Advanced Materials Research Vol 1112 (2015) pp 209-212
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doi:10.4028/www.scientific.net/AMR.1112.209

Submitted: 2014-09-03
Revised: 2015-02-14
Accepted: 2015-02-22

Photocatalytic Activity Inhibition by ZnO-SiO_2 Nanocomposites Synthesized by Sonochemical Method

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Keywords: Ultrasound irradiation, Photodegradation reaction, Zinc oxide nanoparticles, Zinc oxide-silica nanocomposites

Abstract. Here, ZnO particles and ZnO-SiO_2 nanocomposites synthesized by sonochemical method under continuous ultrasound irradiation were reported. For an hour ultrasound irradiated by ultrasonic horn at atmospheric condition, nanorods and spherical structures with crystalline sizes 33 and 17 nm were obtained for ZnO and ZnO-SiO_2, respectively, revealed that silica inhibited the particles and crystal growth. FTIR analysis also indicated that silica covered the ZnO particles. In addition, photocatalytic activity was also inhibited by silica in which ZnO without and with silica had degradation rate 69% and 48%, respectively, to degrade methylene blue solution under direct sunlight irradiation for an hour. The addition of SiO_2 to ZnO gives an advantage in some application to avoid excessive degradation by controlling their photocatalytic activity.

Introduction

ZnO nanostructures have been widely used in many applications such as catalysts, sensors, phosphors, and transparent conducting films because of their wide-band gap of 3.37 eV, high optical gain, and high exciton binding energy of 60 meV [1]. Among many methods to prepare nanostructures materials, it has been demonstrated that ultrasound irradiation can produce a wide range of nanostructure materials [2]. In this method, high power ultrasound with high frequency was introduced into precursor solution resulting in complex reaction mechanism initiated by acoustic cavitation producing local heating up to 5000 K and high pressures about 1000 atmospheres. The collapse occurs in less than a microsecond and very high cooling rate above 10^{10} K per second.

In some application such as photoluminescence material, adding inert materials such as silica is needed to hinder agglomeration between individual ZnO nanoparticles by trapping/capping them in silica matrix [3][4][5]. Another method is coating ZnO by silica layer to control their photocatalytic activity [6] or photoluminescence enhancement [7]. They used tetraethoxylane (TEOS) as a silica source which is relatively expensive and toxic organic material.

Here, we reported the preparation of nanostructured ZnO and ZnO-SiO_2 nanocomposites by ultrasonic irradiation method and comparing their photocatalytic activity method from zinc nitrate and waterglass as zinc oxide and silica sources, respectively, which are relatively inexpensive and green chemical.

Experimentals

Materials and Method. Zinc oxide particles were prepared by dissolving zinc acetate tetrahydrate ($Zn(NO_3)_2.4H_2O$ 98.5%, Merck) into distillate water resulting in 100 mL of 0.2 M zinc nitrate solution. 20 mL of 25% ammonia solution (Merck) was added to the zinc solution to obtain turbid solution. Then, 10 drops of 25% ammonia solution was added to make the solution clear and pH was

10. This solution is called starting solution. Ultrasonic horn (VCX500, 20 kHz, Sonics & Materials, Inc.) was immersed in the starting solution in order to generate high intensity ultrasound wave under nitrogen atmospheric condition and 70°C for an hour in continuous mode irradiation. The generated suspension was washed by centrifugation at 4,000 rpm for 45 minutes, filtered, and dried at 130°C for 12 hours, consecutively, to obtain dry white powder.

To prepare ZnO-SiO_2 particles, 20 mL of 0.1 M colloidal silica prepared from waterglass was added into starting solution that had been sonicated for 45 minutes. The sonication was continued for 15 minutes later to get a total reaction was an hour. The preparation of colloidal silica was explained elsewhere [8].

Characterizations. Powder was characterized their morphology, crystallinity, and chemical bonding by using scanning electron microscopy (SEM, Zeiss Evo MA LS series, operated at 20 kV), x-ray diffractometer (XRD, Phillips, CuKα, θ=1.54 Å, operated at 40 kV and 30 mA), and Fourier transform infrared (FTIR, Perkin Elmer), respectively. The photocatalytic activities of the generated samples were determined by measuring the degradation of methylene blue solution under direct solar irradiation. 70.0 mg of sample was introduced in 50 mL of 10^{-5} M methylene blue solution was stirred in the dark for 30 minutes before irradiated to ensure adsorption/desorption equilibrium. The absorbance of the methylene blue solution was measured using UV-Vis spectrophotometer (Genesys 10uv scanning) which was recorded every 15 minutes for an hour. The measurement was carried out for blank, ZnO added, and ZnO-SiO_2 added methylene blue solution. Because of methylene blue concentration in the solution is directly proportional to the measured absorbance, the degradation efficiency of methylene blue can be calculated using the following equation:

$$\text{Degradation rate (\%)} = (A_o - A)/A_o \times 100\% \quad (1)$$

where A_o is the initial absorbance and A is the absorbance at definite time.

