Solid State Science and Technology, Vol. 25, No 2 (2017) 23-29
ISSN 0128-7389 | *http://journal.masshp.net*

ALUMINIUM DOPED ZINC OXIDE GROWN ON SAND FOR PHOTOCATALYTIC APPLICATION

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ABSTRACT

ZnO and aluminum doped zinc oxide (AZO) nanoparticles grown on microscopic sand particles using the sol-gel method has been applied in the photocatalytic degradation of methylene blue. The doping level was at 0.84 to 6.86 at.% Al with respect to Zn. The use of sand particles as template of ZnO nanoparticles was to enhance the effect by minimizing the agglomeration effect in loose nanoparticles. The doping levels were verified using X-ray diffraction and energy dispersive X-ray spectroscopy. The degradation of methylene blue dye solution was monitored using UV-Vis absorption spectroscopy. The photocatalytic activity has decreased from 10.10 x 10^{-3} min^{-1} for ZnO to 7.90 x 10^{-3} min^{-1} for AZO 0.84 at. % of Al. Then, the photocatalytic activity has increased up to19.10 x 10^{-3} min^{-1} for AZO 3.42 at.% of Al before declining to 15.10 x 10^{-3} min^{-1} at 6.86 at.% of Al.

Keywords: sol-gel; ZnO, nanostructures; photodegradation

INTRODUCTION

The study of semiconductor-based photocatalysis has progressed rapidly since their discovery in early 1970s [1]. Along with several other metal oxide semiconductors (TiO_2 [2, 3], CdS [4, 5] and ZnS [6, 7]), zinc oxide (ZnO) has received a lot of attention due to wide band gap of 3.37 eV, large excitation biding energy of 60 meV, low cost and capability to completely decompose recalcitrant contaminants [8]. Photocatalytic efficiency on ZnO mainly depends on the ability of electron-hole pair formation under UV light irradiation. By reducing the recombination of photoexcited electron and holes, the photocatalytic efficiency were expected to be increase. The most excellent way to increase the charge carrier separation is to dope ZnO with metal oxide such as aluminum, silver, copper and magnesium. Among all, aluminum doped zinc oxide (AZO) has been widely studied for photocatalyst application due to the high

transmittance even at near infrared wavelength [9]. Several technique have been studied in order to increase the quality and density of AZO for photocatalytic efficiency. However, there is still insufficient and controversy over the optimized Al doping content in ZnO as well as the ability of reusable and reproducibility of AZO as photocatalyst. In order to overcome these problems, the synthesis of AZO nanoparticles on sand and the effect of Al doping on the structural, morphology and photocatalytic activity of AZO were investigated.

EXPERIMENTAL

Prior to the growth process, the sand were seeded with ZnO by three cycles of sonicating in the 0.005 M of zinc acetate solution for 15 minutes and then dried at 300 °C for 10 minutes. In order to deposit aluminum doped ZnO nanoparticles, the aluminum nitrate was added to the growth solution at different mol percentage which 1, 3, 5 and 7 mol% Al with respect to Zn. The sand particles were stirred in the growth solution of 0.05 M of zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) at 100 °C for 6 hours. For Al doping the appropriate amount of aluminum nitrate was added to the growth solution. After growth process, the samples were rinse thoroughly in deionized water then calcite at 300 °C for 2 hours. The structural and surface morphologies for each samples was analyzed by field emission electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). For the photocatalytic study, 5 g photocatalyst were added to 100 ml of 10 mg L^{-1} methylene blue (MB) solution under UV light (6 Watt, UVGL-58) with a peak wavelength at 254 nm. The percentage of MB decolorization was recorded by using UV-Vis spectrophotometer for every 15 minutes interval until 150 minutes.

