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Synthesis and Characterization of ZnO/Ag Thin Films as Peat Water Degraders in East Tanjung Jabung Regency, Jambi

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Abstract :
Synthesis and characterization of ZnO/Ag thin film using doctor blade technique as a photocatalyst application, peat water degrading agent has been carried out in Tanjung Jabung Timur Regency. The main ingredients in the manufacture of the thin film are Merck's Zinc Acetate and $AgNO_3$ as the main ingredients of Ag. Thin films were made with Ag doping variations of 0%, 2%, 5%, and 7%. Synthesis of ZnO/Ag using the sol-gel method and making a thin layer using the doctor blade technique. The results of UV-Vis characterization show the band gap values of ZnO/Ag, respectively, which are 3.25 eV, 3.00 eV, 2.65 eV, 2.85 eV. This means that the band gap energy tends to decrease as the doping increases. The results of XRD data analysis showed that ZnO/Ag 0%, 5% and 7% were hexagonal in shape with crystal sizes of 49.99 nm, 41.66 nm, and 41.66 nm, respectively. The best ZnO/Ag degradation ability to peat water is ZnO/Ag doping variation of 5% with the percentage of degradation carried out under UV-Vis lamp of 92.9% for TDS, pH 6.7 and 35.5% TSS.

Keywords: Thin film, photocatalyst, degradation, ZnO/Ag

1. Introduction

ZnO is a group II-VI n-type metallic semiconductor material. ZnO has a wide band-gap (3.37 eV) and is a suitable semiconductor compound in the short wavelength range for optoelectronic applications. The large excitation binding energy (60 MeV) in ZnO crystals can make electron emission efficient at room temperature and efficient in the ultraviolet wavelength range (<400 nm). Excitation of ZnO can be carried out in the visible light wavelength range (400 - 800 nm) and can be made very conductive by adding doping material (Sutanto et al., 2015). One effort to increase photocatalytic activity is by doping ZnO. It can be made with metals or non-metals, resulting in semiconductor-semiconductor, semiconductor-polymer, or semiconductor-metal materials. Doping agents commonly used are silver (Ag), nitrogen (N), aluminum (Al), and titanium oxide (TiO2), etc.

Silver metal (Ag) has tremendous potential as a catalytic and is relatively cost-effective. Based on research (Sutanto and Wibowo, 2015), which has examined Ag-doped ZnO to test the antibacterial effect and photocatalyst test. After the addition of Ag dopant, the bandgap value decreases to 3.1 eV. The tested antibacterial effect of Ag-doped ZnO had poor antibacterial effect compared to Ag-doped ZnO after testing for 4 hours. Photocatalyst tests that have been carried out compare the degradation between ZnO without Ag doping and ZnO with Ag doping, both irradiated with sunlight, both also using variations of Ag doping of 4%, 6% and 8%. When compared, ZnO using Ag doping is able to degrade more than ZnO without doping.
There are several methods for synthesizing semiconductor materials that can be used for photocatalysis. The methods commonly used are sol gel, hydrothermal, solvothermal, metal organic and sonochemical (Kurniawan, 2009). Among the several methods above, the most efficient is the sol gel method, because it is considered easy to use, and its use is very wide, apart from that, the level of particle homogeneity is also very high (Wu et al, 2018).

The use of a thin layer is necessary, because a thin layer can increase the effectiveness of the material as a photocatalyst. One well-known technique is the doctor blade. Doctor Blade is able to deposit a thin layer of glass substrate well. The results are even, because this technique places the liquid on a glass substrate, and then rolls it with a stirring rod, so that the resulting layer is able to be evenly distributed.

