Ag/ZnO photocatalyst for photodegradation of methylene blue

Ni Putu Diantariani1,a, Endang Tri Wahyuni2b, Indriana Kartini2, Agus Kuncaka2

1 Department of Chemistry, Faculty of Mathematics and Natural Science, Udayana University, Bali, Indonesia
2 Department of Chemistry, Faculty of Mathematics and Natural Science, Gadjah Mada University, Yogyakarta, Indonesia
Email: a putu_diantariani@unud.ac.id, b endang_triw@ugm.ac.id

Abstract. Ag/ZnO photocatalysts have been prepared through a coprecipitation method with different Ag loadings. The photocatalysts were characterized by XRD, SEM, XRF, and DRS UV-vis methods. The Ag loadings (1.7–4.4%) slightly decrease the ZnO crystal size from 27.9 to 25.6 nm. There is no effect of Ag loadings on the morphology of photocatalysts that have clustered spherical shape. The Diffuse Reflectance spectra showed the pure ZnO and Ag/ZnO photocatalysts have no significant difference in absorption in UV region, but rise of Ag loading increase the absorption in visible region. Photodegradation of 20 ppm methylene blue (MB) solution was used to evaluate the performance of Ag/ZnO photocatalysts on UV, visible and dark and was compared to pure ZnO. Loading Ag (1.7%) can enhance the photocatalytic activity of photocatalyst, however the excessive of Ag concentration (3.4 and 4.4%) on photocatalysts tend to decrease of photocatalytic activity.

Keywords: Ag/ZnO photocatalyst; methylene blue; photodegradation

1. Introduction
Wastewater contaminated with residual textile dyes has become an important issue especially in third world countries because of its hardly degradation. The photodegradation method using photocatalyst is very potential to decompose textile dyes into simpler and less toxic compounds.

Besides TiO2, ZnO has a great potential to be developed as high performance photocatalyst because it has various advantages such as having a wide direct band gap of 3.37 eV, a large exciton binding energy (60 meV)[1] and high photocatalytic activity[2]. However, ZnO has disadvantage, i.e. the electron-hole photogeneration produced by UV irradiation on ZnO is easy to recombine and it will reduce the photocatalytic activity. Nobel metal particles can improve the photocatalytic performance of ZnO by inhibiting recombination of electron-hole pairs. Schottky barrier in the metal-semiconductor interface can effectively separate electrons-hole because the precious metal can act as an electron sinks [3, 4]. In addition, noble metal extend the photo response of ZnO toward the visible light region [5, 6]. Among all noble metals, silver is the most potential to increase the degradation activity of ZnO and its lowest cost. Modification of ZnO using Ag enhance the photocatalytic activity in UV and visible condition.

The Ag/ZnO photocatalyst can be prepared by several methods such as hybrid induction and laser heating [7], flame spray pyrolysis [8], coprecipitation [9], sol-gel [10], microwave [5], and photo reduction [6]. In this study, the photocatalysts were prepared by coprecipitation method because it was easy, simple and resulted small and uniform particle size [9]. Coprecipitation is the simultaneous
precipitation of more than one compound from a solution. The Ag/ZnO photocatalysts in this research were prepared using a mixture precursor (silver nitrate and zinc nitrate) reacted with sodium carbonate that resulted zinc carbonate and silver carbonate precipitates. After calcination, the mixture carbonate precipitates formed Ag/ZnO. This result characterized using XRD, SEM-EDS, XRF and DRS UV-Vis. The aim of the present work is to characterize Ag/ZnO photocatalysts with various Ag concentration and tested its photocatalytic activity towards methylene blue (MB) under UV and visible condition.

2. Materials and Methods
Silver nitrate (AgNO₃), zinc nitrate tetra hydrate (Zn(NO₃)₂·4H₂O) and sodium carbonate (Na₂CO₃) were analytical grade, purchased from Merck company and used without further purification. Double distilled water was utilized in all experiments.