Results and Discussion

SEM images of pure ZnO and ZnO-SiO_2 synthesized by sonochemical method are depicted in Fig. 1a and Fig. 1b, respectively. The growth of pure ZnO formed nanorods with 160 nm in average diameter and 616 nm in average length. On the other hand, spherical and agglomerate particles seem generated with primary particles less than 50 nm in size. The addition silica during synthesis led to the inhibition of ZnO growth. Silica seemed to coat the ZnO particles or ZnO particles was trapped among silica nanoparticles.

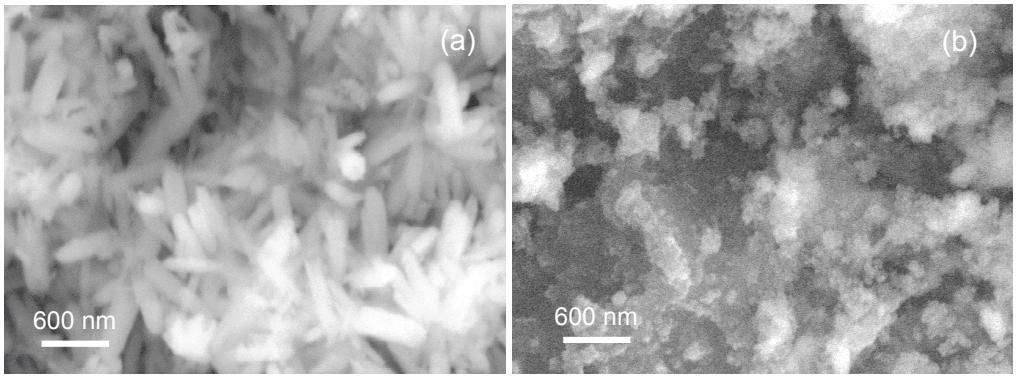

Fig. 1 SEM images of (a) ZnO and (b) ZnO-SiO_2.

Fig. 2 shows the XRD pattern of ZnO and ZnO-SiO_2 particles. Both samples were in agreement with the wurtzite structure ZnO diffraction of hexagonal phase (JCPDS No. 36-1451). Scherrer equation was used to estimate the crystalline size based on the highest peak in XRD pattern characterized by (1 0 1) lattice plane at 2θ=36.253°. Crystalline sizes of ZnO and ZnO-SiO_2 particles

were 33 and 17 nm, respectively. The crystal growth was also inhibited by silica addition during the synthesis.

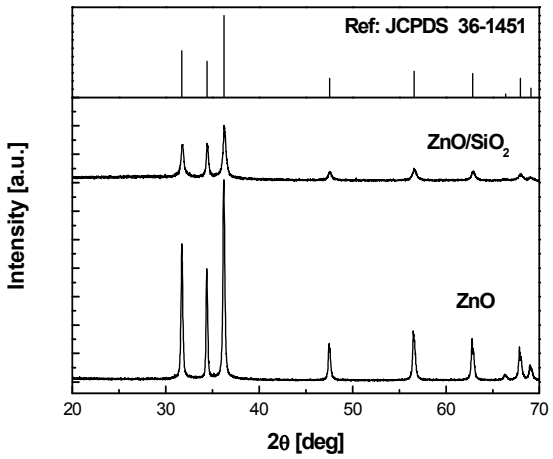

Fig. 2 XRD patterns of ZnO and ZnO-SiO_2 particles.

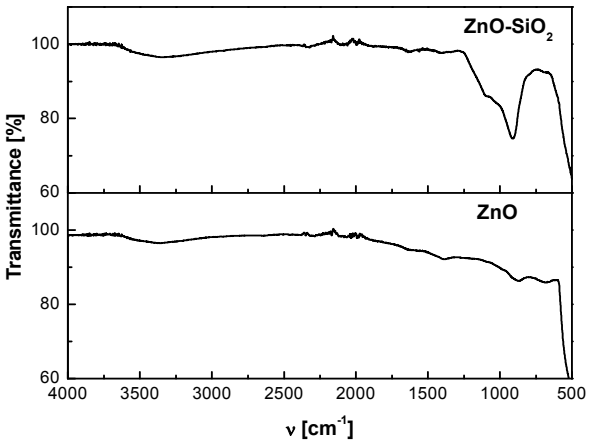

Fig. 3 FTIR spectra of ZnO and ZnO-SiO_2 particles.