RESULTS & DISCUSSIONS

Figure 1 presents the typical FESEM images of the prepared sand-ZnO, ZnO powder and AZO 3.42 at. % of Al respect to Zn samples. All samples show homogeneous, dense and formed of a large number of small particles which the size of particles were less than 100 nm. In term of diameters, AZO 3.42 at. % of Al sample shows smallest sizes compared to the sand-ZnO and ZnO powder which around 24.38 to 47.26 nm. These small particles might increase the surface area of the prepared AZO photocatalyst and enhance its light absorption which might be beneficial for its photocatalytic activity enhancement. The aggregation of small particles in the ZnO powder sample had caused more agglomeration between each other as shown in Figure 1 (e). This leads to a decrease in light utilization rate and lowering photocatalytic activity.

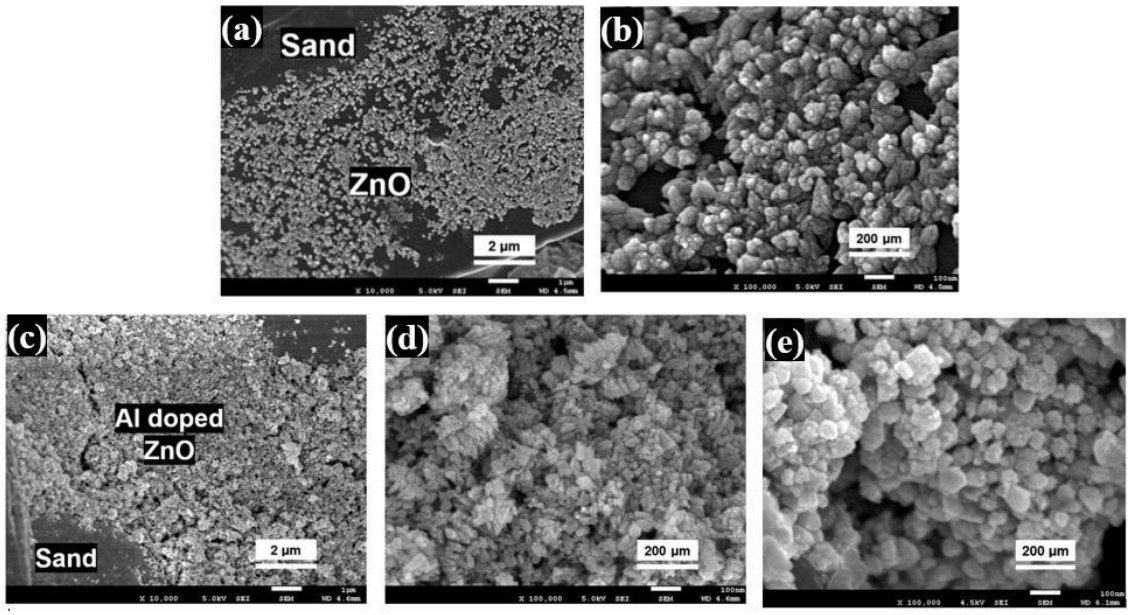
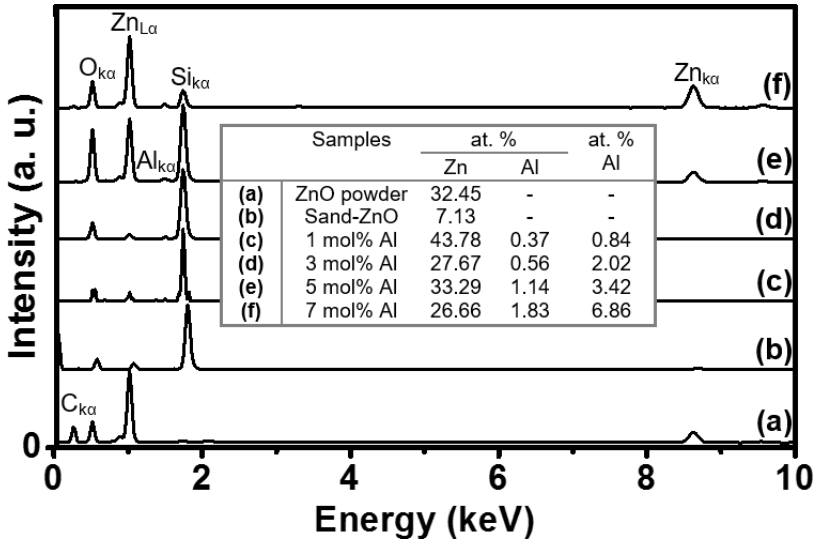


