Eksakta: Berkala Ilmiah Bidang MIPA
VOLUME 22 NO 03 2022, pp 211-222
ISSN : Print 1411-3724 — Online 2549-7464
DOI : https://doi.org/10.24036/eksakta/vol23-iss03/330

Eksakta
Berkala Ilmiah Bidang MIPA
http://www.eksakta.ppj.unp.ac.id/index.php/eksakta

Article

Morphology and Optical Properties Analysis of Cu^{2+} Doped ZnO for Preparation Dye Sensitized Solar Cell (DSSC)

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Article Info

Article history :

Received August 03, 2022
Revised August 28, 2022
Accepted September 04, 2022
Published September 30, 2022

Keywords :

Semiconductor, doped, morphology, dye, transmittance

Abstract. This research reported Cu^{2+} un-doped (pure) and doped ZnO semiconductors with variations in Cu^{2+} concentrations of 3%, 4% and 5% through the sol gel method which aims to determine the morphology and optical properties of ZnO has been investigated. In addition, ZnO film was coated using the doctor blade method with the addition of chlorophyll as a dye sensitizer. Morphological and elemental content tests were carried out using SEM and EDS. The optical properties were analyzed by taking Transmittance data using a UV-Vis Spectrophotometer. SEM analysis with 9900X magnification showed that all samples had small grain sizes and the pores formed were uneven (heterogeneous). The EDS analysis showed that all samples had a higher concentration of zinc by weight than oxygen. UV-Vis Spectrophotometer analysis shows that the transmittance value without dye is lower than using Dye. The addition of Cu^{2+} concentration affects the morphology and optical properties of ZnO. The higher the addition of Cu^{2+} added chlorophyll, the higher the absorbance value, so that the transmittance value decreases. The addition of 4% concentration showed the maximum value of chlorophyll as a sensitizer.

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1. Introduction

Along with the development of human life, energy needs are increasing v. Reserves of fuel sourced from fossils are decreasing over time, so that the need for energy today is increasing [1]. In the year 2050, with the increase in the world's population which reaches 9 billion people accompanied by technological developments and economic growth, the bank predicts that energy needs will double (reach 30 trillion). The most promising alternative energy as a substitute for fossil fuels to overcome the energy crisis in the world is solar energy. Utilizing of sunlight produce energy sources can be increased.

Solar cells are one of the alternative energy that has the potential to be developed. Solar cells are an environmentally friendly energy source because they can convert solar energy sources into electrical energy directly without emitting exhaust gases, and the availability of sunlight throughout the world is abundant [2]. Currently, various solar cells have been manufactured and commercialized using various materials as active layer materials, such as silicon, gallium arsenide, cadmium telluride, amorphous silicon, dye solar cells, organic/polymer solar cells and organic-inorganic hybrid solar cells [3].The development of this solar cell has reached the third generation which was developed by Michael Gratzel in 1991. The solar cell developed by Gratzel is called Dye Sensitized Solar Cell (DSSC) [4]. Dye Sensitized Solar Cell (DSSC) is a type of semiconductor-based solar cell that uses photo electro-chemical phenomena as the basic principle to generate electricity [5]. DSSC has become one of the topics of intensive research conducted by researchers around the world and also the first breakthrough in solar cell technology after silicon solar cells since it was first discovered by professor Michael Gratzel in 1991 [6]. DSSC most used to sensitizer organic to optimize of efficiency by doping metal aluminium/ZnO [7] [8], Ag-doped ZnO [9], Cu co-doping ZnO [10].

