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Structural and Optical Characteristics of Multilayer ZnO Nanorod:TiO2 by DC Magnetron Sputtering for Dye Sensitized Solar Cell (DSSC) Application

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Abstract. The development of Dye-Sensitized Solar Cell (DSSC) technology by utilizing various semiconductors has attracted attention. Among all types of semiconductors, the nanostructure of ZnO is selected due to their unique electrical properties and ease of preparation in various morphologies, and it has been considered a promising material to be applied in DSSC. In this research, the DC magnetron sputtering method was used to prepare ZnO thin films as an efficient alternative to press the charge recombination process that occurs in TiO2-based DSSC. Different thicknesses of TiO2 layers on the FTO conductive glass substrate were made through various sputtering deposition times, while the ZnO nanorod layers were made with a single layer using the hydrothermal method. We used XRD, SEM, UV-Vis, I-V meter, and EIS analysis. Based on these characterization we concluded that multilayer ZnO nanorod:TiO2 coating with a sputtering time of 60 minutes resulted the best performance of DSSC with an efficiency of 0.27%.

1 Introduction

Dye Sensitized Solar Cells (DSSC) are a type of dye-based solar cell. To produce electrical energy, this type of solar cell uses the basic principles of photo electrochemical phenomena [1]. The DSSC arrangement consists of semiconductor oxide, dye, electrolyte, and counter electrode (Pt) [2]. The main advantage of DSSC is its potential to produce high efficiency at low cost. Currently, the maximum efficiency of DSSC has been achieved by the active material TiO2 [3].

TiO2 material is more efficient for converting photons because TiO2 has a nanostructure, has a high surface area, high light absorption ability, high chemical stability and has a long electron lifetime (16 ms) [4]. On the other hand, electron transport in TiO2 is relatively slow, causing high interfacial reactions and limited system efficiency[5][6]. There are various TiO2 fabrication methods, one of which is the sputtering method. In previous research, the DC sputtering method has succeeded in making thin layers of TiO2 with crystallinity that continues to increase as the film thickness increases after post-annealing [7].

Apart from TiO2, there are many semiconductor materials that can be used for DSSC, one of which is ZnO. The ZnO material is widely researched and used because nanostructured ZnO has higher electron mobility than TiO2 [8]. Apart from that, ZnO material is an element that is abundant in nature and has a gap energy of 3.37 eV at room temperature which is almost the same as TiO2, namely 3.2 eV. Furthermore, ZnO material has a high excitation energy of 60 meV and high electron mobility, so that ZnO material has received widespread attention in photocatalytic applications[9]. Apart from that, the ZnO material has lower chemical stability than TiO2, especially under acidic conditions and very low color absorption [10][11]. This condition causes lower power conversion efficiency (PCE) in DSSCs based on ZnO nanoparticles alone compared to TiO2 [11].

Various strategies have been carried out by previous researchers to overcome the weaknesses of the ZnO material, such as coating, synthesis, doping, and composites with other semiconductor materials[12][13]. The fast electron mobility of the ZnO material and the high chemical stability of the TiO2 material are utilized to improve the performance of DSSC [5]. From the results of previous research, it was reported that the use of ZnO material with TiO2 could increase Jsc, Voc and FF by using N719 dye as a sensitizer. This change is related to the formation of a thin TiO2 layer which prevents back transfer of electrons and increases the electron lifetime of the ZnO layer [14].

In this research, ZnO material will be deposited on the FTO substrate using the hydrothermal method. After successfully growing ZnO nanorods, the next step is deposition of the TiO2 target material using the DC Sputtering technique to obtain a multilayer structure. The Sputtering method has the advantage of creating a homogeneous film by controlling the particle size and film porosity [15]. With the sputtering method, oxygen vacancies on the TiO2 surface which prevent electron transport in the system can be overcome by treatment with O2 plasma and Ar plasma to increase reactive activity. Sujuan Wu et.all reported that sputtering TiO2 increases the amount of color absorption, reduces trapping states in TiO2, and suppresses interfacial recombination. [16].