Figure 1: FESEM images of ZnO grown on sand at (a) low magnification and (b) high magnification; (c) and (d) AZO 3.42 at. % of Al grown on sand at low and high magnification, respectively; and (e) ZnO powder at high magnification

The present of Al element in the AZO samples were evidenced by EDX spectra as shown in Figure 2. The amount of Al doped ZnO were calculated by atomic percent (at. %) which leads to 0. 84, 2.02, 3.42 and 6.86 at. % of Al for 1, 3, 5 and 7 mol %, respectively. As the amount of Al doped increases, a strong peak of $Al_{k\alpha}$ appeared for AZO samples at 1.486 keV especially for AZO 6.86 at.
% of Al sample.



	Samples	at. % Zn	at. % Al	at. % Al
(a)	ZnO powder	32.45	-	-
(b)	Sand-ZnO	7.13	-	-
(c)	1 mol% Al	43.78	0.37	0.84
(d)	3 mol% Al	27.67	0.56	2.02
(e)	5 mol% Al	33.29	1.14	3.42
(f)	7 mol% Al	26.66	1.83	6.86

Figure 2: EDX spectra of ZnO powder, ZnO grown on sand and AZO samples

The typical XRD patterns of ZnO powder, ZnO nanoparticles and Al doped ZnO grown on sand are illustrated in Figure 3. Clearly, all samples had showed common ZnO peaks at 31.8^{o}, 34.5^{o}, 36.3^{o}, 47.7^{o}, 56.7^{o}, 63.0^{o} and 69.2^{o}. The peaks position can be indexed to the wurtzite crystal ZnO structure (JCPDS File No. 01-79-2205) and correspond to (100), (002), (101), (102), (110), (103) and (201), respectively as shown in Figure 3 (i). Whereas the others peaks at 39.7^{o}, 40.4^{o}, 42.6^{o}, 45.9^{o}, 50.4^{o}, 55.1^{o} and 60.1^{o} can be indexed to the (012), (111), (200), (201), (134), (022) and (211) reflection planes of quartz based on the JCPDS file no. 46-1045. From the Figure 3 (ii), it also shows that there is a significant shifting and broadening in (101) peak position towards higher 2θ value around 0.42^{o} relative to the pure ZnO with increasing of Al^{3+} content. It indicates that the lattice of ZnO slightly change with Al^{3+} doping due to the formation of stress by ionic radii difference between Zn^{2+} and Al^{3+} [10].

