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Construction of Nanorod-TiO_2/p-Cu_2O Heterostructure Thin Films for Solar Cell Application

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ABSTRACT

This research aimed to develop n-type nanorod structure of titanium dioxide (n-TiO_2)/p-type cuprous oxide (p-Cu_2O) heterojunction thin film solar cell. The nanorod-TiO_2 thin film was fabricated on FTO glass substrate using hydrothermal method by varying the volume of hydrochloric acid (HCl). The volume of HCl being manipulated in the scale of 100, 130 and 160 ml. Based on these findings, the usage of 130 ml HCl was determined to be the optimum value for the fabrication of nanorod-TiO_2. After that, the construction of heterostructure thin film was carried out by deposition of p-Cu_2O material on the n-TiO_2 thin film. The p-Cu_2O was fabricated using new proposed technique, called two-steps electrodeposition method. The deposition time was varied 90, 105 and 120 minutes. Finally, the n-TiO_2/p-Cu_2O thin films were also characterized to determine the optimum condition. Based on the results, the optimum n-TiO_2/p-Cu_2O heterojunction thin films was developed at 105 minutes of electrodeposition time. The structural, morphological, topological, optical and electrical properties of each layer in n-TiO_2/p-Cu_2O thin films were characterized by using X-ray diffraction (XRD), Field emission-scanning electron microscopy (FE-SEM), Atomic force microscopy (AFM), Ultraviolet visible spectroscopy (UV-Vis) and Four-point probe, respectively.

Key words : titanium dioxide; cuprous oxide; thin film; hydrothermal; cyclic voltammetry; electrodeposition

1. INTRODUCTION

Titanium dioxide (TiO_2) nanostructured materials have received large attraction because of their application in various field such as in solar cell, photo-electrochemical applications and photocatalysis [1]. TiO_2 material has been verified as a great candidate for the above applications due to it offered high surface area, stability in solution and good durability in environments [1]. Therefore, the fabrication of TiO_2 nanostructured has appeared as an important research field.

However, the limitation of this material is the 3.2 eV bandgap of TiO_2 which will restricts the absorption of the solar spectrum to only a few percentage [2]. For solving this, a sensitizer material should be added to TiO_2 in order to extend its absorption of the solar spectrum. Many approaches have been conducted to fabricate TiO_2 for photovoltaic application include the use of inorganic semiconductor that are environmentally friendly and cost effective. So, one of the substitute sensitizer materials for solar cell is a metal oxide semiconductor, cuprous oxide (Cu_2O). Cu_2O is an attractive semiconductor material for photovoltaic devices because of its high abundant availability, absorption coefficient, non-toxicity and low production cost [3].

There are many deposition approaches for preparing Cu_2O in thin film such as chemical vapor deposition, electrodeposition, chemical oxidation, anodic oxidation and radio-frequency magnetron sputtering [4]. Electrodeposition is more preferred among those approaches because it is a versatile, low processing temperature, simple and low-cost process [5]. So, p-Cu_2O thin layers deposited on a TiO_2 thin film typically form a p-n heterojunction that will be able to enhance the solar cell performance.

Heterojunction is chosen instead of homojunction because it was recognized that heterojunction can improve the performance of the photovoltaic devices as the best efficiency can be achieved regardless of the metal deposited [6]. Besides, many approaches to improve the photocatalytic activity of TiO_2 have been tested, and many researchers have pointed out that the photocatalytic activity of TiO_2 generally depends on its morphology, crystallinity, and surface area [7]. So, the varying parameters like the different volume of the hydrochloric acid (HCl) used in the synthesis of nanorod-TiO_2 by hydrothermal process will be studied in order to obtain the good sample before conducting the deposition of Cu_2O on nanorod-TiO_2.

Apart from this, the process of electrodeposition of thin film will be taken a longer time due to find an ideal potential value for the deposition of Cu_2O [8]. So, it contributes to time consuming and increase the cost of process. Thus, an additional process prior to electrodeposition process is suggested which is cyclic voltammetry (CV) measurement. With CV measurement, the parameter for the fabrication process can be optimized. In this study, cyclic voltammetry will be used to plot an ideal region of potential range for p-Cu_2O thin film deposited at nanorod-TiO_2. Hence, the main purpose of this study is to fabricate the p-n heterojunction thin films by optimizing its deposition parameter.

