Characterizations of Ag doped ZnO particles via flame pyrolysis method for degradation of methylene blue

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Abstract. Flame pyrolysis is widely used for the fabrication of particles because of great crystallinity and fine size distribution of the products. In this research, ZnO-Ag particle materials have been favourably made by flame pyrolysis. The impacts of Ag loading varying from 0 to 20 wt% on the photocatalytic activity of ZnO-Ag particle under ultraviolet (UV) and sunlight irradiations were studied. ZnO-Ag particles were fabricated based on zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) 0.1 M and silver nitrate (AgNO₃) as a precursor inside a flame reactor. Crystallinity and morphology of ZnO-Ag particles were identified by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. SEM analysis showed that the particles had irregular sphere-like shapes. The XRD patterns showed that the produced ZnO had a wurtzite structure with different crystallite sizes. XRD analysis also confirmed the existence of Ag particles in ZnO-Ag particles after the addition of Ag greater or equal to 5 wt%. The existence of Ag was indicated by the appearance of the XRD peak at 38.1º. The peak at 38.1º increased with the increase of Ag loading. Finally, the photocatalytic activity was evaluated by estimating the degradation of methylene blue aqueous solution under UV and sunlight irradiations. It noted that the most excellent photocatalytic performance was achieved at 5 wt% Ag loading for both irradiations.

1. Introduction

Recently, the textile industry is one of the fastest-expanding industries. Unfortunately, increasing the number of textile industry leads to many environmental issues when the liquid waste is not handled properly. The liquid waste that contains textile dyes are very harmful for living creatures and the ecosystem. Previous researchers mentioned that metal oxides can be applied as materials to degrade the organic waste [1]. Zinc oxide (ZnO) and titanium dioxide (TiO₂) are widely used as catalyst material for degradation of dye pollutants when assisted with photon energy from light. The photocatalytic activity of TiO₂ is influenced by a bandgap of ~ 3.2 eV [2]. While, ZnO has a wider bandgap than TiO₂ which is about ~ 3.37 eV. Thus, ZnO is mostly preferred as photocatalyst material. In addition, ZnO has greater oxidizing ability, greater photocatalytic activity, higher electron transfers and exciton binding energy [3]. However, the application of ZnO particles is very limited to ultraviolet (UV) irradiations with wavelengths below 385 nm [4]. Only 4 % from the total spectrum of sunlight is UV, thus further adjustment is needed when applied on an industrial scale. In addition, the high rate of electron-hole recombination showed that the electron-hole pairs formed can quickly recombine before moving to the photocatalyst area [5]. Therefore, significant efforts are needed to enhance the photocatalytic activity by modifying the surface of ZnO or adding noble metals such as Ag. Kusdianto
et al. [6] stated that the addition of Ag particles reduced the degree of agglomeration and enhanced the photocatalytic performance of these particles.

There are two methods for the fabrication of ZnO-Ag particles, which is by physical and chemical fabrication methods. Sputtering [7], evaporation [8], pulsed laser deposition [9] are widely used for fabrication of the nanocomposite through physical method. Whereas the chemical fabrication method involves sol-gel [10], chemical vapor deposition (CVD) [11], metalorganic CVD [12], hydrothermal [13] or spray pyrolysis [14]. Some of these methods have several significant limitations, such as the requirement of additional steps for further treatments. The flame pyrolysis (FP) method has been favored by researchers because the FP method enables the fabrication of particles via a simple process. On the other hand, the product has high crystallinity and narrow size distribution. Properties of the products, such as: crystallite size, crystalline phase, degree of aggregation and agglomeration, surface area and porosity can also be controlled by adjustment of the flame conditions [15]. In addition, the FP method requires a low-cost source of heating energy (gas fuel) compared to energy sources of spray pyrolysis which is generated by electricity.

In our prior research [16], ZnO-Ag particles have been successfully fabricated using flame pyrolysis, where the obtained results indicated that the best photocatalytic performance was obtained with 5 %wt Ag loading. Unfortunately, the photocatalytic test done in this study was limited under UV light irradiation only. Moreover, controlling the volume of precursor inside ultrasonic nebulizer was required. In this study, particles are synthesized using similar apparatus with our previous study [16], in exception without using a peristaltic pump to reduce the energy consumption. Moreover, the photocatalytic tests were performed not only irradiated under UV light but also sunlight. Further application of the produced particle is used for degradation of organic waste from textile industry in Indonesia. With regard to these problems, the objective of this study is to determine the effect of Ag loading on the characteristics of particles (morphology, particle size, and crystallite size) and the performance of the photocatalytic activity of ZnO-Ag particles under UV and sunlight irradiations. Model for organic pollutant used in this study is methylene blue (MB), because the textile industries commonly use the MB as a synthetic dye.

