods to deposit a photoanode layer of DSSC, such as doctor blade, sputtering and spin coating. However, there are limitations for each of the methods. Electrochemical deposition is a three-electrode, cost-effective method for depositing metal, metallic oxide, and composites. The three-electrode method can also control the coating thickness and chemical composition by varying the deposition potential/current. Zinc Oxide (ZnO) is an n-type semiconductor with a wide bandgap energy value lying in the range of 3.37 eV. In this work, ZnO layers were deposited using an electrodeposition method by varying the time and molarity of the solution. The potential difference used in this experiment was -0.61 V based on the cyclic voltammetry and chronoamperometry using a potentiostat and NOVA software. The qualities of the deposited ZnO have been studied using Scanning Electron Microscopy (SEM) and Ultraviolet-Visible Spectroscopy (UV-Vis) to determine their characterizations.*

***Streszczenie.*** *Istnieje wiele metod osadzania warstwy fotoanody DSSC, takich jak rakla, napylanie katodowe i powlekanie wirowe. Istnieją jednak ograniczenia dla każdej z metod. Osadzanie elektrochemiczne to opłacalna metoda osadzania metali, tlenków metali i kompozytów za pomocą trzech elektrod. Metoda trójelektrodowa może również kontrolować grubość powłoki i skład chemiczny poprzez zmianę potencjału/prądu osadzania. Tlenek cynku (ZnO) to półprzewodnik typu n o wartości energetycznej szerokiego pasma wzbronionego mieszczącej się w przedziale 3,37 eV. W tej pracy warstwy ZnO osadzano metodą osadzania elektrolitycznego, zmieniając czas i molarność roztworu. Różnica potencjałów zastosowana w tym eksperymencie wynosiła -0,61 V w oparciu o cykliczną woltamperometrię i chronoamperometrię z użyciem potencjostatu i oprogramowania NOVA. Właściwości osadzonego ZnO badano za pomocą skaningowej mikroskopii elektronowej (SEM) i spektroskopii w zakresie widzialnym i ultrafioletowym (UV-Vis) w celu określenia ich charakterystyki.* (***Analiza elektroosadzanego ZnO jako fotoanody do ogniw słonecznych***)

**Keywords:**.Zinc Oxide, photoanode, Electrochemical Deposition, SEM, UV-Vis.
**Słowa kluczowe:** Tlenek cynku, fotoanoda, osadzanie elektrochemiczne, SEM, UV-Vis.

## Introduction

Our society requires energy to maintain our quality of life and underlie all other aspects of our economy [1]. Renewable energy technologies promise plentiful, clean energy derived from self-renewing resources, including the Sun, Wind, Earth, and Plants [2]. Solar energy is the radiant light and heat from the sun captured by various methods, including solar power generation, solar thermal energy, such as solar water heating, and solar architecture [3]. A solar cell, also known as a photovoltaic cell, is an electrical device that uses the photovoltaic effect, a physical and chemical phenomenon, to convert light energy directly into electricity using a semiconductor. Solar cells are divided into three generations based on the historical period and the types of materials utilized in their fabrication [4]. This research investigates and discusses the electrochemical deposition of ZnO for the third generation of solar cells. A DSSC is a low-cost solar cell belonging to the thin-film solar cell family. Zinc oxide (ZnO), one of the oldest known semiconductors that is a promising material among the numerous metal oxide materials for photovoltaic applications [5].

Furthermore, toxic substances produce and process most semiconductors, causing environmental problems. Thus, research efforts have been made to develop materials that could guarantee optimal environmental combability, abundance, and photoactivity characteristics, especially in the last decade [6]. As a result, developing novel materials and assembly processes for low-cost solar cells is a viable option [7]–[11]. Accordingly to its low production cost and flexible manufacturing processes, dye-sensitized solar cells (DSSC) have received a lot of interest. Several synthesis methods, such as pulsed laser deposition, chemical vapor deposition, thermal oxidation, sol-gel, photochemical deposition, and electrodeposition, are often utilized to deposit the ZnO thin films. The electrodeposition method has various benefits over other approaches. This is mainly due to its simplicity, cheap equipment cost, ability to produce vast thin films, and control over film thickness. There are two types of electrochemical deposition, which are two-electrode and three-electrode. This research used three-electrode method to deposit ZnO as a photoanode for solar cells [12].

