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Ag MODIFIED ZnO THIN FILMS WITH IMPROVED CRYSTALLINITY AND BAND GAP REDUCTION FOR DEGRADATION OF BATIK DYE EFFLUENTS

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ABSTRACT
This study aims to investigate the effect of silver (Ag) doping on the photocatalytic performance of ZnO thin films for batik wastewater treatment. ZnO precursor was synthesized by dissolving Zinc Acetate Dihydrate in distilled water, stirred at 70°C, followed by the addition of NaOH and titration with triethanolamine (TEA). ZnO-Ag precursor was prepared by adding 4% $AgNO_3$ to the ZnO solution and stirring for 30 minutes. The ZnO-Ag thin film was then deposited on a glass substrate using the sol–gel spray coating method. XRD analysis showed that the crystallite size increased with Ag addition, with the ZnO-Ag film having a size of 62.95 nm, indicating improved crystallinity. SEM images revealed a more heterogeneous particle distribution with finer and more uniform particles in the ZnO-Ag sample. UV-Vis results also indicated a shift in the band gap, supporting better light absorption. Photocatalytic tests showed that ZnO-Ag thin films exhibited superior efficiency in degrading batik dye wastewater compared to pure ZnO films. These findings suggest that Ag doping significantly enhances the photocatalytic activity of ZnO thin films, making them a promising material for eco-friendly wastewater treatment applications.
Keywords: ZnO-Ag thin film, batik wastewater, photocatalyst, spray coating, silver doping, SEM, XRD.
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INTRODUCTION

The batik industry in Indonesia represents a valuable cultural heritage and contributes significantly to the national economy.[1] However, the production process, particularly the dyeing stage, generates large volumes of wastewater containing synthetic dyes and harmful chemicals.[2] Improper treatment and direct discharge of these effluents into the environment have led to serious ecological impacts, such as contamination of surface water and threats to aquatic life and human health.[3] Conventional treatment methods, like sedimentation, are insufficient to address the complex nature of batik dye pollutants. To support sustainable development, especially under Sustainable Development Goal (SDG) 6 Clean Water and Sanitation, there is a growing need to adopt more effective and eco-friendly wastewater treatment technologies. Photocatalysis, an advanced oxidation process that utilizes light-activated semiconductors to degrade organic contaminants, has emerged as a promising solution.[4] This method offers several advantages, such as low energy consumption, potential for solar activation, and the ability to completely mineralize pollutants.[5] Among various photocatalytic materials, zinc oxide (ZnO) is widely studied due to its suitable band gap, non-toxicity, and chemical stability.[6] However, pure ZnO has limitations, such as rapid electron-hole recombination and limited light absorption in the visible range.[7] To overcome these drawbacks, doping with noble metals such as silver (Ag) has been explored. Ag-doping is known to improve charge separation efficiency and enhance light absorption, thus significantly increasing photocatalytic performance.[8] ZnO-Ag thin films have gained attention as photocatalysts due to their unique structural and optical properties.[9] The combination of ZnO and Ag can create a synergistic effect, where ZnO serves as the base photocatalyst and Ag enhances its activity through plasmonic effects and surface interactions.[10] Understanding the crystallinity, surface morphology, and optical characteristics of ZnO-Ag thin films is essential for optimizing their photocatalytic performance in real wastewater applications, such as those from batik industries.[11]

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This study aims to investigate the effects of Ag doping on the crystal structure, morphology, and optical band gap of ZnO thin films prepared via the sol-gel spray coating method. Furthermore, it evaluates their photocatalytic activity in degrading batik dye wastewater. The results are expected to contribute to the development of efficient, low-cost, and sustainable technologies for industrial wastewater treatment, aligning with environmental protection goals and SDG 6 implementation in Indonesia. [12]

EXPERIMENTAL

Material

The materials used in this study include zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), deionized water (Aquades), sodium hydroxide (NaOH), triethanolamine (TEA, $C_6H_{15}NO_3$), and silver nitrate ($AgNO_3$). All chemicals were analytical grade and purchased from Merck KGaA (Darmstadt, Germany).

