SYNTHESIS OF DOUBLE LAYER THIN FILM ZnO/ZnO:Ag BY SOL-GEL METHOD FOR DIRECT BLUE 71 PHOTODEGRADATION

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Abstract

The objective of this paper is to synthesize and to characterize a single and a double layer (DL) ZnO and ZnO/ZnO:Ag thin films and their application for degradation of direct blue 71. DL thin films were deposited on a substrate glass by sol-gel spray coating technique. Amount of Ag doping (2, 4, 6 and 8 %mol) onto ZnO were studied. X-Ray Diffractometer (XRD) and UV-Vis spectrophotometer were used to analyze the structure and optical properties of thin films. Direct Blue 71 (DB71) was used for photocatalytic evaluation under UV light irradiation. XRD result showed that all prepared thin films have wurtzite structure crystall with dominant orientation peak was (002) plane. UV-Vis transmittance spectra showed decreasing transparency of films following the DL preparation and Ag doping concentration. By using envelope method, energy gap of films can be determined. ZnO/ZnO:Ag 6% (DL 6%) indicated the smallest energy gap 3.038 eV. The highest DB71 degradation result under UV light irradiation was reached by DL 6% with 55.43% and 8.56 x 10^{-3} min^{-1} for photocatalytic efficiency and photodegradation rate, respectively.

Keywords: *band-gap energy; microstructure; photocatalyst; semiconductor; spray coating; transmittance;*

Abstrak

SINTESIS LAPISAN TIPIS DOUBLE LAYER ZnO/ZnO:Ag DENGAN METODE SOL-GEL UNTUK FOTODEGRADASI DIRECT BLUE 71. *Tujuan dari paper ini adalah untuk menginformasikan sintesis dan karakterisasi lapisan tipis single dan double layer (DL) ZnO dan ZnO/ZnO:Ag dan aplikasinya untuk degradasi direct blue 71 (DB71). Lapisan tipis DL dideposisi di tas substrat kaca dengan metode sol-gel teknik spray coating. Jumlah doping Ag divariasi (2, 4, 6, dan 8 %mol) dalam ZnO ini diteliti sifat mikrostruktur dan optiknya. X-ray diffractometer (XRD) digunakan untuk menganalisa mikrostruktur dan UV-Vis spectrophotometer digunakan untuk analisa sifat optik. DB71 digunakan untuk evaluasi kemampuan fotokatalitik dibawah iradiasi cahaya UV dari lapisan tipis hasil sintesis. Hasil uji XRD menunjukkan bahwa seluruh lapisan tipis hasil sintesis mempunyai struktur kristal wurtzite dengan puncak dominan pada bidang (002). Hasil uji UV-Vis menunjukkan bahwa spektrum transmitansi dari lapisan semakin menurun dengan kenaikan konsentrasi doping Ag. Dengan menggunakan metode envelope, celah pita energi dapat ditentukan. DL 6% menunjukkan celah pita energi terkecil yaitu sebesar 3,038 eV. Kemampuan degradasi DB71 tertinggi dicapai oleh sampel lapisan tipis DL 6% dengan efisiensi degradasi sebesar 54,43% dan laju fotodegradasi sebesar 8,56 x 10^{-3} min^{-1}.*

Kata kunci: *celah pita energi; mikrostruktur; fotokatalis; semikonduktor; spray coating; transmitansi;*

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INTRODUCTION

Textile industry such as Batik (traditional cloth from Indonesia) does not only affect to economics development, but also has consequence in environmental problem, especially if its waste water is not treated before discharge into the environment. The waste water generally consists of dye stuff that is hardly degraded. Among these stuffs, Direct Blue 71 (DB71) is considered as the most toxic and hardest degraded (Boumaza *et al.,* 2014; Bulut *et al.,* 2007; Saien *et al.,* 2009).

The application of pretreatment method is required to reduce the toxicity content of this waste. Besides using biological treatment, physical treatment has advantage in long life cycle and relatively fast process. One of the methods is by using photocatallytic process. Photocatalytic process is a degradation method for pollutant by using oxidation process over photocatalyst material such as TiO_2, Ag-ZnO, WO_3. To improve the oxidation process, the selection of photocatalyst material is very important (Al-areqi *et al.,* 2014; Khoa *et al.,* 2012; Chen *et al.,* 2010). The materials produce electrons and holes on conduction band and valence band. The electrons and holes then produce hidroxyl and superoxide ions that effectively will decompose the organic compound.

