Fabrication of ZnO-SiO₂ Nanocomposite Materials Prepared by a Spray Pyrolysis for the Photocatalytic Activity under UV and Sunlight Irradiations

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Abstract. ZnO is the most widely used for photocatalytic application among various semiconductor materials. The photocatalytic performance of ZnO can be enhanced by doping with other materials. In this study, ZnO-SiO₂ nanocomposites have been successfully fabricated by gas-phase method via spray pyrolysis. The effect of temperature of spray tubular furnace reactor ranging from 300 to 600 °C on the photocatalytic activity of ZnO-SiO₂ nanocomposites were investigated. Colloidal SiO₂ with concentration at 1 %wt was used as dopant to ZnO particles. The pristine ZnO was also synthesized at temperature of 400 °C for comparable. Zn(OH)₂ acetate and water glass were used as the precursors for fabrication ZnO˗SiO₂ nanocomposites. At first, the water glass was synthesized by sol-gel method to produce colloidal SiO₂ nanoparticles and then mixed with zinc acetate before subjecting to the spray reactor. The produced nanocomposite materials were collected by an electrostatic precipitator. Scanning electron microscopy and energy-dispersive X-ray (SEM-EDX), X-ray diffraction (XRD), and Fourier-transform infrared (FTIR) were used for characterization the products. While UV-Vis spectrometry was used to measure the concentration of methylene blue (MB) before and after irradiations. SEM images indicated that the morphology of particles was as sphere-like structures with interwoven nanoplate and the agglomeration of particles can be suppressed by adding SiO₂. The average particle size of the produced nanocomposite decreased with increasing synthesis temperature. XRD analysis also confirmed that the crystallite size increased with increasing temperature. Finally, the photocatalytic activity of the ZnO-SiO₂ nanocomposites were calculated by evaluating the methylene blue degradation aqueous solution under UV and sunlight irradiations. MB degradation efficiency under UV light was much lower than that of under sunlight irradiation. It also showed that the best photocatalytic performance reached 96 % when the synthesis temperature was set as high as 400 °C with SiO₂ concentration at 1 %wt under sunlight irradiation.

1. Introduction
Now a day, increasing the organic pollutants derived from dyes have paid more attention because they are not easily biodegraded [1]. There are many methods reported by previous studies to degrade the organic pollutants, such as by electrochemical, absorption, oxidation, reverse osmosis, ion-exchange, sonocatalytic, and photodegradation [2-5]. Photocatalysis method is one of the most promising method to degrade the organic pollutants because it can be conducted in atmospheric pressure and ambient temperature and not expensive. This method can convert the organic pollutants into water and carbon dioxide when the photon energy of incident light is greater or equal to the band gap energy of catalyst material used [1, 2]. For application in photocatalysis, ZnO is the most widely used as catalyst material among the semiconductor materials because it has wide band gap, strong oxidation ability, cost-
effectiveness, non-toxicity, high chemical stability, and so on [2, 3]. However, the application of ZnO particles in the photocatalysis has some limitations due to electron-hole recombination and very limited to ultraviolet (UV) region [1, 2, 6]. Therefore, significant efforts have been made to enhance the photocatalytic activity of ZnO which is by modification the surface of ZnO [2, 7], adding noble metals [3] or SiO2 nanoparticles [1, 8], and formation of ZnO film [9].

In this study, colloidal SiO2 is used as a dopant in ZnO matrix because it is relative ease of preparation, large specific surface area, non-toxic, and compatibility with other materials [1]. Moreover, SiO2 can be used as support to prevent the growth of ZnO particles and enhance the contact area between catalyst and water [9]. ZnO-SiO2 nanocomposite can be prepared by liquid and gas phase methods. Sol-gel, co-precipitation, solid dispersion method, chemical synthesis, and biosynthesis are widely used to fabricate ZnO-SiO2 via liquid phase [1, 2, 9-12]. Using liquid phase method to produce nanocomposites has some advantages due to a simple process. Experiment can be carried out at ambient temperature and atmospheric pressure. Unfortunately, it involves a great number of processing steps. Widiyastuti et al. [13] used consecutive sol-gel and flame-assisted spray-drying to produce ZnO-SiO2. However, the application of the produced nanocomposites is limited to the photoluminescence. On the other hand, controlling the temperature inside the flame reactor may be difficult. To overcome this limitation, ZnO-SiO2 is synthesized by spray pyrolysis in the present study. The source of heat energy comes from the electricity making the adjustment of temperature inside tubular reactor becomes much easier in comparison with the flame method. It is also not required for further treatment to handle the solvent because the solvent evaporates during heating. Another advantage in this study is that colloidal SiO2 is synthesized from water glass, where this precursor is much cheaper than other silica sources (tetra ethoxy silane (TEOS) and hexa methyl disiloxane (HMDSO)). Furthermore, water glass is non-toxic if compared with TEOS and HMDSO. Our hypothesis, the adjustment of furnace temperature may alter the properties of the produced nanocomposite resulting the difference photocatalytic performance. Therefore, the objective of this study is to investigate the effect of furnace temperature on the photocatalytic activity of ZnO-SiO2 prepared by spray pyrolysis. The photocatalytic activity is evaluated by measuring the degradation of methylene blue (MB) under UV and sunlight irradiation. We believe that the obtained results will give new insight in fabrication method of ZnO-SiO2 via gas phase method using spray pyrolysis and perhaps it can be applied in textile industries to degrade the organic liquid waste caused by textile dyes.