2 Experimental Methods

The process of making the DSSC device begins with cleaning the FTO substrate with ethanol, then soaking it with soapy water and Aquades, then sonicating it for 15 minutes each and dipping it in acetone at a temperature of 65ºC. Synthesis of ZnO nanoseed uses zinc acetate dyhydrate with the following chemical reaction equation:

Zn + 2CH3COOH + 2H2O → Zn(CH3COO)2·2H2O + H2 (1)

Zinc acetate dyhydrate (Zn(CH3COO)22H2O) was dissolved in ethanol with a stirrer for 2 hours then deposited with spin coating at a speed of 2000 rpm for 20 seconds for homogeneous results and heated on a hotplate at 100ºC for 15 minutes, 300ºC for 15 minutes and at a temperature of 500ºC for 30 minutes. ZnO nanorods are grown via the hydrothermal method with zinc nitrate tetrahydrate solution with the following chemical reaction:

Zn + 2HNO3 → Zn(NO3)2 + H2 (2)

ZnO + 2HNO3 → Zn(NO3)2 + H2O (3)

Zn(OH)2 + 2HNO3 → Zn(NO3)2 + 2H2O (4)

Zinc nitrate tetrahydrate (Zn(NO3)24H2O was dissolved in deionized water with a stirrer for 1 hour and hexamethylentetramine was added as a provider of OH- [17]. The hydrothermal temperature used was 100ºC for 6 hours, then heated at 500ºC for 1 hour. Synthesis TiO2 uses the DC sputtering method with variations in sputtering time (30 minutes, 60 minutes and 90 minutes). The sputtering process uses DC power 80 Watt, pressure 9 × 10-1 Pa, gas flow rate Ar 60 sccm and O2 plasma 20 sccm, water press control of 35%, and substrate rotation of 5 rpm. Through the sputtering process, the TiO2 target material will scatter microscopic particles, then be collided with high-energy particles from the Ar plasma which are scattered and go in all directions, including the substrate, thus forming thin film.

The next step is the characterization stage, XRD testing is used to identify the crystalline phase in the material by determining the lattice structure parameters and to obtain the particle size of the nanocrystals. SEM cross section to determine the surface morphology and distribution of nanoparticles and SEM EDX to detect the concentration of elements contained in the sample. Meanwhile, to find out the optical properties of the film, you can see the results of UV-Vis characterization. The deposition electrode was soaked in D205 dye solution for 24 hours. Next, the ZnO nanorod:TiO2 photoanode was combined with a commercial Pt counter electrode and dripped with TDE mosalyte electrolyte solution for I-V meter testing. DSSC efficiency values are obtained by I-V meter testing using a solar simulator and Keithley 2602A to determine parameters such as Isc, Jsc, FF, and Voc so that DSSC efficiency values can be obtained and by analyzing the results of the Electrochemical Impedance Spectroscopy (EIS) test using Gamry Echem Analyst you can studied in detail the charge transfer mechanism in the cell as well as the electron lifetime value.

3 Results And Discussion

In this research, the ZnO Nanorod:TiO2 multilayer film was successfully deposited on the FTO substrate using the hydrothermal method for growing ZnO nanorods and using the Sputtering method for deposition of the TiO2 layer for 60 minutes. Crystal size analysis can be done using XRD characterization. Several ZnO peaks were identified in the (010), (002), (011), (012), and (110) hkl planes with 2θ diffraction angles of about 32º, 34º, 36º, 47º, and 57º respectively when matched with the database COD-1011258 obtained through the Crystallography Open Database and the resulting crystal phase is hexagonal wurtzite which belongs to the P63MC space group.