Zinc Oxide (ZnO) is photocatalyst semiconductor II-VI group with wide direct band-gap (3.3 eV) and highest binding free excitation energy (60 meV) (Poongodi *et al.,* 2015; Nair *et al.,* 2011). ZnO was abundant, low cost and harmless to environment (Lam *et al.,* 2012). Several study showed the effectiveness of ZnO is higher than TiO_2 in azo dye stuff photodegradation application (Sakthivel *et al.,* 2003). Although photocatayst material in powder form is much more efficient, but it has disadvantages due to separation difficulties and require more time for centrifugation and filtration (Bagheri *et al.,* 2014; Sariouglu *et al.,* 2005). Therefore, the implementation of using thin film is proposed. Several methods to synthesize ZnO thin films usually use pulsed laser deposition (PLD) (Tarwal *et al.,* 2011), spray pyrolysis (Vijayalakshmi *et al.,* 2008), metal oxide chemical vapour deposition (MOCVD) (Biethan *et al.,* 2012) and sol-gel (Sutanto *et al.,* 2014). Among them, sol-gel spray coating become the best option because it is easy and economically low cost. The improvement of photocatalytic efficiency has been proposed such as introducing Ag doping into semiconductor (Gouvea *et al.,* 2002; Sutanto *et al.,* 2015). Li *et al.* (2014) showed that double layer semiconductor could also increase the photocatalytic efficiencies. The objective of this paper were to synthesize and to characterize the double layer thin film ZnO/ZnO:Ag prepared by sol-gel spray coating method. The double layer thin film of ZnO/ZnO:Ag was applied to degrade the pollutant in dyes textile industry especially DB71.

Experimental

Material

Zinc Acetate dehydrate ($Zn.(COOCH_3)_2.2H_2O$), 2-propanol (IPA) and Monoethanolamine (MEA) were used to synthesize ZnO precursor. Silver acetate (CH_3COOAg) was used as Ag source. Substrate glass for deposition was cleaned using acetone, methanol and de-ionized (DI) water. All chemical was supplied from Merck Germany, except silver acetate from Sigma Aldrich, Swiss. Direct blue 71 (DB71) was triazodirect dye with chemical structure showed in Figure 1 (molecule wieght : 1029,86 g/mol, C.I. No: 34140, λ_{max} = 584 nm). It was purchased from local dye shop "Jerman" Pekalongan, Indonesia.

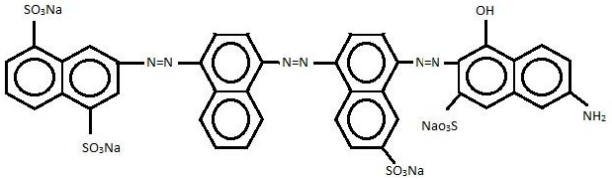


Figure 1. Chemical structure of Direct Blue 71 (DB71)

Preparatin of double layer thin film ZnO/ZnO:Ag

Zinc Acetate was dissolved in 2-propanol (IPA) with solution concentration of 0.5 M. The solution stirred for 30 minutes at room temperature. MEA was added into the solution at mol ratio of 1:1 and stirred again for 30 minutes until a clear solution is obtained. In order to make Ag doping by adding CH_3COOAg into solution and stirred for next 30 minutes. Doping variation was adjusted for 2, 4, 6 and 8 % mol. The *sol-gel* precursor was sprayed to glass substrate with temperature 450^oC and allowed for an hour. For *single layer* only ZnO solution was sprayed, while *double layer* ZnO:Ag solution was sprayed after ZnO layer. The prepared thin film was characterized by using Shimadzu XRD 6100/7000 for structure analyzis and mini UV-Vis Shimadzu 1240 SA for optical measurement.

