Effect of concentration double layer ZnO/ZnO:Ag on optical and photocatalytic properties

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Abstract. ZnO is a semiconductor material that advantages in various applications, especially for photocatalysts. The catalytic activity of ZnO is much better than other materials, because ZnO can absorb light in a wider spectrum. The double layer ZnO/ZnO:Ag with various concentrations of 0.1 M, 0.3 M, and 0.5 M has been successful deposition. Double layer ZnO/ZnO:Ag deposition was carried out by sol-gel method and spray coating deposition technique. The results showed that the concentration of double layer ZnO/ZnO:Ag increased with the increase of the absorbance value. From the transmittance spectrum attempt was made to estimate the value of energy band gap of the samples. Double layer ZnO / ZnO:Ag energy gap in the range 3.2-3.3 eV. The energy gap of Double Layer ZnO/ZnO:Ag decreases with increasing concentration to 0.5 M. Double layer ZnO/ZnO: Ag 0.5 M has the smallest energy gap of 3.21 eV. Photodegradation testing was carried out to determine the ability of samples to photocatalytic activity at methylene blue dye. The optimum photocatalytic activity is indicated by the largest percentage of degradation. The largest percentage of degradation was shown by Double layer ZnO/ZnO:Ag 0.3 M at 81.5%.

1. Introduction

The disposal of industrial waste in the textile industry contributes to water pollution due to dissolved dyes [1]. The textile industry uses dyes as coloring agents. The dye that is widely used is Methylene Blue. Methylene blue dye with chemical formula C₁₆H₁₈ClN₃S is a poisonous aromatic hydrocarbon compound and is a cationic dye with very strong adsorption power. It is generally used as a dye for silk, wool and textiles [2]. Photocatalysts are currently a promising technique for water purification compared to other conventional methods [3]. The photocatalyst process occurs when the energy from the light matches the band gap energy of the semiconductor material, a chemical transformation will occur so that it converts the inorganic and organic compounds in the material into water and carbon dioxide [4]. ZnO is a semiconductor that has attracted a lot of attention from researchers because ZnO has many advantages for various advantages in various applications, especially for photocatalysts [5]. The catalytic activity of ZnO is much better than that of other materials because ZnO can absorb light in a wider spectrum than other materials. So that various studies on ZnO are now increasingly being looked at by researchers. Several methods to synthesize ZnO thin films usually use coprecipitation method [6], thermal decomposition method [1], spray pyrolysis [7], and sol-gel [8]. Sol-gel processing as an attractive method for the synthesis of ZnO thin films has many advantages over other deposition techniques [9]. Among these methods, sol-gel deposition is the best choice because it is easy and has...
low economic costs [10]. The increase in photocatalytic efficiency has been investigated by adding Ag doping to semiconductors [7]. Previous research showed that the presence of 4% Ag doping in ZnO was able to best degrade methylene blue dyes with a 4 hour exposure time [11]. In addition to doping, the addition of solution concentration has an effect on its shape, optical properties, and photocatalytic activity. The addition of molar concentration will affect the thickness of the layer. This will affect the morphology and optoelectronic properties [9]. Depositing using double layer technique on semiconductors can increase the efficiency of photocatalytic activity [10]. This research will carry out a study of making double layer ZnO/ZnO:Ag with various concentrations of Zinc 0.1 M, 0.3 M, and 0.5 M which are deposited on a glass substrate using the sol-gel method using the thermal spray coating technique at temperature annealing 300 °C for degradation of water contaminated by textile waste methylene blue. This research is expected to produce Double layer of ZnO / ZnO: Ag on a glass substrate with a suitable energy band gap value to maximize the activity of photocatalysts to degrade water contaminated with methylene blue textile waste. Furthermore, the band-gap value will be studied and its effect on degradation of methylene blue textile waste.