2. Materials and method

2.1. Material and experimental set up

Zinc acetate dehydrate (Zn(CH$_3$COO)$_2$.2H$_2$O) 99.5 % (E. Merck, D-6100 Darmstadt, F.R. Germany) and silver nitrate (AgNO$_3$, E. Merck, D-6100 Darmstadt, F.R. Germany) was used as the precursor for this experiment. Zinc acetate was dispersed to distilled water using a sonicator for 10 minutes forming a homogenous 0.1 M zinc acetate. Silver nitrate was fed to the zinc acetate mixture with various weights ranging from 0 to 20 %wt and subjected to a sonicator for making homogenous suspension. The prepared precursor was then poured in to the ultrasonic nebulizer.

Fabrication of ZnO-Ag through flame pyrolysis was done using an apparatus as shown in Figure 1. An ultrasonic nebulizer was utilized to produce droplets from the precursor. Compressed air was used as a carrier gas to carry the droplets into the flame reactor with a flow rate of 3 L/min (LPM). Liquefied petroleum gas (LPG, commercial grade, PT. Pertamina) was used as fuel and compressed air was used as the oxidizer with a flowrate of 0.4 LPM and 33.33 LPM, respectively. The droplets produced by an ultrasonic nebulizer was then passed through the flame reactor and the decomposition of precursor occurred in here to produce the particles. The particles were then collected in the electrostatic precipitator as a powder collector. The temperature of the electrostatic precipitator was kept constant at 120 °C to avoid the condensation, while the applied voltage was set at 40 kV. Non-condensable gases were drawn by the vacuum pump and the uncollected particles are captured in the water trap. Detail of this experiment can also be seen in our prior research [16].
2.2. Characterizations

ZnO-Ag particles was analyzed by X-ray diffraction (XRD, X’pert Philips) operated at 40 kV and 30 mA with 2θ ranging from 10 - 80°, scan speed of 10 °/min, and sampling point of 0.02°. This characterization was done to observe the crystallite size and crystalline phase of the generated particles. Furthermore, the morphology of the powder was also analyzed by scanning electron microscopy (SEM, FlexSEM1000, Hitachi High Technologies). The particle size distribution was measured by sampling a few hundreds of the particles using ImageJ software.

Photocatalytic activity of ZnO-Ag was finally estimated to measure the performance of the produced particles for the degradation of MB (Sigma-aldrich, C.I.52015) aqueous solution under UV light (220 V, 10 W) and sunlight irradiation. The intensity of the sunlight was periodically monitored by intensity meter. For photocatalytic test, 10 mg of particles was put in to 40 ml of MB solution and was stirred for 30 minutes in a dark condition to obtain an adsorption-desorption equilibrium. Afterwards the solution was exposed to either UV or sunlight for 210 min. 4 ml of the sample was taken with an interval of 30 min and then centrifuged. UV-VIS spectrophotometry (Thermo Scientific Genesys 10s) was used to determine the concentration of MB before and after irradiation with the wavelength of 664 nm. The percent MB degradation efficiency under both irradiations was calculated by using the following equation [17]:

\[
\text{Degradation} = \frac{C_0 - C_t}{C_0} \times 100\% 
\]

\( C_0 \) and \( C_t \) represents the concentration of MB before and after \( t \) irradiation. Whereas, the rate constant \( (k) \) of MB degradation is governed by the pseudo-first-order Langmuir-Hinshelwood kinetics [18]

\[
C_t = C_0 e^{kt} \text{ or } -\ln(C_t/C_0) = kt \tag{2}
\]

By plotting the \(-\ln(C_t/C_0)\) versus time, the value of \( k \) can be obtained by the slope of the fitted line.
3. Results and discussion

3.1. SEM analysis

The SEM analysis results of ZnO-Ag with different Ag loadings are shown in Figure 2. The morphology of the produced particles was observed as a spherical shape. It can also be observed that more agglomeration of particles occurred for the pristine ZnO in comparison with the additional of Ag particles to the ZnO. The agglomeration of particle can be diminished by increasing the Ag loading. Interestingly, the shape of the particles remains as spherical shape even as the Ag loading increased. The resulting tendency of this research is in a coincident according to the research by Liu et al. [5]. The agglomeration of particles is due to their magnetic dipoles interaction with each other [19].