Semiconductors are materials with electrical conductivity that are between insulators and conductors with a large energy gap <6 eV [11]. Semiconductors have a band gap energy (Eg) between 0-4 eV while insulators have a band gap energy above 4 eV and conductors have a band gap energy below 0.5 eV [12]. Semiconductors that are often used in DSSC are metal oxides (ceramic) such as TiO_2, SnO_2 and ZnO [13]. The Zinc oxide (ZnO) is a one of semiconductor type which quite interesting to be applied to various things such as Dye Sensitized Solar Cell (DSSC) because it can be a good electrical conductor if doped with the appropriate atoms [14]. The ZnO is a type of n-type semiconductor from groups II-VI which has a wide band gap of 3.2 eV at room temperature [15]. The weakness of ZnO is that it has poor electrical properties, optical properties and unit structure so that it is repaired by doping. Doping is a process of inserting another atom into a semiconductor [16]. In this study, the Zno semiconductor will be doped by Cu^{2+} using the sol gel method. It aims to improve the conductivity properties due to the increase in the band gap in the ZnO structure. This is because Cu can replace Zn ions when doping occurs. Sol gel is one method that is often used to synthesize catalysts. The other hand, ZnO/CuO doping purpoded to improve band gap as organic solar cell [17]. Not only for solar cell, but for antimicrobial and antioxidant applications [18] [19], supercapacitor [20], piezoelectric applications [21], charge carrier and catalytic activity [22]. The process of forming inorganic compounds through chemical reactions in solution at low temperatures in which a phase change occurs from colloidal suspension (sol) to form a continuous liquid phase (gel) is the definition of the sol gel method itself [13][23][24]. The hydrolysis stage, condensation stage, aging stage, drying stage and calcination stage are the stages of synthesis using the sol gel method [25] [26].

The aims for this research is making Cu^{2+} un-doped and doped ZnO semiconductors via sol gel method for variations in concentrations of 3%, 4% and 5%, and the addition of chlorophyll as a dye sensitizer. Determine the surface morphology of un-doped ZnO and Cu^{2+} doped ZnO which were characterized using Scanning Electron Microscope (SEM). Analysis of optical properties by measuring transmittance using an Ultraviolet-Visible (UV-Vis) Spectrophotometer and measuring elemental content by using Energy Dispersive Spectroscopy (EDS) testing.

2. Experimental Section

2.1. Sample Preparation

In this study, samples of Cu^{2+} doped and ZnO un-doped were used. The tools which used are glassware, magnetic stirrer (Lab-Line instruments), stirrer bar, porcelain cup, analytical weight (Ohaus pioneer PX423/E) oven (Memmert Un30), *furnace* (Nabertherm), *Scanning Electron Microscope* (phenom Prox G5), Uv-Vis Spectrophotometer (spectrophotometer orion), preparation glass. Materials which used are zink (II) asetat dihidrat $Zn(CH_3COO)_2.2H_2O$, Copper (II) asetat monohidrat $Cu(CH_3COO)2.H_2O$, isopropanol, *di ethylamine*, aquadest, alcohol, Moringa leaves (*Moringa oleifera)*, Polyethylene Glycol (PEG 400).