In 2020, Vallejo et al studied thin ZnO/Ag films using the sol-gel method and doctor blade technique with doping variations of 1%, 3% and 5%. The lowest bandgap energy (Eg) can be found at 1% Ag concentration, namely 2.95eV. For the highest photocatalyst test, it was found at a concentration of 5% with a Bandgap energy (Eg) of 3.10 eV and a degradation percentage of methylene blue of 44.8%. Meanwhile, in 2021, Rasouli et al have degraded Methyl Orange Dye using the precipitation-irradiation method at doping variations of 1%, 2% and 3%. The bandgap energy (Eg) in each variation obtained is the same as 3.22 eV. Meanwhile, for photocatalytic activity, doping is very efficient at 2% with a degradation percentage of 80%. In this research, the author will make a thin layer of ZnO/Ag, synthesize it using the sol gel method and thin layer deposition using the doctor blade method, and carry out Ag doping variations of 0%, 2%, 5% and 7%. Characterization can be carried out using an X-ray Diffractometer (XRD), UV-Vis Spectrophotometer and Characterization using XRD, aiming to see the crystal size, crystal structure and distance between planes. Characterization uses a UV-Vis Spectrophotometer to see the energy band gap and absorbance after carrying out a photocatalytic test of the ZnO/Ag thin layer.

2. Research Methods

Materials

Zn-acetate, isopropanol, ethylene glycol, $AgNO_3$ were analytical grades from Mercks

Research Stages

This research includes the process of synthesizing Ag-doped ZnO using the sol gel method, growing a thin layer of ZnO/Ag on a glass substrate using the doctor blade technique, characterization and analysis using a UV-Vis spectrophotometer, XRD, and photocatalytic activity tests under UV-Vis lights.

Synthesis of ZnO/Ag Using the Sol Gel Method

The ZnO/Ag solution was made with 3.514 0.5M zinc acetate dissolved in 30 mL of isopropanol at room temperature. The solution was stirred for 15 minutes at 60°C, then 0.089 mL of ethylene glycol solution was added in a stirrer until the solution was homogeneous. 15 minutes later, $AgNO_3$ was added to the stirrer with a doping variation of 0.2%, 5%, 7% at a temperature of 85°C with constant stirring, waited for 15 minutes, then the suspension was covered with aluminum foil and the finished solution was stored in a closed bottle.

Deposition of ZnO/Ag Thin Layers Using the Doctor Blade Technique.

The ZnO/Ag thin layer deposition process was carried out using the Doctor Blade technique. The solution that has been formed is smeared on the stirring rod, then the stirring rod is rolled onto the glass substrate. The thin layer that has been formed is then dried on a hotplate, then the heating process is carried out. The heating process is carried out at a sintering temperature for 1 hour at a temperature of 500°C.

Analysis and Characterization of ZnO/Ag

Characterization and analysis were carried out after making a thin layer of ZnO/Ag which had been subjected to temperature variations. The first characterization is to use XRD to see the crystal structure, then continue with a UV-Vis spectrophotometer to see the gap energy.

3. Results and Discussion

Gap Energy

A UV-Vis Spectrophotometer is used to determine the energy band gap value. Doping is done to reduce the energy band gap value. In this research, samples were tested using a wavelength of 200-800 nm. The data obtained is transmittance data which will be used to determine the gap energy value of the TiO2/Ag thin layer. The Transmittance value graph can be seen in Figure 1.

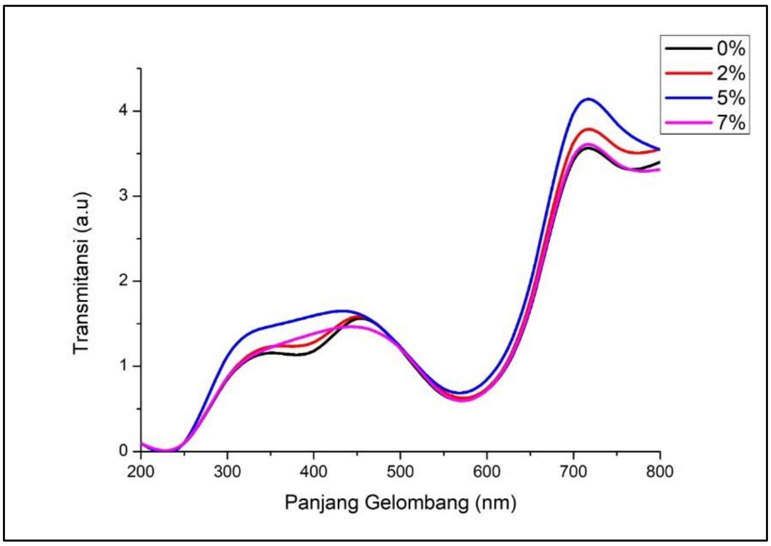

Figure 1 Transmittance Spectrum of ZnO/Ag Thin Film with 0%, 2%, 5%, and 7% doping