Understanding applied materials science requires material characterization. Material characterization combines approaches to determine a material's structure at various scales and its link to its attributes and behavior [13]–[16]. Typically, a material's microstructure is characterized by a physical action at that size, and this data can predict larger-scale traits. Scanning Electron Microscopy (SEM) is a technique used to examine the surface topography of materials, such as structures, cracks, defects, pollutants, or corrosion. UV-Vis Spectroscopy is a frequently used method for determining a sample's absorption of light or transparency. It uses a spectrophotometer to determine the wavelengths of light flowing through a sample and generates a plot of intensity (percent T) against wavelength [17].

## Experimental

*Sample Cleaning*

The dimensions of ITO glass were 50 mm x 50 mm with a thickness of 1.1 mm and a sheet resistance of 10-15 /square. First, 1.5 cm × 2 cm pieces of the microscope glass substrate and ITO were cut using a laboratory glass cutter. Next, the substrates were washed with liquid detergent and sonicated for 30 minutes in isopropyl alcohol (IPA) using an ultrasonic cleaner. The substrates were then

placed in ethanol and sonicated for 30 minutes to eliminate organic residues. After that, the substrates were washed five times with deionized water (DI), and then they were dried in an oven at 100°C until the water marks disappeared. The process of the sample cleaning is summarized in Figure 1.

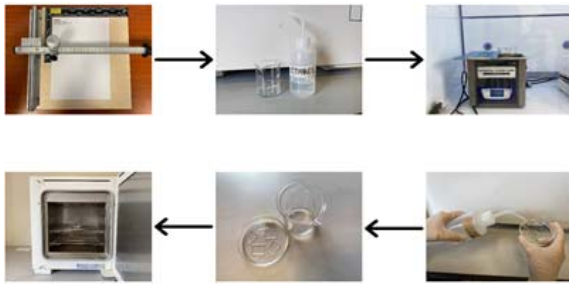

Fig 1: Summary of the sample cleaning process.

**Preparation of Zinc Oxide Solution**

1. Reagents. The chemical reagents used in this work were analytical grade. Zinc nitrate hexahydrate **($Zn(NO_3)_2.6H_2O$)**, 98%, Sigma Aldrich) was used as zinc and oxygen sources. All the aqueous solution was prepared using distilled water.
2. Electrodeposition configuration and characterization techniques of the ZnO thin films.

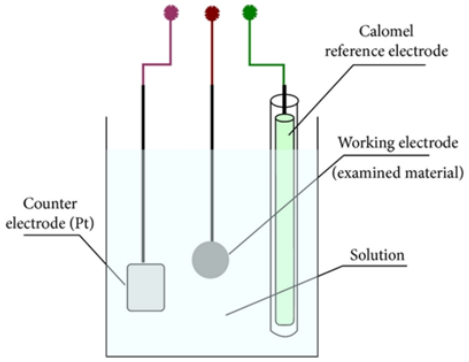


Fig. 2: The illustration of the three-electrode setup for electrodeposition process.

Figure 2 shows the example of the three-electrode system used in this project. The platinum electrode, working electrode, and calomel reference electrode were replaced with platinum plate, ITO-coated glass, and Ag/AgCl, respectively. The system was connected to a potentiostat to supply potential or voltage into the electrochemical deposition system. Zinc nitrate hexahydrate added with sodium hydroxide until reached the pH of 5.74 was used as solution for the deposition process. The thin zinc oxide films were electrodeposited in an aqueous solution at 90°C. After the deposited ZnO onto ITO-coated glass substrates is acquired, the samples were sent to the lab for characterization.

The deposited ZnO onto ITO glasses was evaluated by measuring the absorbed chemical light using Ultraviolet-visible (UV-Vis). The UV-Vis measured the intensity of light that passes through the sample concerning the intensity of light through a reference sample. Then, the samples were evaluated for the surface morphology and the elemental of the photoanode layer using Scanning Electron Microscopy (SEM). SEM is a technique that produces images of a sample by scanning it with a beam of electrons.

**Results & Discussion**

**Electrodeposition of Zinc Oxide**

1. Zinc Oxide as Photoanode The deposition of ZnO thin films with different times

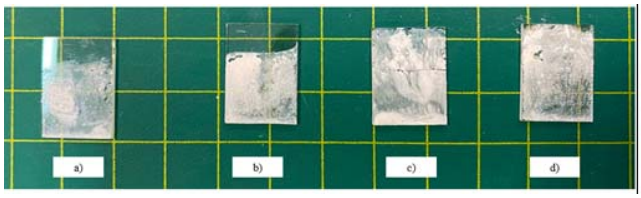


Fig. 3: The ZnO was deposited for a) 20 minutes, b) 30 minutes, c) 40 minutes, and d) 50 minutes, respectively, under deposition potentials of -0.61V at 90°C and pH value of 5.74.

