Deposition of 2-6 mol%-doped ZnO Photocatalyst Thin Films by Thermal Spray Coating Method for E.coli Bacteria Degradation

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Deposition of Ag 2~6 mol%-doped ZnO Photocatalyst Thin Films By Thermal Spray Coating Method for E.coli Bacteria Degradation

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Abstract. ZnO doped with 2~6 mol% Silver (Ag) photocatalyst thin films has been deposited on a glass substrate by thermal spray coating with a temperature deposition of 250°C. A gel of ZnO:Ag precursor has been synthesized by sol-gel route from aqueous/alcoholic solution of zinc acetate dehydrate and silver nitrate mixture at room temperature. The morphology of ZnO:Ag films was investigated using scanning electron microscopy (SEM). 3D SEM images of ZnO:Ag thin films show the rough morphology with roughness mean square (RMS) of 150 to 195 nm. The grain size of ZnO:Ag films were found in the range 76.5 to 304.8 nm. The photoactivity examination of ZnO:Ag photocatalyst films shows the E.coli bacteria degrade up to 99.99% under sunlight irradiation for 4 hours.

Introduction

Heterogeneous photocatalyst is currently considered as a promising technique for the purification of water compared with other conventional methods [1, 2]. This water purification process uses the principle of the semiconductor. The photocatalytic process occurs when energy from the light is attuned to be in line with the band gap energy of a semiconductor material for chemical transformations to happen [3]. One of the semiconductors that now gain the attention of researchers as a photocatalyst material is Zinc Oxide (ZnO). Semiconductor-based photocatalytic degradation of pollutants has several advantages including being more effective, economical, and environmentally friendly [4]. Several studies have been carried out by several methods to improve the photocatalytic activity of ZnO. One of them is doping ZnO with transition metal nanostructures. Increasing the concentration of transition metal doping into ZnO will result in the change of energy level that in turn improves its physical and optical properties [5]. The transition metal silver (Ag) is suitable for ZnO doping to enhance its photocatalytic activity. In addition, Ag doping has advantages due to its nature as an antibacterial used to control the growth of bacteria in a variety of applications [6]. Previous research reported that Ag-doped ZnO increased photocatalytic activity [7]. There are methods available to deposit a thin layer of ZnO:Ag such as co-precipitation [5], spray pyrolysis [8], and sol-gel [9].

In this study, a thin layer of ZnO:Ag was deposited using sol-gel method on a glass substrate by thermal spray-coating. It was then examined as a photocatalyst to degrade organic pollutants. In addition, the microstructure and its influence in degrading the presence of E.coli bacteria as organic pollutants were also studied.

Experiment

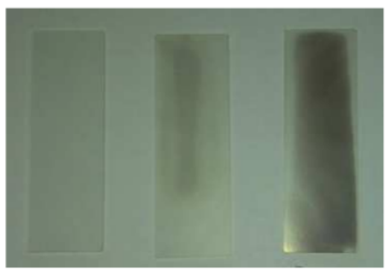
The precursor solution for depositing ZnO:Ag was made using the sol-gel method. Zinc Acetate dehydrate ($Zn(COOCH_3)_2.2H_2O$) was dissolved in 2-propanol ($CH_3CH(OH)CH_3$) at room temperature at a concentration of 0.3 M. Monoethanolamine (MEA) was then dropped into the solution and stirred using a magnetic stirrer at a temperature of 70°C for 30 minutes to form the sol-gel of ZnO. The sol-gel of ZnO:Ag was obtained by adding Ag doping with a concentration of 2~6% into ZnO solution as it was stirred for 30 minutes until the sol-gel ZnO:Ag 4% became.

The glass substrate was earlier cleaned according to the RCA (Radio Corporation of America) method with acetone and methanol for 10 min in ultrasonic bath to remove organic impurities. The glass substrate was washed with distilled water for 8 minutes and dried with spraying compressor. The dried glass substrate was then placed on a hot plate at a temperature of 250^{o}C for 10 minutes. The ZnO and ZnO:Ag thin films were deposited on a glass substrate by using thermal spray coating at a temperature of 250ºC for 1 hour. After deposition, the films were annealed at a temperature of 450ºC for 1 hour.

The microstructure of ZnO:Ag thin films was examined using SEM. The influence of dopant Ag on the shape and surface morphology of the ZnO thin film were analyzed. Then, the photocatalytic activity of ZnO:Ag was evaluated onthe solution containing the E.coli bacteria under sunlight irradiation. The solution containing the bacteria E.coli (30 ml) was poured into a container that contains ZnO:Ag thin films. After that, photo degradation process was performed by irradiating the sample under the sunlight for 4 hours. The solution after photodegradation was then characterized by Total Plate Counter (TPC) to determine the amount of the bacteria present after the photo degradationby ZnO and ZnO:Ag.