Fig. 3 shows the FTIR spectra of the samples characterized the type of chemical bonding of pure ZnO and ZnO-SiO_2 particles. FTIR spectra of pure ZnO and ZnO-SiO_2 particles showed the presence of bands at around 3,500 cm^{-1} corresponding to O-H stretching vibrations of the absorbed water. The spectra of ZnO-SiO_2 particles had the additional broad band at around 1,000 cm^{-1} corresponding to Si-O-Si asymmetric stretching vibration. This spectrum indicated that the silica coated on ZnO particles that has been confirmed by previous investigation [6].

Fig. 4 shows absorbance of methylene blue solution characterized the photocatalytic methylene blue decomposition in the presence of ZnO and ZnO-SiO_2 particles. The highest absorption spectrum of methylene blue occurred at wavelength of 664 nm arises from the chromophore in methylene blue. This wavelength was selected to calculate the degradation rate of methylene blue. ZnO particles shows higher photocatalytic activity than that of ZnO-SiO_2 nanocomposites. The rate of the methylene blue degradation is higher for ZnO particles.

ZnO shows higher photocatalytic activity indicated by the absorbance or the concentration of the methylene blue more decreased than that of ZnO-SiO_2.

Fig. 5 shows the degradation rate of methylene blue solution by ZnO and ZnO-SiO_2 acted as photocatalysts. For an hour sunlight irradiation, the degradation rate of methylene blue by ZnO and ZnO-SiO_2 were 69% and 48%, respectively. Silica lowered the degradation rate of ZnO acted as a layer to inhibit the migration of active photocatalyst (ZnO) to the surface [6].

Summary

ZnO nanorods and ZnO-SiO_2 spherical nanocomposites were successfully synthesized by sonochemical method under continuous ultrasound irradiation. Crystalline size of ZnO-SiO_2 was smaller than that of ZnO nanorods revealed that silica inhibited the crystal growth of ZnO. Degradation rate methylene blue by ZnO nanorods was higher than by ZnO-SiO_2 spherical nanocomposites. Silica acted as inhibitor for photocatalytic reaction of methylene blue solution by active area of ZnO.

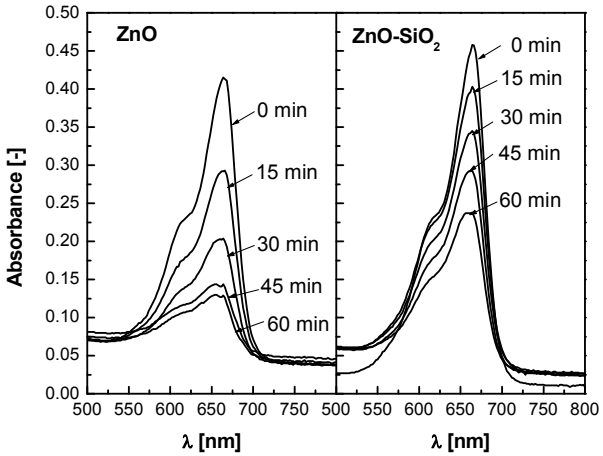

Fig. 4 Absorbance spectra of methylene blue solution in the presence of ZnO and $ZnO-SiO_2$ under direct sunlight at various time.

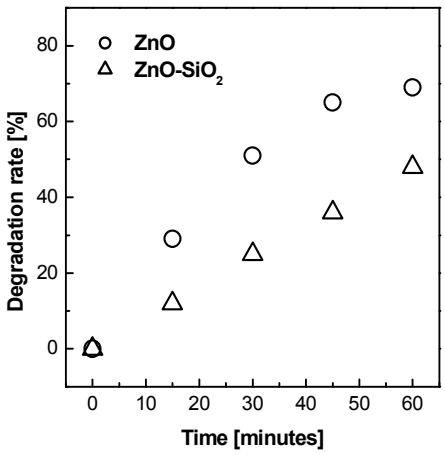

Fig. 5 Degradation rate of methylene blue in the presence of ZnO and $ZnO-SiO_2$ under direct sunlight at various time.

Acknowledgements

Research Grant sponsored by Directorate General for Higher Education, Ministry of Education and Culture of Indonesia under scheme of research collaboration and international publication (No. SP DIPA-023.04.2.414964/2014) is gratefully acknowledged. We also extend our gratitude to Mr. Septono Sanny Putro and Mr. Mohammad Rahmatullah for assistance with the experiment.

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