As illustrated in Figure 3, the ZnO samples were deposited using varied deposition durations of 20, 30, 40, and 50 minutes. Initially, the deposition was initiated using ITO glass as the working electrode on which ZnO would deposit. From the observation, the homogeneity of the ZnO layer deposited in 30 minutes was the best compared to the other samples.

2. The deposition of Zinc Oxide thin films with different molarity.

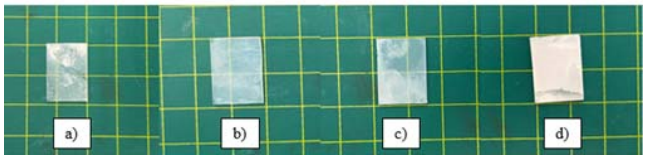


Fig. 4: The ZnO was deposited for a) 15 minutes and 0.01M, b) 30 minutes and 0.01M, c) 15 minutes and 0.1M, and d) 30 minutes and 0.1M, respectively, under deposition potentials of -0.61V at 90'C and pH value of 5.74.

As illustrated in Figure 4, the ZnO sample was deposited by varying the molarity of the solution. 0.01M and 0.1M of the solution were used to perform the electrodeposition for 15 and 30 minutes for each molarity. The sample with 0.1M for 30 minutes has the best uniformity compared to others.

**UV-Visible Spectroscopy (UV-Vis)**

1. Absorption spectra of ZnO thin film with different deposition times.

Absorption spectra examine the energy absorbed by electrons when they transition between energy levels in a metal. Each element has a different absorption spectrum, which may be used to identify the unidentified substances. The data in Figure 5 show the absorption spectra for ZnO thin films deposited at different time. It can be seen that at the wavelength of 300 nm to 1000 nm, the ZnO thin film deposited in 40 minutes of deposition time has the highest absorbance, whereas the ZnO thin film deposited in 20 minutes has the lowest absorbance. The ZnO thin film deposited in 20 minutes exhibits low absorption because of non-uniform layer of ZnO thin film, as can seen in Figure 3

In addition, as illustrated in Figure 6, the bandgap energy of ZnO thin film can be extracted from the UV-vis data. The ZnO thin film deposited in 30 minutes has a band gap of 3.46 eV which is close to the typical value of bandgap energy for ZnO, which is 3.37 eV.

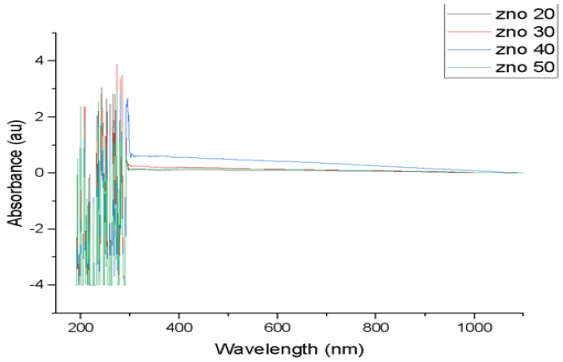


Fig.e 5: Absorption spectra of ZnO thin film with different deposition time (20, 30, 40 and 50 minutes with fix molarity of 0.01M.

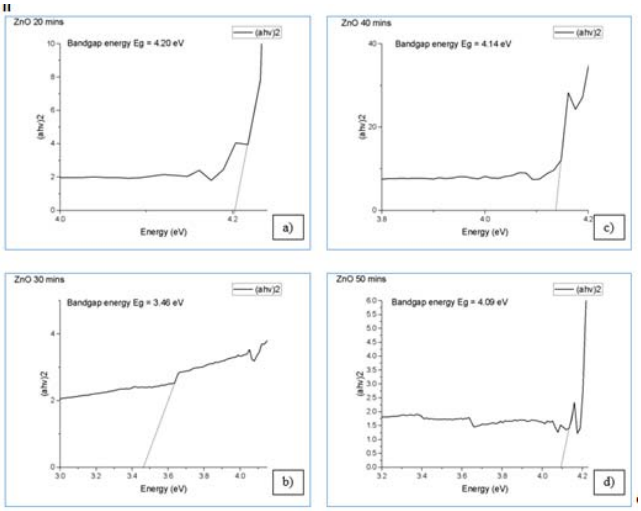


Fig. 6: Bandgap of deposited ZnO thin film on ITO glass with different the deposition times; a) 20 minutes, b) 30 minutes, c) 40 minutes, and d) 50 minutes.