Figure 1 shows the transmittance spectrum of the ZnO /Ag thin film. Figure 1 shows that there is light interference on the substrate surface. The addition of Ag dopant to ZnO also reduces the transmittance value. It can be seen that at wavelengths of 450-500 there is a very sharp decrease. Wavelengths of 400nm-800nm are included in visible light, so the resulting transmittance is higher. As the doping given increases, the transmittance will increase, this occurs at a wavelength of 600nm-800 nm. The increase in the transmittance spectrum can be clearly seen at a wavelength of 700 nm. It can be seen that the higher the doping given to the sample, the higher the transmittance percentage.

Table 1 Energy Band Gap Values of ZnO/Ag Thin Films

Percentage of ZnO/Ag Thin Film	Energy Band Gap (eV)
0%	3,25 eV
2%	3,00 eV
5%	2,65 eV
7%	2,85 eV

Table 1 shows the energy band gap values of the ZnO/Ag thin film which was synthesized using various doping. In the table it can be seen that the energy bandgap with Ag doping variations is 0%, 2%, 5%, and 7%. In table 1, the energy bandgap value for ZnO without doping is 3.25 eV, ZnO/Ag 2% is 3.00 eV, ZnO/Ag 5% is 2.65 eV and ZnO/Ag 7% is 2.85 eV. The higher the Ag doping percentage, the energy bandgap value tends to decrease. The most optimal reduction in energy bandgap was obtained with the addition of 5% doping, namely 2.65 eV. The addition of silver (Ag) in this research aims to reduce the band gap so that the greater the addition of Ag doping to ZnO, the energy band gap tends to decrease (Sistesya and Sutanto, 2013).

XRD Characterization

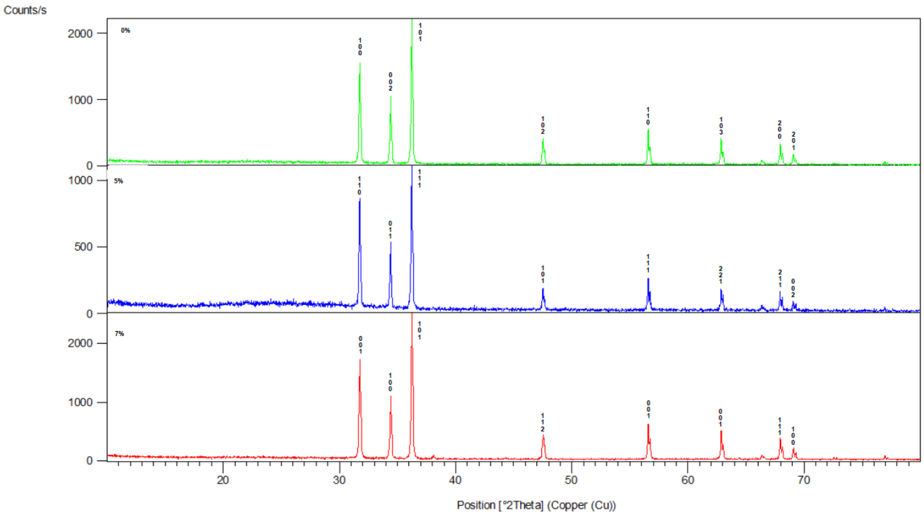

Figure 2. XRD Characterization of ZnO/Ag Thin Film with doping variations of 0%, 5% and 7%

