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Preface of the editorial team

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The Editorial team of Proceedings the second International Seminar on New Paradigm and Innovation on Natural Sciences and its Application in 2012 (ISNPINSA-2) expressed gratitude to God the All-Knowing and the Supreme for the successful publication of these proceedings. This book, we present to all participants of the 2nd ISNPINSA, who had participated in this regular scientific meeting held at Hotel Santika Premier, Semarang, Indonesia on October 4, 2012, and for the continuity of communication between scientists both inside and outside the country and strengthen the cooperation that already exists as well as creating a new partnership.

The publication of ISNPINSA-2 proceedings, we made in two versions which are hard copy and soft copy. The soft copy edition of the second ISNPINSA proceedings created in *.pdf, in addition the text and images in the file could not be copied because it is protected. This needs to be done in the context of protection of copyright authors and avoiding plagiarism. In these proceedings, papers are sorted by alphabetical order of the first author of each paper. This is done to facilitate the reader in searching particular paper that want to read. In the proceedings, some papers only found in abstract form only, as some authors stated does not want to publish full papers in these proceedings or because the author was too late to send full papers by the date we have set. Nevertheless, we hope this limitation does not diminish the value of the proceedings that have been published.

Regarding the implementation of the 2nd ISNPINSA and publishing these proceedings, we would like to thank and express our appreciation to the authors who have worked well accordingly the proceedings can be issued as expected, as well as all those who have supported the success of the overall activity. Also our thanks goes to all committees who have worked hard in the implementation of this great activity.

Sincerely

The Editorial team

Proceedings the second ISNPINSA

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Deposition of ZnO Thin Films by Spray Coating Technique for Photocatalytic and Photochemical Degradation of Methylene Blue

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ABSTRACT

Deposition of a thin layer of Zinc Oxide (ZnO) on glass substrates by spray coating techniques has been done. ZnO is a semiconductor with band gap energy of ~ 3.2 eV and has the properties as oxidation photo catalysts that will transform harmful compounds and toxic substances in water into harmless compounds. ZnO thin film deposition is conducted by making gel ZnO with dissolving zinc acetate dehydrate ($Zn(COOCH_3)_2 \cdot 2H_2O$) into a solution of isopropanol ($(CH_3)_2CHOH$) and monoethanolamine (MEA: $HOCH_2CH_2NH_2$) at room temperature with a concentration of 0.3 M zinc acetate and the molar ratio is 1:1. ZnO gel is placed on the spray hole and sprayed on a glass substrate which has been heated at a temperature of 250°C at a pressure of 70 psi to form a thin layer. A thin layer is sintered at a temperature of 450°C for 2 hours. A ZnO thin layer then used as a photocatalytic and photochemical degradation of methylene blue (MB) with and without stirring. The microstructure analysis by using XRD show that the thin layers having polycrystalline wurtzite structure with orientations (100), (002), (101) and (110). EDS characterization showed that thin layers of ZnO consists of 50.27% and 49.73% zinc and oxygen atomic, respectively. ZnO photocatalyst reaction by using ultra violet light (UV) for 3 hours has been reduces the concentration of MB until 97.05%. A high percentage of color degradation MB performed by treatment with stirring.

Keywords: ZnO, Spray Coating, Thin Film, Color Polutan, Photo Catalyst, Glass Substrate

1. INTRODUCTION

Some recent decades, the developments of industrial sector have an impact on environmental degradation, particularly water resources. The presence of organic contaminants including dyes in wastewater has been an important problem in many countries since the textile industry is widely developed. Synthetic dyes are extensively used in textile dyeing, paper printing, color photography, pharmaceutical, cosmetic, and other industries [1]. Approximately 10,000 different dyes and pigments are used industrially, and over 0.7 million tones of synthetic dyes are produced annually worldwide. Major classes of synthetic dyes include azo, anthroquinone and triaryl methane dyes, and many of them are toxic or contain carcinogenic compounds with long turnover times. Approximately 15% of the dyes produced worldwide are lost within wastewater during synthesis and processing [2].

