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Effect of Molarity on Double Layer Photocatalytic Activity ZnO/ZnO:Ag for Metanil Yellow Degradation

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ABSTRACT

Double layer (DL) ZnO/ZnO:Ag has been synthesized with variations in molarity of 0.1, 0.3, 0.5, and 0.7 M and its application as a degrading agent for methanil yellow dye. This study aims to determine the effect of the molarity of the DL ZnO/ZnO:Ag on crystallinity and photocatalytic activity for methanil yellow degradation. DL ZnO/ZnO:Ag was synthesized using sol-gel technique and deposited with spray coating technique. The results of DL ZnO/ZnO:Ag were characterized by XRD to determine the crystallinity and particle size. The photocatalytic activity was carried out by immersing the DL ZnO/ZnO:Ag layer in 10 ppm methanil yellow solution and irradiating it with UV light for 4 hours and then tested using UV-Vis spectroscopy to get the percentage of methanil yellow degradation. The results showed that the crystallinity of the DL ZnO/ZnO:Ag for all molarity variations had a hexagonal wurtzite structure. Grains size increase as molarity increases from 0.1 to 0.5 M. However, if the concentration continues to be increased to 0.7M, the grain size decreases. Photocatalytic activity is increasing every hour, as indicated by the increasing percentage of degradation. Precursor in 0.5 M has the maximum percentage of degradation is 25.32%.

Introduction

The increasing number of population and the number of industries will have an impact on environmental changes, one of which is a decrease in water quality (Goel & Chaudhary, 2018). The decrease in water quality over the last few years is due to the rapidly growing industrialization of pollution to cater the needs of a growing population (Masunga et al., 2020). Some industries such as the paper, textile, ink and paint industries dispose of dye in the aquatic system in large amounts which are contaminants that can be toxic in water (Sangari, 2018). The textile industry uses various types of dyes, one of which uses azoic dyes. The most which is used widely dyes are azoic dyes which when used as a dye then approximate 70% usage, but about 12% of this azoic dye is wasted in water. The disposal of azoic dyes into water is very dangerous because of the stable azo group (-N=N) so that it cannot decomposed (Masunga et al., 2020).

Methanil yellow or often called acid yellow 36 is one of the azoic dyes that is often used in the textile industry. Metanil yellow is a dye that is difficult to degrade and is hepatotoxic and can cause cancer. (Masunga et al., 2020). Metanil yellow has a chemical group $C_{18}H_{14}N_3O_3SNa$ which if consumed in the long term can cause eye irritation and liver damage (Gita Bhernama et al., 2017). Previous studies have shown that azo methanol yellow enters the human body through food and beverage consumed was contain water has been contaminated with Metanil Yellow

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which can cause toxic effects on various physiological systems and enter the bloodstream. When the Methanyl Yellow dye reaches various organs of the human body, the cell metabolism will be disrupted resulting in vital organs in the body experiencing a state of oxidative stress which can be harmful to human health (Ghosh et al., 2017).

To overcome this problem, a photocatalyst utilization technology was introduced as a photo degradation of pollutants. A more promising water purification technique than conventional method is using photocatalyst (Baruah et al., 2012). Semiconductor that is often chosen among transition metal oxides is zinc oxide (ZnO) because it has many advantages (Priyadharshini et al., 2022). ZnO has many advantages due to its high thermal and chemical resistance, photocatalytic (Anggita & Sutanto, 2016), antimicrobial and antibacterial properties (Azizi et al., 2013). ZnO is an advantageous photocatalyst material due to the band gap energy 3.37 eV which has a higher electron mobility and a better lifetime than TiO2. (Taheri et al., 2017). ZnO is a material that can be used as a photocatalyst. ZnO in the form of nanoparticles is able to degrade dyes better than TiO2 because ZnO nanoparticles have a relatively high surface area. (Priyadharshini et al., 2022).

Pure ZnO cannot be used directly in most applications because it still has poor optical properties caused by point defects such as Zn interstitial or vacancies of oxygen atoms (Al-Jawad et al., 2018). To overcome the weakness of these optical properties, it is necessary to add dopants. addition of dopants can increase the energy between the valence band and the conduction band (Masunga et al., 2020). Silver (Ag) dopant addition has been extensively studied due to the ion's larger size, high solubility and minimum orbital energy of 8 (Hosseini et al., 2015). Ag-doped ZnO can increase photocatalytic activity. This is due to the substitution of Ag atoms in the Zn atomic sites into the ZnO lattice (Tarwal & Patil, 2011).

The effect of molar variations on ZnO affects the thickness of the coating. Increasing the thickness of the coating will affect the morphology and optoelectronic properties (Taheri et al., 2017). Previous studies with double layer (DL) deposition on semiconductors can increase the activity of photocatalytic semiconductors (Sutanto et al., 2015). The DL ZnO/ZnO:Ag in previous studies could degrade methylene blue better than the ZnO single layer and an increase in the molar concentration of the DL ZnO/ZnO:Ag could reduce the energy gap (Anggita et al., 2021). This research will study the manufacture of DL ZnO/ZnO:Ag using the sol-gel method and will be varied with various molar concentrations of Zinc 0.1M, 0.3M, 0.5M, and 0.7M with the aim of knowing the crystallinity and the ability of photocatalytic activity in degrading dyes methanil yellow.