![SEM images of the ZnO-Ag particles, showing the top views, with different Ag loading at: (a) 0%, (b) 0.01%, (c) 0.1%, (d) 1%, (e) 5%, and (f) 20%.](image)

Figure 3 shows the particle size distributions of the ZnO and ZnO-Ag particles at different Ag loading. The particle size distribution was estimated using ImageJ software by measuring several hundreds of samples from the particle images. The size of ZnO-Ag particles decreased when Ag loading increased. The particle size obtained for ZnO, ZnO-Ag 0.01%, 0.1%, 1%, 5%, and 20% were 6462 nm, 6292 nm, 3344 nm, 2509 nm, 1029 nm, and 943 nm, respectively. In our previous study using peristaltic pump for controlling the volume of precursor (the volume was kept constant), the particle size distribution was reported in range of 40-70 nm [16]. If we compare the particle size distribution of these results with our previous study, it seems that the particle size in this study is much greater as much as twenty to one hundred times. It can be simply concluded that the agglomeration can be diminished by controlling the volume of the precursor. By controlling the volume, we believe that the concentration of the precursor inside the nebulizer can also be kept constant in resulting the homogeneous droplets size produced by the nebulizer. In contrast, the concentration of precursor inside the nebulizer will change time by time due to the droplet generation. The concentration of precursor became more concentrated with the increase of time, and the droplet size will vary every time. These phenomena can be used as explanation why the agglomeration occurred in this study. Previous studies also reported that a high concentration of the precursor can result in a heterogeneous higher particle diameter and local aggregation of Ag particle [1, 20].
3.2. XRD analysis

X-ray diffraction (XRD) pattern was recorded to determine the crystallite size and crystalline phase of ZnO-Ag particles, and the results can be seen in the Figure 4 including the Joint Committee on Powder Diffraction Standards (JCPDS) of the ZnO (JCPDS card No. 36-1451) and Ag (JCPDS card No. 04-0783). The peaks at 31.78°, 34.39°, 36.25°, 47.50°, 56.6°, 62.84°, and 68.09° can be observed for the pristine ZnO. All these peaks are match with the peaks from JCPDS of ZnO with the plane orientations in sequence are (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), and (1 1 2), respectively. It indicates that the ZnO was successfully synthesized by flame pyrolysis. Moreover, the detected peaks are similar to the ZnO phase with the wurtzite hexagonal crystal structure, which is the most thermodynamically stable phase for ZnO.

Figure 4 also shows that the existence of Ag particles in the ZnO cannot be detected when the Ag loading was less than 5 %wt, indicated by the disappearance of Ag peaks at 38° and 44°. This may be due to the small amount of Ag loading in the particle. Interestingly, eight peaks can be seen when Ag loading was greater or equal to 5 %wt at 31.84°, 34.39°, 36.23°, 38.0°, 47.65°, 56.66°, 62.99°, 68.04° and 75.87°. These peaks can be assigned to the presence of Ag particles at 38.0° with plane orientation of (1 1 1). The crystal structure of Ag was face-centered cubic (FCC).

The mean crystallite size of particles (D) was determined using the Scherrer equation [16].

$$D = \frac{k \lambda}{B \cos \theta}$$  \hspace{1cm} (3)

Here, k is the constants, where the value of k is 0.94, \(\lambda\) is CuK\(\alpha\) radiation source (\(\lambda\)) is = 0.15418 nm, B is full-width at half-maximum (FWHM) suitable to XRD peaks, and \(\theta\) (theta) is a half the angle of the peak. Based on the estimation using Eq. (3), the crystallite size of ZnO-Ag with different Ag loading at 0.01%, 0.1%, 0.2%, 1%, 5%, and 20% were 35.84, 28.66, 13.85, 23.49, 29.98, 24.24, and 31.13 nm, respectively. The average crystallite size (D) for the pristine ZnO was greater than ZnO-Ag particles, because ZnO particles had a tendency to agglomerate. This tendency is similar with the particle size distribution based on the SEM images. This is because particles would lower surface

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Figure 3. Particle size distribution of the ZnO-Ag particles with different Ag loading at: (a) 0%, (b) 0.01%, (c) 0.1%, (d) 1%, (e) 5%, and (f) 20%.
energy due to the large ratio of surface area to volume. In addition, the magnetic characteristic of ZnO particles tends to be attractive, thus making aggregation due to magnetic dipole interactions between particles. If we compare these results with our previous study, the crystallite size in this study is slightly greater than that of previous study (3-9 nm).

