Effect of Fe Addition on Zno Thin Films for Photodegradation Under UV and Halogens Light

by Eko Hidayanto

Effect Of Fe Addition On Zno Thin Films For Photodegradation Under UV And Halogens Light

Heri Sutanto, Ilham Alkian, Vitalis Janu Pramunditya, Mukholit, Eko Hidayanto, Inten Rafika Duri, and Priyono

Abstract: ZnO:Fe thin film has been successfully deposited on subtracted glass using sol-gel method with spray-coating technique. This study aims to degrade rhodamine B using ZnO with addition of 2, 4, 6, 8, and 10 wt.% solution of Fe. Optical properties characterization showed the highest transmittance of ZnO:Fe 4% (96.8%) while the lowest transmittance of ZnO:Fe 2% (53.5%). The highest absorbance is performed by ZnO:Fe 2% (0.271) and the lowest absorbance by ZnO:Fe 4% (0.014). Calculation of magnitude thin film energy band gap shows values of 3.24; 3.29; 3.27; 3.25; and 3.24 eV. Results of contact angle testing using contact angle meter showed the greatest contact angle by thin-film ZnO:Fe 2% (62.52^{o}) with the smallest contact angle by ZnO:Fe 4% (50.66^{o}). In UV light irradiation, the highest degradation efficiency is produced by ZnO:Fe 4% thin film of 86.14% and the lowest efficiency is produced by ZnO:Fe 2% thin film of 81.37%. In the irradiation using halogen light, the highest degradation efficiency was produced by ZnO:Fe 2% film by 68.70%, while the lowest degradation efficiency was produced by ZnO:Fe 4% film (58,87%).

Index Terms: Contact angle, halogen light, photodegradation, sol-gel method, spray coating, thin film, ZnO:Fe

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1. INTRODUCTION

Pollution is one of current problems that should be paid attention to and need to be immediately solved. Colored waste is a source of environmental pollution that can cause toxic effects and reduce light penetration in waters [1]. Several methods of colored wastes degradation such as biodegradation, ozonation, and chlorination require expensive costs in its operations, thus they are less effective to be implemented in Indonesia [2]. Photodegradation is an alternative method that offers low cost and easy operation. This method utilizes photocatalyst material derived from semi-conductor materials, such as TiO_2, ZnO, Fe_2O_3, CdS, etc. [3]. ZnO is a good anoxidation as a photocatalyst, especially in colored waste degradation applications [4, 5]. ZnO energy band gap of 3.37 eV and 60 MeV excitation energy make this material important for atoptic ultraviolet and blue-ray based devices [6]. However, the nature contains very small ultraviolet, i.e., about 4% of sunlight received by the earth [7]. To improve the ability of photocatalysts and broaden the absorption spectrum, it is necessary to provide doping of metals, non-metals, or precious metals to be able to change the level of energy, electrical and optical properties [8]. Fe as anabundant metal is believed to be an effective dopant to reduce band gap and change the initial properties of ZnO.

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The growth of ZnO:Fe thin films is carried out by the sol-gel method, while depositioning in the subtraction is done by spray-coating technique. This method was chosen because it is affordable, does not use vacuum chamber, homogeneous composition, controlled thickness of the refractive layer and the faid microstructure [9, 10]. Thin film formed is then used for degradation of rhodamin B dyes under UV and halogens.

2 MATERIAL AND METHOD

2.1 Instruments and Materials

Instruments used are Spray Gun (Krisbow HS-80, KW 1200333), Compressors (Krisbow, AS 186), UV-C and Halogen Lamps, Magnetic Stirrer Hotplates (Yellow Line, Yellow MAG HS 7), Digital Balance (VMC, VB 304 models), UV-Vis Spectrophotometer (Shimadzu, 1240 SA), and digital anglemeter. While the materials used are Sealing glass, Zinc Acetat Dehydrate (Sigma Aldrich, 97%), Isopropanol (Merck, 99.5%), Acetone (Merck, 99.5%), Methanol (Merck, 99.9%), Monoethanolamine (MEA), Aquades, Iron (III) Nonahydrate (Fe (NO3) 3.9H2O), Rhodamine B (C28H31N2O3Cl), and Methylene Blue (C16H18ClN3S).