Results and discussion

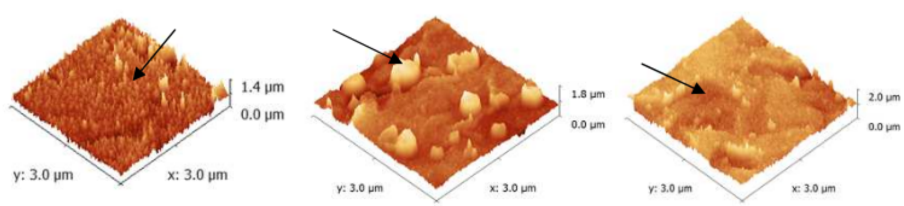
Fig. 1 shows the micrograph of ZnO:Ag thin film deposited on glass substrates by spray coating for different Ag concentrations (2 – 6%). It can be seen that adding Ag into ZnO precursor solution resulted in dark brown coating. In the other words, the transparency of the thin film is reduced by adding Ag.



(a) (b) (c)

Fig. 1. The ZnO:Ag films deposited on glass substrates with various Ag composition (a) 2%; (b) 4%; and (c) 6%.

Fig. 2 depicts 3D SEM image of ZnO:Ag thin film with an area of 3x 3 µm2 for various Ag contents. The 3D image reveals the film has rough morphology with non-uniform Ag distributed on the film surface. The RMS roughness value of ZnO:Ag thin films is tabulated in Table 1. The roughness RMS of 520 nm was observed for pure ZnO thin films. The addition of Ag into ZnO decreases RMS roughness of that films. Similar results have been reported by Tsay et al.,. The ZnO thin film surface with Ag doping has smoother surface than a film without Ag. The addition of Ag into ZnO decreased the roughness surface of that film [10].



ZnO:Ag(2%) ZnO:Ag(4%) ZnO:Ag(6%)

Fig. 2. 3D SEM image of ZnO: Ag thin films.

Table 1. The RMS value of ZnO:Ag thin films.

Sample	RMS (nm)	Grain Size (nm)
ZnO	520	-
ZnO:Ag 2%	150	76,5
ZnO:Ag 4%	195	304,8
ZnO:Ag 6%	167	173,4

The ZnO:Ag 4% thin film posseses higher RMS value than the ZnO:Ag thin films because the surface of ZnO:Ag 4% thin film is in a ganglia shape and it has large grains of 304.8 nm in size that are present uniformly on the surface. The increase in particle size leads to improved roughness and surface area [11]. Higher surface area enhances vacancy oxygen and increases diffusion process among organic and inorganic molecules with catalyst and it also correlates to photocatalyst activity [12]. The least rough RMS of 150 nm was observed for ZnO:Ag 2% thin film. The low roughness resulted from uniform small grains distributed on film surface. In addition, the grain size of ZnO:Ag 2% thin film is 76.5 nm and smaller than the others. Reduced grain size leads to less rough surface [10].

Photocatalytic ability of ZnO and ZnO:Ag thin films to degrade bacteria was examined using TPC. TPC measurement gives information about bacteria population which is present in a medium. In this research, photocatalytic ability of ZnO and ZnO:Ag thin films to degrade E.coli bacteria was evaluated in the water containing E.coli under sunlight irradiation for 4 hours. The sample of water after photodegradation was then analyzed using TPC. Table 2 shows the amount of E.coli and degradation percentage for all samples. The bacteria contained in all samples were reduced from 10^{10}/ml to 10^5/ml. These results show that ZnO and ZnO:Ag thin film possess photocatalytic ability. The percentage value of degradation for all samples is comparable. Degdradation of E.coli bacteria is found to be 99.9977% for pure ZnO thin film. This result reveals that ZnO thin film has good photocatalytic ability even without Ag dopant. It is well known that ZnO is a semiconductor that also has antibacterial property. That antibacterial activity destroys microorganism cell membrane. Wang et al. have pointed out that ZnO can destroy bacteria membrane with hydrogen peroxide it produces or by the proximity between surface of ZnO and bacteria [13]. The addition of Ag into ZnO increases degradation ability of pure ZnO due to the Ag antibacterial property. Therefore, the photocatalytic activity of ZnO is improved [6,7].