Characterization using XRD with undoped ZnO, the smallest energy band gap, and the maximum Ag doping. XRD Characterization Results: The ZnO/Ag thin layer has a wurtzite phase and a hexagonal crystal structure. ZnO/Ag is adjusted to JCPDS data with reference number 01-079-2205. The 2θ peak that appears is 36.25o with each hkl ZnO/Ag 0% (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) while ZnO/Ag 5% and 7% 100), (002), (101), (102), (110), (103), (200), (112), (201) , (004), (202). Based on JCPDS data, the ZnO/Ag thin layer has 5% ZnO/Ag lattice parameters and has a hexagonal crystal structure with axes a=3.2501 Å and c=5.2071 Å and 7% ZnO/Ag with axes a=3.2499 Å and c=5.2066.

The crystal size can be obtained using the Scherrer equation. With the values λ= 0.156 nm and k= 0.9, these two values are definite constants, and do not change. The 2θ value taken is the value with the highest intensity, equal to 36.25o, with a FWHM value of 0.1440, so from these data it is known that the crystal size is 49.99nm for ZnO/Ag 0% and 41.66 nm for ZnO/Ag 5% and 7 %. This thin layer is in the nanometer realm, because the crystal size is below 100 nm.

Photocatalyst Test

The photocatalysis process requires 3 main components, namely a light source, target compound, and catalyst. The light source used is a UV-Vis lamp, the target compound is Peat Water and the catalyst is a thin layer of ZnO/Ag. Testing with a UV-Vis lamp was carried out at 1602 lux meters. Photocatalytic activity was carried out in a 100 mL beaker, filled to 60 mL, then the glass substrate was inserted.

(a) (b)

Figure 3. Peat water in Dendang District (a) Before Photocatalysis (b) After Photocatalyst Test

Figure 3 (a) shows the situation before the degradation test, while Figure 3 (b) shows peat water that has been degraded with a ZnO/Ag photocatalyst with variations of 0%, 2%, 5% and 7% Ag. Visually, the peat water is cloudy and there is a color change that is not very significant from the peat water before the degradation test was carried out compared to the test that has been carried out.

pH

The determination of pH was carried out using a pH meter dipped in a 250 ml beaker with the pH carried out on each sample, namely the Ag percentage of 0%, 2%, 5%, 7%. Obtained before the degradation test was 3.42. After degradation, the results obtained are shown in Table 2.

Table 2. pH test results

Sample Type	pH Before Photocatalyst Test	pH After Photocatalyst Test
ZnO/Ag 0%	3,42	5,6
ZnO/Ag 2%	3,42	6,4
ZnO/Ag 5%	3,42	6,7
ZnO/Ag 7%	3,42	6,6

Table 2 shows the pH test results after irradiation for 4 hours using a UV-Visible lamp. For the degradation test with pH parameters, the pH value of 0% ZnO/Ag was 5.6, the pH of 2% ZnO/Ag was 6.4, the pH of 5% ZnO/Ag was 6.7 and for the pH of 7% ZnO/Ag it was 6.6 . The optimal pH test results are at a doping variation of 5% with the resulting pH being 6.7. These results show that the higher the Ag doping variation, the smaller the energy bandgap and the effect on the pH photocatalyst test. The smaller the energy bandgap, the photocatalyst is able to absorb the acid content of peat water. Even though the color of peat water does not change significantly, based on the increase in pH in the table above, it shows that the addition of various Ag doping can degrade peat water. This is because the moving electrons will leave holes in the valence band and will act as a compound breaker in the peat water so that it can increase the pH towards neutral.

TDS (Total Dissolved Solid)

In this research, the TDS parameter test was carried out using a TDS meter dipped in a 250 ml beaker with TDS carried out on each sample, namely the Ag percentage of 0%, 2%, 5%, 7%. The results obtained before the degradation test were 1200 mg/L. After degradation, the results obtained are shown in Table 3.