2. Research Methodology

2.1. Materials and experimental setup

Materials used in this study were zinc acetate dehydrate (Zn(CH3COO)2.2H2O, 99.5%), water glass (Na2O.nSiO2.mH2O, 8% Na2O, 27% SiO2), potassium hydroxide (KOH) and MB (C16H18ClN3S). These chemicals were purchased from Merck and used as received without further purification. In this case, zinc acetate and colloidal silica particles were used as the precursor for producing ZnO-SiO2 nanocomposites. The colloidal silica particles were prepared based on a method reported by Widiyastuti et al. [13] and Qomariah et al. [14]. Briefly, water glass was diluted with a distilled water to obtain the concentration of colloidal solution as much as 0.1 M at ambient temperature. After that, the water glass solution was converted into silicic acid solution by removing sodium ions through the cation exchanger filled with AmberliteTM IR120 resin (Dow Chemical). Formation of gel was observed indicating that the removing of sodium ions with the cation exchange process was successfully completed. Potassium hydroxide 0.1 M was then added drop by drop to reach the pH of 8 under continuously agitation to form colloidal silica. In the current research, colloidal silica at 1 % based on the weight percent of zinc acetate was used. The particle size distribution of the prepared colloidal silica was obtained as large as 10 nm using dynamic light scattering [14]. While, zinc acetate was dispersed to distilled water to obtain 0.1 M under sonication for 10 min. The colloidal silicate and the prepared zinc acetate were mixed under sonication for making homogenous suspension. The prepared precursor was then poured into the ultrasonic nebulizer.
Figure 1 shows a schematic diagram of the fabrication method of ZnO-SiO$_2$ using spray pyrolysis. Droplets were generated by an ultrasonic nebulizer (Omron) operated at 1.7 MHz. Peristaltic pump was utilized to flow the fresh precursor into the nebulizer in order to keep the constant volume of the precursor inside a nebulizer [3]. We assumed that the concentration of the precursor can be kept constant by controlling the volume level inside the nebulizer. The generated droplets were then carried to the tubular reactor by compressed air as a carrier gas with a flow rate of 2 L/min (LPM). The tubular reactor was heated by using electricity source and varied at temperature in range of 300 – 600 ºC. The solvent evaporation and decomposition of precursor occurred in the heated tubular reactor to produce ZnO-SiO$_2$ nanoparticles. The generated nanoparticles were then collected in the electrostatic precipitator with applied voltage at 40 kV. To avoid condensation, the temperature in the electrostatic precipitator was maintained constant at 120 ºC.

![Figure 1. Schematic illustration of ZnO-SiO$_2$ nanoparticles prepared by spray pyrolysis.](image)

2.2. Characterizations
X-ray diffraction (XRD, X’pert Philips) operated at 40 kV and 30 mA was used to observe the crystalline phase and crystallite size of the produced ZnO-Ag nanocomposites. Other parameter settings of XRD analysis were 2$\theta$ ranging from 10 - 80o, scan speed of 10 o/min, and sampling point of 0.02o. Scanning electron microscopy (SEM, FlexSEM1000, Hitachi High Technologies) was used to see the morphology of the particles. The chemical composition of the produced nanocomposites was measured by energy-dispersive X-ray spectroscopy (EDX). The distribution of particle size was estimated by measuring few hundreds of the particles using ImageJ software. Fourier-transform infrared (FTIR) was used to identify the hydroxyl group of the produced nanocomposites.