The major issue related to these organic compounds in large quantities in wastewater is their chemical stability and low biodegradability in water systems, which is potentially harmful to the eco-environment. As a consequence, an effective and economic technique needs to be developed to reduce the concentrations of these contaminants before releasing the wastewater into the aquatic environment. Among the several techniques developed in wastewater treatment, advance oxidation processes (AOP) are increasingly used as for the reduction of organic contaminants in a variety of wastewaters from different industrial plants. The AOP are usually driven by hydroxyl radicals produced in the system [3,4]. The advantage of AOP is the conversion of organic compounds to less toxic molecules. In perfect conditions, it is possible to oxidize the organic molecules completely to CO_2 and H_2O .

Oxide semiconductors, such as TiO_2 and ZnO are very promising photocatalysts, especially for the degradation of organic pollutants dissolved in solution. Although they both exhibit the same band gap of about 3.3 eV, ZnO has been shown to be more efficient in the photodegradation of organic compounds under UV-light illumination [5-8]. For instance, Neppolian et al. [8] compared the efficiency of different semiconductor photocatalysts, such as TiO_2 , ZnO, SnO_2 , ZrO_2 , $\alpha-Fe_2O_3$, WO_3 , and CdS, in the photodegradation of an azo dye in aqueous solution under identical experimental conditions using sunlight as the energy source. From this comparative study, ZnO emerged as the most active photocatalyst. The zincite nanostructures were used as potential photocatalysts for water purification based on the decolorization of dyes [10,11]. Lizama et al. reported ZnO is the most efficient photocatalyst for photodegradation of reactive blue 19. Although most of the studies investigating the photocatalytic behavior of ZnO have been carried out with powder materials, it requires long time sedimentation or centrifugation process for separation of particles. It would be preferable to use zinc oxide films instead of particles because they would not require a final separation process. The photocatalytic decomposition of toluene, salicylic acid and 4-

chlorophenol with sun light in an oxygenated aqueous suspension has been studied under nanocrystalline hexagonal ZnO photocatalyst [12]. The ZnO thin films can be prepared through many techniques such as hydrothermal method, sol-gel, RF magnetron sputtering, chemical vapor deposition, thermal vaporization, laser ablation, E-beam Evaporation, ion beam assisted deposition and spray pyrolysis [13]. Among these methods, spray pyrolysis technique (SPT) provides a simple route of synthesizing thin films because of its simplicity, low cost; in addition, this photoelectrocatalysis could be used for the production of large area thin films. This technique appears to offer a great deal of hope in treating hazardous and toxic chemical wastes into harmless end-products at ambient temperature with minimum intermediates. In view of the advantages of heterogeneous photoelectrocatalysis in the treatment of wastewater, it has been aimed to decolorize and degrade the textile effluent by using spray deposited ZnO thin films.

In this work, the deposition of ZnO thin films by spray coating technique and its photoactivity for methylene blue (MB) were reported. The prepared material was characterized by X-ray diffraction (XRD), scanning electron microscopy with energy dispersive analysis (SEM-EDS), and UV-Visible absorbance spectrophotometry (Shimadzu UV-1601).

2. MATERIALS AND METHOD

ZnO thin films deposited on glass substrate using sol-gel method by spray-coating technique. Prior to deposition, glass substrates were etched by immersing the substrate in 2% HF and then cleaned of organic impurities by soaking substrate into acetone and methanol each for 5 minutes with ultrasonic bath. Furthermore, the substrate immersed into the DI water and then dried with nitrogen gas sprayed.