2. The deposition of Zinc Oxide thin films with different molarity and times.

The data in Figure 7 exhibit the absorption spectra for ZnO thin films deposited at different time and molarity. From the graph, the ZnO thin film deposited in 30 minutes of deposition time with 0.1M has the highest absorbance, whereas the ZnO thin film deposited with 0.01M in 15 and 30 minutes has the lowest absorbance. These two samples have low absorption because of the non-uniform layer of ZnO thin film, as can be seen in Figure 4.

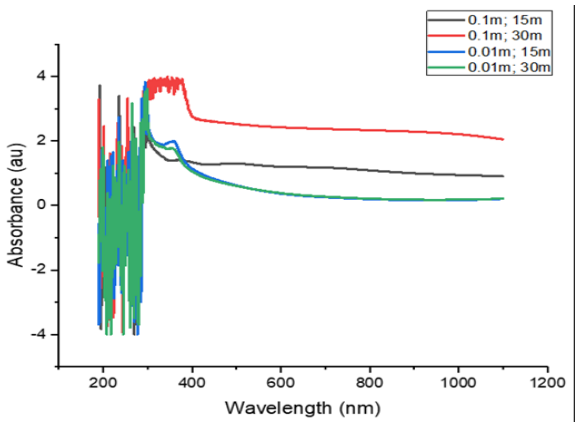


Fig. 7: Absorption spectra of ZnO thin film with different deposition times (15 and 30 minutes) for each molarity of 0.01 and 0.1 M.

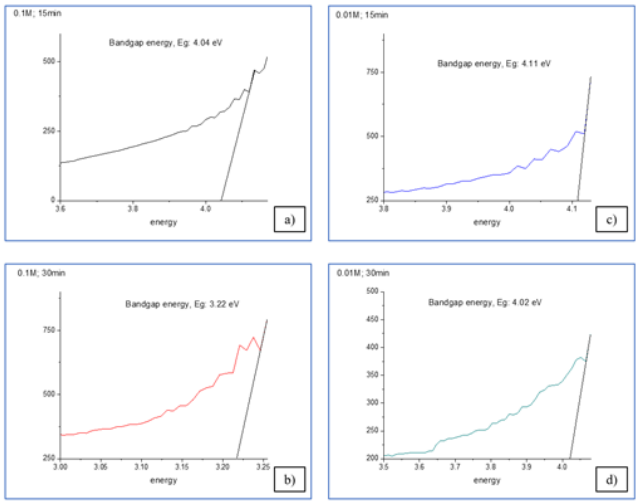


Fig. 8: Bandgap of deposited ZnO thin film on ITO glass with different in molarity and deposition times; a) 0.1M and 15 minutes, b) 0.1M and 30 minutes, c) 0.01M and 15 minutes, and d) 0.01M and 30 minutes.

In addition, as illustrated in Figure 8, the bandgap energy of ZnO thin film can be extracted from the UV-vis data. The ZnO thin film deposited in 30 minutes with 0.1M has a band gap of 3.22 eV, which is close to the typical value of bandgap energy for ZnO, which is 3.37 eV.

**Scanning Electron Microscopy (SEM) Analysis of ZnO thin films with Different Deposition Time and Molarity**

SEM analysis was used to investigate the surface morphology of ZnO thin films deposited at different times and molarity.

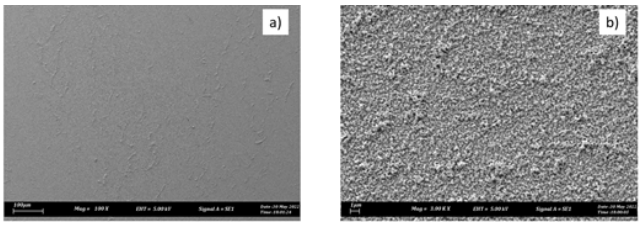


Fig. 9: The ZnO thin film deposited under deposition potentials of -0.61V with the molarity, 0.01M at 15 minutes of deposition time; a) magnification of 500 and b) magnification of 3000.