Photocatalytic activity measurements

DB71 10 mg/L solution was made by dilution in water. The dye solution was poured into the box with volume 40 mL for each sample. The samples were labeled with no photocatalyst, ZnO, ZnO/ZnO:Ag (DL 2, 4, 6, and 8 %). 10 Watt UV lamp was used as photon source. The dye solution was sampled every 15 minutes up to 90 minutes. Photocatalytic eficiency (E_f) was calculated by using this equation :

$$E_f(\%) = \left(1 - \frac{C_t}{C_0}\right) x100\% \qquad (1)$$

where C_0 and C_t were initial concentration and final concentration of dye solution.

RESULTS AND DISCUSSION

Structure Analysis

XRD pattern of ZnO pure, ZnO:Ag and DL were showed in Figure 2. There are three main peaks

in 2θ = 31.72°, 34.42° and 36.22° which show lattice orientation (100), (002) and (101), respectively. Figure 2 also showed that ZnO on the thin films surface have wurtzite structure matched with JCPDS No. #361451.

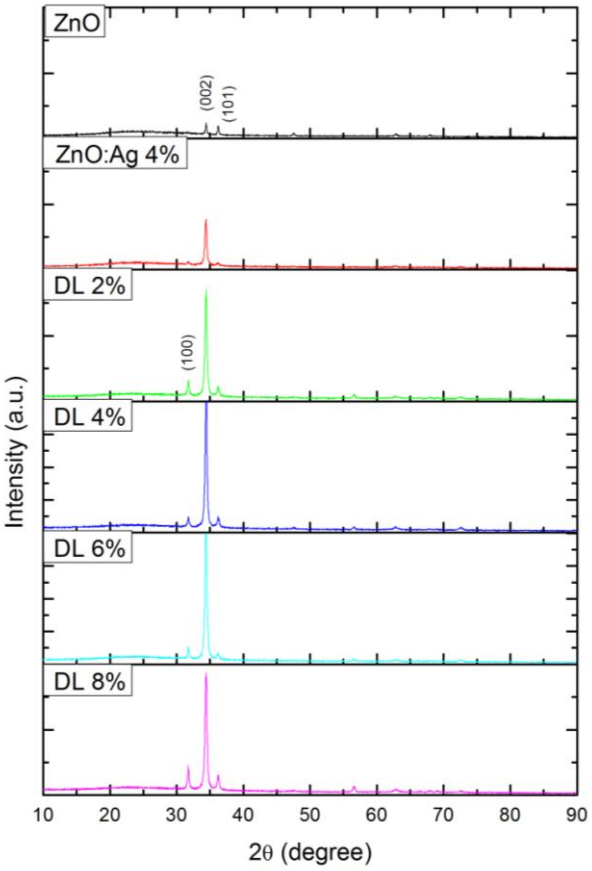


Figure 2. XRD spectra of ZnO, ZnO:Ag 4% and DL (2%, 4%,6%and 8%) thin films

In the ZnO film, the obtained polycrystalline structure. Only two dominant peaks on (002) and (101) orientation, meanwhile (100) did not appear. These both of peaks were shortest than other prepared thin films. The ZnO:Ag thin film has better crystalinity than ZnO film. It was seen by appearance among the three peaks,the (002) orientation shows the highest peak. In the XRD result, crystal quality on double layer thin film is better than single layer thin film.

There was enhancement of main peaks (002) in ZnO:Ag 4%, DL 2% and DL 4% films. Meanwhile, in DL 6% and DL 8%, the crystal quality decreases. It may be caused by replacement of Zn^{2+} ion (radius of 0.65 Å) by Ag^{+} ion (radius of 1.02 Å) obtained A_gZn ion (Xu *et al.*, 2015). The existance of Ag was confirmed by appearance of peak in 2 θ = 56,64° according to (103) orientation matched by

JCPDS No.#411402. The average crystallite size of ZnO was shown on Table 1. The size was calculated according to Scherrer equation on (002) peak:

$$d = \frac{0.89\,\lambda}{D\,cos\,\theta} \qquad (2)$$

where d, λ, D and θ were crystalite size, x-ray wavelength used (1.54016 Å), *Full Width at Half Maximum* (FWHM) and degree of peak, respectively. The crystallite size(grain size) of single layer decreases by introducing Ag from 24.88 nm became 20.04 nm in ZnO and ZnO:Ag 4%, respectively. In contrast, for double layer, the grain size of thin film increase by increasing Ag concentration from 19.64-22.01 nm and the highest grain size was reached by Ag doping of 4% mol.