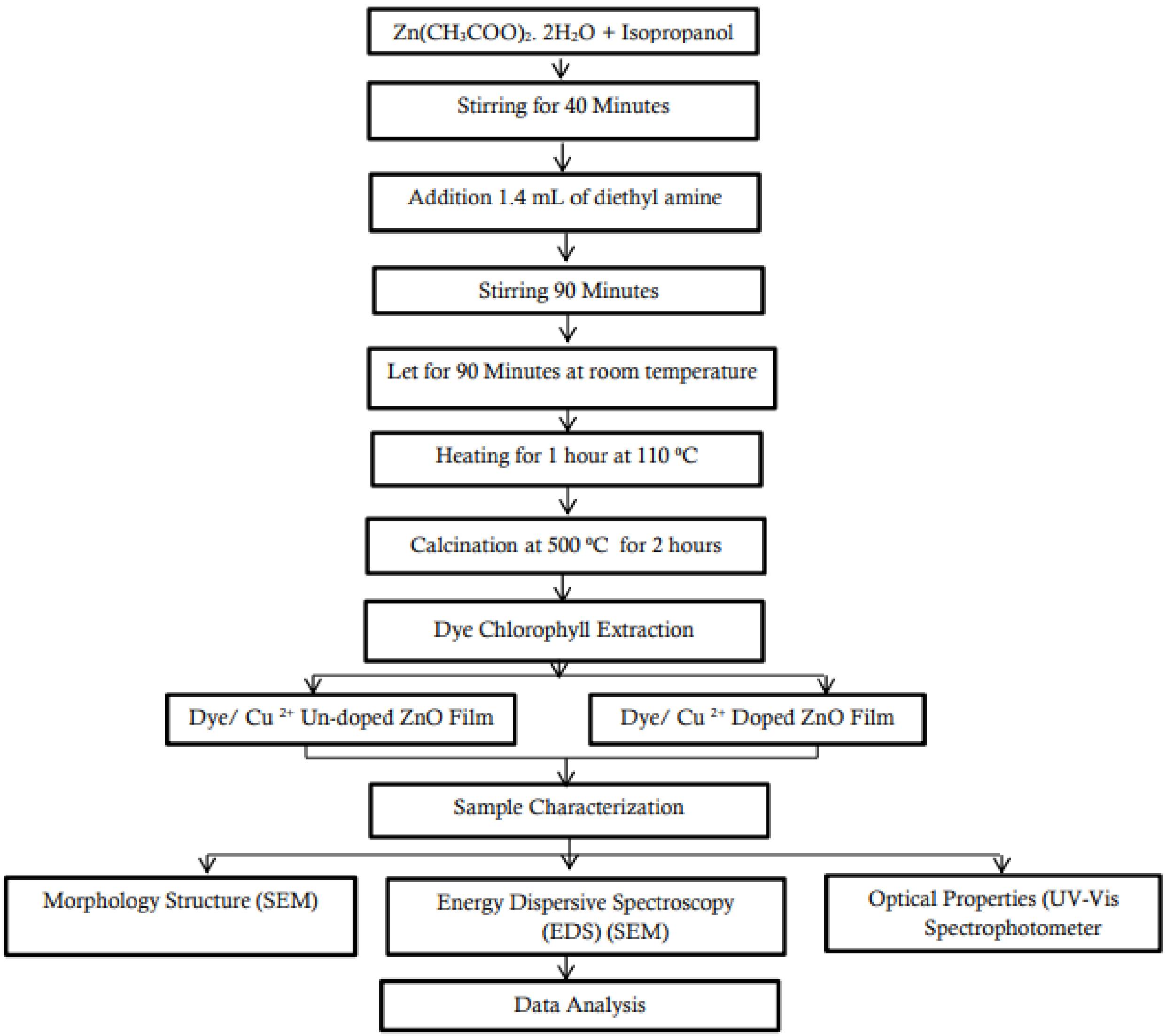

Figure 1. Schematic/Flowchart of Research

The next step synthesized ZnO used sol gel method, the first preparing about 2.7437 grams precursor Zinc Acetate Dehydrate $Zn(CH_3COO)_2$ $2H_2O$ were dissolved by adding 50 ml of isopropanol, then stirring using a magnetic stirrer for 40 minutes. The next step for Cu un-doped ZnO has no addition for $Cu(CH_3COO)2.H_2O$, but it was the addition of 1.4 mL of diethyl amine. The other hand for Cu doped ZnO, it has to add $Cu(CH_3COO)2.H_2O$ 3%, 4% and 5% respectively and stirred again used a magnetic stirrer for 90 minutes. Let stand for 12 hours, followed by the removal of water content by heating in the oven for 1 hour at a temperature of 110°C. After it becomes a gel, it is then put into a furnace at a temperature of 500°C for 2 hours [16]. Then grind it using a mortar so that it is obtained in the form of a fine powder.

The dye is made by extracting chlorophyll from natural ingredients, namely Moringa leaves *(Moringa oleifera)* in small scissors until smoothed then put into a glass jar to be macerated (soaked) with 95% alcohol solvent, then covered with aluminum foil. Simmer for 24 hours after which the mixture is shared using sharing paper [14]. The mixture is evaporated using a magnetic stirrer until the solvent is gone. ZnO film without chlorophyll dye was made by coating ZnO pasta to glass. Preparation as much 0.017 grams, then put it into the mortal, dripping with Polyethylene Glycol as much as three drops. Mixed and mashed using a pestle, the solution was coated on a glass substrate used the casting method and then dried using a hot plate, after which it was characterized using UV-Vis. Then, ZnO film with addition chlorophyll dye was same as with before step, only different in addition dye.

2.2 Measuring Sample and Data Analysis

The morphological characterization of un-doped and doped Cu^{2+} ZnO semiconductors using SEM (Scanning Electron Microscope). The sample is placed on a stub pin that has been attached to adhesive carbon tape. Then the sample is sprayed to remove any light particles that may stick. Then the sample is coated using a sputter coater with the target material used, namely Au/Pd. The sample was coated for 60 seconds at a current of 20 mA. Furthermore, the sample is inserted into the SEM using a *SE* detector with a working distance of 12.1mm with 10kV ETH and magnification 9900x. The characterization of optical properties was measured by UV Vis Spectrophotometer at a wavelength of 300 nm-800 nm. This is done to determine the absorption area of each sample measured. Elemental content was determined to use Energy Dispersive Spectroscopy (EDS) testing.