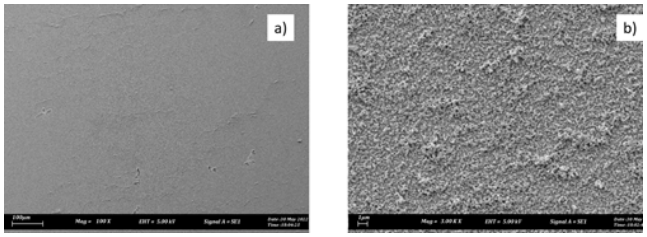


Fig. 10: The ZnO thin film deposited under deposition potentials of -0.61V with the molarity, 0.01M at 30 minutes of deposition time; a) magnification of 100 and b) magnification of 3000.

Figure 9 and Figure 10 provide SEM images of ZnO thin films at magnifications of 100 and 3000 for 0.01M samples of ZnO thin films deposited at 15 and 30 minutes, respectively. From the SEM images, no significant different were observed in terms of the density and uniformity

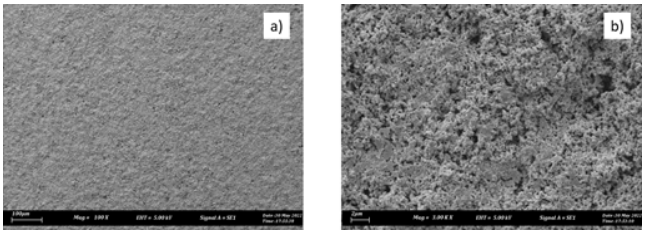


Fig. 11: The ZnO thin film deposited under deposition potentials of -0.61V with the molarity, 0.1M at 15 minutes of deposition time; a) magnification of 100 and b) magnification of 3000.

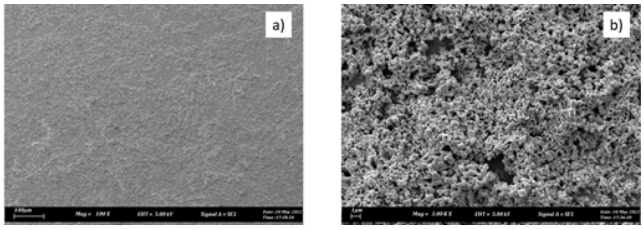


Fig. 12: The ZnO thin film deposited under deposition potentials of -0.61V with the molarity, 0.1M at 30 minutes of deposition time; a) magnification of 100 and b) magnification of 3000.

On the other hand, Figures 11 and 12 provide SEM images of ZnO thin films at magnifications of 100 and 3000 for 0.1M samples of ZnO thin films deposited at 15 and 30 minutes, respectively. SEM image in Figure 11 shows that the ZnO thin film deposited in 15 minutes has a better uniformity in comparison to the ZnO thin film deposited in 30 minutes.

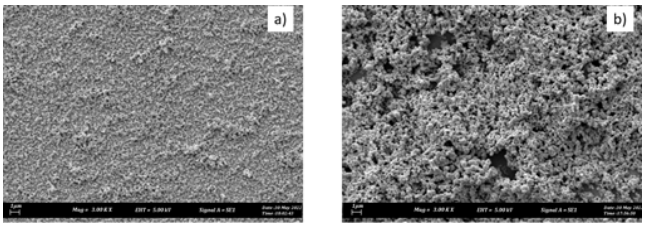


Fig. 13: Comparison of the electrodeposited thin film ZnO using aqueous solution of 0.01M and 0.1M in 30 minutes.

The SEM images in Figure 13 show the comparison between the samples of the electrodeposited ZnO thin films (0.01M at 30 minutes and 0.1M at 30 minutes). It can be observed that thin films of ZnO deposited with 0.1M have high density and larger particle size in comparison to the thin films of ZnO deposited with 0.01M. The molarity of aqueous solution plays an important role in the particle size and density of the thin film.

**Conclusion**

Zinc oxide (ZnO) thin films have been successfully electrodeposited using the electrochemical deposition method from an aqueous zinc nitrate solution at 90°C. The deposition time for the electrodeposition has been varied into 20, 30, 40, and 50 minutes. By observing the uniformity of the deposited layers, it can be concluded that deposited zinc oxide for 30 minutes has the best uniform coating. For the different molarity solutions, the deposited layers of ZnO thin films for 0.01M and 0.1M with deposition times of 15 and 30 minutes also exhibited good uniformity. From the SEM images, it can be observed that a greater the molarity of the aqueos solution leads to a higher density of ZnO thin films. Beside that, the sample for the deposition time at 15 and 30 minutes with the same molarity gave barely any difference in their morphologies. Finally, the data from the Uv-Vis characterizations show that the sample with 0.1M at 30 minutes deposition time has the best absorbance compared to the other samples.

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