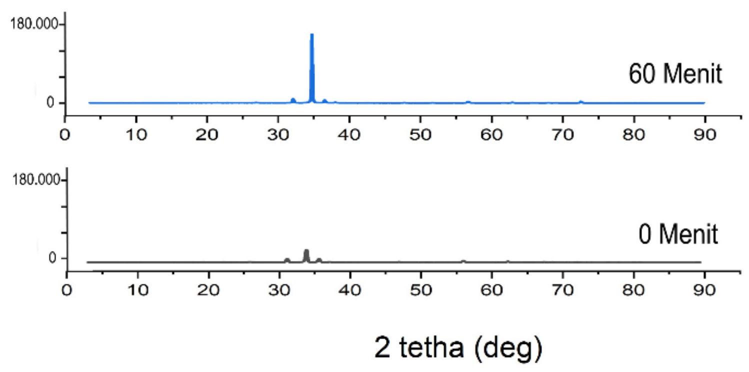
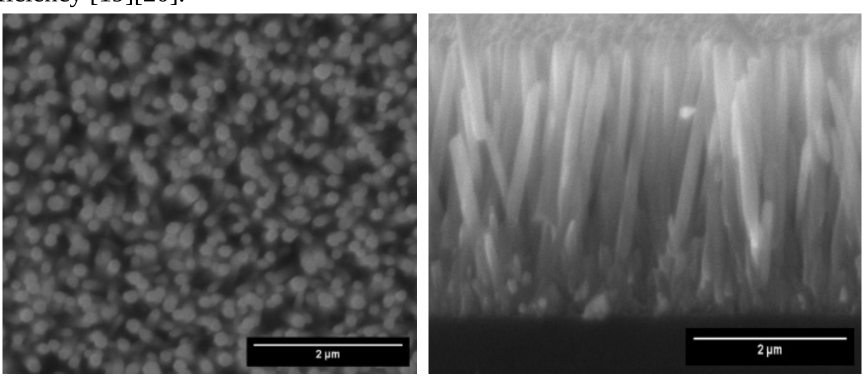


Figure 1. Multilayer ZnO nanorods/TiO_2 diffraction pattern.

The crystal size of ZnO nanorods was calculated using the Debye-Scherer equation resulting in the crystal grain size for pure ZnO nanorods being 40.64 nm with a crystallinity of 42% while for multilayer ZnO nanorods:TiO2 it had a crystal size of 54.71 nm with a crystallinity of 60%. The increase in crystal grain size is in accordance with the increase in peak intensity as shown in Figure 1. The larger the crystal size, the smaller the diffraction peak will be and the FWHM value will also decrease and the higher the peak intensity, the more crystalline the material will be. [18].

The morphology of the ZnO Nanorod:TiO2 multilayer film is shown in Figure 2. At the same magnification (50,000 x), the ZnO:TiO2 nanorods have varying diameters. These results were then analyzed using the ImageJ program to measure the cross-sectional diameter of 25 randomly selected samples of nanorods. Next, the diameter measurement results were processed using the normal distribution equation and the resulting pure ZnO rod diameter was 83.3 nm with a rod length of 4.11 µm, while the ZnO Nanorod:TiO2 film with a sputtering time of 60 minutes had a rod diameter of 65.9 nm. and rod length 4.40 µm. This large change in rod diameter and length shows that the addition of the TiO2 layer causes the rod to become smaller and longer. A small rod diameter will increase load mobility and increase the Jsc value, while rod thickness or length is useful for increasing conversion efficiency [19][20].



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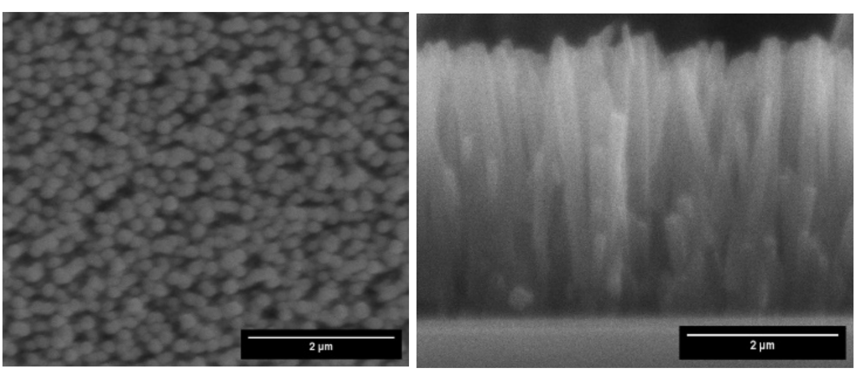
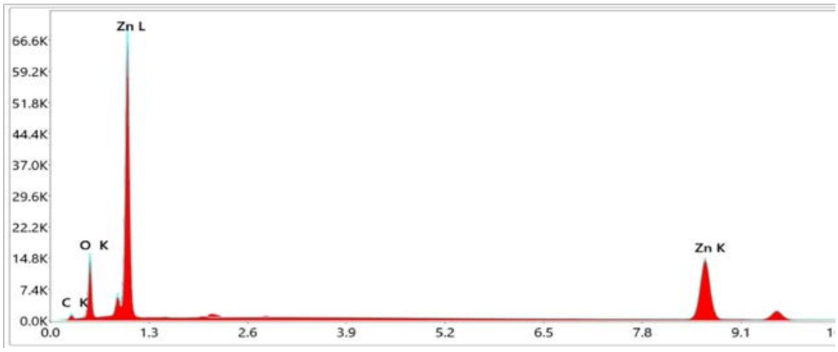


