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3rd iSNPiNSA

International Seminar on New Paradigm and Innovation on Natural Sciences and its Application

Developing Innovation and Application of Applied Sciences for Sustainable Development

PROCEEDINGS

Diponegoro University
2013

The 3rd International Seminar on

New Paradigm and Innovation on Natural Sciences and its Application 2013

"Developing Innovation and Application of Applied Sciences for Sustainable Development"

Organized By :

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PREFACE

Good Morning Ladies and Gentlement
On behalf of the Organizing Committee, i would like to warmly welcome you to the 3rd Internasional Seminar on New paradigm and Innovation on Natural Sciences and Its Application (ISNPINSA). This seminar has been successfully conducted since 2011 and therefore becoming an annual event since then. The theme of ISNPINSA this year is Developing Innovation and Its Application of Applied Sciences for Sustainable Development.

The aims of this seminar are to facilitate brain storming and state of the art information in field of sciences and mathematic; to increase innovation of technology that can be applied in industries; to contribute in formulating strategy to increase the role of science for the community; and to stimulate collaboration between industries, researchers and government to increase community welfare.

We divided the parallel session in this seminar into specific topic that can accommodate the field range from chemistry, physics, biology, mathematics and the science related to them. By inviting the speakers from academics and industries, we hope that this event can be a bridge between researchers, scientists and industries in order to foster developing innovation and its application to support sustainable development.

In closing, I wish to express my gratitude to all speakers, presenters and participants in this seminar. I hope that we can have a fruitful and productive discussion, brain storming and presentation that can increase and develop our understanding in sciences. I take this opportunity to thank the organizing committee for this seminar and the Faculty of Science and Mathematics for the necessary funding. The various sponsors are also thanked for their kind hospitality.
Thank you

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Deposition of ZnO:Ag Photocatalyst Using Spray Coating Technique and Its Application for Methylene Blue and Methylene Orange Photodegradation

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ABSTRACT

ZnO:Ag thin films have been successfully deposited on glass substrates by spray coating technique with various Ag content of 2%, 3%, 4% and 5%. The ZnO:Ag thin films used to photodegrade the dye methyl orange and methylene blue using ultraviolet (UV) irradiation. ZnO:Ag solution was synthesized by dissolving zinc acetate dehydrate (ZnAc) in isopropanol then monoethanolamine (MEA) and Silver nitrate added into that solution at room temperature. The concentration of zinc acetate was 0.3 M and the molar ratio of MEA : ZnAc was 1:1. The solution was stirred by a magnetic stirrer at a temperature of 70°C for 30 minutes to obtain a clear and homogeneous solution. ZnO:Ag gel was sprayed on a glass substrate and then heated at temperature of 400^{o}C for 15 minutes. Optical properties of ZnO:Ag thin films were characterized by using UV-Vis spectroscopy. The research showed that the incorporation Ag into ZnO can enhance photocatalytic activity due to the Ag depressed the recombination rate. In addition, the higher ion Ag concentration was decreased bandgap energy. The photocatalityc activity of ZnO:Ag could degraded methyl orange dye up to 42.68% for ZnO: Ag 4%, 45.45% for ZnO: Ag 5% and the degradation of methylene blue dye is reached up to 99.21% for ZnO:Ag 4% and the ZnO: Ag 5% thin films could degraded up to 100% under UV irradiation for 10 hours.

Keywords: *ZnO:Ag, Photocatalyst, Thin Films, Spray coating, Methyl Orange, Methylene blue.*

1. INTRODUCTION

In the last decade, environmental problems become increasingly serious with industrial development and population growth [1]. One of the many industries that cause waste liquid dyes is textile industry. Methylene Blue (MB) is one ingredient that is widely used as a textile dye, wool and silk. Methylene blue is toxic aromatic hydrocarbons and a cationic dye with a very strong adsorption power. Methyl orange (MO) and methylene blue are carcinogenic and mutagenic, so it needs an effective alternative to degrade these compounds. Oxidation catalyst semiconductor photocatalyst to degrade organic compounds by converting it into CO_2 and H_2O [2]. Photocatalytic degradation of organic pollutants using nanoparticulate semiconductors has been investigated to solve environmental problems. Among the various semiconductor photocatalysts are used to eliminate pollutants and toxic waste treatment, semiconductor Zinc Oxide (ZnO) is used extensively because it has the advantages of high photosensitivity, thermal stability and good chemical at room temperature, low cost and non - toxicity. Moreover, ZnO nanomaterials have the ability to form a greater photocatalytic activity than TiO_2 in terms of discoloration of reactive blue 19 textile anthraquinone dye, in aqueous suspension and protocatechuid acid oxidation [3, 4]. Current research on the creation and application of ZnO thin films attracted much attention for various purposes. In addition to applications in the ultraviolet emission, ZnO thin films also have important applications in non - volatile memory, pH sensors, varistors, acoustic wave devices, optical waveguides, solar cells, and biosensors [5-7]. This is due to ZnO is an n-type semiconductor material with a band gap of 3.4 eV and a binding energy of 60 MeV [8].