Optical measurements

The prepared thin films showed that they have a fine and homogenous surface (Ilican *et al.*, 2007; Bhira *et al.*, 2000; George *et al.*, 1988). It was seen by fringes pattern on UV-Vis transmittance spectra in Figure 3. The fringes were caused by surface reflection without much absorption on bulk material (Manifacier *et al.*, 1976). Transmittance spectra showed that pure ZnO thin film has highest transparency about 91 %. Transparency decreased in the visible region by addition of Ag-4 % mol to 78% and decreased again in double layer thin film from 65% to 40% by increasing Ag. This decrease might be caused by scattering of grain boundary and visible light absorption of Ag nanoparticles (Tarwal *et al.*, 2011).

Figure 4 showed the absorbance spectra as a function of wavelength in the ZnO, ZnO:Ag and double layer thin films with doping variation. The ZnO thin film showed a sharp absorption at wavelength below 380 nm and after the addition Ag, both single and double layer absorption shifted to higher wavelength (lower energy). It showed that the addition of Ag shifted the absorption ZnO spectra. Previously studies (Karyoui *et al.*, 2015; Chen *et al.*, 2013; Bahnemann, 2004) reported that the appropriate wavelength absorption by ZnO will increase electron transfered from valence band to conduction band. The generated holes were very important for formation of hydroxyl radicals that are used for degradation of pollutants. Absorbance spectra wavelength shifted toward to visible light (red shift) by increasing Ag on single or double layer. It was seen that double layer 6% thin film shifted toward to visible light more dominant than others. That means double layer 6% could absorb larger wavelength spectrum or smaller photon energy. It was so important in photocatalytic application, since visible light responsive photocatalyst was more interesting studies by researchers in this field.

Table 1. The crystallite size of ZnO on (002) plane

Films	FWHM (θ)	FWHM (rad)	d (nm)	a (Å)	c (Å)
ZnO	0.3305	0.0058	24.88	3.0068	5.2079
ZnO:Ag 4%	0.4103	0.0072	20.04	3.0094	5.2124
DL 2%	0.4187	0.0073	19.64	3.0077	5.2095
DL 4%	0.3737	0.0065	22.01	3.0065	5.2074
DL 6%	0.4157	0.0073	19.78	3.0079	5.2098
DL 8%	0.4099	0.0072	20.06	3.0077	5.2094

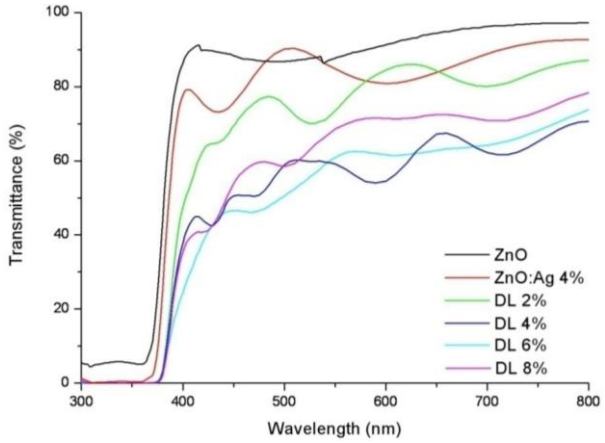


Figure 3. UV-Vis transmittance spectra with various prepared films.