3. Results and Discussion

This result showed a changing that occurred during the synthesis of Cu un-doped ZnO were zinc (II) acetate di-hydrate $Zn(CH_3COO)_2.2H_2O$ in 50 mL of isopropanol which had been stirred and added dyethylamin to produce a white color. The results that have been left overnight and in an oven at 110°C for 1 hour produce a yellowish color. The product which has been heated in a furnace at a temperature of 500°C for 2 hours produces a white sol and some of it is black which is the result of evaporation of dyethylamin. Furthermore, after being mashed it produces a light gray powder.

The samples of ZnO doped Cu^{2+} for concentrations of 3%, 4% and 5%: Zinc (II) acetate di-hydrate $Zn(CH_2COO)_2.2H_2O$ in 50 mL isopropanol which has been stirred with added Copper (II) $Cu(CH_3COO)_2.2H_2O$ diethyl amine produces a blue color . The results have been left overnight and in the oven at 110°C for 1 hour. The result of the sample with a concentration of 3% becomes light blue compared to other samples and the sample with a concentration of 4% becomes a bright blue color compared to the sample with a concentration of 5%. The three samples were heated at a temperature of 500°C for 2 hours, after the mixture was produced in the furnace, there were white and black parts. The resulting white color is the desired result. The results of the three samples obtained after being mashed were dark gray powder. This happens because of the Cu^{2+} content that is still remaining in the sample [12].

3.1 Morphological Analysis of Cu un-doped ZnO Semiconductor

The Scanning Electron Microscope (SEM) characterization aims to see the surface morphology of the Cu^{2+} un-doped and doped ZnO semiconductors and also to determine the elements contained in the semiconductor by testing Energy Dispersive Spectroscopy (EDS).

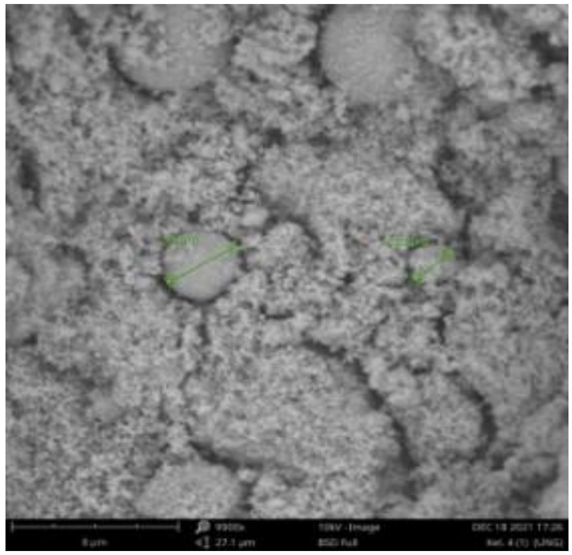

Figure 2. Morphology of Cu Un-doped ZnO

Figure 2 showed SEM result for Cu^{2+} un-doped ZnO semiconductor sample with a magnification of 9900x. Based on the figure shows that the particle size (average: 3.04 µm). The size of the grains and pores formed between the particles are not evenly distributed (still heterogeneous), experiencing agglomeration which is still fused with one another.

Table 1. Energy Dispersive Spectroscopy (EDS) of Cu^{2+}un-doped ZnO Semiconductors

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
30	Zn	Zinc	33.36	67.16
8	O	Oxygen	66.64	32.84

From the Table 1 it showed that Oxygen has a higher atomic concentration than Zn. On the other hand, the concentration of Zn by weight is greater than that of oxygen. This in the process causes Zn to bind oxygen into oxides, causing a nucleation process, and causing the same size distribution to be formed [13].

3.2 Morphological Analysis of the 3% Concentration of Cu^{2+} doped ZnO Semiconductor

Based on Figure 2, with a magnification of 9900x for the sample of Cu^{2+} doped ZnO semiconductor with a concentration of 3%, it can be seen that the particle size is not evenly arranged, there are still some clumps caused by one particle with another particle still fused (agglomerated).