2.2 Research and Variables

Fixed variables in this study were raw material of ZnO, hotplate temperature 60 °C, 180 minutes degradation time and deposition temperature 450 °C. The independent variables in this study were the addition of Fe in ZnO of 2, 4, 6, 8, and 10%, as well as the light sources used, namely UV lamps and Halogen. The dependent variable in this study is optical characteristics and degradation efficiency.

2.3 Synthesis Sol-Gel ZnO:Fe

Zinc acetatdehydrate (Zn (CH3COO)2.2H2O) 0.5 M is dissolved in isopropanol, stirred with a magnetic stirrer at 60^{o}C for 15 minutes. Solution is added Monoethanolamine (MEA), stirred for 15 minutes at 60^{o}C until the solution transparent. Then adding ferrititritrate (Fe (NO3)3.9H2O) with concentration variations of 2, 4, 6, 8, and 10% and then stirred for 15 minutes at 60^{o}C temperature. Synthesized product is then deposited with a spray-coating technique on the substrate laced on a 450^{o}C hot plate.

2.4 Degradation and Characterization

Rhodamine B 10 ppm solution is prepared by dissolving 10 mg of powder into 1 liter of distilled water. ZnO:Fe thin film according to the percentage of concentration is put into solution and carried out degradation using UV lamps and halogens for 180 minutes. Thin films and degradation results were characterized using a Shimadzu UV-Vis 1240 SA device

3 RESULT AND DISCUSSION

ZnO:Fe thin films has been successfully made using sol-gel method with spray coating technique. Samples with addition of Fe variation of 2, 4, 6, 8, and 10% are shown in Fig 1. Although itis not significant, the effect of adding Fe can be observed visually by shifting color of film from white to yellowish.

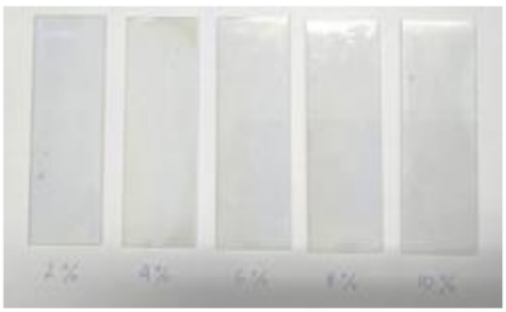


***Fig. 1**. ZnO:Fe 2-10% thin films*

Analysis of ZnO:Fe thin film transmittance in the 300-800 nm spectrum range is shown in Fig 2. Refers to wavelength spectrum of 400 nm, the highest value is ZnO:Fe 4% thin film, amounting to 96.8%, while the lowest value obtained ZnO:Fe 2% thin film by 53.5%. In the contrary, absorbance analysis shown in Figure 2, the wavelength spectrum of 400 nm highest value was ZnO: Fe 2% by 0.271, while the lowest value was ZnO:Fe 4% by 0.014. However, generally the increase in Fe concentration causes a decrease in transmittance and an increase in absorbance. It is due to the replacement of Zn atoms by Fe atoms which will form the distance among close particles. The greater concentration of Fe dopants, the greater agglomeration possible, thus the film will get thicker. Thick films indicate that more molecules are involved in absorbing light energy and less light is passed on. To determine the size of the ZnO:Fe thin films energy band gap, the tauch's plot method is used. As a result, the energy band gap values of ZnO:Fe 2-10% are 3.24; 3.29; 3.27; 3.25; and 3.24 eV. Energy band gap changes that decreases with the addition of doping concentrations is caused by a shift in the spectrum redshift. The change in the energy band gap value of the redshift of the semi-conductor II-VI doping metal transition is associated with the interaction of the sp-d spin electron band and the electron d transition metal s-d and p-d exchanging interaction cause narrower energy band gap [11].