b)

Figure 2. The morphology of Multilayer ZnO nanorods/TiO_2 characterized by SEM a) Pure Zno Nanorod and b) With 60 minutes sputtering duration



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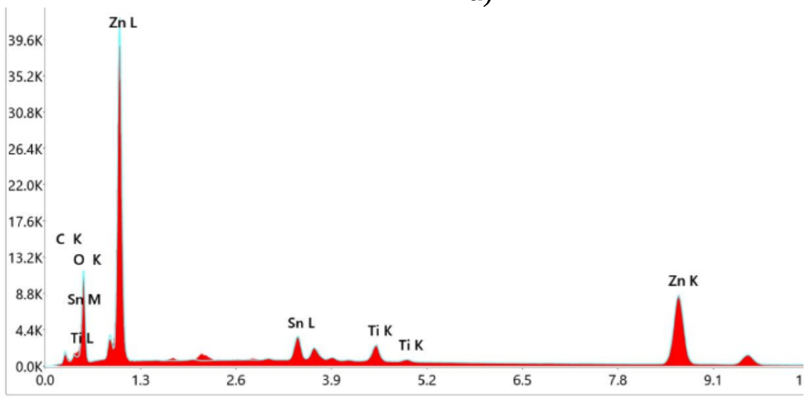


b)

Figure 3. The compositoin of a) Pure Zno Nanorod and b) Multilayer ZnO *Nanorod*:TiO_2 with 60 minutes sputtering duration characterized by SEM

Table 1. Wt% Composition of ZnO/TiO_2-FTO substrate

Sample		Wt%	
	Zn	O	Ti
Pure ZnO	67,5	20,4	0,0
Multilayer ZnO Nanorod:TiO2	52,5	22,5	2,8

Furthermore, the morphology of ZnO:TiO2 is viewed in terms of porosity. From the porosity analysis as shown in Fig. 3. The porosity of the film increased from pure ZnO to multilayer ZnO Nanorod:TiO2 with a sputtering time of 60 minutes, namely from 53.59% to 65.48%. Based on the results of this analysis, decreasing the nanorod diameter causes an increase in film porosity. The denser the pores will result in a decrease in the ability of the electrolyte to penetrate the membrane so that the transfer of electrons from the electrolyte to the photosensitizer becomes slower. This condition will result in lower DSSC efficiency values [21].
The optical properties and band gap energy of ZnO nanorod:TiO2 films were characterized using a UV-Vis spectrophotometer.

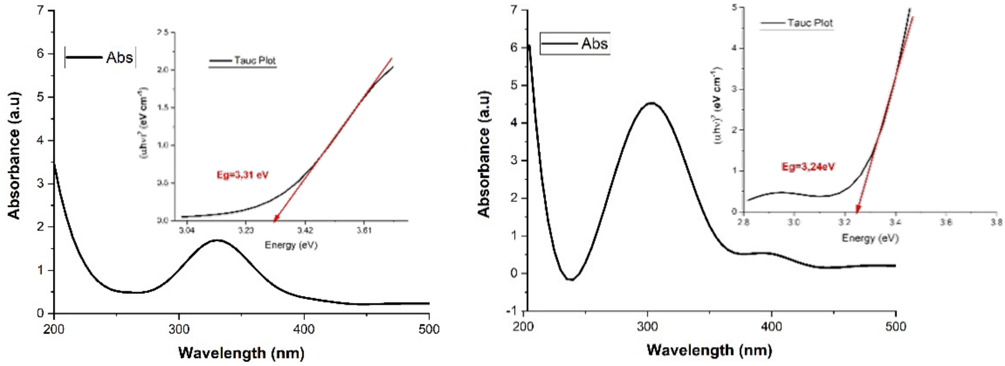


Figure 4. Absorbance of a) Pure ZnO *Nanorod* and b) Multilayer ZnO *Nanorod*:TiO_2