Table 3. TDS Degradation Percentage

Percentage Variation	Degradation time (hour)	Initial Concentration C_0 (mg/L)	Final Concentration C_t (mg/L)	Degradation Percentage (%)
ZnO/Ag 0%	4	1.200	208	82.6
ZnO/Ag 2%	4	1.200	111	90.75
ZnO/Ag 5%	4	1.200	85	92.9
ZnO/Ag 7%	4	1.200	88	92.6

Based on table 3, the TDS for the ZnO /Ag test samples with Ag doping variations of 0%, 2%, 5% and 7%, where all sample treatments have succeeded in reducing TDS levels. Based on table 3, the percentage of degradation at 0% ZnO/Ag is 82.6%, degradation at 2% ZnO/Ag is 90.75%, degradation at 5% ZnO/Ag is 92.9% and 7% ZnO/Ag is 92.6%. Based on the TDS degradation percentage, it shows that the higher the Ag doping variation, the energy band gap can be reduced so that the ability to degrade peat water with TDS parameters tends to be greater with the most effective percentage for reducing TDS levels being a 5% Ag sample with a degradation percentage of 92.9%.

TSS (Total Suspended Solid)

In this research, the TSS parameter test was carried out using the gravimetric method based on SNI 6989.3.2019 which was carried out on each sample, namely the Ag percentage of 0%, 2%, 5%, 7%. The TSS results obtained for peat water before the degradation test were 48 mg/L. After degradation, the results obtained are shown in Table 4. The presence of TSS contained in peat water is a source of pollution because these solids block the entry of sunlight into the water and ultimately the microorganisms in the water will die because they do not receive an adequate supply of sunlight. Suspended solids have properties that can be differentiated from the solution because the particle size is larger than 1 mm and this size contributes to the turbidity of peat water (Rahmadani et al, 2017).

Based on table 4, the results of the TSS parameters for the ZnO /Ag test samples show a sample percentage of 0%, 2%, 5% and 7%, all sample treatments have succeeded in reducing TSS levels. It is known that the most effective percentage for reducing TSS levels is sample 5 % Ag. When the sample is applied to the medium for TSS testing, the addition of Ag to ZnO can increase the effectiveness of the catalyst. The higher the modification percentage, the lower the TSS content in peat water. This is caused by the photocatalyst which has formed a wider surface and the pores are open so that it is able to adsorb water. The results of the percentage of photocatalytic degradation of peat water on TSS levels can be seen in table 4.

Table 4. Percentage of TSS Degradation

Percentage Variation	Degradation time (hour)	Initial Concentration C_0 (mg/L)	Final Concentration C_t (mg/L)	Degradation Percentage (%)
ZnO/Ag 0%	4	48	32,86	31.5
ZnO/Ag 2%	4	48	31,08	35.25
ZnO/Ag 5%	4	48	30,95	35.5
ZnO/Ag 7%	4	48	36,84	23.25

When exposed to a UV-Visible lamp for 4 hours, the 5% ZnO/Ag thin layer tested gave the highest degradation percentage. This indicates that the peat water has been degraded in this 5% sample the most among the other percentages. A decrease in the percentage of degradation occurred in samples with a doping variation of 7%. This is because too much Ag causes the ZnO particles to be covered by a layer of Ag. This also causes the energy band gap to increase and affects the degradation percentage, where the final concentration of the TSS test is not too far from the initial concentration and shows a percentage of around 23.25%, which shows that this percentage is lower than the percentage of other samples.

Conclusion

Overall, with the addition of Ag doping on ZnO, this occurs. Decreased Band Gap energy, where the smallest band gap is at 5% ZnO/Ag, namely 2.65 eV. The addition of Ag doping to ZnO for the peat water photocatalyst test shows that the higher the Ag doping, the photocatalyst test value on the pH parameter is close to optimum neutral around 6.7, while for the TDS and TSS parameters, adding high doping variations can reduce TDS and TSS levels with the most optimum degradation percentages, namely 92.9% and 35.5%. XRD results show that ZnO/Ag crystals are 0%, 5 %, and 7% of the resulting crystal structures are Hexagonal (Wurtzite) with crystal sizes of 49.99nm, 41.66nm, 41.66nm respectively.

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