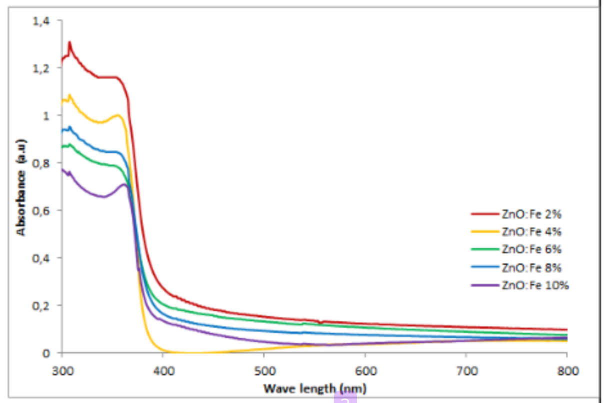


***Fig. 2**. Absorbance spectrum of ZnO:Fe thin films*

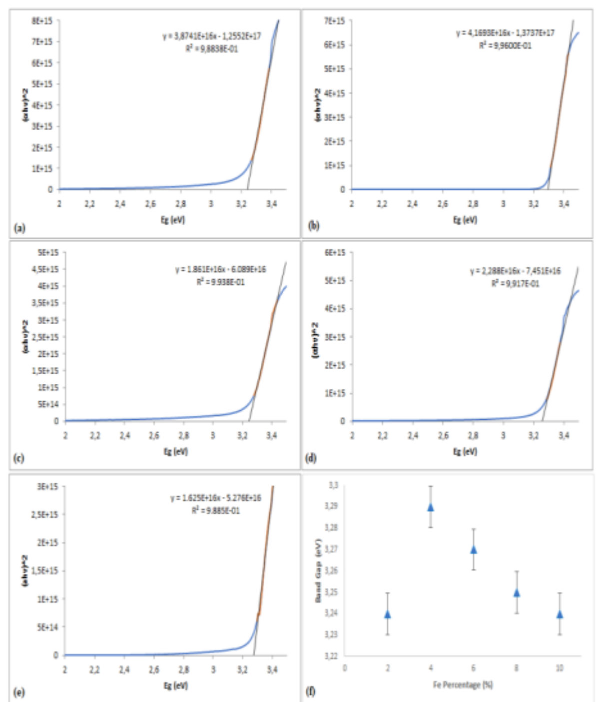
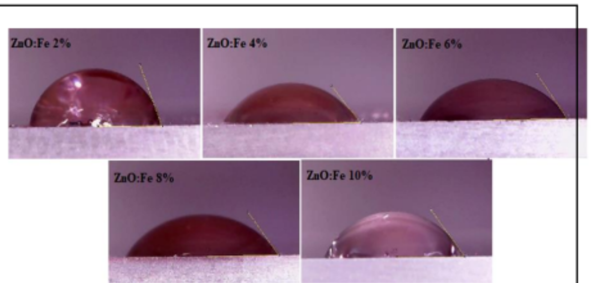


***Fig. 3**. Determination of energy band gap (a) ZnO: Fe 2% (b) ZnO: Fe 4% (c) ZnO: Fe 6% (d) ZnO: Fe 8% (e) ZnO: Fe 10% (f) Redshift shift according to the addition of Fe concentrations of 2-10%*

Hydrophilicity analysis of ZnO:Fe film was carried out using contact anglemeter which was then processed using imageJ software (Fig 4). Table 1 shows the results of contact angle testing, where the largest contact angle (62.52°) is owned by a thin film of ZnO:Fe 2%,and the smallest contact angle (50.66°) is owned by ZnO:Fe concentration of 4% Fe. In general, ZnO:Fe thin film has good hydrophilic properties, because the contact angle formed is less than 90°. It happens allegedly because there are hydrophilic molecules in the thin film, ie molecules that can interact well with H_2O. The difference of the contact angle valuesis related to the difference of the gap energy values and the resulting degradation efficiency.