Finally, the performance of photocatalytic activity of the produced ZnO-SiO$_2$ nanocomposite was tested using MB aqueous solution under sunlight and UV light (220 V, 10 W) irradiations. Intensity meter was used to record the intensity of the sunlight periodically and conducted on a sunny day. The sample was prepared by dispersing 10 mg of nanocomposite into 40 ml of MB solution under stirring for 30 min in a dark condition. This procedure was attributed to obtain the equilibrium of an adsorption-desorption. After that, the samples were exposed to either UV light or sunlight for 210 min. Degradation of methylene blue was monitored every 30 min by measuring the absorbance of MB using UV-Vis spectrophotometry (Thermo Scientific Genesys 10s). The concentration of MB was obtained by converting the measured absorbance using the calibration curve of MB. The degradation of MB was calculated using same equation as reported in our previous study [15]:

$$\text{Degradation} = \frac{c_a - c_t}{c_a} \times 100\%$$  \hspace{1cm} (1)
Here, $C_0$ is the initial concentration of MB and $C_t$ is the concentration after $(t)$ irradiation. Photocatalytic performance was then investigated by plotting $-\ln(C_t/C_0)$ versus time, where the slope of the fitted line represents the value of $k$.

3. Results and Discussion

3.1. XRD results

Figure 2 shows the XRD patterns of ZnO-SiO$_2$ nanocomposites produced by spray pyrolysis at different temperatures ranging from 300 to 600 $^\circ$C including the pristine ZnO at 400 $^\circ$C. Selecting the pristine ZnO at temperature of 400 $^\circ$C is caused by which the highest photocatalytic activity was obtained at this temperature (data not shown).

It is shown that the peaks at 31.8º, 34.4º, 36.3º, 47.5º, 56.6º, 62.9º, and 68.1º appear in the XRD patterns indicating the existence of ZnO with the phase of wurtzite hexagonal crystal structure. Moreover, all these peaks are consistent with the ZnO peaks from the Joint Committee on Powder Diffraction Standards (JCPDS) which correspond to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), and (1 1 2) plane orientation, respectively. It indicates that spray pyrolysis method with varying temperatures is able to synthesize ZnO nanoparticles. The same peaks were also observed when flame pyrolysis was used to produce ZnO nanoparticles using zinc acetate as precursor [3]. Unfortunately, the existence of SiO$_2$ in the nanocomposite cannot be detected because the SiO$_2$ has an amorphous phase. This result is in a good agreement with result reported by Qomariah et al. [14], where there was no significant peaks can be detected by XRD analysis using various concentrations of SiO$_2$.

Scherrer equation was then used to estimate the crystallite size ($D$) of the produced nanocomposite as expressed in Equation (2) [2, 15]:

\[ D = \frac{k \lambda}{B \cos \theta} \]

Here, $k$ is the constants (0.94), $\lambda$ is the CuK$_\alpha$ radiation source (0.15418 nm), $B$ is the full-width at half-maximum (FWHM) and $\theta$ is a half the angle of the peak. The crystallite size estimated by Equation (2) for ZnO-SiO$_2$ with different temperature at 300, 400, 500, and 600 $^\circ$C were obtained as large as 11, 14, 17, and 19 nm, respectively. While the crystallite size for the pristine ZnO at 400 $^\circ$C was 16 nm. It can be simply concluded that increasing temperature will slightly increase the crystallite size of the
nanocomposite. This is because the energy provided to form crystal structure becomes greater in resulting the larger crystallite size. This result has same tendency with the results reported by previous studies which mentioned that the increasing temperature produced the particle with larger crystallite size [15, 16].

3.2. SEM observation
The morphology of the nanocomposites with different temperatures was observed by SEM as depicted in Figure 3. The morphology of the produced nanocomposite was observed as sphere-like structures with interwoven nanoplate. In general, the morphology of particles does not alter significantly by changing the temperature of furnace reactor from 300 to 600 ºC. This morphology is quite different when compare to the nanoparticles produced by liquid phase, where the shape is mostly spherical [17]. We believe that the effect of temperature may contribute in the formation of the produced nanoparticles. Moreover, Figure 3 also indicates that the more agglomeration of particles occurs when the pristine ZnO is used in comparison with the addition of SiO₂ nanoparticles.