2. Methods
This research to be carried out is generally divided into 4 stages: (1) the process of making ZnO sol gel and ZnO: Ag sol-gel with a concentration of 4% and a molar concentration of zinc 0.1 M, 0.3 M, and 0.5 M. The mechanism for making the solution; Zinc acetate dehydrate (Zn (COOCH₃)₂.2H₂O) is dissolved into a solution of isopropanol ((CH₃)₂CHOH) and dripped with monoethanolamine (MEA: HOCH₂CH₂NH₂) adjusts the expected concentration of Zinc at room temperature [12]. Then the solution is annealed using a magnetic stirrer at a temperature of 70°C for 30 minutes until a clear and homogeneous ZnO solution is obtained. While the ZnO: Ag solution is obtained from the sol-gel ZnO solution which is still stirred at a temperature of 70°C then Silver Nitrate (Ag (NO₃)) powder is added as doping with a percentage of 4% of the number of moles from Zinc (Zn). (2) double layer deposition process ZnO and ZnO: Ag 4% on glass substrate Double layer ZnO/ZnO:Ag deposition process on glass substrate using spray coating technique. Glass substrate that has been heated to 300°C for 15 minutes sprayed with ZnO solution with a deposition temperature of 300°C, then sprayed with ZnO: Ag with the same deposition temperature. Annealing with a temperature of 300°C for 1 hour on the hotplate, followed by the sintering process again at 500°C for 1 hour using a furnace with the aim of producing silver nanoparticles from silver nitrate solution and embedding them evenly on the ZnO surface [12]. (3) testing the photodegradation of methylene blue by means of methylene blue textile waste liquid with a concentration of 10 ppm placed in glass containers coated with Double layer ZnO/ZnO:Ag and then placed into a UV lamp reactor. All samples were exposed to UV light within a span of 8 hours. (4) optical properties testing with solid UV-Vis test to get the band gap value and photocatalyst testing with liquid UV Vis test to determine the degradation ability of methylene blue.

3. Result and Discussion

3.1 Optical Properties
The transmittance graph between single layer ZnO and ZnO:Ag is shown in Figure 1. It was found that the optical transmission of ZnO was about 82% and ZnO:Ag increased about 93%. The presence of spectrum fluctuation is caused by the interference phenomenon on thin films [13]. In addition, the increase in optical transmission value is due to the presence of Ag doping, this is due to the increase in free electrons as a result of the presence of Ag. The increase in transmission can be caused by a decrease in optical scattering caused by densification of film crystals [14].
Optical transmission experienced by Double layer ZnO/ZnO:Ag is shown in Figure 2. Double layer optical transmission is lower than single layer. This decrease is due to grain boundary scattering and visible light absorption of Ag nanoparticles. The decrease in transmission occurred at Double layer ZnO/ZnO:Ag 0.1 M to 0.5 M, namely 91% to 78%. Transmission decreases with increasing zinc concentration. This shows that the greater the concentration, the less transparent it is because the more atoms make it up which makes it more difficult for light to pass [15]. The reduction in transmission is also due to an increase in optical scattering caused by grain boundaries and an increase in film thickness. The grain boundary density increases with increasing zinc concentration. This is what can reduce optical transmission [12].
Figure 3. Band gap plot of $(\alpha h\gamma)^2$ vs energy single layer

Figure 3 shows that the optical band gap energy of the ZnO film obtained is about 3.22 eV less than ZnO:Ag which is 3.25 eV. This increase in the energy bandgap of ZnO compared to ZnO:Ag is known as the Moss-Burstein shift. With the presence of Ag doping in the zinc oxide layer, the donor electron occupies a state at the lower edge of the conduction band [13]. Therefore, the ZnO:Ag band gap is larger than the ZnO band gap.

Figure 4. Band gap plot of $(\alpha h\gamma)^2$ vs energy double layer ZnO/ZnO:Ag

| Sample                  | Single Layer ZnO  | DL ZnO/ZnO:Ag  |
|-------------------------|-------------------|----------------|
| ZnO                     | 3.22              |                |
| ZnO:Ag                  | 3.25              |                |
| Double layer ZnO/ZnO:Ag 0.1 M | 3.28              |                |
| Double layer ZnO/ZnO:Ag 0.3 M | 3.25              |                |
| Double layer ZnO/ZnO:Ag 0.5 M | 3.20              |                |
Table 1 was found that the gap energy of Double layer ZnO/ZnO:Ag was around (3.21-3.28) eV as shown in Fig. 4. The band-gap decreased with increasing Molar concentration of zinc. It can be seen that the band gap value decreases with increasing concentration of zinc from 0.1 M to 0.5 M. Double layer ZnO/ZnO: Ag 0.5 M has the smallest band gap energy of 3.21 eV. The amount of energy gap shows the amount of energy used by the movement of electrons across the valence band to the conduction band. The energy gap decreases with increasing layer concentration due to the large number of ZnO molecules that fill and agglomerate. The large number of ZnO involved and this agglomeration results in an increasing absorbance value so that more energy is absorbed by the material [16]. If the width of this energy gap gets smaller, the transition of electrons from the valence band to the conduction band will increase so that the double layer layer will be more conductive.