Table 2. Total E.coli degradation before and after photodegradation for 4 hours.

Sample	total *E.coli* / ml	% Degradation
Control	3.30×10^{10}	0
ZnO	7.50×10^5	99.9977
ZnO:Ag 2%	1.00×10^6	99.9970
ZnO:Ag 4%	1.61×10^5	99.9995
ZnO:Ag 6%	3.40×10^5	99.9990

Summary

ZnO and ZnO:Ag thin films with various Ag contents (2-6%) have been successfully grown on a glass substrate by thermal spray coating method. The microstructure and effect for photocatalyst application were also studied for the degradation of E.coli bacteria in water. The presence of Ag dopant on the microstructure of ZnO thin film affects the shape and size of grains in the film. The grain size increases up to 304.8 nm by 4%Ag doping. Alteration in the microstructure also affects photocatalytic activity. Ag dopant added to ZnO resulted in better ZnO photoactivity. This is proven by the decline in the number of E.coli bacteria after being treated with ZnO:Ag, compared to ZnO. Degradation percentage of ZnO:Ag (99.99951%) is greater than the degradation percentage of pure ZnO (99.99773%).

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References

[1] S. Baruah, and J. Dutta, Nanotechnology applications in pollution sensing and segradation in agriculture, a review. Environ. Chem. Lett. 7 (2009) 1-14.

[2] L. Chen, T. ThanhThuyn, C. Huang, J. Li, L. Yuan, and C. Qing Yun, Synthesis and photocatalytic application of Au/Ag nanoparticle-sensitized ZnO films, Appl. Surface Science 273 (2013) 82-88.

[3] A. Fujishima, T.N. Rao, and D.A. Tryk, Titanium dioxide photo catalysis, Journal of Photochemistry and Photobiology, C: Photochemistry Reviews 1 (2000) 1-21.

[4] J. Zhi-Gang, P. Kuan-Kuan, L. Yan-Hua, and Z. Rong-Sun, Preparation and photocatalytic performance of porous ZnO Micro rods Loaded with Ag, Journal of Trans. Nonferrous Met. Soc. 22 (2012) 873-878.

[5] R. Chauhan, A. Kumar, and R.P. Chaudary, Synthesis and characterization of silver doped ZnO nanoparticles, Journal of Scholar Research Library 2 (2010) 378-385.

[6] J. S. Kim, E. Kuk, K. N. Yu, K. Jong-Ho, S. J. Park, L. H. Jang, K. S. Hyun, P. Y. Kyung, P. Y. Ho, H. Cheol-Yong, K. Yong-Kwon, L. Yoon-Sik, J. D. Hong, and C. Myung- Cho, Antimicrobial effects of silver nanoparticles, Nanomedicine: Nanotechnology, Biology, and Medicine 3 (2007) 95-101.

[7] N. L. Tarwal, and P.S. Patil, Enhanced photo electrochemical performance of Ag–ZnO thin films synthesized by spray pyrolysis technique, Electrochemical Acta. 56 (2011) 6510-6516.

[8] S. K. Panda, and C. Jacob, Preparation of transparent ZnO thin films and their application in UV sensor devices, Solid-State Electronics 73 (2012) 44-50.

[9] M. H. Habibi, and R. Sheibani, Nanostructure silver-doped zinc oxide films coating on glass prepared by sol–gel and photochemical deposition process: Application for Removal of Mercaptan, Journal of Industrial and Engineering Chemistry 19 (2013) 161-165.

[10] C. Y. Tsay, and W. C. Lee, Effect of dopants on the structural, optical and electrical properties of sol-gel derived ZnO semiconductor thin films, Journal of Current Applied Physics 13 (2013) 60-65.

[11] J. B. You, X.W. Zhang, Y. M. Fan, Z. G. Yin, P. F. Cai, and N. F. Chen, Effect of the morphology of ZnO/Ag interface on the surface-plasmon-enhanced emission of ZnO films, J. Phys. D: Appl. Phys. 41 (2008) 205101C.

[12] J. C. Chang, M.H. Hsu, Y. C. Weng, C. Y. Tsay, and C. K. Lin, Hierarchical ZnO nanorod-array Films with enhanced photocatalytic performance, Journal of Thin Solid Films 528 (2013) 167-174.

[13] C. Wang, L. L. Liu, A. T. Zhang, P. Xie, J. J. Lu, and X. T. Zou, Antibacterial effects of zinc oxide nanoparticles on E.coli K88, African Journal of Biotechnology 11 (2012) 10248-10254.

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