2. PROCEDURE

In this work, nanorod-TiO_2 was fabricated by several steps which are substrate preparation, solution preparation, hydrothermal and characterization. Firstly, a conductive side of FTO glass substrate is determined using a multimeter and wrapped with PTFE Teflon tape after undergoes cleaning process. Then, a solution consists of HCl is mixed with a 120 ml of DI water and stir for 5 minutes. 4 ml of TBOT is added to the solution drop by drop using the disposable dropper and stir for 10 minutes. Next, the hydrothermal process was carried out by pouring the solution into an autoclave after the substrates were placed into it in slanted position. The autoclave is then put into the oven with 150 °C for 16 hours. After 16 hours, the autoclave is taken out from the oven and cooled down to room temperature with several hours. The hydrothermal process was continued with different volume of HCl. Table 1 tabulated the established parameters used in the fabrication of nanorod-TiO_2 using hydrothermal. Several samples of nanorod-TiO_2 thin film have been characterized by using XRD, FE-SEM, AFM, UV-Vis and Four-point probe for its structural, morphological, topological, optical and electrical properties to determine its optimum condition.

Next, the construction of p-n heterojunction thin film was done by depositing the p-Cu_2O on the optimum n-TiO_2 thin film. There are several steps needed to be carried out in order to fabricate p-Cu_2O thin film, namely solution preparation, substrate preparation, cyclic voltammetry measurement, two-steps electrodeposition, and characterization test. A deposition area of 1 cm x 1 cm on the conductive side of nanorod-TiO_2/FTO substrate is formed using the Nittoflon adhesive tape. Cyclic voltammetry measurement was done in order to optimize the deposition parameter of p-Cu_2O. The CV solution was prepared by using an aqueous solution containing of 0.4 M copper (II) acetate monohydrate $(Cu(OAc)_2$, 3.0 M lactic acid ($C_3H_6O_3$) by potentiostat electrolysis. The pH solution was adjusted by adding the potassium hydroxide (KOH) until reached pH 12.5. The CV measurement was conducted by implementing a three-electrode system where the substrate, platinum foil and silver/silver chloride (Ag/AgCl) electrode are served as working, counter, and reference electrodes, respectively. A graph of I versus E will show at the monitor, and the potential value for deposition of p-Cu_2O on n-TiO_2 will be analyzed. While the two-steps electrodeposition for the fabrication of p-Cu_2O was carried out as same in the CV's procedure, but this process was varied by different deposition time (90, 105 and 120 minutes) at pH 12.5 and water bath temperature of 60 °C. Table 2 shows the established electrodeposition parameters for p-Cu_2O electrodeposition. Lastly, the p-n heterojunction thin films were also characterized to determine the optimum condition.

Table 1: Established parameters used in fabrication of nanorod-TiO_2 thin film

Parameters	Measurable value		
Duration (hours)	16		
Temperature (°C)	150		
TBOT volume (ml)	4		
DI water volume (ml)	120		
HCl volume (ml)	100	130	160

Table 2: Established parameters used in p-Cu_2O electrodeposition.

Sample	Potential (V vs Ag/AgCl)	Adjustment deposition time with two-steps method (minutes)	Total Deposition time (minutes)
1	-0.4	60 + 30	90
2	-0.4	60 + 45	105
3	-0.4	60 + 60	120

3. RESULTS

Three sections of the results to be discussed which are the fabrication of nanorod-TiO_2 thin film by hydrothermal method, cyclic voltammetry measurement and the fabrication of p-Cu_2O on nanorod-TiO_2/FTO substrate by electrodeposition method.

3.1. Fabrication of Nanorod-TiO_2 Thin Film

The structural, morphological, topological, optical, electrical and photoelectrochemical properties of nanorod-TiO_2 thin film are analysed using different characterization tools to determine its optimum condition.

3.1.1 Structural properties

X-ray diffraction (XRD) is used to investigate the structural properties of the nanorod-TiO_2 thin film. The orientation of the n-TiO_2 samples are examined by XRD. Figure 1 shows the XRD pattern results of n-TiO_2 thin film prepared by using hydrothermal method with the variation of HCl volume at temperature of 150 ºC for 16 hours. The phase formation of TiO_2 structure is confirmed by using Powder Diffraction Standards Committee (JCPDS) data at position of 2θ, where the range is between 20 to 80^o.