Methods

2.1 Preparation of Double Layer ZnO/ZnO:Ag

The process of making ZnO and ZnO:Ag solutions using the sol-gel method. ZnO sol-gels were prepared by dissolving Zinc acetate dehydrate (ZnAc: $Zn(COOCH_3)2.2H_2O$ and monoethanolamine (MEA: $HOCH_2CH_2NH_2$) in isopropanol solution ($(CH_3)_2CHOH$) at room temperature (Nagayasamy et al., 2013). The concentration of ZnAc used in this study was 0.1M, 0.3M, 0.5M, and 0.7M and the molar ratio of MEA and ZnAc was 1:1. The ZnO solution was stirred and annealed at 70°C for 30 minutes to obtain a clear and homogeneous ZnO sol-gel. Ag was prepared by adding Silver Nitrate to ZnO solution with a percentage of 4% of the number of moles of ZnAc then stirring and annealing at 70°C for 30 minutes to obtain a homogeneous ZnO:Ag sol-gel.

Spray coating technique is a technique used to deposit double layers of ZnO/ZnO:Ag. This spray coating technique is done by spraying ZnO sol-gel on a glass substrate at 300C for 1 hour, then spraying ZnO:Ag sol-gel on top of the ZnO layer for 1 hour at the same temperature. After the ZnO/ZnO:Ag layer is formed, the sintering stage is continued. This sintering stage by placing a DL ZnO/ZnO:Ag in a furnace at 500°C to produce silver nanoparticles embedded on the ZnO surface.

2.2 Characterization

XRD (X-Ray Diffraction) was carried out to determine the crystal structure and grain size formed on DL ZnO/ZnO:Ag. The crystal size was determined using the Scherrer method based on the width of the x-ray diffraction peaks. Calculation of crystal value using Equation 1 (Nagayasamy et al., 2013).

$$D = K\frac{\lambda}{\beta cos\theta} \qquad (1)$$

D is the crystal size of the material, K is constant (0.9), λ is X-ray wavelength used, β is the FWHM value of the selected peak, θ diffraction angle.

2.3 Photocatalytic Analysis

The photocatalytic ability of DL ZnO/ZnO:Ag to degrade Methanol yellow dye is using UV-Vis spectroscopy to obtain the percentage of degradation. The method used is to take small samples every hour

from a solution of methanil yellow dye that has been treated with DL ZnO/ZnO:Ag which is irradiated with UV light for 4 hours every hour. To calculate the percentage of degradation using Equation 2 (Ali et al., 2015).

$$\text{Degradation}=(C_0 - C_t)/C_0 \times 100\% \qquad (2)$$

Co is the concentration before being given treatment and Ct is the concentration after being given treatment.

Result and Discussions

3.1. Structural Properties of Double Layer ZnO/ZnO:Ag

Figure 1
The result XRD pattern of DL ZnO/ZnO:Ag

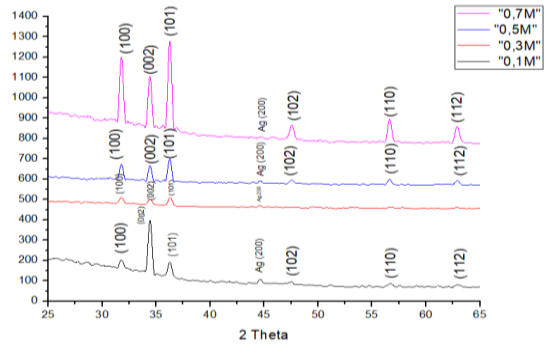


Figure 1 is the result XRD pattern of DL ZnO/ZnO:Ag. All XRD pattern results show that all samples are polycrystalline. From the XRD pattern that has been obtained, show lattice orientation [100], [002], [101], [102], [110], [112] which indicate that the pattern of the hexagonal wurtzite crystal structure of ZnO (Tarwal & Patil, 2011)(Jabeen et al., 2017) and there is a lattice orientation [200] at an angle of 2θ 44.04° which indicates the Ag phase with a face centered cubic (fcc) crystal structure according to data of JCPDS 36-1451 and JCPDS 4-0783 (Azizi et al., 2013).

The absence of an impurity phase at the diffraction peak indicates that Ag ions have been successfully incorporated into the ZnO matrix structure (T. Ali et al., 2018)(Tarwal & Patil, 2011). The diffraction peaks of ZnO and Ag did not shift with increasing molarity. The absence of a shift in the XRD peaks made it possible that the number of substituted Ag ions at the Zn site was not significant. The very low doping of Ag and the difference in radii between the Ag and Zn ions resulted in the separation of Ag particles at the ZnO crystallite grain boundaries (Karunakaran et al., 2011) (Georgekutty et al., 2008). The addition of molarity to the ZnO/ZnO:Ag double layer affects the high peak intensity which will affect the crystallinity (Mohammadi et al., 2010). Crystal size is influenced by the FWHM value, where the higher the intensity, the smaller the FWHM value and the greater the crystal size (Masruroh et al., 2013). The diffraction peak of ZnO [101] increases in intensity with increasing molarity, this will affect the crystal size. To get the crystal size, you can use the Scherrer equation (eq. 2.1) so that the crystal size is obtained as Table 1.