Several attempts to be made to improve the photocatalytic activity by doping with metal or non-metallic or composite forming such semiconductor/semiconductor, semiconductor/polymer or semiconductor/metal. ZnO on doping with certain elements will optimize the electrical properties as well as its optics properties. Many methods are used for ZnO deposition, such as atom beam sputtering, combustion, spray pyrolisis, sol-gel, metal organic chemical vapor deposition, pulsed laser deposition, etc. [9-10]. Modification of ZnO semiconductors with noble metal atoms has attracted attention because of the presence of such atoms can improve the reduction process thus improving the photocatalytic degradation process. Among the precious metals, silver (Ag) was chosen because of the tremendous potential as catalytic, anti-bacterial, non-toxicity and relatively cost-effective. In addition, ZnO nanoparticles: Ag can act as electron wells, thus increasing the photogenerated electron and hole, increasing the number of hydroxyl atoms on ZnO surface, facilitating the occurrence of electron and hole trapping, all of which will increase the photocatalytic efficiency of ZnO [11]. In this study, conducted studies with doping ZnO layers making silver (ZnO:Ag) by using the method of variation percent Ag sol - gel spray coating techniques. Photocatalyst thin layer of ZnO:Ag deposition results are used to degrade dyes MB and MO with the help of UV light irradiation.

2. EXPERIMENTAL METHOD

The production process of solution of ZnO and ZnO: Ag is performed using the sol-gel method. The mechanisms of the preparation of the solution are as follows. Zinc Acetate in hydrate (Zn. $(COOCH_3)_2.2H_2O$) dissolved in 2-propanol (CH_3CH (OH) CH_3) at room temperature at concentrations of Zinc Acetate 0.3 M. Then Monoethanol Amine (MEA) was dropped into the solution and stirred using a magnetic stirrer at a temperature of 70°C for 30 minutes, then added Ag doping from silver nitrate to obtain a homogeneous solution.

Thin film deposition process of ZnO and ZnO:Ag on glass substrates was conducted using spray coating techniques. Before the deposition, the glass substrates cleaned first with acetone and methanol for 10 min with ultrasonic washing system to remove organic impurities such as fats and oils. Subsequently washed with Aquabides glass for 10 minutes and dried. The dried glass substrates placed on a hot plate with a temperature of 400^oC for 10 minutes, and then at the same temperature with a solution of ZnO sprayed evenly. The same treatment is given to spraying ZnO:Ag in the glass substrate. After the deposition process, the coating is allowed to stand for 1 hour at a temperature of 400^oC before temperatures finally lowered slowly to room temperature.

Deposition results of ZnO:Ag thin layer was tested its compositions using Energy Dispersive X-ray (EDX) and optics properties using UV-Vis Spectrophotometer (Ultra Violet-Visible) at wavelengths of 200-800 nm. The data obtained were used to determine the transmittance and band gap energy. Thin layer of ZnO:Ag is then used to degrade dyes MB and MO. Solution of MB and MO 10 ppm by volume of 30 ml, placed in a container that already contains a layer of ZnO:Ag, the next test with illuminated photodegradation of dyes using light from a UV lamp for 6 hours. In addition, samples of MB and MO dye degradation products were also tested to determine the ability it absorbance photo degradation.

3. RESULTS AND DISCUSSION

The EDX measurement was carried out in order to analyzed atomic composition of ZnO:Ag thin films deposited on glass substrate by spray coating technique. Fig. 1 shows EDX spectrum of ZnO:Ag thin film for Ag content of 4%. As can be seen in Fig. 1, the atomic composition of thin film is nonstoichiometry and dominated by Zn atom. It is indicate that Zn atom more reactif at higher deposition temperature than deposition temperature for ZnO at 250^oC, as previoulsy reported. Increasing temperature lead to increase Zn reactivity and result in oxygen desorption. Beside, the result also show that Ag atomic composition in the sample was found to be 5.29% which higher than that composition in starting solution (4%).