The chemicals used, zinc acetate dehydrate ($\text{Zn}(\text{COOCH}_3)_2 \cdot 2\text{H}_2\text{O}$), isopropanol ($(\text{CH}_3)_2\text{CHOH}$), monoethanolamine (MEA: $\text{HOCH}_2\text{CH}_2\text{NH}_2$), and methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot x\text{H}_2\text{O}$) were supplied by Merck Chemical. ZnO thin film deposition is conducted by making gel ZnO with dissolving zinc acetate dehydrate into a solution of isopropanol and monoethanolamine at room temperature with a concentration of 0.3 M zinc acetate and the molar ratio is 1:1 and stirred for 30 minutes. 50 ml ZnO gel is placed on the spray hole and sprayed on a glass substrate which has been heated at a temperature of 250°C at a pressure of 70 psi to form a thin layer. A thin layer is sintered at a temperature of 450°C for 2 hours with atmospheric pressure.

The structural properties were studied by Philips X-ray diffractometer PW-1710 using $\text{Cu K}\alpha$ (with $\lambda=1.5405 \text{ \AA}$) radiation in the span of 10–60°. Surface morphology and compositions of the thin film was studied with JEOL JSM-6360 Scanning Electron Microscope with Energy Dispersive Spectroscopy analysis (SEM-EDS). Optical absorption study was carried out in the wavelength range 200–800 nm, using Spectrophotometer (Shimadzu model UV-1601). Photooxidation reaction of methylene blue (MB) was carried out in a 1000 mL glass beaker. The beaker was charged with 500 mL aqueous solution of 10 ppm MB. Sources of UV radiation from the sun radiation directly on a glass beaker containing 10 ppm MB sample solution. Tests performed photo degradation of the MB dye color concentration for 3 hours (from 9 am to 12 am). The UV-Vis spectrophotometer absorption is used the photo degradation analysis.

3. RESULTS AND DISCUSSION

3.1. Crystal Structure of ZnO Thin Films

XRD patterns of the ZnO thin film crystal structure grown on glass substrate with spray coating technique is shown in Figure 1. Through the identification data using the JCPDS program (Joint Committee on Powder Diffraction Standards) no PDF# 361451 can be seen that XRD of ZnO thin films in Figure 1 shows that the films have polycrystalline structure with orientation are (100), (002), (101) and (110). A thin layer deposition results are polycrystalline due to the deposition process was performed at low temperatures.

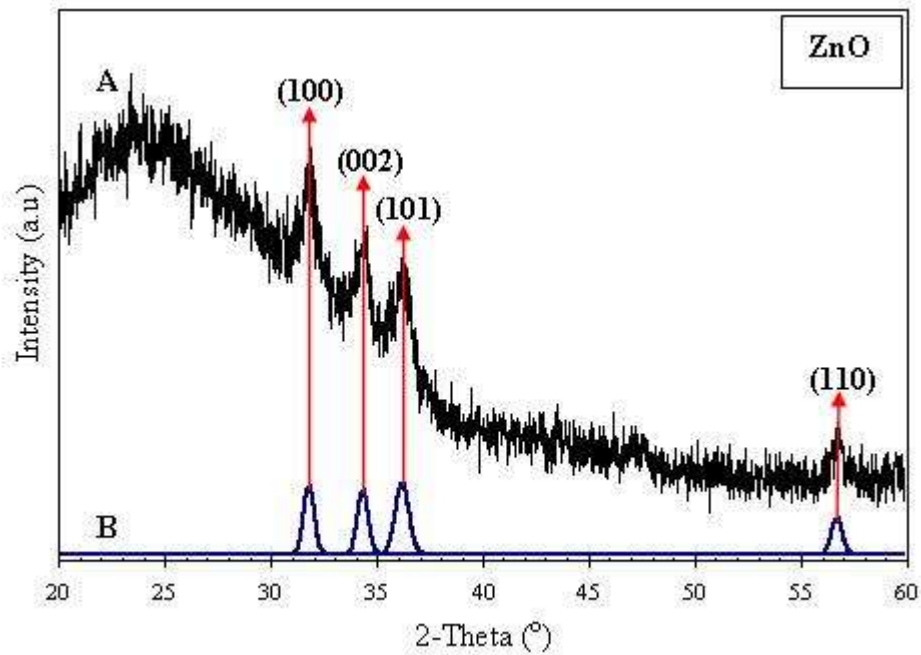


Figure 1. XRD pattern of ZnO thin films: (A) Original, and (B) Fitting by Gauss Function