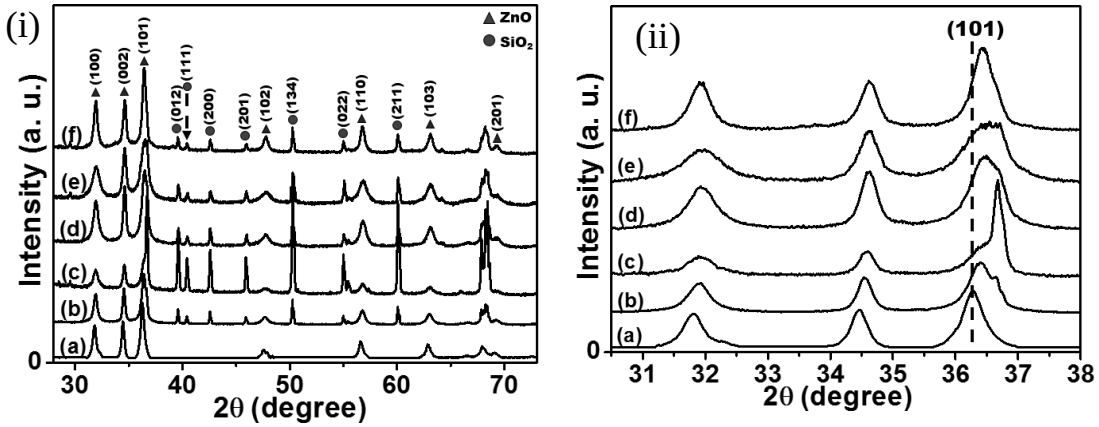


Figure 3: (i) and (ii) XRD patterns of (a) ZnO powder, (b) sand-Zno and Al doped ZnO grown on sand for (c) 0.84 at. % Al, (d) 2.02 at. % Al, (e) 3.42 at. % Al and (f) 6.86 at. % Al

The photocatalytic activities of sand-ZnO, ZnO powder and AZO catalysts were evaluated by measuring the degradation of 100 ml MB solution under UV irradiation as shown in Figure 4. The photocatalytic activity of sand-ZnO had been found to be better than ZnO powder which was able to degrade MB solution approximately 78.52 % at 150 minutes compared to 64.41 % of ZnO powder. It indicated that the ZnO grown on sand made a great improvement on the efficiency of photocatalytic activities by minimizing the agglomeration effect in loose nanoparticles as well as prevent ZnO nanoparticles to stack together during growth process. The influence of the Al doping level was at 0.84 to 6.86 at. % Al with respect to Zn on the degradation of MB solution was investigated. The photocatalytic activity slightly decrease for the AZO 0.84 at. % compared to sand-ZnO. This phenomenon occurred might be due to the presence extra electron from Al element that caused fast recombination rate of photogenerated electron-hole pair during photodegradation process. Along with the increasing of Al

doped in the AZO samples from 0.84 at. % to 3.42 at. %, the time of MB solution degradation were shortened as well as the photocatalytic activities were increased from 72.47 % to 93.81 % for 150 minutes as shown in Figure 5 (a). As the doping level of Al continued increase to 6.86 at. %, the photocatalytic activity was decreased by 3.51 %. The relatively high doping level of Al seems to be detrimental to the photodegradation reaction of MB by promoting the charge pair combination [11]. Contrarily, the charge pair separation probably occurs effectively for AZO photocatalysts at low doping level of Al. It was prove that with an appropriate Al content, it will optimize its role of photogenerated electron trapping.