Synthesis of ZnO and ZnO-Ag Precursors

The ZnO precursor was prepared by dissolving zinc acetate dihydrate in deionized water and stirring with a magnetic stirrer at 70 °C. A NaOH solution was added, followed by dropwise titration with TEA to adjust the pH and stabilize the sol.[13] The mixture was stirred for 30 minutes until a homogeneous solution was obtained. To synthesize the ZnO-Ag precursor, $AgNO_3$ was added to the ZnO solution at a concentration of 4% (w/w), followed by continuous stirring for another 30 minutes.

Deposition of ZnO-Ag Thin Film

The ZnO-Ag thin film was deposited onto pre-cleaned glass substrates using the sol–gel spray coating technique. The substrates were maintained at 250 °C during deposition. After coating, the films were dried in an oven at 200 °C for 30 minutes and subsequently calcined in a furnace at 450 °C for 2.5 hours to remove residual organics and promote crystallization.

Characterization Techniques

Optical properties were analyzed using UV-Vis spectrophotometry to determine the band gap energy. The crystal structure was examined using X-ray diffraction (XRD) to determine the crystallinity and phase composition. Surface morphology and elemental composition were observed using Scanning Electron Microscopy (SEM).

Photocatalytic Activity Test

The photocatalytic performance of the ZnO-Ag thin film was evaluated by degrading synthetic batik wastewater under light irradiation for 6 hours. The turbidity reduction was measured as an indicator of dye degradation efficiency.

RESULTS AND DISCUSSION

The crystal structure of ZnO and ZnO-Ag thin films was analyzed using X-ray Diffraction (XRD). As shown in Fig.-1, diffraction peaks corresponding to ZnO were observed at 2θ = 31.84°, 34.52°, and 36.25°, associated with the (100), (002), and (101) crystal planes. After doping with 4% Ag, additional peaks appeared at 2θ = 38.07° and 44.75°, which correspond to the (111) and (200) planes of metallic silver, confirming the presence of Ag in the ZnO lattice. Figure-1 shows the diffraction patterns of ZnO and ZnO-Ag thin films.

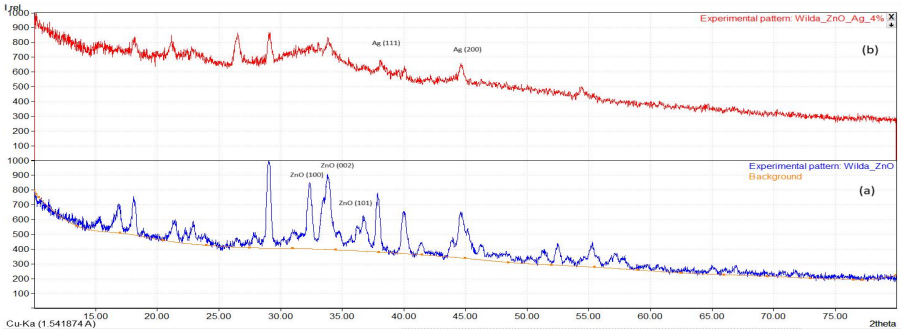


Fig.-1: XRD Pattern of (a) ZnO Thin Film and (b) ZnO-Ag Thin Film

The reduction in peak intensity and the broadening of ZnO peaks in ZnO-Ag samples indicate a slight increase in microstrain or a reduction in crystallite size. However, crystallinity remained good, as shown in the calculated FWHM values and crystal size using the Scherrer equation (Table-1). The ZnO-Ag thin film showed a larger average crystallite size (62.95 nm) compared to pure ZnO (27.32 nm), indicating improved crystal quality upon Ag incorporation. The incorporation of silver (Ag) into ZnO crystal structures typically influences crystallinity and microstructural characteristics due to differences in ionic radius and valence state.[14] Ag^{+} ions (ionic radius ~1.26 Å) are larger than Zn^{2+} ions (ionic radius ~0.74 Å), and when Ag^{+} substitutes or interacts with Zn^{2+} in the lattice, it can induce lattice distortion or defect formation.[15-17] This alteration can lead to changes in peak intensity, broadening, and shifts in diffraction angles in the XRD pattern. Moreover, the presence of Ag atoms on the grain boundaries may promote crystal growth during the thermal process, which can contribute to the increase in crystallite size observed in Ag-doped ZnO thin films.[18] Table-1 shows that the full width at half maximum (FWHM) value decreases with Ag doping. This indicates that the crystallinity of the Ag-doped thin film is good. These results indicate that the ZnO-Ag thin film is able to reduce the full width at half maximum (FWHM) value.[19] Furthermore, the average crystal size of the thin film is calculated using the Scherrer formula.[20]

$$D = \frac{K\,\lambda}{\beta\,COS\,\theta}$$

Where the crystal size is denoted by the symbol D, the constant (for oxide materials = 0.94) is denoted by K, is the wavelength denoted by λ of the X-ray source used (in this study λ = 1.5406 Å) β is the FWHM size, and θ is the diffraction crystal peak. Based on the results of the crystal size calculation, it shows that the presence of Ag doping on ZnO thin films causes an increase in crystal size. Similar results show that the crystal quality of ZnO thin films increases significantly with the presence of Ag doping.[9]