From the results obtained, there are four main peaks at 27.45, 36.08, 41.23 and 54.32^o which correspond to [110], [101], [111] and [211] plane of the TiO_2 orientation, respectively. The XRD pattern also shows that the n-TiO_2 were well crystalized and all planes are pure rutile TiO_2 structure on top of the conductive side of FTO glass substrate. It can be observed that when the HCl volume increases from 100 to 130 ml, the peaks become sharper and narrower. But for 130 to 160 ml, the FTO structure immerged in the XRD pattern and the peak of TiO_2 becomes shorter due to the thickness of the rods was decreased and the crystallinity of rutile phase was gone. The results obtained was similar to the previous study conducted by N. Noor Kamalia and her partners about the influence of HCl volume on the growth of TiO_2 [9]. Therefore, it can be concluded that the peak of TiO_2 increased when the HCl volume increased from 100 to 130 ml, but it decreased when the volume of HCl increased from 130 to 160 ml. According to the results obtained, 130 ml of HCl appeared to be the optimum condition for the growth of nanorod-TiO_2 on FTO substrate.

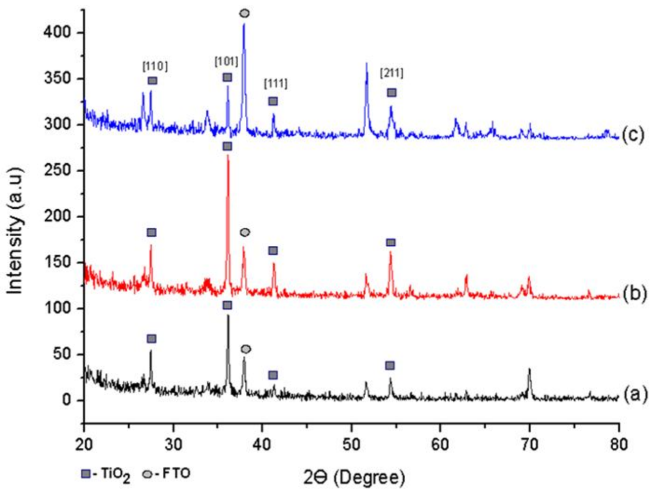

Figure 1: XRD patterns of the nanorod-TiO_2 thin films prepared by different volume of HCl: (a) 100, (b) 130, (c) 160 ml.

3.1.2 Morphological properties

The morphology of the n-TiO_2 thin films were examined by using FE-SEM (JEOL JSM-7600F). Figure 2 shows the FE-SEM images of n-TiO_2 thin film prepared by 100, 130 and 160 ml of HCl, respectively. According to the figures, all the samples have verified the presence of nanorods on the FTO substrate. The results also showed that the morphologies of the nanorod TiO_2 were affected by the volume of HCl. For 100 ml, the TiO_2 thin film have more nanorods growth on the FTO substrate and when the HCl volume increased to 130 ml, the size of the rods become smaller which lead to surface area improvement. However, when the HCl increased until 160 ml, the growth of nanorods have been diminished on the FTO substrate and some of the rods have become thinner as shown in Figure 2. In addition, the thickness of the rods of TiO_2 also affected by the volume of HCl. Table 3 shows the data of TiO_2 thickness that measured from the cross section during FE-SEM characterization process. The thickness of the nanorod TiO_2 has decreased to the increment of the volume of HCl. Based on the previous study, the increasing of the volume of HCl has produced smaller and thinner TiO_2 nanorods on FTO glass substrate [9].

Table 3: The thickness of the n-type nanorods of TiO_2 on the FTO glass substrate

Volume of HCl (ml)	Thickness (μm)
100	3.23
130	2.56
160	2.08

3.1.3 Topological properties

In this research, the average surface roughness of the TiO_2 samples was examined by using Atomic Force Microscopy (AFM). Table 4 showed the average roughness of the samples. As seen in the table below, the average surface roughness of the samples increased with the increment of the volume of HCl. The average surface roughness of the sample with 100 ml HCl was the smallest compared to all other samples. However, the highest average surface roughness was the sample with 160 ml HCl. This can be explained by the number of small grains which was recorded to be highest when the volume of HCl as a chelating agent increasing. Thus, the topological properties of the TiO_2 would be influenced by the volume of HCl used in the hydrothermal method.