The XRD results of fitting a Gaussian functions obtained Full Width at Half Maximum (FWHM) values were used to calculate the grain size of the thin film using Scherrer equation:

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

where D is the crystallite size or average grain size (nm), K is a Scherrer constant (0.9 for oxide material), λ is the X-ray wavelength and θ is the Bragg angle. The results of XRD data processing can be used to determine the crystal grain size as is shown in Table 1. From Table, the average grain size of ZnO thin film is 15.9 nm. The result shows that the sol gel method with spray coating technique can be used for depositing ZnO thin film with crystal grain size up to nanometer scale.

Table 1. The position of diffraction angle 2-theta, FWHM values, and crystallite size of the varied diffraction field orientation of ZnO thin films.

Diffraction Orientation Field	Diffraction Angle 2θ (°)	FWHM (°)*	Grain Size (nm)
(100)	31.786	0.508	16.268
(002)	34.319	0.505	16.472
(101)	36.169	0.639	13.084
(110)	56.697	0.508	17.776

* Full width at half maximum

3.2. Composition and Surface Morphology of ZnO Thin Films

Analysis of atomic composition using EDS (Figure 2.a) on a thin film of ZnO formed aims to determine the constituent atoms of the layer. In Figure 2.a shows the results of ZnO layer composition, which X-axis is an energy-dispersive and Y-axis is the atoms dispersive intensity. EDS test results indicate that the constituent atoms of ZnO thin film on glass substrate is zinc (Zn) and oxygen (O) with %At atomic composition (percent atomic material) consisted of 50.27% zinc (Zn), and 49.73% oxygen (O). The result shows that the ZnO layer deposited on the glass substrate was stoichiometric. The more stoichiometric synthesis of the results showed the less impurity atom in the material. The results of this study indicate that the sol-gel method with spray coating technique has able to deposition of thin layers of materials, especially oxides based.

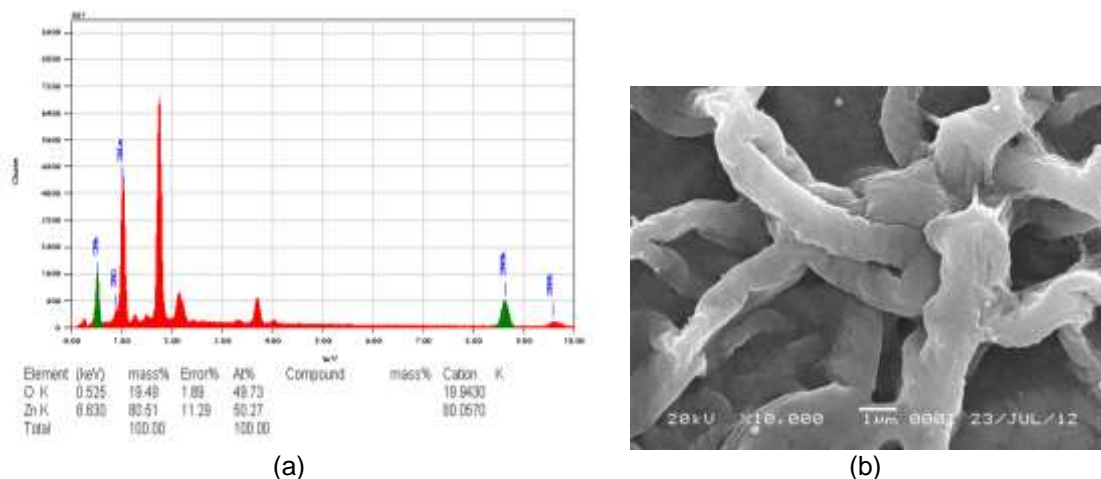


Figure 2. (a) The EDS analysis and (b) Surface image morphology of ZnO thin films on glass substrate deposited by spray coating technique.