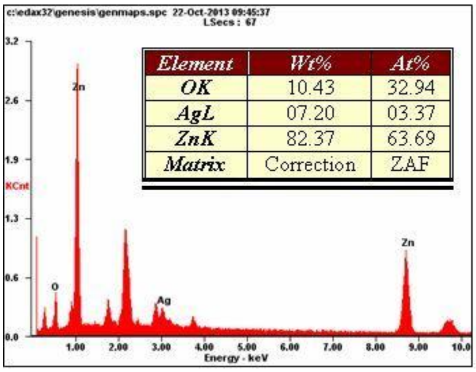


Figure 1: The EDX spectrum of ZnO:Ag thin films deposited on glass substrate by spray coating technique.

The optical properties of ZnO:Ag thin films was investigates by UV-Vis spectrophotometer. The transmittance spectra of ZnO:Ag thin films for Ag composition of 4% and 5% is shown in Fig.2. It can be seen that all the thin films possess transmittance close to 100%. It is suggest that ZnO:Ag thin films transparent to visible light. However, there is slightly difference in transmittance for both ZnO:Ag thin films. The ZnO:Ag (4%) is more tranparent than the ZnO:Ag (5%). The sharp decline in transmittance occur at wavelenght of 415 nm and 406 nm for ZnO:Ag (4%) and ZnO:Ag (5%) thin films, respectively. It is suggest those thin films absorp UV irradiation with corelated to optical transition mechanism. From the transmittance measurement, the band gap of thin films was estimated by using Tauc's plot method as express in the equation $\alpha^2 \propto (h\upsilon - E_g^{op})$ with E_g^{op} is optical band gap, α is absorbance coefficient, and $h\upsilon$ is photon energy [13]. The band gap was found to be 3.15 eV and 3.05 eV for ZnO:Ag 4% and 5%, respectively. By comparison to pure ZnO band gap (3.35 eV), the Ag doping lead to decrease that band gap. Ag doping causes an increase in the number of donor atoms in the conduction band and then form an additional gap that impact on the width of the band gap for the electron excitation.

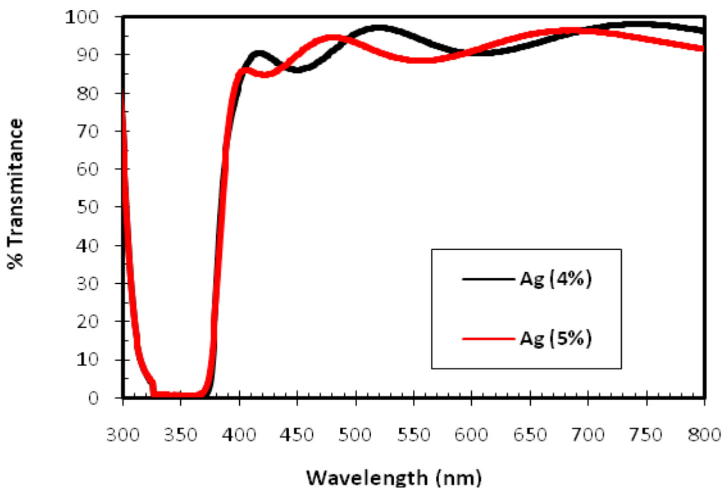
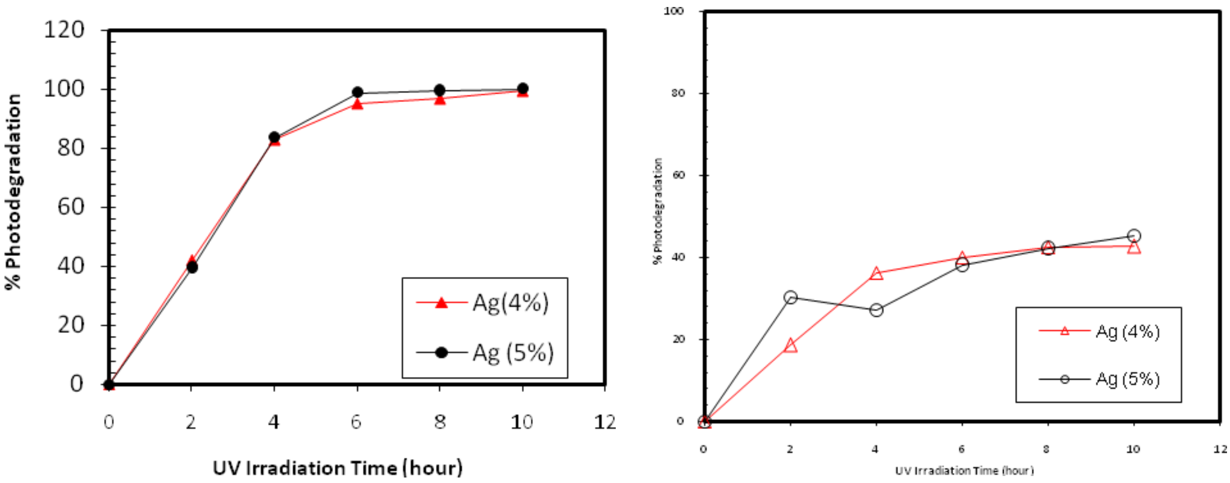