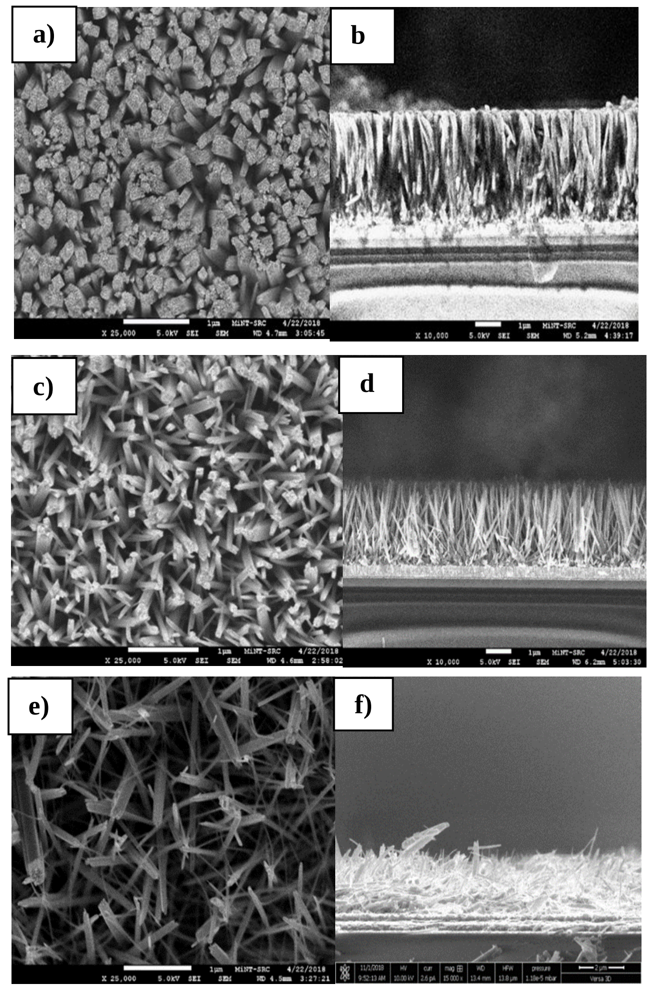

Figure 2: FE-SEM images of the nanorod-TiO_2 thin films with different volume of HCl: (a -b) 100, (c-d) 130, and (e-f) 160 ml respectively

Table 4: Surface roughness of the nanorod-TiO_2 thin films

Sample	Surface roughness (nm)
100 ml HCl	23.28
130 ml HCl	37.73
160 ml HCl	78.62

3.1.4 Optical properties

The optical properties of the n-TiO_2 thin films were determined by using UV-Vis spectroscopy. First, the absorbance of the TiO_2 has been determined. Figure 3 shows the absorbance of the TiO_2 thin film. From the figure, it can be observed that, all the TiO_2 nanorods samples exhibit high absorbance properties for wavelength below than 400 nm and it is represented by band gap energy of 3.0 eV. Hence, the band gap energy obtained was similar to the previous study in [10-13].

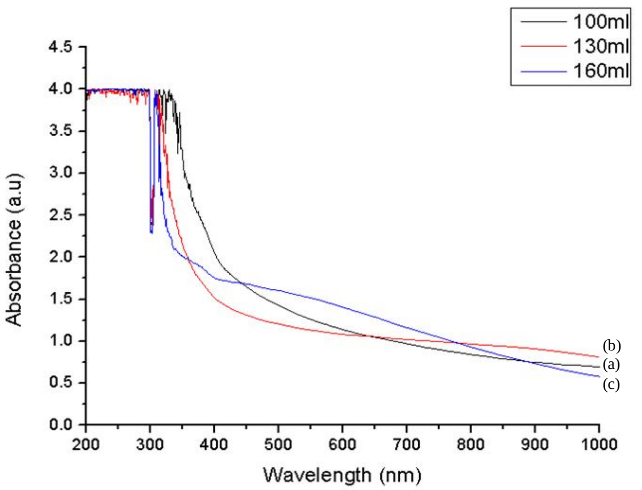

Figure 3: Absorbance spectra of the nanorod-TiO_2 thin films prepared with different volume of HCl: (a)100ml, (b) 130ml, (c) 160ml, respectively

3.1.5 Electrical properties

In this study, Four-Point Probe is used to determine the electrical properties of the n-TiO_2 thin films. The sheet resistivity of the thin film can be determined by using Four-Point Probe. Table 5 shows the sheet resistivity of the n-TiO_2 thin films with different volume of HCl. From the results obtained, the sheet resistivity increased when the volume of HCl increased. This means that the conductivity of the TiO_2 thin film is decreased with the increment of HCl volume

Table 5: Resistivity of the n-TiO_2 thin films.