Table-1: Diffraction Angle, FWHM, and Crystallite Size of ZnO and ZnO-Ag Thin Film

Sample	Angle 2θ	FWHM (10^3 rad)	Crystal size (nm)
Thin Film ZnO	36.25	5.59	27.32
Thin Film ZnO-Ag	38.07	2.44	62.95

Surface morphology of the films was examined using SEM, as shown in Fig.-2. ZnO thin films exhibit relatively uniform and compact grain structures, indicating a successful deposition process. Meanwhile, the ZnO-Ag thin film shows a more heterogeneous particle distribution with smaller grains evenly spread across the surface, which could enhance photocatalytic performance by increasing active surface area.

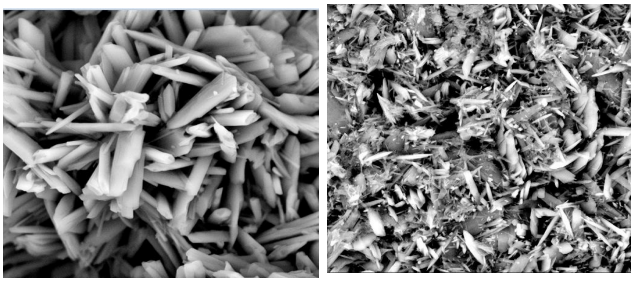


Fig.-2: SEM Images of (a) ZnO Thin Film and (b) ZnO-Ag Thin Film

Some agglomeration was observed in ZnO films, due to particle clumping during the calcination process.[21] This could reduce surface activity in localized regions. In contrast, the ZnO-Ag film displayed finer and better-dispersed particles, supporting its superior photocatalytic activity.[22] The optical properties of the films were investigated using UV-Vis spectroscopy. As presented in Fig.-3, ZnO-Ag thin films exhibited a red shift in the absorption edge compared to pure ZnO films, indicating a decrease in band gap energy. The band gap was calculated from the Tauc plot $(\alpha h\nu)^2$ vs hν and shown in Fig.-4.

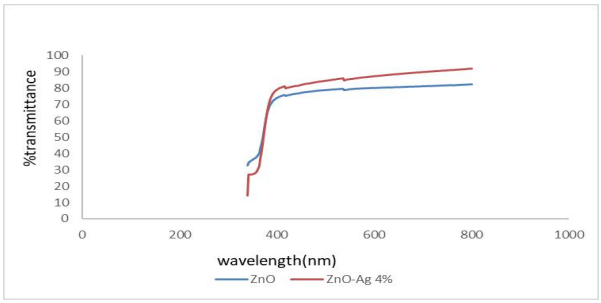
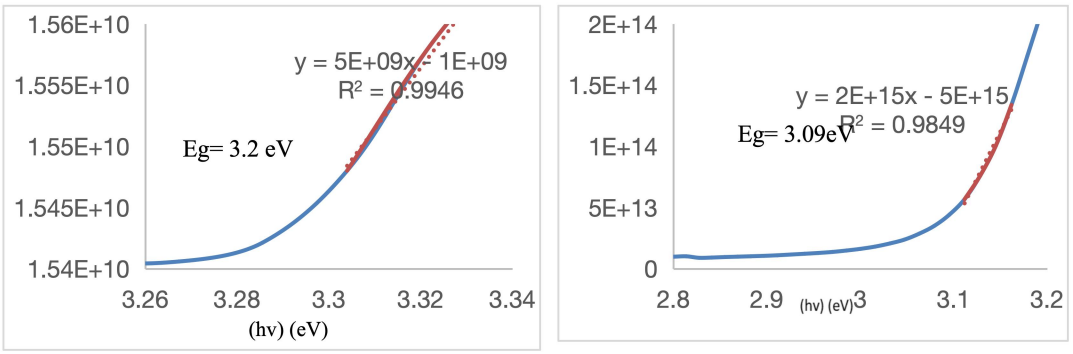