![Figure 3. SEM images of ZnO-SiO₂ nanocomposites prepared by spray pyrolysis at different temperatures ranging from 300 to 600 ºC including the pristine ZnO at temperature of 400 ºC.](image)

Figure 4 shows the particle size distributions of ZnO-SiO₂ nanoparticles at different temperatures as well as the pristine ZnO at temperature of 400 ºC. ImageJ software was utilized to calculate the particle size distribution by measuring several hundreds of particles from the SEM image. It is found that the particle size decreases with the increase of furnace reactor temperature. The possibility of this phenomena may be attributed due to nucleation process. At higher temperature, the nucleation becomes faster resulting higher concentration of nanoparticles. In contrary, the nucleation will be slow at lower temperature allowing the nanoparticles to grow and become larger. Interestingly, the particle size of pristine ZnO is larger than that of ZnO-SiO₂ at same temperature of 400 ºC. It means that the existence of SiO₂ particles in the nanocomposite is able to suppress the particle growth resulting to decrease the size. Moreover, the presence of SiO₂ can inhibit the agglomeration of ZnO particles as reported by Widiyastuti et al. [13]. The tendency of this result is also similar with reported by Ali et al., where the addition of SiO₂ reduced the agglomeration of particles by pressing the particle growth [9].
Figure 4. Particle size distribution calculated by ImageJ software of ZnO at temperature of 400 ºC (a) and ZnO-SiO2 nanocomposites at temperatures of 300 ºC (b), 400 ºC (c), 500 ºC (d), and 600 ºC (e).

Figure 5. EDX mapping of ZnO-SiO2 nanocomposites at temperature of 400 ºC (a) and %mass of Si analyzed by EDX spectroscopy of ZnO-SiO2 nanocomposites at different temperatures ranging from 300 to 600 ºC (b).

Based on the SEM images, it is difficult to differentiate SiO2 nanoparticles from the ZnO-SiO2 nanocomposites, because the particle size of SiO2 is much smaller than that of ZnO. Further observation using field emission SEM (FE-SEM) or transmittance electron microscopy should be addressed. In this study, we used EDX mapping and EDX spectroscopy to detect the existence of SiO2. Figure 5(a) shows the distribution of particles by EDX mapping, where the sample is mostly dominated by red colour representative as Zn. While, Figure 5(b) depicts the elemental analysis of Si in the sample with various temperatures. It is clearly observed that the existence of Si is detected by EDX spectroscopy in which the Si concentration is in the range of 0.2-0.9 %mass. However, it may be difficult to make conclusion using this graph, because the tendency is not comparable. In the current report, we cannot explain why the concentration of Si is difference in various temperatures. More experiments should be conducted to explain these phenomena.
3.3. Photocatalytic activity

Photocatalytic activity of ZnO-SiO$_2$ nanocomposites can be evaluated by measuring degradation efficiency of MB and the rate constant. MB degradation efficiency after irradiation with UV and sunlight are shown in Figure 6. It is obviously observed that the degradation of MB under UV irradiation is much lower than that of sunlight irradiation. The maximum degradation efficiency of MB under UV irradiation can reach up to 58% when SiO$_2$ was added to ZnO at temperature of 400 °C. Whereas, the degradation efficiency can attain 96% under sunlight irradiation for ZnO-SiO$_2$ prepared at 400 °C. In general, it can also be seen that the addition of SiO$_2$ is able to enhance the photocatalytic performance. These results are in a good agreement with the result as reported by previous studies [2, 8, 9].

![Figure 6](image1.png)

Figure 6. Methylene blue degradation efficiency as a function of irradiation time of the ZnO-SiO$_2$ nanocomposites at different temperatures including the pristine ZnO under UV (a) and sunlight irradiations (b).

![Figure 7](image2.png)

Figure 7. Plot ln($C_t/C_0$) versus irradiation time of the ZnO-SiO$_2$ nanocomposites at different temperatures including the pristine ZnO under UV (a) and sunlight irradiations (b).

Photocatalytic performance can also be expressed by plotting $-\ln(C_t/C_0)$ versus irradiation time in resulting the slope of the fitted line which represents the value of $k$ as shown in Figure 7. It can be concluded that the best photocatalytic performance is obtained when SiO$_2$ was added into ZnO and synthesized at temperature of 400 °C. Moreover, the addition of SiO$_2$ into ZnO particles shows better photocatalytic performance than that of using pristine ZnO. It was reported by Stanley et al. [2] that the
existence of SiO₂ nanoparticles in the ZnO enhances the efficiency of separation process of electron-hole recombination and creates new active sites during photocatalytic process. This is ascribed due to interaction between ZnO particles and SiO₂.