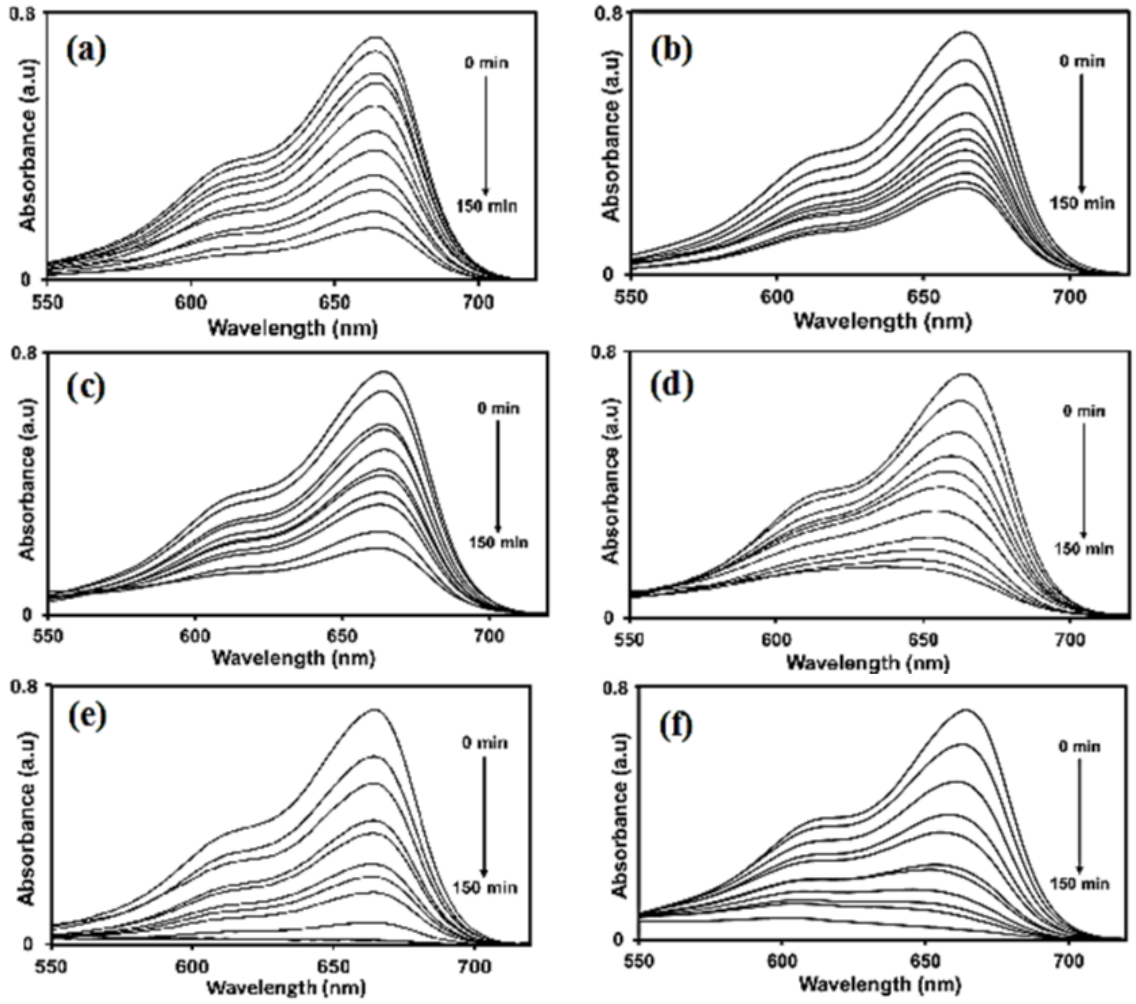


Figure 4: UV-Vis absorption spectra showing photocatalytic degradation of 100 ml MB solution under UV light using: (a) sand-ZnO, (b) ZnO powder, (c) 0.84 at. % Al, (d) 2.02 at. % Al, (e) 3.42 at. % Al and (f) 6.86 at. % Al as photocatalyst

The photocatalytic activities of sand-ZnO, ZnO powder and AZO nanoparticles grown on sand for the degradations of MB were illustrated in Figure 5. The photocatalytic activities of the AZO photocatalyst change with the Zn contents where the photocatalytic

activities of AZO samples showed increasing until it reach at AZO 3.42 at. % of Al sample with photocatalyst reaction rate constant, k was 19.10 x 10^{-3} min^{-1} and photodegradation percentage was 93.81% for 150 minutes. The lowest photocatalytic activity was observed at ZnO powder with k value was 6.80 x 10^{-3} min^{-1}. It was then followed by AZO 0.84 at. %, sand-ZnO, AZO 2.02 at. % and AZO 6.86 at. % of Al where k values are 7.90 x 10^{-3} min^{-1}, 10.10 x 10^{-3} min^{-1}, 11.50 x 10^{-3} min^{-1} and 15.10 x 10^{-3} min^{-1}, respectively.