Degradation is done by irradiating two variations of irradiate sources namely UV lamps (<400 nm) and visible light of halogen lamps. When the ZnO:Fe thin film absorbs irradiate from UV and halogens, transfer of electrons occur from the valence band to the conduction band to produce electron and hole pairs. If this condition can be maintained, the process of rhodamine B degradation will take place optimally. The resulting electrons can reduce O_2 to superoxide radicals (O_2–*) while holes can react with OH- ions in water to form

TABLE 1

CONTACT ANGLE OF ZNO:FE THIN FILM

Thin Film	Θ (°)
ZnO:Fe 2%	62,52
ZnO:Fe 4%	50,66
ZnO:Fe 6%	53,76
ZnO:Fe 8%	52,19
ZnO:Fe 10%	55,55

hydroxyl radical compounds (OH*) [12]. Superoxide radical compounds and hydroxyl radical compounds play a role in the degradation process of rhodamine B. However, formation of electron and hole pairs is an unstable condition and naturally will soon undergo recombination. Function of Fe doping in ZnO is to inhibit the recombination process. It happens because the Fe^{3+} dopant ion forms a new energy level that can trap electrons so that it does not immediately fall on the valence band and the degradation process can take place quickly [13,14]. The degradation rate of each irradiation is determined by analyzing the optical character of the sample every 30 minutes, as shown in Fig 5a and 5b. As a result, in the UV light ZnO:Fe 4% thin film produces the highest degradation efficiency (86.14%), while the lowest efficiency is produced by ZnO:Fe 2% thin film (81.37%). On the contrary, in the irradiation using visible light halogen lamps, the highest degradation efficiency was produced by a ZnO:Fe 2% thin film of 68.70%, while the lowest degradation efficiency was produced by a ZnO:Fe 4% thin film of (58.87%). Different levels of photocatalytic efficiency at each increase in dopant concentration are associated with a balance between absorption of visible light and potential of the valence edge band [15]. Nevertheless, the degradation ability generally corresponds to the energy band gap values that have been analyzed previously

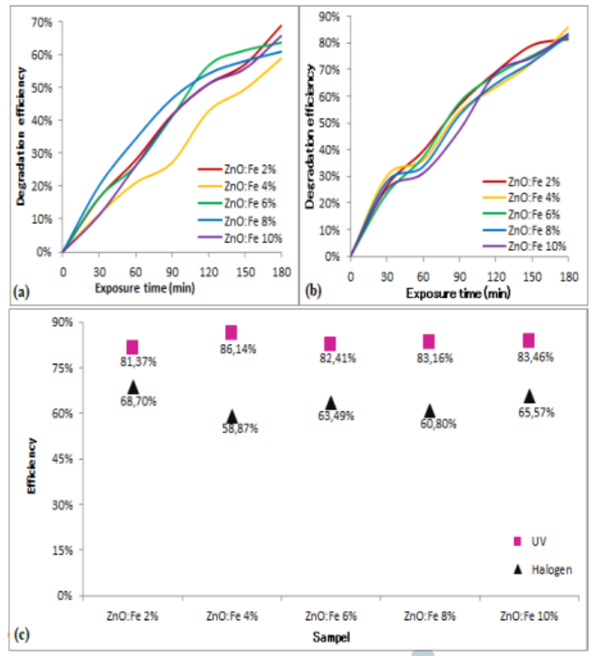


***Fig. 5**. (a) Degradation Efficiency under visible light irradiation (b) Degradation efficiency under UV irradiation (c) Comparison of degradation efficiency*

ZnO:Fe film 4% with the lowest energy band gap is effective for degradation in visible light irradiation. Whereas ZnO:Fe 2% and 10% films with the highest energy band gap are effective for degradation in UV irradiation. In this study, irradiation using UV seems more advantageous than using halogen visible light, because the decrease in energy band gap due to the addition of Fe concentration is in the range of 3.2 eV which is UV absorption. In addition to the light absorption factor, the catalytic efficiency of the ZnO:Fe film may also be affected by crystal size [16] therefore it needs to be further investigated.

4 CONCLUSION

ZnO:Fe thin films has been successfully made using sol-gel method with spray coating technique. Band gap value with the addition of Fe dopant is 3.24; 3.29; 3.27; 3.25; and 3.24 eV. ZnO: Fe 4% films produce the highest degradation efficiency (86.14%) under UV light and ZnO: Fe 2% films produce the highest degradation efficiency (68.70%) under halogen light.

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