Figure 4 shows the maximum absorbance peak of the two samples, which is at a wavelength between 300-350 nm. The conduction band edge of ZnO is slightly higher than that of TiO2 resulting in an induced electron transfer from the conduction band of ZnO to the conduction band of TiO2 [22]. Figure 5. Also shows the absorbance value and wavelength range of the ZnO nanorod:TiO2 film as well as the gap energy value using the Tauc Plot method with analysis for the direct band gap. Maximum absorbance occurs at a wavelength of 300 nm which has a gap energy of 3.24 eV, namely in the ZnO Nanorod:TiO2 multilayer.
The photovoltaic properties of the DSSC device, which is arranged in the form of a ZnO nanorod:TiO2/FTO sandwich photoanode and counter electrode with dye D205 as a dye and mesolyte as an electrolyte, were then tested using a solar simulator to determine the I-V characteristics of the system and to assess the performance of the resulting DSSC.

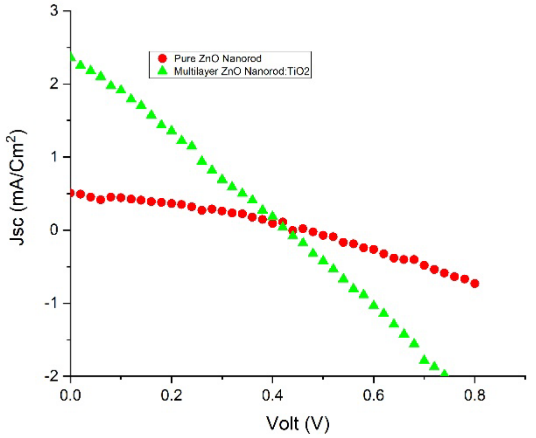


Figure 5. Graph of the relationship between J-V

DSSC photovoltaic parameters are shown in table 2.

Table 2. DSSC photovoltaic parameters

	Pure ZnO Nanorod	**Multilayer ZnO Nanorod: TiO2**
Area (cm2)	0,25	0,25
Jsc (mA / cm2)	0,50	2,23
Voc (V)	0,35	0,52
Fill Factor	0,23	0,35
Efficiency (%)	0,08	0,27

Based on Table 2, the addition of TiO2 with a sputtering duration of 60 minutes to the ZnO nanorods layer succeeded in increasing the Jsc value and efficiency. This increase shows that TiO2 plays a role in suppressing electron recombination [23]. In pure ZnO samples the Jsc value is very low, causing low DSSC efficiency. After adding TiO2 the Jsc value increases so that it can increase efficiency from 0.08% to 0.27%. This increase in efficiency is mainly caused by the large gap energy, porosity, thickness and diameter of the nanorod as shown in Figure 20. A small gap energy value will make the photoexcitation process more effective so that it will increase the number of photo electrons produced. Zhang et al also reported that in their research the efficiency of DSSC became more promising as the TiO2 optical gap energy decreased [24]. Furthermore, increasing porosity, thickness and decreasing rod diameter will increase the surface area so that the number of color molecules attached to the surface increases and will increase the Jsc value which will have an effect on increasing DSSC efficiency. [25].