![XRD spectra of ZnO-Ag with different Ag loadings ranging from 0.01% to 20% including the pristine ZnO.](image)

**Figure 4.** The XRD spectra of ZnO-Ag with different Ag loadings ranging from 0.01% to 20% including the pristine ZnO.

### 3.3. Photocatalytic activity

Photocatalytic activity of the ZnO-Ag composite irradiated by sunlight and UV light are shown in Figures 5 and 6. It can be observed from Figure 5 that the degradation of MB solution increased with an increase of irradiation time and Ag loading. However, as the concentration of Ag exceed 5% the degradation efficiency decreased. These results are in a good agreement with the result reported by Xie et al [21], where there is an optimum concentration of dopant for obtaining the best performance of photocatalytic activity. Addition of dopant greater than the optimum condition will cause a decrease of the degradation rate. It is also an agreement with Elsellami et al [22], where higher mass percentage can decrease the degradation rate because the Ag doping can prevent light penetration to the photocatalyst. Kusdianto et al [16] reported that the most excellent photocatalytic performance was obtained when the Ag loading was 5% wt under UV irradiation, where % degradation of MB reached up to 65%. In this study, the highest degradation efficiency of MB under UV light and sunlight irradiations was obtained at 57% and 99% after 210 minutes of irradiation, respectively. It can be concluded that % degradation of MB in this study is lower than that of reported by our previous study. This can be attributed due to the produced particles in this study was much bigger than the previous one, resulting in the decrease of surface area. Thus, reducing the contact between catalyst particles and MB. Figure 6 also shows that the efficiency of MB degradation after irradiation with sunlight is higher than that of UV irradiation, it is due to the localized surface plasmon resonance (LSPR) of metallic Ag in the ZnO-Ag particles system [23]. Estimation of the rate constant for the photocatalytic activity were found by the determination of the slope from Figures 6 (a) and (b). It shows that the photocatalytic activity at Ag 5% wt was the most effective among other conditions.
The mechanism of photocatalytic activity with different Ag loading have been explained details in our previous study [16]. In this study, however, we try to propose the different mechanism of photocatalytic activity under UV and sunlight irradiations. Generally, degradation of MB is an oxidative process which is illustrated in Figure 7. UV and sun light irradiations may have different roles for ZnO and Ag particles in the electron-hole pair generation, transport, and separation in the particle [5]. Figure 7 (a) illustrates how the catalyst material induced by UV light with a higher energy than the band gap energy of ZnO. The photon energy from UV light excites the electron (e-) from the valance band (VB) of ZnO to the conduction band (CB) and generates a hole (h+). For the ZnO-Ag particles, the generated electrons were attracted to the Ag particles, where electron recombination was inhibited due to the fermi energy level of the ZnO-Ag. The generated holes can interact with water or hydroxyl group resulting in hydroxyl radical species that can interact with the pollutant to degrade the MB solution. While, the different mechanism after irradiation with sunlight is depicted in Figure 7(b). It can be seen that the Ag particles were also photoinduced and cause the electrons to be excited. These electrons can adsorb oxygen molecules and generates superoxide radical anions (O_{2}^{-}). The superoxide radicals are also able to degrade the MB solution [5, 24].
**Figure 7.** Schematic illustration of photocatalytic mechanism of ZnO-Ag particles under (a) UV and (b) visible light irradiations.

**4. Conclusions**

The ZnO-Ag composite materials have been successfully synthesized by one step process using flame pyrolysis. The effect of Ag loading in the particles on the photocatalytic activity were investigated by exposing them to UV and sunlight irradiations. The SEM analyses confirmed the formation of ZnO-Ag particles with a spherical shape. In the absence of Ag particles, the produced particles showed more agglomeration. The addition of Ag particles decreased the agglomeration of particles. The particle size distribution in this study was much bigger than the previous study where peristaltic pump was used for controlling the volume of precursor. In this study, particle size decreased with increasing Ag loading. XRD results showed the phase structure of the produced ZnO was wurtzite hexagonal. The crystallite size of the particles showed no significant difference. The presence of Ag particles can be identified by XRD when the Ag loading was higher or equal to 5 %wt.

Photocatalytic activity of the particles was evaluated by measuring the degradation efficiency of methylene blue under UV and sun light irradiations. ZnO-Ag particles was found to be a better photocatalyst than that of the pristine ZnO. The best photocatalytic activity for the particles was obtained at 5 %wt Ag loading. The degradation efficiency of ZnO-Ag under UV light irradiation was lower than sunlight irradiation. The degradation of MB reached 56% under UV light irradiation, while it can attain up to 99 % with sunlight after 210 min of irradiation. These results indicate that most of the MB can be degraded by the ZnO-Ag particles.

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