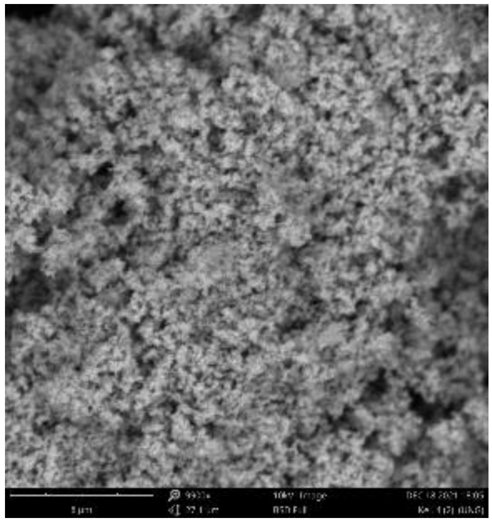

Figure 3. Scanning Electron-Microscope of 3% Cu^{2+} doped ZnO Semiconductor

Based on the results of the SEM measurement, the particle size of the sample has an average of 6.6μm with a magnification of 9900x.

Table 2. Energy Dispersive Spectroscopy (EDS) of 3% doped ZnO Semiconductor

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
30	Zn	Zinc	38.07	71.53
8	O	Oxygen	61.93	28.47

Table 2 shows that oxygen has a higher atomic concentration than zinc with a difference of 3.86 and zinc has a higher weight concentration than oxygen with a difference of 43.06 nm.

3.3 Morphological Analysis of ZnO doped Cu^{2+} Semiconductor with 4% Concentration

The addition of 4% concentration showed that the morphology of the formed ZnO was still tightly bound to one another. The pores have not been clearly formed, and it can be seen that there are bulk particles with a larger size.

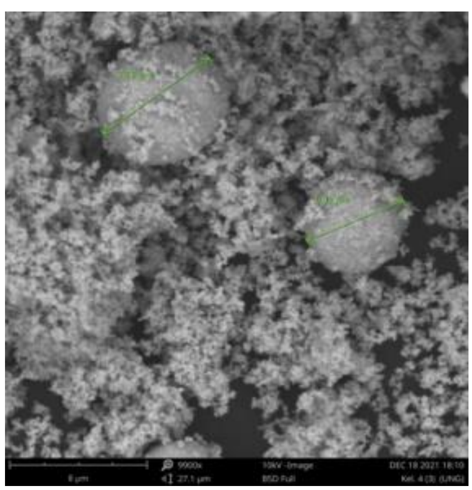

Figure 4. Scanning Electron Microscophy of 4% Cu^{2+} doped ZnO Semiconductor

The image was performed at a magnification of 9900x, where the average particle size was 6.8µm. These results indicate that the particles are still agglomerated.

Table 3. Energy Dispersive Spectroscopy (EDS) of 4% doped ZnO Semiconductor

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
30	Zn	Zinc	86.60	96.35
8	O	Oxygen	13.40	3.65

From table 3, it can be seen that oxygen has a higher atomic concentration than zinc with a difference of 73.2 and zinc has a higher weight concentration than oxygen with a large difference of 92.7.

3.3 Morphological Analysis of the 5% Concentration of Cu^{2+} Doped ZnO Semiconductor

The following is the morphology of the ZnO sample with the addition of 5% Cu^{2+}. The shape of the particles is not homogeneous. And tends to agglomerate so that the particles formed are not evenly distributed.

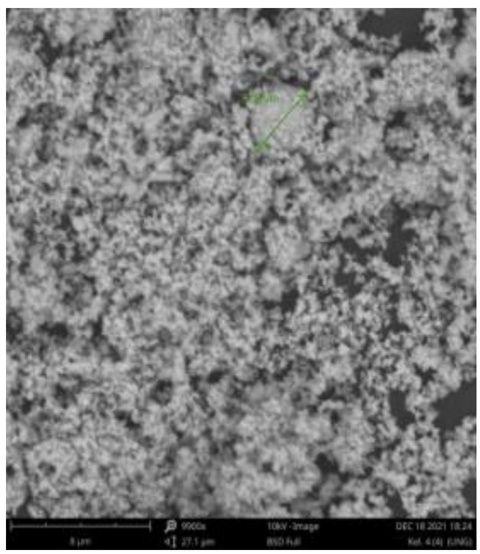

Figure 5. Scanning Electron Microscope of 5% Cu^{2+} doped ZnO Semiconductor

The average size of the particles formed in Figure 5 is 4.08 µm. This size is still very large. It appears that the boundaries between grains are not clearly visible because the surface is very tight and still very uniform, so that pores are not clearly formed. However, there are visible particles formed.