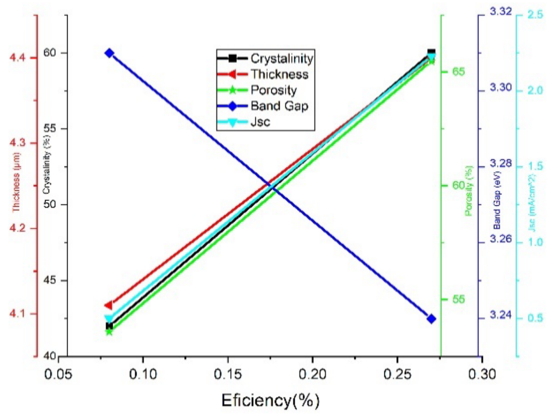
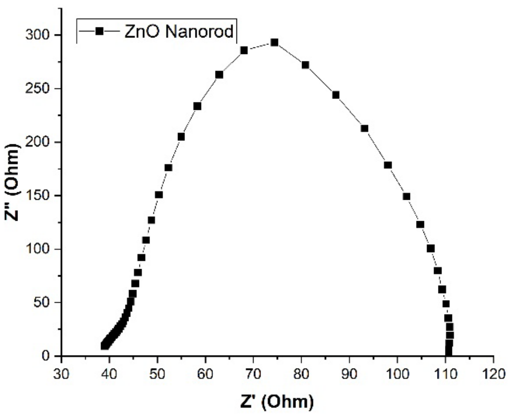
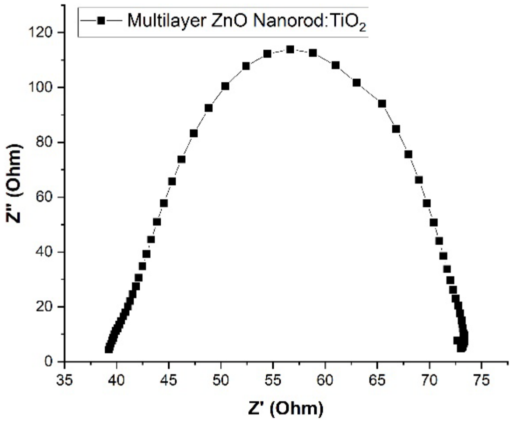


Figure 6. Graph of the relationship between all parameters measured and efficiency

Electrochemical impedance spectroscopy measurements were carried out to investigate the dynamics of the charge transfer process in the DSSC. Measurements are made around Voc when no current flows through the external circuit and the frequency range is between 100 mHz to 100 kHz. The graph of the EIS DSSC ZnO nanorod:TiO2 measurement results is shown in Figure 6.





a) b)

Figure 7. Nyquist Plot of EIS data for a) ZnO *Nanorod* b) Multilayer ZnO *Nanorod*:TiO_2

Ideally, in EIS DSSC measurements, 3 semi circles will appear, namely the first semi circle is related to the interaction between the counter electrode and the electrolyte, while the second semi circle is related to the Rct value (charge transport resistance) and the interaction between the photoanode and the electrolyte. Meanwhile, the diffusion phenomenon that occurs in the system is explained in the third semicircle. Based on Figure 21, it can be seen that there is only one semi circle. This is caused by overlapping between semi circles [26][27].

Table 3. Summary of EIS analysis results for DSSC

Sample	Rct (Ω)	fmax (Hz)	τ (s)
Pure ZnO	15,79	130,7	0,0012
Multilayer ZnO Nanorod:TiO2	6,03	74,6	0,0021

Table 6 shows the results of EIS data analysis, the Rct value experienced a significant decrease from pure ZnO Nanorod to multilayer ZnO Nanorod:TiO2. A small Rct value is indicated by the smallest semicircle with a low fmax, namely 74.6 Hz, resulting in a longer electron lifetime. By decreasing the frequency, electrons entering the conduction band will remain stable for a long time [26]. Table 6 also shows that the electron lifetime value increases as the Rct (charge transport resistance) value decreases. These results show that the multilayer thin layer ZnO nanorod:TiO2 with a sputtering duration of 60 minutes provides fast electron transport, shortens the electron transfer distance, longer electron lifetime and lower recombination rate, thereby causing an increase in DSSC efficiency. [27].

4 Conclusion

A multilayer thin layer of ZnO nanorod:TiO2 was successfully deposited on the FTO glass substrate with DC power parameters of 80 Watt and pressure of 9 × 10-1 Pa at a sputtering duration of 60 minutes. Various parameters that have been tested show interrelated results. The multilayer ZnO nanorod:TiO2 structure shows an increase in DSSC performance compared to pure ZnO-based DSSC and leads to an increase in electron lifetime, namely 2.1 ms with an Rct (charge transport resistance) value of 6.03 Ω.

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