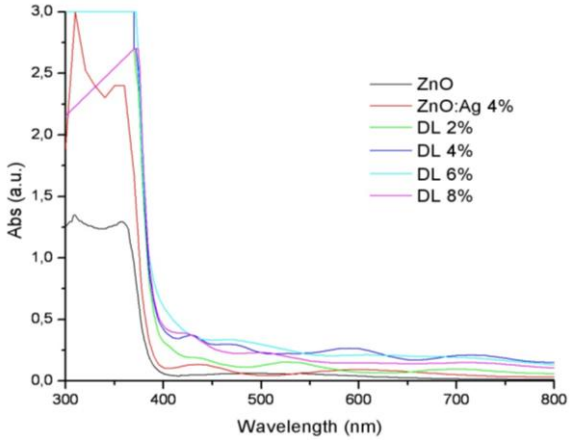


Figure 4. Absorbance spectra with various prepared films

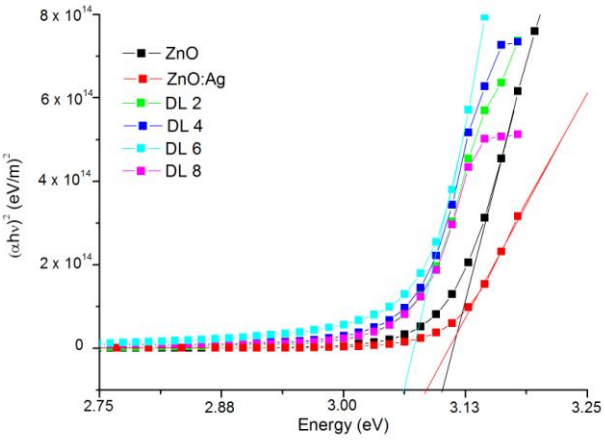


Figure 5. Optical band-gap energy of prepared thin films

In order to calculate direct band-gap of semiconductor, the absorption coefficient and band-gap follow the equation :

$$(\alpha\, h\nu)^2 = B\left(h\nu - E_g\right) \qquad (3)$$

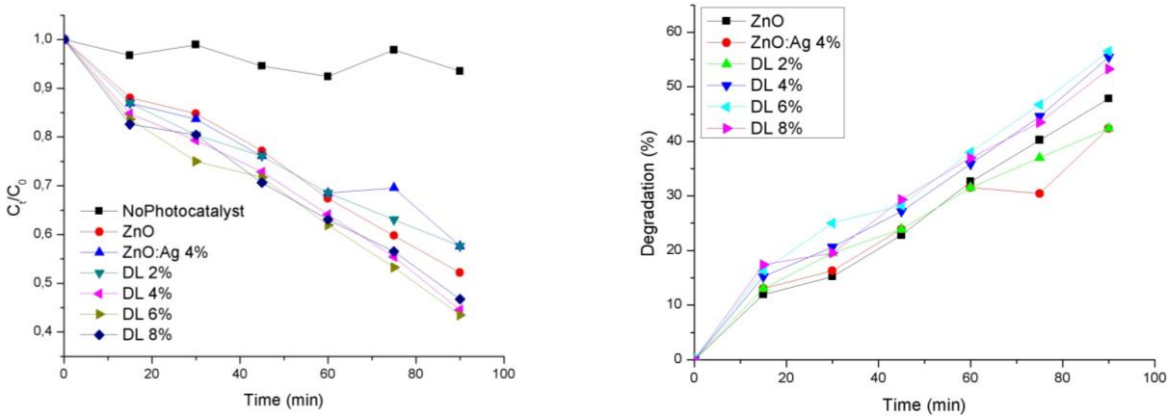
where α is absoption coefficient, hν is photon energy, B is constant and Eg is optical band-gap energy. If a plot $(\alpha h\nu)^2$ ~ hν, Eg can be obtained by linear extrapolation on the curve $(\alpha h\nu)^2 = 0$. The plot of energy of all prepared thin films was shown in Figure 5. The absorption coefficient α follows the equation :

$$\alpha(v) = 2.303\frac{A}{t} \qquad (4)$$

where A is optic absorbance and t is thickness of film. Optical band-gap energy of ZnO film was obtained about 3.103 eV smaller than the result was obtained by Tarwal *et al.* (2011). For Ag doping thin film on single and double layer, the band-gap were about 3.038 – 3.081 eV. Band-gap decreased with increasing Ag concentration. It indicated that the subtitution of Zn^+ by Ag^+ (Jeong *et al.*, 2007).