Table 4. Energy Dispersive Spectroscopy (EDS) of 5% Cu^{2+}doped ZnO Semiconductor

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
30	Zn	Zinc	33.26	67.07
8	O	Oxygen	66.74	32.93

From table 4, it can be seen that oxygen has a higher atomic concentration than zinc and zinc has a higher weight concentration than oxygen.

Based on the results of the Scanning Electron Microscope characterization, the sample that has the smallest particle size is the un-doped sample, which is 3.8 m and for the sample and for the doped Cu^{2+} which has the smallest particles, the sample with a concentration of 5% is 4.08 m. This shows that the variation of Cu doping affects the morphology of ZnO, the higher the concentration of Cu doping, the smaller the particle size. Variations of Cu doping also have an effect on increasing ZnO agglomeration and poor particle homogenitis [29]. This is in accordance with the explanation that the higher the variation of the Cu doping concentration, the smaller the particle size [30] .

3.4 Optical Characterization of Cu^{2+} Doped and Un-doped ZnO Films without the Addition of Chlorophyll Dye

Figure 6 shows the relationship between wavelength and transmittance for each sample. The first sample is a sample with a doping concentration of 3%, the second sample with a concentration of 4% and the third sample with a concentration of 5%. Initially, the third sample has a higher transmittance value than the second sample. Then the transmittance value of the second sample increases until it exceeds sample 3.

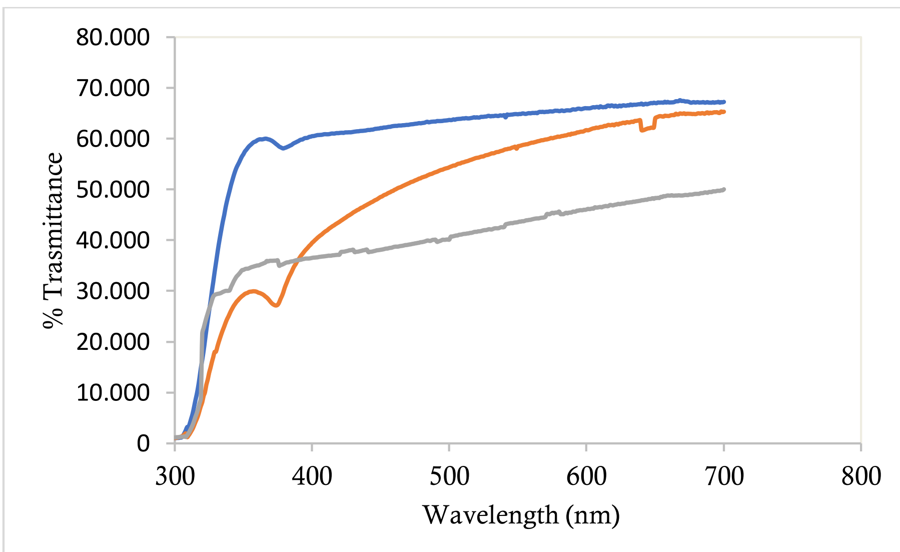

Figure 6. Graph of ZnO Doped Cu Samples without Chlorophyll (— 3%, — 4%, — 5%)

From the graph, it is found that increasing doping concentration results in lower transmittance values. This is evidenced by the minimum transmittance value of sample 3 with a doping concentration of 5%. From these results, an increase in the percentage of unstable transmittance is obtained, where there is a decrease in the transmittance value at a certain wavelength. This can be caused by an uneven surface or film thickness. Increasing the concentration causes the absorbance value in the sample to increase as well, thereby reducing the transmittance value. However, if the addition of Cu is done linearly, the figure shows a decrease in 5% Cu. The number of molecules and elements in the sample plays an important role in absorbing photons. The maximum transmittance from the graph was 366 nm of wavelength.