X-ray diffraction pattern of the samples were recorded using X-ray diffractometer (XRD-6000 Shimadzu) with Cu Kα radiation (λ=1.5406 Å) under the conditions of 40 kV and 30 mA. X-ray diffraction (XRD) pattern were recorded between 3° and 80° 2θ at scan speed of 5°minute⁻¹ giving a step size of 0.02 and step time of 0.24 s. Scanning Electron Microscope (SEM; PEI Inspect 550) equipped with Energy Dispersive X-ray Spectroscopy (EDS) was used to capture SEM image for observing the sample morphology and it was operated at an acceleration voltage 20 kV. The composition of synthesized powders was analysed by x-ray fluorescence (XRF; PANalytical tipe Minipal 4). UV-Vis diffuse reflectance spectra (UV-vis DRS) were recorded in wavelength range of 200-800 nm using a Shimadzu UV–2450 spectrophotometer. The degradation extent was monitored by Thermo Scientific Evolution 201 UV-vis Spectrophotometer.

2.1. Synthesis of Ag/ZnO photocatalysts
Ag/ZnO photocatalysts were produced by coprecipitation method. In synthesis process, 50 mmol of Zn(NO₃)₂·4H₂O and (0 mmol; 0.77 mmol; 1.57 mmol; and 2.34 mmol) of AgNO₃ were dissolved with 50 mL of bidistillated water respectively and homogenized. Then 125 mL 0.5 M Na₂CO₃ was poured drop-wise into the mixture and the reaction was done under vigorous stirring at room for 15 minutes. The formed precipitate was filtered and washed several times with bidistillated water and dried up in oven at temperature 110°C. The precipitates were powdered and sieved with 200 mesh sieve. The powders were calcined at 400°C for 4 hours to form Ag/ZnO photocatalysts.

2.2. Photocatalytic activity
Photodegradation experiments were performed in a photocatalytic reactor. The reactor consisted of three Sankyo Denki G20T10 UV-C lamp for UV reactor, three Philips TLD 18W/54-765 lamp for visible reactor, stirrer and 12 glass vessels with 50 mL capacity. The vessels were filled with 20 mL of 20 ppm MB and 20 mg of photocatalyst. The suspension was stirred during photodegradation reaction for 4 hours. When the reaction was finished, the remains MB was analysed by using a UV-Vis spectrophotometer 1800 Shimadzu at wavelength of 663 nm to determine percentage of photodegradation.

3. Results and Discussions
3.1. Crystallography and Morphology of Ag/ZnO photocatalysts
Fig. 1 shows XRD patterns of pure ZnO and Ag/ZnO photocatalysts with different Ag contents (1.7-4.4%). All powders exhibit the typical pattern of hexagonal Wurtzite structure for ZnO (JCPDS File No. 36-1451). It was showed by sharp diffraction peaks at 20 31.8°, 34.4°, 36.3°, 47.6°, 56.7°, 62.9°, 68.0° and 69.2°. The (Ag(3.4%)/ZnO and (Ag(4.4%)/ZnO showed a series of diffraction peaks at 20 38.1°, 44.3° and 64.5° which are assigned to the silver nanoparticle with face center cubic (fcc) structure (JCPDS File No. 04-0783). The peak intensity of Ag slightly increases with the Ag loading increase for the Ag/ZnO photocatalyst. Meanwhile, the Ag's typical peak does not appear in the XRD pattern of Ag(1.7%)/ZnO because of its small concentration in photocatalyst.
Figure 1. XRD pattern of (a) pure ZnO, (b) Ag(1.7%)/ZnO, (c) Ag(3.4%)/ZnO and (d) Ag(4.4%)/ZnO.

It is found that Ag loading in the Ag/ZnO photocatalyst causes the XRD peak position of ZnO shifts to a low 2θ angle. According to Bragg’s equation $n\lambda=2d\sin\theta$, the smaller sin $\theta$ value, the larger the d spacing. It is observed that the value of d increasing with increasing of Ag loading in Ag/ZnO photocatalysts. The enlargement of the XRD basal spacing (d) implies that Ag diffuse into the lattice of ZnO [11].