DB71 photodegradation test

The photocatalytic activity of thin films ZnO, ZnO:Ag and ZnO/ZnO:Ag was indicated by DB71 degradation under UV irradiation. Figure 6(a) showed decreasing DB71 concentration each interval period. Under UV light, DB71 without photocatalyst showed no significant decrease in concentration. Enhancement photocatalytic activity was shown by double layer with Ag doping in Figure 6(b). The double layer 6% showed the highest photocatalytic efficiency (E_f) c.a. 56.52% in 90 minutes irradiation. It might due to addition of Ag, the generated electron and hole increased more than pure ZnO. It also resulted in more production of hydroxyl ions and enhaching the photodegradation reaction. In addition, the influence of the double layer inhibited recombination process, so that the oxidation process could take longer.



(a) (b)

Figure 6. Photocatalytic degradation (a) and photocatalytic efficiency (b) with various prepared films.

DB71 photocataytic degradation kinetics was described by Langmuir – Hinshelwood models and photocatalytic degradation rate (r) was given by :

$$r = -\frac{dC}{dt} = \frac{k_r K_{dye}\, C}{1+K_{dye}\, C} \qquad (5)$$

where dC/dt is degradation rate (mgL^{-1} min^{-1}), C is dye concetration (mgL^{-1}) at irradiation time (t), k_r is the rate constant ($min^{-1}gL^{-1}$) and K_{dye} is dye adsorption coefficient by catalyst surface (L mg^{-1}). In this study, we used low concentration DB71 dye. The first order kinetic rate with apparent rate constant k_{app} (min^{-1}) follows this equation (Juang *et al.*, 2010) :

$$ln\left(\frac{C_t}{C_0}\right) = -k_r K_{dye}\, t = -k_{app}\, t \qquad (6)$$

Apparent rate constant can be determined from slope of the linear plot $-\ln(C_0/C_t)$ versus time (t) (Figure 7). Apparent rate constant increase by addition of Ag in double layer, whereas in single layer decreased. The highest rate constant was achieved by DL 6%. That means DL 6% has best degradation rate. Each apparent rate constant of thin films could be seen in Table 2.

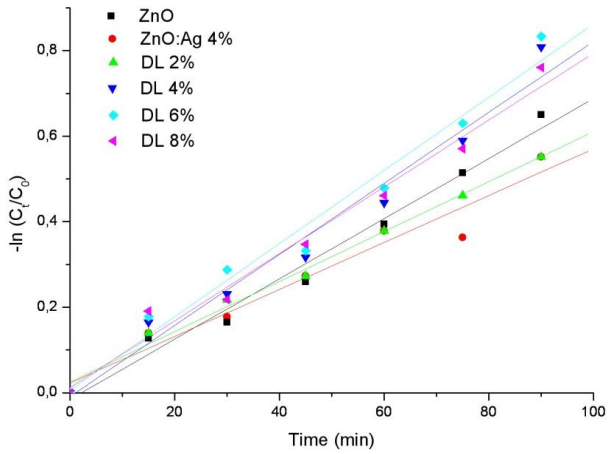


Figure 7. Photodegradation kinetic with various prepared films

Table 2. Apparent rate constant of DB 71 degradation

Films	K_{app} x 10^3 (min^{-1})	R^2
ZnO	7.00	0.97901
ZnO:Ag 4%	5.48	0.9463
DL 2%	5.85	0.98961
DL 4%	8.30	0.96683
DL 6%	8.56	0.97147
DL 8%	7.82	0.97486

CONCLUSION

Double layer thin film of ZnO/ZnO:Ag was succesfull deposited on glass substrat by sol gel spray coaing method. All prepared thin films were hexagonal wurtzite structure. The addition of Ag into ZnO did not significantly affect the crystal structure, but increase dominant peak in (002) plane. It was also seen that double layer thin films have better crystalinity than single layer. The calculation from Scherrer equation showed that crystallite size of ZnO have a tendency of getting smaller with addition of single layer from 24.88 nm on ZnO and 20.04 nm on ZnO:Ag 4% thin film. For double layer thin film have a tendency to increase crystallite size with increasing of Ag doping from 19.64 nm to 22.01 nm with the highest increasing was DL 4%. The band-gap of thin films were getting smaller with addition Ag in single and double layer and the smallest energy gap was owned by DL 6%. The highest DB71 degradation result under UV light irradiation was reached by DL 6% with 55.43% and 8.56 x 10^{-3} min^{-1} for photocatalytic efficiency and photodegradation rate, respectively.

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