Pulse laser deposition (PLD) technique for ZnO photocatalyst fabrication

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Abstract. The pulsed laser deposition (PLD) technique has been employed to fabricate zinc oxide ZnO thin film for photocatalytic application. Nd:YAG laser, with the wavelength of 1064 nm and energy of 30 mJ was used in our experiments for the ablation process. The thin film was deposited into a glass as the substrate then it was characterized for its structure and optical properties. The ZnO thin film has good morphology with the grain size smaller than 100 nm and hexagonal wurtzite crystal structure. The measured UV absorbance is able to predict its band gap energy, where it was found to be around 3.25 eV. For photocatalytic function, the film was tested to reduce the concentration of Rhodamine B (RdB). During 6 hours exposure under the sunlight, the concentration of RdB has been reduced down to 9% in comparison to its initial concentration indicating the film works as a good photocatalyst.

1. Introduction

The water treatment by employing photocatalyst has become a significant issue to reduce the pollutant of the water [1, 2]. Some pollutant were released from industries to surrounding areas, such as the textile industries, pharmaceutical industries, paper-pulp industries, etc. [3-6]. ZnO as the thin film has been proven as a great photocatalyst for water treatment [7-9]. Aal et al. mentioned in their work that h. The photolysis of TCP using UV irradiation reaches 91.00 ppm after 225 min, whereas its photocatalytic using the UV irradiation in the presence of the nanostructured ZnO thin film catalyst TCP was complete after 60 min [8]. Balcha et al. were also able to develop ZnO base photocatalyst to reduce the concentration on methylene blue. They used the sol-gel method to establish ZnO nanostructures, where higher aspect ratio and intentional inclusion of defects can lead to even higher photocatalytic activity by appropriately modifying the synthetic routes [9].

Some of the methods to deposit the thin film above the substrate have become one important discussion since each way has its good points and unique feature. Pulsed laser deposition, PLD, is one type of thin film deposition technique, which is known to be very simple, easy to control and producing high-quality film [10, 11]. This method is also known to be a green approach method and provides the chance of future possibilities on combining ZnO nanostructures with other elements as dopant material to increase the function of ZnO.
In this paper, we would like to present our recent work on PLD technique using Nd:YAG was chosen to produce the ZnO thin film for photocatalyst application. FESEM, XRD, UV-Vis spectroscopy and photoluminescence characterization were firstly conducted to obtain the structure and optical properties of the produced ZnO thin film. The film was tested as photocatalyst to reduce the Rhodamine B (RdB) concentration under the sunlight exposure.

2. Experimental Methods
2.1 ZnO thin film fabrication
The schematic diagram of this experiment is shown in figure 1. The PLD system consists of Quanta-Ray Spectra-Physics Nd-YAG laser with the wavelength of 1064 nm, energy of 30 mJ and frequency of 10 Hz. The laser beam was focused into the sample by a 150 mm focal length plano-convex lens. The laser beam was focused into a ZnO pellet target attached on a rotation holder inside the vacuum chamber. The vacuum chamber was operated at the pressure of 1.5 torr. The generated plasma, which appeared in plasma plume containing atoms and ions, was then deposited into the substrate. The substrate was attached into a substrate holder at 5 cm distance with an angle of 45° from the center of the target. The PLD process was conducted for 30 minutes to fabricate the ZnO thin film. More detail experiment set-up can be seen in Figure 1, where the target-substrate was arranged inside the chamber.

ZnO pellet used in this experiment was prepared by mixing ZnO powder with several drops of PVA 2% and press the mixture using a pellet press machine. Pellet was then heated on an oven at the temperature of 500 °C for 5 hours. We used glass as the substrate for XRD, UV-Visible spectroscopy, photoluminescence (PL) spectroscopy and photocatalyst characterization. For FESEM characterization, we used the silicon wafer as a substrate (same set-up for both substrates). The purpose of this action was to improve the image quality on FESEM analysis. After the PLD process the samples (the substrates with the ZnO thin film coating) was keep in the oven with temperature of 200 °C for 5 hours.

2.2 Structure and optical characterization
Field-Emission Scanning Electron Microscopes (FESEM) and X-ray diffraction (XRD) unit have been used to observe the structure of ZnO nanoparticles. Using JEOL JIB 4610F FESEM with EDS mapping, we were able to obtain some information such as the morphology, the grain size, percentage of atomic weight and the distribution of ZnO nanostructures. The XRD from Rigaku was used to study the crystal structure of ZnO thin film. The optical properties were conducted using UV-Visible (UV-Vis) and photoluminescence (PL) spectroscopy to analyze the absorbance and luminescence of the thin film. This analysis is also very useful to predict the band gap energy of the thin film sample.