Analysis of atomic composition using EDS on a thin layer of ZnO formed aims to determine the constituent atoms of the layer. Figure 2.b shows the SEM image of the surface morphology of ZnO thin film grown on a glass substrate. The Figure shows that the image of the ZnO surface morphology is composed of a group of rod-shaped granules with a diameter of about 1.153 μm . The pattern of grain growth of the ZnO layer in the form is a laterally growth islands to form a layer.

3.3. ZnO Photocatalytic for Methylene Blue



Figure 3. Photoactivity of ZnO thin film for 10 ppm dye MB solution: (A) Without treatment, (B) with treatment using ZnO thin film and stirring of 3 hour, and (C) with treatment using ZnO thin film and without stirring.

For testing the ability of photocatalytic reaction to the degradation of water pollutants it used a 10 ppm methylene blue dye standard. The photocatalytic reaction was carried out in a glass container containing a deposited ZnO for methylene blue solution and then exposed to direct sunlight. Irradiation is performed for 3 hours on the methylene blue solution. Each container is treated differently by stirring using a magnetic stirrer and without stirring.

From Figure 3 it is clear that the results of treatment with ZnO showed methylene blue became clear water, which indicates the degradation of color pollutants due to the activated ZnO photocatalyst coating by UV radiation from sunlight. The sunlight was able to excite the pair of electron and holes the surface of ZnO. Excitation of electrons from the valence band to the conduction band will produce a group of hydroxyl radicals ($\cdot\text{OH}$), which is a strong oxidizing agent, so as to oxidize organic compounds. These radicals are continuously formed during ZnO irradiated with sunlight. The radicals will attack the pollutants that exist in the water pollutant methylene blue dye will be degraded.

The photocatalytic activity was investigated by means of the degradation of methylene blue (MB) in an aqueous solution. The ZnO thin films were placed in a beaker that contained 500 mL of 10 ppm MB and they were then irradiated with sunlight for 3 h (09.00 am – 12.00 am). After irradiating process, the concentration of residual MB was determined by a UV-vis spectrophotometer. The degradation of MB can be calculated by the following formula:

$$\text{Degradation(\%)} = \frac{[C_0 - C_t]}{C_0} \times 100 = \frac{[A_0 - A_t]}{A_0} \times 100 \quad (2)$$

where C_t and A_t are the concentration or absorbance at 665 nm of the MB solutions after irradiation in 3 h, while C_0 and A_0 are the concentration or absorbance at 665 nm of the MB solutions before irradiation.

Table 2 shows the absorbance test results. It can be seen that the radiation from the sun for 3 hours in a solution of MB was able to degrade the concentration of MB up to 29.22%. With the use of ZnO photocatalyst without stirring was able to degrade the concentration of MB up to 73.73% and the degradation rate rises to 97.05% with stirring. This suggests that mixing can improve the efficiency degradation due to the continuous interaction of the surface of the ZnO layer and the MB solution.

Table 2. The analysis concentration of MB samples and percentage of degradation of MB after treatment by ZnO thin film photocatalyst.

Treatment	Absorbance	% Degradation
Initial sample (without treatment)	0.746	0
Direct irradiation sunlight with stirring	0.528	29.22
Direct irradiation sunlight with ZnO and without stirring	0.196	73.73
Direct irradiation sunlight with ZnO and stirring	0.022	97.05

4. CONCLUSION

The polycrystalline ZnO thin films on glass substrates by sol-gel method of spray-coating technique with sintering temperature of 450°C have been successfully deposited. The films have an average grain size of 15.9 nm. The SEM image of ZnO thin films showed that the surface morphology is composed by a group of rod-shaped granules with a diameter of about 1.153 μm . The pattern of grain growth of the ZnO layer in the form is a laterally growth islands to form a layer. ZnO photocatalyst reaction by using ultra violet light (UV) for 3 hours has reduces the concentration of MB. A high percentage up to 97.05% of color degradation MB was performed by applying treatment ZnO film and stirring.

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