The crystallite size of the ZnO NPs and Ag NPs of the photocatalysts were calculated using the Scherrer equation (Eq. 1) [12]:

$$D = \frac{0.89\lambda}{\beta\cos\theta}$$  \hspace{1cm} (1)

where D is the crystallite size, $\lambda$ is the X-ray wavelength of 1.5406 Å, $\beta$ is the FWHM of the diffraction peaks (its conversion value to rad) and $\theta$ is Bragg diffraction angle. The crystallite size of ZnO NPs is found to be 26.7; 27.9; 27.4 and 25.6 nm for pure ZnO, Ag(1.7%)/ZnO, Ag(3.4%)/ZnO and Ag(4.4%)/ZnO, respectively. While crystallite size of Ag NPs is found 38.1 nm and 36.9 nm for Ag(3.4%)/ZnO and Ag(4.4%)/ZnO respectively. The ZnO and Ag crystallite size slightly decrease by increasing Ag concentration in photocatalysts.

The morphologies of pure ZnO and Ag/ZnO photocatalysts were investigated by using Scanning Electron Microscope (SEM). Fig. 2 (a-d) shows the SEM image of pure ZnO, Ag(1.7%)/ZnO, Ag(3.4%)/ZnO and Ag(4.4%)/ZnO respectively. There is no effect of Ag loadings on the morphology of photocatalysts. All photocatalysts showed the same morphology shape, which is clustered spherical. It appears from SEM image that the Ag(4.4%)/ZnO photocatalyst has the smallest particles size, as also showed by XRD data.
Figure 2. SEM images of (a) pure ZnO, (b) Ag(1.7%)/ZnO, (c) Ag(3.4%)/ZnO and (d) Ag(4.4%)/ZnO.

Energy Dispersive X-ray Spectroscopy (EDS) analysis (Fig. 3) confirms that the Ag/ZnO photocatalysts only consists zinc, silver and oxygen. The composition of element in photocatalysts were also determined by using X-ray Fluorescence. The percentage of Ag of photocatalysts increase with increasing the mmol of AgNO$_3$ precursor reacted in synthesis process. The percentage of Ag on photocatalysts synthesized by reacted 50 mmol of Zn (NO$_3$)$_2$.4H$_2$O and (0.77 mmol; 1.57 mmol; and 2.34 mmol) of AgNO$_3$ were 1.7, 3.4, and 4.4 % respectively.

Figure 3. EDS spectrum of Ag/ZnO photocatalysts.
3.2. Optical properties of Ag/ZnO photocatalysts

The UV-vis diffuse reflectance spectra were measured to examine the light absorption properties of the samples in UV and visible region (200-800 nm) and to determine its band gap energy. The UV-vis diffuse reflectance spectra of pure ZnO and Ag/ZnO photocatalysts are displayed in Fig. 4. Silver loading on ZnO is observed to shift the absorption edge to a longer wavelength, i.e. from 407 nm (pure ZnO) to 410-421 nm (Ag/ZnO). This absorption wavelength allows the Ag/ZnO catalysts to be active in the visible region. The absorption shift may be resulted by the diffusion of the metallic silver into the crystal lattice of the semiconductor structure that the silver to be dispersed or inserted between the conduction and valence bands of the host material. The shift increases with the increasing Ag amount in ZnO because more Ag inserted into the gap so that the gap becomes narrower than that of pure ZnO, shifting in the absorption wavelength to increase [11].