![Figure 1. (a) LIBS experiment set-up, (b) ZnO pellet as the target and (c) glass (left) and silicon wafer (right) as the substrate.](image-url)
2.3 Photocatalyst testing
The photocatalyst effect was tested directly under the sunlight. The petri dish was prepared for the sample with and without ZnO thin film. The tested glasses (with and without ZnO thin film) were placed inside the petri dish and then 10 ml of Rhodamine B (RdB) suspension was filled in the petri dish. The placement of the ZnO thin film and the RdB suspension can be seen in figure 2. The concentration of RdB is 0.1% (mass to volume) for both petri dishes. All samples were exposed under the sunlight for 6 hours. The absorbance spectrum of the RdB suspension was measured in every 2 hours for 6 hours sunlight exposure. The absorbance is related to the concentration of RdB in the suspension. Our data analysis was expected to obtain the reduction (%) of the concentration of RdB.

3. Results and Discussion
3.1 ZnO thin film structure
Figure 3 (a) shows FESEM images of ZnO thin film coated on a silicon wafer surface. The thin film was measured with the potential of 15.0 kV and magnification of 100k×. It can be observed that the grains are found to be smaller with size less than 100 nm, and morphologies be dense and continuous. The grains are uniformly distributed and get a good adhesion to the substrate which is believed as the annealing effect on the thin film. The EDS mapping of the thin film can be seen at figure 3 (b). Through the result, it is safe to assume that the ZnO thin film has been formed. The atomic weight (at%) of both element Zn and O almost have same portion, with at% of Zn is slightly higher than O, which might be due to some oxygen vacancy of the ZnO crystallite structure. Figure 4 presents the XRD characterization of the film. The thin film sample exhibits hexagonal wurtzite structure of ZnO showing preferred orientations along (100), (002), and (101). Crystallite size along (002) crystallographic plane for this sample, as calculated by Debye Scherrer formula, lies on 24.13 nm.

3.2 Optical properties of ZnO thin film
Optical properties were analyzed using UV-visible and photoluminescence (PL) spectroscopy. The spectrums are presented on figures 5 (a) and (b) respectively for absorbance and PL spectrum. The absorbance the optical absorbance varies between 0% and 10% in the wavelength range of 400–800 nm. In the UV region the absorption is more than 90%. The spectral data recorded shows the strong cut off at 381.57 nm, where the absorbance value is at minimum. The formula, \( E = h \times c \times \lambda^{-1} \), where \( \lambda \) is the cut off wavelength, was used to calculated the band gap energy. From the calculation, it was found that the band gap energy of ZnO thin film to be at least 3.25 eV.

![Figure 2. Photocatalyst testing set up for the ZnO thin film.](Image)
Figure 3. (a) The ZnO thin film surface which was taken using FESEM at the potential of 15.0 kV with the magnification of 100,000x, and (b) the EDS mapping analysis of the thin film.

Figure 4. The XRD analysis of the ZnO thin film.

The photoluminescence data exhibits two peaks at 387.2 and 555.6 nm. The first peak presents in the UV region at 387.2 nm and it is known as the near-band edge luminescence. This peak is much stronger than the second peak which appears at green luminescence region at 555.6 nm. This green luminescence is most often attributed to oxygen vacancy in ZnO and the target of the PLD includes oxygen, thus oxygen vacancy is assumed to be reduced. The occurrence of the two peaks are opposite of each other, at the time the green luminescence is strong; the near-band edge luminescence is relatively smaller or disappear from ZnO. When the green luminescence is weaker, the near-band edge luminescence becomes stronger [12].

3.3 Photocatalyst application
The photocatalytic function for as prepared ZnO thin film was tested by applying the thin film as a catalyst to reduce the concentration of Rhodamine B (RdB). A thin film coated on glass was attached inside a petri dish, and 10 ml RdB was filled into the petri dish. The petri dish was exposed under the sunlight for 6 hours. This observation was conducted by comparing the degradation of RdB with and
without (only glass sample) ZnO thin film. The absorbance spectrum was measured using a UV-vis spectrophotometer in every two hours to measure the degradation of RdB.