This transition of electrons from the valence band to the conduction band is increasingly having an important role in its application for photodegradation. The resulting electrons react with oxygen to produce superoxide anion radicals. Meanwhile, the holes will react with water molecules to produce hydroxyl radicals. These two reactants work together to decompose organic and inorganic compounds [5]. With the presence of Ag doping in double layer ZnO/ZnO:Ag, it can increase its photocatalytic efficiency by preventing recombination [11]. Electron photogeneration in the ZnO conduction band can move to Ag particles, resulting in good photocatalytic activity and will affect the degradation process of methylene blue.

3.2 Photocatalytic Properties
Photodegradation testing was carried out to determine the ability of single Layer ZnO, ZnO:Ag and Double layer ZnO / ZnO:Ag photocatalytic activity against methylene blue dye with a concentration of 10 ppm (parts per million) for 4 hours. The results of photodegradation testing can be seen in the absorbance graph as shown in Figure 5. If the absorbance value decreases, the dye will decrease and the color of the liquid will be clearer.

![Figure 5. Absorbance of dye by single layer and double layer](image-url)
Table 2. Degradation of Methylene Blue

| Time (hour) | ZnO | ZnO:Ag | Double layer ZnO/ZnO:Ag 0.1 M | Double layer ZnO/ZnO:Ag 0.3 M | Double layer ZnO/ZnO:Ag 0.5 M |
|-------------|-----|--------|------------------------------|-------------------------------|-------------------------------|
| 1           | 9.125 | 7.750  | 28.500                       | 10.750                        | 14.625                        |
| 2           | 24.125 | 37.625 | 46.500                       | 26.000                        | 48.875                        |
| 3           | 46.375 | 42.625 | 50.375                       | 48.875                        | 55.250                        |
| 4           | 68.125 | 60.375 | 57.250                       | 81.500                        | 75.250                        |

The results obtained from Table 2 show that the double layer ZnO/ZnO:Ag layer is a photocatalyst material that is able to degrade methylene blue dye better than single layers ZnO and ZnO:Ag. This can be seen from the large percentage of double layer degradation which is higher than the single layer. The largest percentage of degradation was double layer Zn/Zn:Ag 0.3 M which was able to degrade methylene blue by 81.5%. Double layer ZnO/ZnO:Ag has been proven to be the most effective because combining semiconductors can reduce the electron-hole recombination rate which will increase its photocatalytic activity [17].

Giving Ag particle doping can also increase the photocatalytic activity of the double layer. This is due to the contribution of Ag, namely the number of electrons and holes produced is more increased than the single layer ZnO. By increasing the number of electrons and holes, it will produce more hydroxyl ion production and increase the photodegradation reaction [18]. The electrons on the semiconductor surface will be trapped by Ag particles. Ag particles in ZnO act as electron charge carriers [19]. Ag particles carry electron charges in metal hydroxides and can react by capturing electrons in solution such as O$_2$ to form superoxides. The next step, the hole will react with metal hydroxide, namely zinc which is contained in the H$_2$O solution which forms hydroxyl radicals as a strong oxidizer to oxidize the methylene blue dye, so that the chemicals in the methylene blue dye will be degraded. Furthermore, the double layer effect inhibits the recombination process, so the oxidation process may take longer [10]. These radicals will work continuously as long as the double layer ZnO / ZnO: Ag is exposed to sunlight.

4. Conclusion

Double Layer ZnO/ZnO:Ag with various concentrations of 0.1 M, 0.3 M, and 0.5 M has been successfully deposited on the glass substrate. Obtained Double Layer optical transmission is lower than single layer. This decrease is due to grain boundary scattering and visible light absorption of Ag nanoparticles. The decrease in transmittance occurred between Double layer ZnO/ZnO:Ag 0.1 M to 0.5 M, namely 91% to 78%. Transmission decreases with increasing zinc concentration. The bandgap energy owned by Double layer ZnO/ZnO:Ag ranges from (3.21 to 3.28) eV. Band-gap energy decreases with increasing Molar Zinc concentration. It can be seen that the band gap value decreases with increasing concentration from 0.1 M to 0.5 M. Double layer ZnO/ZnO:Ag 0.5 M has the smallest band gap energy of 3.21 eV. The photocatalytic activity of double layer ZnO/ZnO:Ag was able to degrade methylene blue dye better than single layer ZnO and ZnO: Ag. This can be seen from the large percentage of double layer degradation is higher than the single layer. The largest percentage of degradation was double layer ZnO/ZnO:Ag 0.3 M which was able to degrade methylene blue by 81.5%. Double layer ZnO/ZnO: Ag has the best photocatalytic activity because combining semiconductors can reduce the rate of electron-hole recombination which will increase its photocatalytic activity.

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