![Figure 4. DR spectra of (a) pure ZnO, (b) Ag(1.7%)/ZnO, (c) Ag(3.4%)/ZnO and (d) Ag(4.4%)/ZnO.](image)

The band gap energy of photocatalysts determined based on its adsorption edge wavelength according to equation $E_g = \frac{1239}{\lambda}$ nm. The band gap energy of pure ZnO and Ag/ZnO photocatalyst are displayed in table 1. The shift of absorption edge of photocatalyst to a longer wavelength with Ag loading resulted smaller band gap energy. Therefore, increasing of Ag loading in Ag/ZnO photocatalyst gradually decreased the value of band gap energy.

| Photocatalyst   | Adsorption wavelength (nm) | Band gap energy (eV) |
|-----------------|---------------------------|----------------------|
| pure ZnO       | 407                       | 3.05                 |
| Ag(1.7%)/ZnO   | 410                       | 3.02                 |
| Ag(3.4%)/ZnO   | 416                       | 2.98                 |
| Ag(4.4%)/ZnO   | 421                       | 2.94                 |
3.3. Photodegradation testing

The photocatalytic activity of photocatalyst was evaluated by photodegradation of MB. Fig. 5 shows the percentage of photodegradation of MB by different sample over the same periods of time under UV light, visible light and dark condition.

![Figure 5. Percentage of photodegradation of MB (a) without photocatalyst, (b) pure ZnO, (c) Ag(1.7%)/ZnO, (d) Ag(3.4%)/ZnO and (e) Ag(4.4%)/ZnO photocatalysts under UV light, visible light and dark condition.]

In general, the addition of photocatalysts increases the percentage of MB degraded under UV and visible radiation. Reactive oxygen species, which are superoxide radical (·O$_2^-$) and hydroxy radical (·OH) that is formed when photocatalysts are irradiated with UV or visible light play a role in degrading MB [13]. Thus the percentage of photodegradation MB increases with the addition of photocatalysts. However, the percentage of photodegradation under UV radiation was twice as high as visible radiation. The little decrease of $E_g$ with loading of Ag on ZnO photocatalyst give a contribution to the low of photodegradation activity under visible irradiation. In addition, photodegradation activity in dark conditions also increases with the addition of photocatalysts. This is caused by the adsorption of MB by photocatalysts. The adsorption capability possessed by photocatalysts plays an important role to increase the concentration of dyes around photocatalyst particles to accelerate and increase its photocatalytic activity.

The Ag loading in ZnO photocatalysts increase the percentage of photodegradation both in the UV and the visible light region. This was because Ag NPs has a lower energy level compared to ZnO NPs so that the electrons in the conduction band of ZnO can move to Ag nanoparticles. Ag NPs in this case act as electron sinks that can trap the photogeneration electrons from semiconductor thereby increasing the efficiency of electrons-holes photogeneration separation and resulting the increasing of photocatalytic activity of ZnO. Loading Ag NPs on ZnO semiconductor can overcome the weakness of the photocatalyst that is caused by easy recombination of electron-hole photogenerated. Recombination of these electron-hole pairs certainly reduced the formation of hydroxy radicals that has function to degrade the pollutants and finally will reduce the photocatalytic activity of photocatalyst [5, 14]. Loading Ag NPs on photocatalysts enhance the photocatalytic activity from 93.56% (pure ZnO) to 98.38% (Ag(1.7%)/ZnO) under the UV irradiation and from 43.04 (pure ZnO) to 48.60% (Ag(1.7%)/ZnO) under the visible irradiation. The enhance in the percentage of photodegradation of MB by Ag loading in the visible region was also caused by an increase in the intensity of the visible light absorption as shown in Fig. 4. However, although there is an increase of intensity of the visible
light absorption on Ag(3.4%)/ZnO and Ag(4.4%)/ZnO, the photodegradation activity tend to decrease. A possible reason is that the Ag NPs also act as recombination centres at high Ag concentration in Ag/ZnO photocatalyst [3]. Thus the excessive loading of Ag on Ag/ZnO photocatalyst cause reduction of oxygen radical forming so that the photocatalytic activity decrease. This reduction of photodegradation MB with the excessive loading of Ag occurs both under UV and visible irradiation condition.