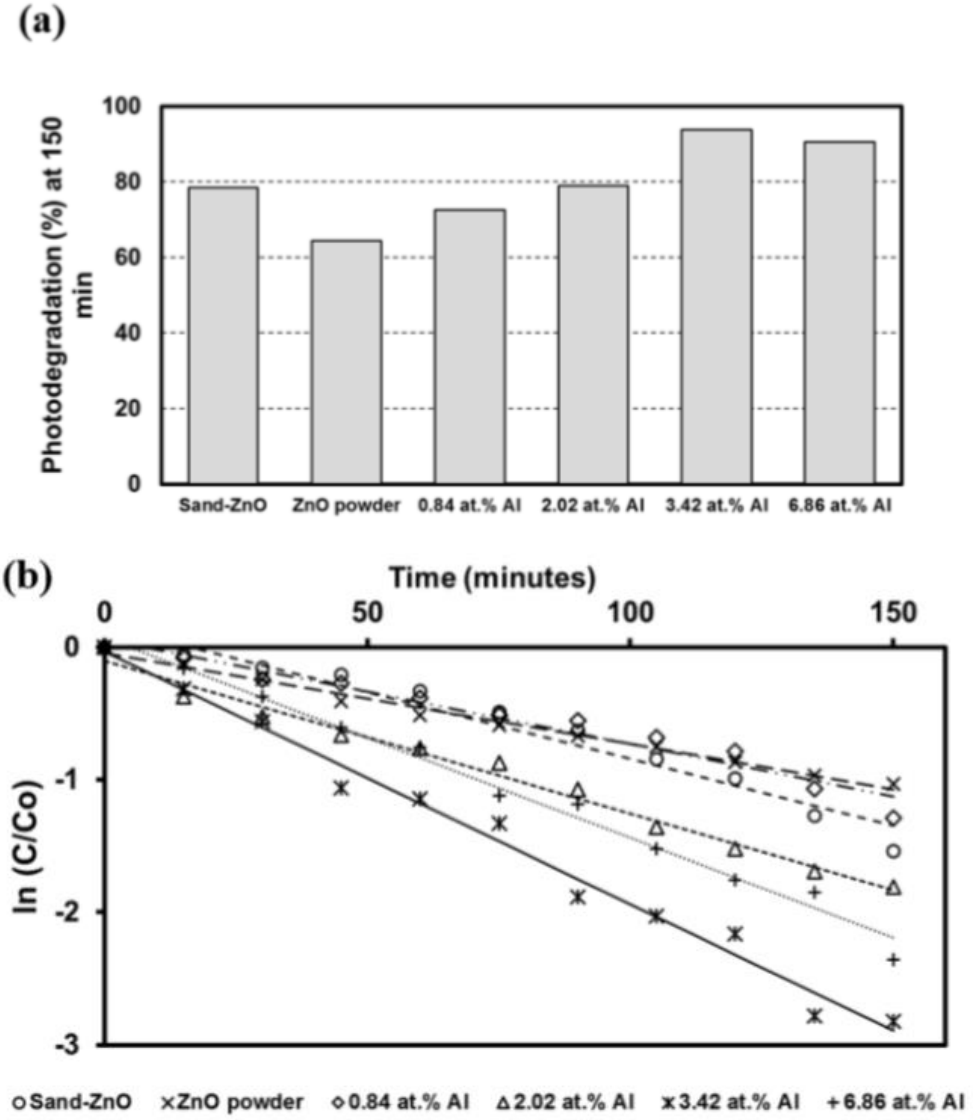


Figure 5: (a) The percentage of photodegradation MB solution at 150 minutes and (b) linear plots of ln (C/C_o) for the photodegradation of MB in the presence of sand-ZnO, ZnO powder and AZO samples

CONCLUSION

In conclusion, ZnO and AZO were successfully growth on the microscopic sand particles by using sol-gel method. Photocatalytic experiments were carried out using MB as a photodegradable organic compound under UV irradiation. It was showed that the doping of Al into ZnO did not change significantly the crystal structure and light absorption property of ZnO. Moreover, the diameters of AZO slightly decreased compared to ZnO powder and sand-ZnO. By decreasing the diameters of AZO, the surface area will increase and leads to increase the photocatalyst activity for MB degradation. AZO 3.42 at. % of Al showed the highest photocatalytic activity for the degradation of MB where the value of the reaction rate constants was 19.10×10^{-3} min^{-1}. Based on results, the photocatalytic activities were found to be affected by the agglomeration of ZnO and doping level of Al.

ACKNOWLEDGEMENT

This work is supported by Postgraduate Research Grant (Project Code: PG110-2015A) funded by the Institute of Research Management & Monitoring, University of Malaya.

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