Figure 7 also shows that the photo degradation of MB under sunlight irradiation is much higher than that of using UV light irradiation. It is because the existence of SiO₂ nanoparticles in the ZnO matrix is able to widen the spectrum to visible region due to surface plasmon resonance effect of SiO₂ particles. This result is in good agreement with Stanley et al., where the effect of SiO₂ was able to shift the absorption peak into visible region at 434 nm. It is well known that the sunlight consists of about 48% visible region [18]. It means that the photocatalytic process can be done not only limited in the UV region but also in the visible region. This can be obtained by irradiation with sunlight in resulting the higher photocatalytic activity.

Figure 8. FTIR spectra ZnO-SiO₂ nanocomposites prepared by spray pyrolysis at different temperatures ranging from 300 to 600 °C.

It can be seen form Figure 7, the photocatalytic performance of the ZnO-SiO₂ nanocomposite increases from temperature 300 to 400 °C, while it then decreases after the increase temperature at 500 and 600 °C. Generally, the photocatalytic performance is influenced by many parameters, such as: surface area, diameter of particle, pore size, crystallinity, crystalline size, morphology of particle, addition of foreign materials, and so on. Based on our results, the particle size decreases with increasing temperature and the crystallinity also increases with increasing of temperature. However, we believe that the photocatalytic activity may be not significantly affected by the particle size and crystallinity. We think that the most dominant factor to affect the performance of photocatalytic in this study is attributed due to existence of hydroxyl group of the produced nanocomposites. As mentioned in our previous study [3], the mechanism of photocatalytic activity is initiated by generating of electron and holes after irradiation with photon energy. Holes are then reacted with hydroxyl to produce hydroxyl radicals. These radicals are strong enough to degrade the MB for producing water and carbon dioxide [9]. To investigate the hydroxyl group in the produced nanocomposites, we used FTIR analysis as depicted in Figure 8. The area around the peak at 3400 cm⁻¹ was measured using simple method to compare the number of hydroxyl group as quantitatively. The area at temperature of 300, 400, 500, and 600 °C is found as 2758, 5835, 2727, and 2316, respectively. Based on this area, it can be concluded that the synthesis ZnO-Ag at temperature of 400 °C give the highest area among them indicating the highest number of hydroxyl group. The reason why synthesis temperature at 400 °C producing the best photocatalytic performance can be explained by this phenomenon. Cheng et al. [19] also reported that
the activity of photocatalytic is mostly influenced by hydroxyl ions in comparing with crystal structure. They also used FTIR to estimate the number of hydroxyl group in the nanocomposites.

4. Conclusions

The fabrication of ZnO-SiO₂ nanocomposite using gas-phase method via spray pyrolysis has been successfully conducted. The effects of furnace temperatures ranging from 300 to 600 °C on the morphology and crystallite size of the produced nanocomposite as well as their photocatalytic activities were investigated. SiO₂ nanoparticles were successfully fabricated using water glass as a precursor. The XRD analyses indicated that the ZnO produced in this study was hexagonal wurtzite structure. The crystallite size increased with increasing the temperature. Moreover, the SEM analyses indicated that the morphology of ZnO-SiO₂ nanocomposite had as sphere-like structures with interwoven nanoplate. The average particle size decreased with increasing the temperature of furnace. On the other hand, the particle size of the pristine ZnO synthesized at temperature of 400 °C was slightly larger than that of ZnO-SiO₂. XRD and SEM analyses did not show the exactly of the existence of SiO₂ in the nanocomposite, but using EDX mapping and EDX spectroscopy can observe the presence of SiO₂ in the nanocomposites.

Activity of photocatalytic of the produced nanoparticles was investigated by measuring the photodegradation of MB under UV and sun light irradiations. It was found that the existence of SiO₂ in the nanocomposite showed better photocatalytic performance than that of using pristine ZnO for both conditions. The best photocatalytic performance was obtained when ZnO-SiO₂ synthesized at 400 °C was used under UV and sunlight irradiations. The FTIR observation also indicated that the highest number of hydroxyl group was obtained at temperature of 400 °C. Degradation efficiency under sunlight irradiation was also higher than UV light. The maximum efficiency of MB degradation under UV irradiation reached up to 58 %, while it attained 98 % under sunlight irradiation.

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