Sample	Resistivity (x 10^7 Ω/sq)
100 ml HCl	1.23
130 ml HCl	2.84
160 ml HCl	7.53

3.2 Cyclic Voltammetry (CV) Measurement

CV was used to determine the suitable range of potential for the deposition of p-Cu_2O thin film. In this study, a CV is conducted after the selection of an optimum TiO_2 thin film and before the process of depositing the p-Cu_2O on n-TiO_2 to form p-n heterojunction thin film. The CV is conducted by using the TiO_2 sample with 130 ml of HCl as the substrate. Figure 4 illustrates the cyclic voltammetry results by using the TiO_2 sample prepared by 130 ml of HCl. Based on the results, it can be observed that there are two cathodic regions have been recognized. The reduction reaction of Cu^{2+} to Cu^+ and then to Cu_2O is indicated by the first region which occurred form -0.3 until -0.7 V vs. Ag/AgCl while the second region is started around -0.7 V vs. Ag/AgCl and it is attributed to reduction reaction of Cu^{2+} to Cu. These findings are corresponding to the previous studies in [14] that have reported that a constant range of the potential to deposit p-Cu_2O was around -0.2 to -0.8 V vs. Ag/AgCl for the first region and second region around -0.8V. Thus, it can be concluded that the potential range obtained in this CV measurement is valid.

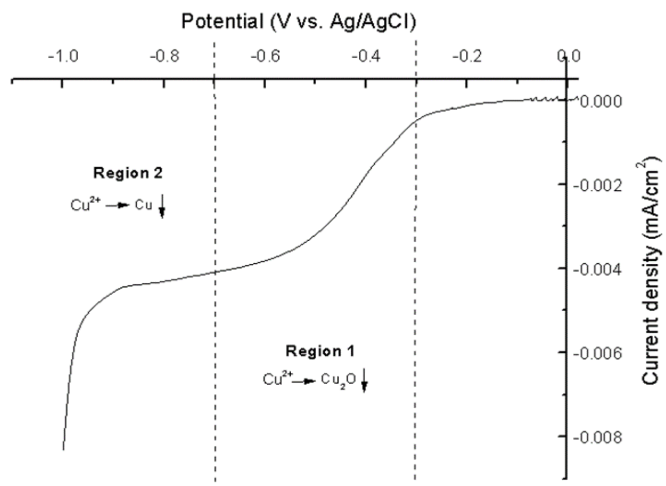

Figure 4: Graph of cyclic voltammetry measurement for p-Cu_2O electrodeposition

3.3 Fabrication of p-Cu_2O on Nanorod-TiO_2/FTO substrate

The structural, morphological, topological, optical, electrical and photoelectrochemical properties of nanorod-TiO_2/p-Cu_2O heterojunction thin film are also analysed using different characterization tools to determine its optimum condition.

3.3.1 Structural Properties

The orientation of the p-Cu_2O thin films are examined by X-Ray Diffraction (XRD). The result of the XRD is observed and showed in Figure 5. From the result obtained, there are several peaks detected at 29.7, 36.5, 43.4, 63.2 and 74.3^o which correspond to [110], [111], [200], [220] and [222] of the orientation of p-Cu_2O, respectively. Based on the results obtained through the XRD characterization, the highest peaks observed among the samples is 36.5^o. This means that the p-Cu_2O is successfully deposited on n-TiO_2/FTO substrate with orientation of [111] which corresponding with the previous finding by F. Mohamad *et. al.* that shown the dominant orientation for p-Cu_2O thin film was [111] at 36.5^o [15]. The highest peak was located at the sample that had been deposited for 120 minutes, while the lowest was the deposition time of 90 minutes. This result can be related with the past study by N. Arifin *et al.* which stated that the longer deposition time, the sharper and longer the diffraction peaks of Cu_2O phase [16]. This also means that the thickness of Cu_2O that contributes to the XRD intensity will be increased as the deposition time increased. So, it can be concluded that the increment of intensity would improve the structural properties of Cu_2O as the deposition time increased.