Fig.-3: Transmittance Spectra of ZnO and ZnO-Ag Thin Films

The results of optical properties testing show that the absorption edge of the ZnO-Ag thin film shifts to a longer wavelength (redshift) than the ZnO thin film. According to the theory of optical absorption, the relationship between the absorption coefficient (α) and the photon energy (hv) for direct transition is $(\alpha hv)^2 = hv - Eg$, where Eg is the energy band gap of the thin film.[23] Figure-4 shows the energy band gap of the ZnO and ZnO-Ag thin films.



(a) (b)

Fig.-4: Band Gap Energy of (a) ZnO and (b) ZnO-Ag Thin Films

The band gap narrowing in ZnO-Ag films is attributed to the creation of localized states by Ag doping, which facilitates electron excitation and light absorption in the visible region. This enhancement is favorable for photocatalytic applications under UV and visible light.[24] Photocatalytic degradation of batik dye wastewater was performed under UV irradiation for 6 hours using both ZnO and ZnO-Ag thin films. As shown in Fig.-5, the ZnO-Ag thin film showed a significantly higher degradation percentage than pure ZnO, especially at longer durations. Figure-5 is a diagram of the measurement of the % degradation value of Tegalan batik wastewater after undergoing treatment using ZnO-Ag thin film under UV light for 6 hours.

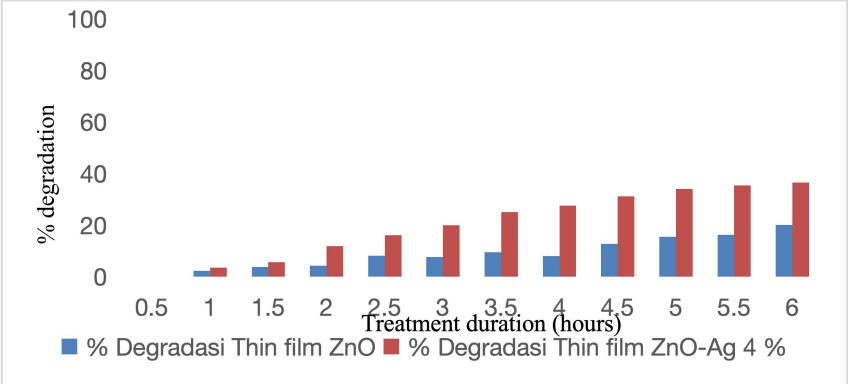


Fig.-5: Measurement Diagram of % Degradation of Tegalan Batik Wastewater after Undergoing Treatment Using ZnO-Ag Thin Film Material

This improvement confirms that Ag incorporation enhances charge separation and reduces recombination of photogenerated electron-hole pairs, which are crucial for efficient photocatalysis. Thus, ZnO-Ag thin films represent a promising material for practical wastewater treatment. The findings of this study align with Sustainable Development Goal (SDG) 6 Clean Water and Sanitation, by providing a low-cost and effective method to treat industrial dye wastewater from the batik industry. The development of ZnO-Ag thin film photocatalysts supports environmentally sustainable solutions for water purification in small-scale and rural industries.

CONCLUSION

This study demonstrates that Ag doping significantly enhances the structural and functional properties of ZnO thin films. The incorporation of 4% Ag resulted in improved crystallinity, as indicated by increased crystallite size, and more uniform surface morphology, as shown in SEM analysis. Optical characterization revealed a reduction in band gap energy, enabling broader light absorption. Most notably, the ZnO-Ag thin film exhibited superior photocatalytic activity in degrading batik dye wastewater compared to pure ZnO. These findings suggest that ZnO-Ag thin films are promising photocatalyst materials for wastewater treatment applications. As such, this research directly supports Sustainable Development Goal (SDG) 6 Clean Water and Sanitation, by promoting environmentally friendly methods for industrial wastewater management. Further studies are recommended to optimize Ag concentration and evaluate the long-term stability of the photocatalyst in real industrial conditions.

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CONFLICT OF INTERESTS

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AUTHOR CONTRIBUTIONS

The present work is related to *SDG-6: Clean Water and Sanitation*. All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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