Table 1
Grain size of Double layer ZnO/ZnO:Ag

Molar Concentration (M)	2θ (°)	hkl	FWHM (°)	d-spacing (nm)	Grain Size (D) (nm)	Mean Grain Size (nm)
0.1	31.7768	100	0.3149	0.2816	26.22	28.20
	34.4271	002	0.2755	0.2605	30.18	
0.3	31.7583	100	0.2755	0.2818	29.97	32.58
	34.4294	002	0.2362	0.2605	35.20	
0.5	31.8021	100	0.2362	0.2814	34.96	38.60
	34.3327	002	0.1968	0.2612	42.23	
0.7	31.8006	100	0.3149	0.2814	26.22	28.20
	34.4117	002	0.2755	0.2606	30.18	

Grains size increase as the molarity increases from 0.1M to 0.5M. The increase in molarity resulted in the number of zinc ions contained, so that the kinetics of ZnO growth was faster and resulted in high intensity (Baneto et al., 2014)(Sakthivelu et al., 2011). The increase of intensity indicate that the increase of crystallite size (Afaah et al., 2019). However, if the concentration continues to be increased to 0.7M, the grain size decreases. This is because the addition of increasing concentrations can affect nucleation, so that new sites appear to host thin film formation (Baneto et al., 2014).

3.2 Photocatalytic Performance of Double Layer ZnO/ZnO:Ag

The photocatalytic activity of DL ZnO/ZnO:Ag in degrading methanil yellow dye at a concentration of 10 ppm (parts per million) for four hours showed a decrease in the absorbance value can be seen in Table 2.

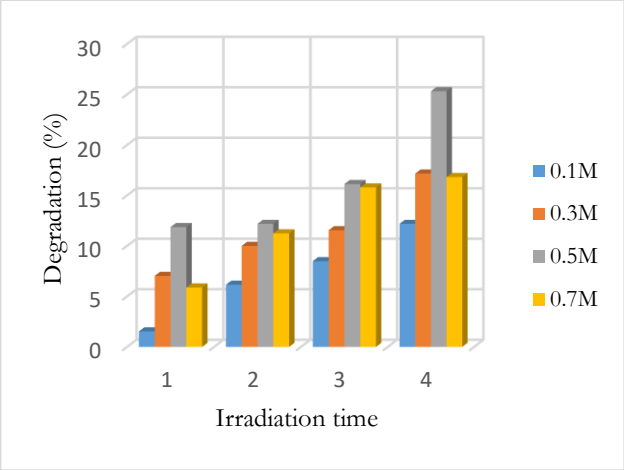
Table 2
Percentage Degradation of Double Layer ZnO/ZnO:Ag

Irradiatin Time (hour)	Degradation (%)			
	0.1M	0.3M	0.5M	0.7M
1	1,54	7,03	11,86	5,88
2	6,16	10	12,18	11,24
3	8,49	11,55	16,13	15,79
4	12,18	17,16	25,32	16,82

Table 2 shows an increase in the percentage of degradation with increasing time of UV exposure to the ZnO/ZnO:Ag double layer. The degradation percentage also increased according to the increase in molarity from 0.1M – 0.5M. However, there was a decrease in degradation when the molar concentration reached 0.7M. Increased molar concentration can increase the production of electrons and holes so as to produce more hydroxyl ions. The more hydroxyl ions will bind to free radicals and will increase the photocatalytic activity. The double layer can inhibit the electron-hole recombination process so that the oxidation and reduction processes that occur on the catalyst surface take longer and can increase photocatalytic activity (Sutanto et al., 2015).

The presence of Ag ions on the surface of ZnO can inhibit electron-hole recombination, thereby increasing its photocatalytic activity (Jia et al., 2012). As the concentration of Ag increases, the photocatalyst activity of ZnO:Ag should also increase. However, the results showed that the photocatalytic activity of the ZnO/ZnO:Ag double layer decreased when the molar concentration reached 0.7M. This can be caused when the Ag content reaches above the optimal value limit, Ag metal can act as an electron-hole recombination center due to the electrostatic force of negatively charged silver and positively charged holes making it easy to recombine and reduce its photocatalytic activity (Jia et al., 2012).

Figure 2
Percentage degradation of double layer ZnO/ZnO:Ag



4. CONCLUSION

The crystallinity of the ZnO/ZnO:Ag double layer for all molar variations had a hexagonal wurtzite structure. Grains size increase as the molarity increases from 0.1M to 0.5M. However, if the concentration continues to be increased to 0.7M, the grain size decreases. Photocatalytic activity is increasing every hour, as indicated by the increasing percentage of degradation. The degradation percentage also increased according to the increase in molarity from 0.1M – 0.5M. However, there was a decrease in degradation when the molar concentration reached 0.7M. The 0.5M molar variation has the maximum percentage degradation with a percentage value of 25.32%.

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