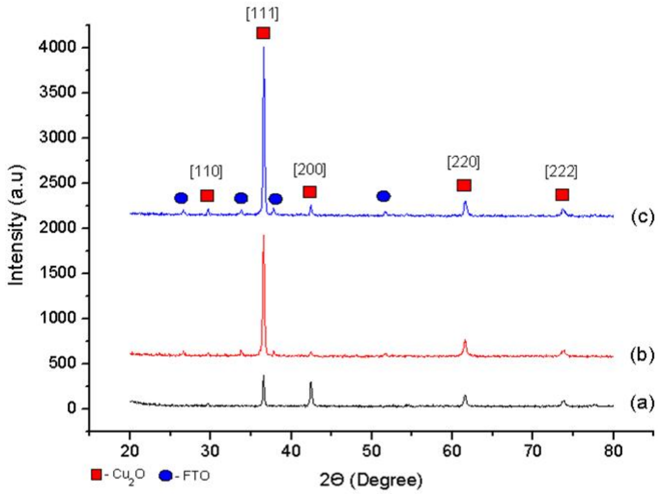

Figure 5: XRD pattern for p-Cu_2O with different deposition time of (a) 90 (b) 105 and (c) 120 minutes, respectively

3.3.2 Morphological Properties

The morphological properties of the p-Cu_2O deposited on n-TiO_2/FTO substrate were examined by the FE-SEM. The overview of the samples that prepared by 90, 105 and 120 minutes of deposition time was shown in Figure 6 that consists of its top view and cross-section. Based on the results obtained from FE-SEM, it has been proven that there is presence of Cu_2O on TiO_2/FTO substrate as the pyramid triangular shapes structure can be observed in all FE-SEM images. This results also believed that corresponding to the [111] plane of Cu_2O. All samples with different deposition time seem growth fully covered the n-TiO_2/FTO substrates. From the results, it can be observed that the shape of the Cu_2O gradually changed from small pyramidal shape into more compact triangular shape as the increment of deposition time. Table 6 shows the data of the n-TiO_2/p-Cu_2O thickness that measured from the cross section during FE-SEM characterization process. The thickness of the thin films has increased to the increment of deposition time. These results were consistent with XRD results and can be corresponded to the previous study by B. M. Fariza *et al.* who claimed that the increase of deposition time would increase the intensity of Cu_2O peaks as more compact and closer particles were formed on the substrate [18].

Table 6: The thickness of the n-TiO_2/p-Cu_2O thin film

Total deposition time (minutes)	Thickness (μm)
90	4.93
105	5.36
120	5.72

3.3.3 Topological Properties

The average surface roughness of each n-TiO_2/p-Cu_2O thin films which had been deposited at different time was taken using AFM. Table 7 showed the average roughness of each sample. From the results obtained, it was observed that the roughness increased as the deposition time increased. The sample deposited at 120 minutes showed the highest roughness which is 36.17 nm compared to others. This result was corresponding with previous finding by N.M. Arifin *et al.* that declared that the deposition time had a strong influence on the film growth [18]. Hence, the longer the deposition time, the higher the surface roughness of the deposited thin film.

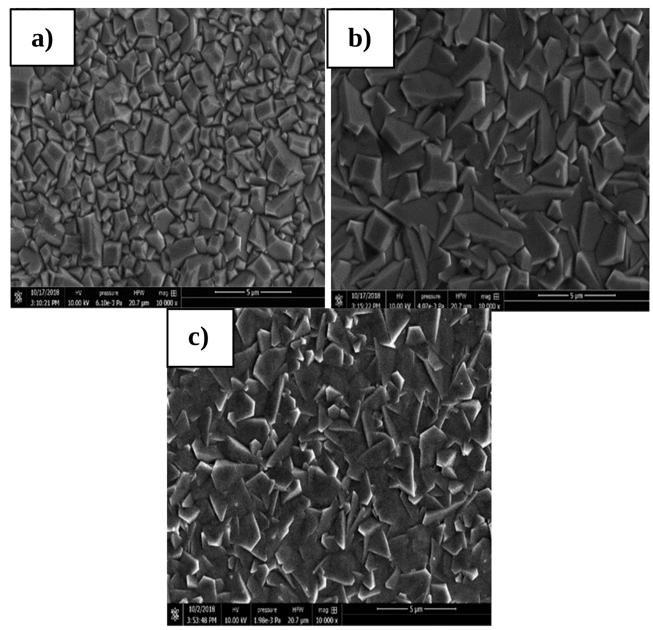

Figure 6: FE-SEM images of p-Cu_2O deposited on n-TiO_2 thin film with different deposition time of (a) 90 (b) 105 (c) 120 minutes

Table 7: Average surface roughness of the n-TiO_2/p-Cu_2O thin films.