4. Conclusions
Ag/ZnO photocatalysts with different Ag loadings have been successfully prepared by coprecipitation method. An appropriate amount of Ag loading enhances the photocatalytic activity of ZnO photocatalyst under UV and visible light radiation. Ag/ZnO photocatalyst has a potential for MB degradation due to its easy to synthesize and good photocatalytic performance under UV and visible irradiation.

Acknowledgement
The authors thank the University of Gadjah Mada for providing the research facilities, and the Directorate General of Higher Education for funding this research.

References
[1] Andrade G R, Nascimento C C, Júnior E C S, Mendes D T and Gimenez I F 2017 ZnO/Au nanocatalysts for enhanced decolorization of an azo dye under solar, UV-A and dark conditions J. Alloys Compd. 710 557-66
[2] Sakthivel S, Neppolian B, Shankar M, Arabinndoo B, Palanichamy M and Murugesan V 2003 Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO2 Sol. Energy Mater. Sol. Cells 77 1 65-82
[3] Divband B, Khatamian M, Eslamian G K and Darbandi M 2013 Synthesis of Ag/ZnO nanostructures by different methods and investigation of their photocatalytic efficiency for 4-nitrophenol degradation Appl. Surf. Sci. 284 80-6
[4] Xu F, Yuan Y, Wu D, Zhao M, Gao Z and Jiang K 2013 Synthesis of ZnO/Ag/graphene composite and its enhanced photocatalytic efficiency Mater. Res. Bull. 48 6 2066-70
[5] Liu H, Hu Y, Zhang Z, Liu X, Jia H and Xu B 2015 Synthesis of spherical Ag/ZnO heterostructural composites with excellent photocatalytic activity under visible light and UV irradiation Appl. Surf. Sci. 355 644-52
[6] Liu Y, Wei S and Gao W 2015 Ag/ZnO heterostructures and their photocatalytic activity under visible light: effect of reducing medium J. Hazard. Mater. 287 59-68
[7] Wang R, Xin J H, Yang Y, Liu H, Xu L and Hu J 2004 The characteristics and photocatalytic activities of silver doped ZnO nanocrystallites Appl. Surf. Sci. 227 1-4 312-7
[8] Height M J, Pratsinis S E, Mekasuwandumrong O and Praserthdam P 2006 Ag-ZnO catalysts for UV-photodegradation of methylene blue Appl. Catal. B, 63 3-4 305-12
[9] Jazi F S, Parvin N, Rabiei M, Tahiri M, Shabestari Z M and Azadmehr A R 2012 Effect of the synthesis route on the grain size and morphology of ZnO/Ag nanocomposite J. Ceram. Process. Res. 13 5 523-6
[10] Benhebal H, Chaib M, Salmon T, Geens J, Leonard A, Lambert S D, Crine M and Heinrichs B 2013 Photocatalytic degradation of phenol and benzoic acid using zinc oxide powders prepared by the sol–gel process Alexandria Eng. J. 52 3 517-23
[11] Wahyuni E T and Roto R 2018 Titanium Dioxide; Material for a Sustainable Environment, ed D Yang (London: IntechOpen Limited)
[12] Nezamzadeh-Ejhieh A and Khodabakhshi-Chermahini F 2014 Incorporated ZnO onto nano clinoptilolite particles as the active centers in the photodegradation of phenylhydrazine J. Ind. Eng. Chem. 20 2 695-704
[13] Kuriakose S, Choudhary V, Satpati B and Mohapatra S 2014 Facile synthesis of Ag–ZnO hybrid nanospindles for highly efficient photocatalytic degradation of methyl orange Phys. Chem.
[14] Trandafilović L V, Whiffen R K, Dimitrijević-Branković S, Stoiljković M, Luyt A S and Djoković V 2014 ZnO/Ag hybrid nanocubes in alginate biopolymer: synthesis and properties Chem. Eng. J. 253 341-9