Figure 6a shows the absorbance spectra of RdB every two hours for six hours of exposure under the sunlight for both samples, with and without ZnO thin film. The absorbance of the RdB suspension sample shows very significant reduction by applying ZnO thin film. The absorbance indicates the concentration of RdB in its liquid. Figure 6 (b) presents the degradation of RdB concentration (%) in the liquid with and without ZnO thin film as photocatalyst. At the first two hours exposure under the sunlight, the ZnO thin film is able to reduce almost 30% of the RdB concentration; while at 4 hours and 6 hours exposure it reduces 82% and 91% of RdB concentration. Our experiment also confirmed that without ZnO thin film the concentration of RdB drops down to around 71% after 6 hours sunlight exposure in comparison to its initial concentration before the sunlight exposure. Ultraviolet of the sunlight is able to break down the chemical bonds such that the pollutants or the color of sample fades away. Dyed textiles and watercolors are some objects which are easier to experience bleaching effect. More detail explanation of this phenomenon can be studied on photochemical processes for water treatment [13].

It is commonly assumed that the photocatalytic dye degradation occurs due to the production of reactive oxygen species (ROS) under illumination. The photocatalytic reactions were initiated when ZnO particle absorbs photons with energies higher than that of its band gap energy from the lighting. As the ZnO thin film was exposed under the sunlight, the high intensity of light was well absorbed such that the ROS, such as superoxides (O$_2^-$), hydroxyl radicals (OH•) and hydrogen peroxide (H$_2$O$_2$) was produced in much more significant amount. The degradation of the dye solution is due to the reaction of hydroxyl radicals in solution upon irradiation by UV light. Hydroxyl radicals are very strong oxidizing agent, which can easily react with the RdB molecules and cause the decoloration of the original solution.

In our experiment, both sample show the reduction of RdB concentration. However, with the inclusion of ZnO thin film in our photocatalytic experiment has shown a great reduction of the RdB concentration, down to 9% in comparison to the initial concentration. This result is an indication that the ZnO thin film produced by pulsed laser deposition is able to work as a good photocatalyst.
Figure 6. The absorbance spectrum of RdB which was exposed under the sunlight (a) and the RdB degradation (%) during the sunlight exposure for 6 hours (b) with and without ZnO thin film.

4. Conclusions
The fabrication of ZnO thin film using pulsed laser deposition technique has been conducted. The structure was analyzed using TEM and XRD. The film was nicely coated on its substrate with the grain size under 100 nm. The XRD exhibits the hexagonal wurtzite structure of ZnO showing preferred orientations along (100), (002), and (101). Based on UV absorbance spectrum, the band gap energy was determined to be at least 3.25 eV. The film has been applied as photocatalyst for Rhodamine B degradation. PLD seems to be very promising method to develop good photocatalyst and some wavelength is suitable to produce good quality thin film. During 6 hours exposure under the sunlight, the concentration of RdB has been reduced down to 9% in comparison to its initial concentration indicating the film works as a good photocatalyst. The photocatalytic efficiency can also be improved, by adjusting the PLD parameters such as the laser energy and the laser exposure time.

Acknowledgments
This work was funded by “Program Insinas Riset Pratama 2018” from Ministry of Research, Technology and Higher Education Indonesia.

References
[1] Umar M and Aziz H A 2013 Photocatalytic Degradation of Organic Pollutants in Water (Organic Pollutants - Monitoring, Risk and Treatment) ed Rashed M N (IntechOpen) p 195
[2] Sagawe G, Brandi R J, Bahnemann D, and Cassano A E 2003 Chem. Eng. Sci. 58 2587
[3] Zaharia C and Daniela S 2012 Textile Organic Dyes –Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview (Organic Pollutants Ten Years After the Stockholm Convention – Environmental and Analytical Update) ed Puzyn T (IntechOpen) p 55
[4] Saini R D 2017 IJChER 9(1) 121
[5] Chandra R, Raj A, Yadav S, and Pathl D K 2009 Environ. Monit. Assess. 155 1
[6] Gadipelly C, González A P, Yadav G D, Ortiz I, Ibáñez R, Rathod V K and Marathe K V 2014 Ind. Eng. Chem. Res. 53(29) 11571
[7] Jongnavakita P, Amornpitoksuka P, Suwanboon S, and Ratana T 2012 Thin Solid Films 520(17) 5561
[8] Aal A A, Mahmoud S A, and Aboul-Gheit A K 2009 Mater. Sci. Eng. C 29 831
[9] Balcha A, Yadav O P, and Dey T 2016 Environ. Sci. Pollut. Res. 23(24) 25485
[10] Villanueva Y Y, Liu D R, and Cheng P T 2006 Thin Solid Films 501 366
[11] Tsoutsouva M G, Panagopoulos C N, Papadimitriou D, Fasakic I, and Kompitsas M 2011
Mater. Sci. Eng. B 176 480
[12] H. Shalish, H. Temkin, and V. Narayanamurti 2011 Phys. Rev. B 69 245401
[13] O. Legrini, E. Oliveros, and A. M. Braun, 1993 Chem. Rev. 93(2) 671