Sample	Surface roughness (nm)
90 minutes	11.18
105 minutes	27.60
120 minutes	36.17

3.3.4 Optical Properties

The optical properties were determined by UV-Vis. The absorbance of the samples was obtained before determining the band gap of the deposited p-Cu_2O on n-TiO_2 thin films. The absorbance of the samples was shown in Figure 7. Based on the figure, all samples exhibit high absorbance value with the increment of wavelength at 600 nm. This finding is parallel to the previous study by B. M. Fariza *et.al.* which showed an offset of absorbance for Cu_2O thin film at about

600 nm [19]. While the bandgap (Eg) of the three samples is obtained by extrapolating the plot of $(\alpha h\nu)^2$ vs $(h\nu)$. The band gap is found to be 1.8 – 2.16 eV. This result was corresponded with earlier study by M. Fariza *et al.* which claimed that band gap for Cu_2O thin film is about 1.8 - 2.16 eV [14].

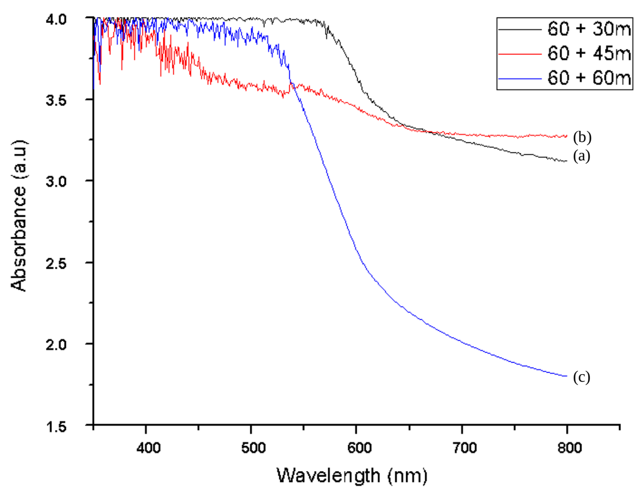

Figure 7: Absorbance spectrum of p-Cu_2O deposited on n-TiO_2 thin film with different deposition time of (a) 90 (b) 105 (c) 120 minutes

3.3.5 Electrical Properties

The sheet resistivity of the samples was obtained by using Four Point Probe. Table 8 tabulates the sheet resistivity of n-TiO_2/p-Cu_2O thin films. From the table, it showed that the sheet resistance of the thin films increased as the deposition time increased. This might be due to the increase of the thickness of thin film when the electrodeposition time increase, so the Cu_2O layer tend to growth on the n-TiO_2/FTO substrate and results in relatively high sheet resistance and resistivity [16]. Hence, the sheet resistivity of the sample will be increased with the increment of deposition time.

Table 8: Sheet resistivity of the n-TiO_2/p-Cu_2O thin films.

Sample	Resistivity (x 10^7 Ω/sq)
90 minutes	4.01
105 minutes	9.27
120 minutes	10.91

4. CONCLUSION

In summary, the n-TiO_2/p-Cu_2O heterojunction thin films have been fabricated successfully. For the n-type nanorod TiO_2 thin films, it has been fabricated using hydrothermal method. Based on the characterization results, it can be concluded that the TiO_2 sample with 130 ml of HCl is the optimum thin film among all the samples. This is because based on the structural properties, this sample showed the highest peak of TiO_2 at the XRD pattern results compared to other samples. In addition, it showed a good morphology result in FE-SEM image where the nanorods are grown better on the FTO substrate and having an optimum thickness as compared to others. For the fabrication of p-n heterojunction thin films, the cyclic voltammetry measurement was conducted successfully before the electrodeposition process in order to optimize the deposition parameter of p-Cu_2O on TiO_2/FTO substrate. While for the n-TiO_2/p-Cu_2O heterojunction thin films, it has been fabricated successfully by the new two-step electrodeposition method. Based on the characterization results, it can be concluded that the n-TiO_2/p-Cu_2O sample prepared by 105 minutes of deposition time is the optimum thin film among all the samples. This is because this sample exhibits an optimum XRD peak compared others. In addition, it showed a good morphological result in FE-SEM image where the shape of Cu_2O gradually changed from small pyramidal shape into more compact triangular shape and fully covered all the n-TiO_2/FTO substrate. Lastly, it also exhibits an optimum condition in electrical properties where its sheet resistivity value is not high and nor low.

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