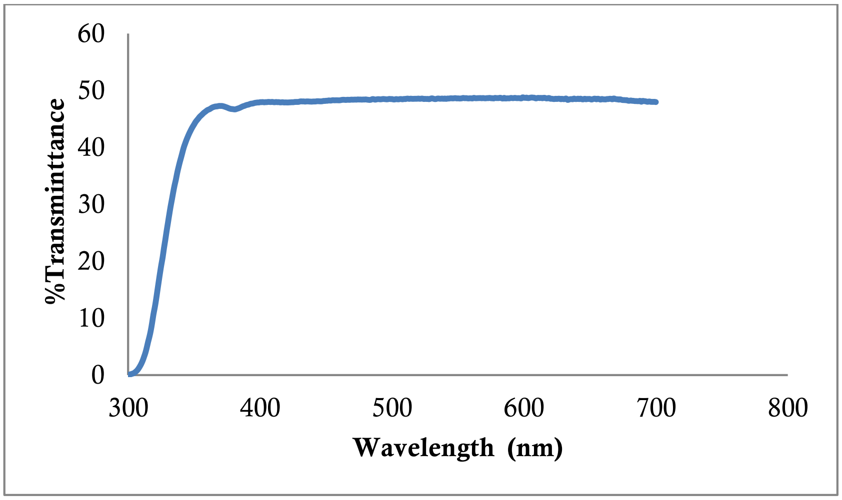

Figure 7. Transmittance of Un-doped Cu^{2+} ZnO Film without the addition of Dye Chlorophyll

Changes in the transmittance value of ZnO can be seen in the range of 316 nm-360 nm. The transmittance maximum were 360 nm of wavelength. It was likely the previous result [17]. This is very different from Figure 7 which Cu doping occurs. The changes in the graphs in the two images are because Cu causes the replacement of the Zn core, thus affecting the absorbance value. The addition of concentration causes the absorption value to be greater and the transmittance value to decrease. This film showed the highest transmittance about 70-80% in visible wavelength [31].

3.5 ZnO Doped Cu Film with Addition of Chlorophyll Dye

There is a change in transmittance at 355 nm and 625 nm wavelengths. This shows the effect of chlorophyll in which this pigment consists of chlorophyll a and chlorophyll b. The change in transmittance indicates the presence of a molecule that plays a role in absorbing photons that are passed through the sample.

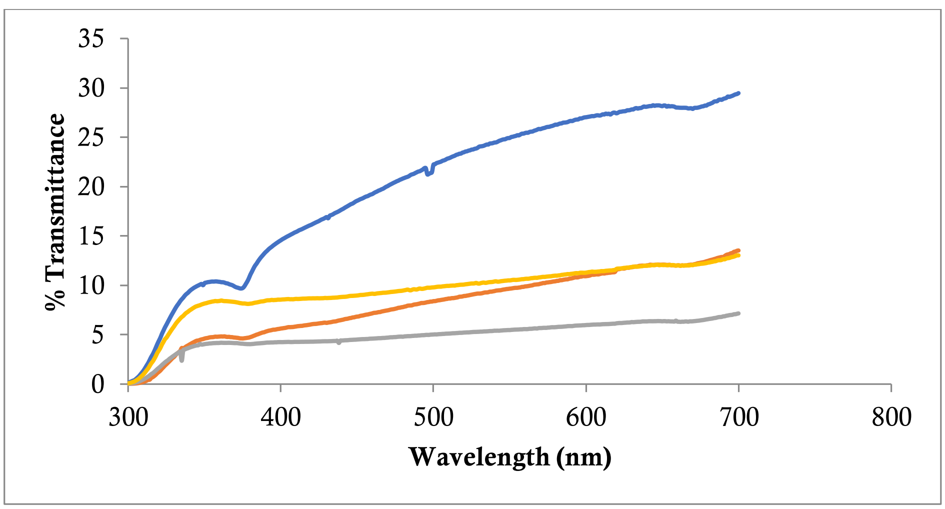

Figure 8. Transmittance of ZnO with the addition of Chlorophyll (Un-dopped Cu), Doped Cu used concentration various (3% Cu, 4% Cu dan 5%)

The graph from above shows the comparison results by using UV-Vis Spectrophotometry for Undopped, Cu Dopped ZnO semiconductors with concentration variations of 3%, 4% and 5%. The transmittance value in the undoped layer was higher than the doped layer with variations in concentration. The difference in transmittance value is also influenced by uneven film coating techniques which greatly affects its performance. The film thickness most influenced for this case. Based on the graph in Figure 8. The addition of Cu with a concentration of 4% added chlorophyll showed the lowest transmittance value. This indicates that the low transmittance has a higher absorption ability. This indicates that the chlorophyll pigment is able to act as a sensitizer.

4. Conclusion

The addition of Cu^{2+} with various concentrations affects the pore morphology and optical properties of the ZnO semiconductor. The higher the concentration, the higher the ability to absorb photons and the lower the transmittance value. Likewise with the addition of chlorophyll which acts as a sensitizer, capable of absorbing photons that are passed at a certain wavelength. Thus, this film can be used for preparation of solar cells, especially the DSSC type.

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