Figure 2: The UV Vis transmittance spectra of ZnO:Ag thin films on glass substrate deposited by spray coating technique.

The result of UV Vis spectrometer measurement for control solution of methyl orange (MO) shows that the solution has the absorption spectrum at 463 nm, while the methylene blue (MB) at a wavelength of 664 nm. The photocatalytic activity was investigated by means of the degradation are MB and MO in an aqueous solution. The ZnO:Ag thin films were placed in a beaker glass that contained 500 mL of 10 ppm MB, MO and they were then irradiated with 10 watt UV lamp for 0 to 10 h. After irradiating, the residual concentration of MB and MO was determined by a UV Vis spectrophotometer. The degradation of MB or MO can be calculated by the following formula: Degradation (%) = [(Co - Ct) / Co] x 100% = [(Ao - At) / Ao] x 100 %, where Ct and At are the concentration or absorbance after irradiation, and Co and Ao are the absorbance or concentration before irradiation. The concentration analysis of MB or MO after treatment by using UV Vis Spectrophotometer. Photodegradation test results with ZnO:Ag in MB and MO dye samples shown in figure 3 .



(a) (b)

Figure 3: Degradation rate of: (a) MB, and (b) MO with ZnO:Ag with varied time of UV irradiation.

Figure 3 shows the photodegradation rate of MB and MO 10 ppm by ZnO:Ag photocatalyst thin film. It can be seen that the longer UV irradiation result in increase the percentage of MB dye degradation of about 99.21 % for ZnO : Ag 4% and 100% for ZnO:Ag 5%, while the percentage of MO dye degradation is 42.68% for ZnO layers of 4% Ag and 45.45 % for coating ZnO:Ag 5%. Percentage degradation of MB is greater than the percentage degradation of MO. This is because the wavelengths of absorption of MB lower than the absorption wavelength of MO. In other words the energy required to break the bonds of MO dye should be higher than the MB. In addition, it also found that percentage degradation of MO and MB by ZnO:Ag 5% is higher that that ZnO:Ag 4%. It sugesst that the degradation rate increases as incresing Ag doping. Ag act as trap electrons from the semiconductor and induces holes to form hydroxyl radicals that reasonable for degradation of organic species. Ag doping can significantly improve the efficiency of photocatalytic degradation of MO and MB.

4. CONCLUSION

The composition analysis shows that the Zn/O (% ratio) in ZnO:Ag thin film is nonstoichiometry and dominated by Zn atom. The optical property measurement shows that ZnO: Ag thin film is tranparent and the increasing in Ag doping lead to reduce that tranparency. The energy band gaps of photocataluyst thin films are 3.15 Vand 3:.05 eV for ZnO:Ag (4%) and ZnO:Ag (5%). Addition in composition of Ag on ZnO structure reduces the band gap energy. The photocatalyst activity of ZnO:Ag (5%) thin film can degrade MB dye up to 100% and up to 45.45% for MO dye. The presence of Ag on ZnO structure improved that photoactivity for MB degradation. The low photoactivity of ZnO:Ag to degrade MO dye is due to narrow band gap (3.15 eV).

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Glucose Content of Sago Waste After Acid Pre-Treatment Hydrolysis for Bioethanol Production

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