Electrospray synthesis and photocatalytic activities of ZnO-SiO$_2$ composites particles

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Abstract. A new and rapid method for zinc oxide (ZnO) and ZnO-SiO$_2$ (ZS) composite particles by the simple electrospray method was reported. Free agglomeration and smaller particle size of ZS composite obtained with an increase in the applied voltage that correlates with the charge repulsion within the particles. The presence of silica inhibited the ZnO particles and crystal growth. The XRD and FTIR spectra indicated that silica covered the ZnO particles. Smaller ZS molar ratio with higher applied voltage had a significant role in minimizing the agglomeration of the particle production. This suggested a morphological control of the composite through electrospray. The results of the photocatalytic degradation of methylene blue (MB) in aqueous solution revealed that the presence of silica effectively inhibited the photocatalytic activity of ZnO particles in which the ZnO without and with silica had degradation rate 85% and 63%, respectively. The effect of silica amount to the ultraviolet (UV) shielding property of ZnO particles also examined.

1. Introduction

In recent decade the ZnO nanoparticle has attracted a lot of attention for wide application because this metal oxide has unique optical and electrical properties which are not observable in the bulk counterparts [1,2]. It has various functions such as for catalysts, sensors, cosmetic materials, pigments, photoluminescence material and transparent conducting film [3-9]. This is because it has wide-band gap around 60 MeV [10]. In general, the ZnO particle is easily agglomerate in the colloidal solution [11]. In particular, for the special application such as for UV attenuation, an inert material such as colloidal silica particle usually added to the ZnO colloidal solution. The silica particle is a transparent material which did not disturb the nature properties of ZnO [12-14]. In addition, the gel formation should be avoided in this application.

Recently, a number of investigations such as hydrothermal, sonochemical, co-precipitation, and spray pyrolysis has been published in preparing the ZnO-SiO$_2$ composite [9, 15-18]. The process typically consists of the sol preparation and the composite production process. However, the composite particle produced from the general process typically agglomerate. This is due to the natural characteristic of ZnO particle which can easily agglomerate. A hydrothermal, sonochemical, and sol-gel can produce a homogeneous and controllable particle morphology, but these methods have several disadvantages such as long reaction time and multi-step process. Spray pyrolysis method is promising for composite production in one-step process. However, it needs a higher reaction temperature which means the higher energy is required. In comparison with the established method, it is necessary to develop a one-step and
efficient process involved the short production time to synthesize the composite particle. The use of electrospray process can specially use in this regard. The used of electrospray process instead of conventional spray drying has been increased by several authors [19-21]. As compared with conventional spray drying process, this method offers a higher production yields, high purity product and has a dramatically lower evaporation temperature. This is due to the produce droplet can lose the solvent to the environmental air only by the diffusion process at room temperature. The droplet formation was initiated and affected by the applied voltage. The high electric field concentration induces the emission of fine spray of charged droplet [22]. It is important to generate a small droplet size in order to obtain higher surface area. Several composite particles have been developed through this process. For example, Ag/ZnO, CdSe/ZnS, carbon-polymer, ZnSnO$_3$/PMMA, any kinds of other composite [19, 23-25]. Based on the author best knowledge, the electrospray method is a new process for producing ZnO-Silica composite particle. The published report related to this composite formation is found to be limited.

The present work describes a new and one-step process of ZnO and ZS composite using electrospray method. The advantage of this method is the short production time of the composite. A wide range of chemical and physical parameters can be tuned to obtain a controllable morphology. These parameters include solution composition, flow rate, and the applied voltage. Here we reported that under an appropriate set of condition, the electrospray method can be employed to obtain a controllable ZS composite particle. The photocatalytic activity of produce particles was also reported. The presence of silica particle found to be affected the inhibition of ZnO photocatalytic activity.

2. Materials and Methods

2.1 Materials
The composite was prepared from natrium silicate (Na$_2$SiO$_3$, 27%, Merck) as silica source and zinc acetate (C$_4$H$_6$O$_4$Zn, 2H$_2$O, Merck) took as ZnO source. Ethanol (C$_2$H$_6$O, 90%, Merck) was as a solvent. The model azo dye methylene blue (Merck) for photocatalytic test was used as received. All the chemicals were reagent grade and used without further purification.

2.2 Methods
The colloidal silica solution was prepared by a method established by author previous research [26]. Sodium silicate diluted in distilled water to reach 0.1 M. The solution passed through cationic resin (Amberlite™ IR 120, Dow Chemical) to remove the sodium ion. The resulting solution pH was adjusted to 11 point by added 0.1 M potassium hydroxide (KOH) solution drop-by-drop. The ZnO colloid was prepared by dispersing zinc acetate in ethanol. Ultrasonic treatment was performed to the resulting solution to increase the zinc acetate dispersion. The dispersion was put into distillation apparatus at 80°C to dilute the zinc acetate. The resulting solution was put in cold environment at 5°C followed by the addition of 0.14 M LiOH solution drop-by-drop to form ZnO colloid.

![Figure 1. The experimental apparatus of electrospray process](image)

To prepare the ZS composite, the prepared colloidal precursors which have different characteristic were mixed with a different ZnO and SiO$_2$ molar ratio. The resulting colloid was put in the plastic syringe with 0.5 mm diameter of the needle tip. To maintain the continuity of liquid supply, a syringe pump was used at fix feeding rate 1 mL/h. The needle tip was connected with the positive terminal of high voltage
generator or in vice versa. While the negative terminal was connected to collector with approximately 10 cm away from the needle. The experimental apparatus is clearly described at Figure 1.

2.3 Surface Characterizations
The characteristics of the colloidal solutions (SiO₂, ZnO, and ZS composite) were measured using the Zetasizer nano ZSP (Malvern Instruments, Ltd., Malvern, U.K.). The results were presented in detail in Table 1. To examine the size distribution and the morphology of the prepared particles, a Hitachi FlexSEM 1000 high resolution scanning electron microscope was used to obtain the SEM micrographs. The X-ray diffraction (XRD) of the powder samples were taken in the 2θ range of 10-80°. FT-IR spectra were recorded using IRAffinity-1S (Shimadzu Corp, Japan).

| Ratio          | Zeta Potential (ζ) |
|----------------|--------------------|
| SiO₂           | -38.6 mV           |
| ZnO            | -10.4 mV           |
| ZnO : SiO₂ (4:1)| -18.3 mV           |
| ZnO : SiO₂ (1:4)| -30.2 mV           |
| ZnO : SiO₂ (1:1)| -25.1 mV           |

2.4 Photocatalytic Activity Measurement
The photocatalytic activity of pure ZnO and ZS composite particles were evaluated by measuring the photodegradation of methylene blue (MB). It has been extensively used to be an indicator of photocatalytic activity. The prepared particles (0.1 g) were introduced to a 100 ml of 10⁻⁵ M methylene blue aqueous solution. The solution was stirred in a dark room for 30 minutes to ensure the adsorption/desorption equilibrium of MB and then irradiated under direct sunlight for 2 hours. The absorbance of the MB was recorded in a regular interval every 10 minutes using a UV-Vis spectrophotometer (Genesys 10 UV-Vis Spectrophotometer, Waltham, MA) at 600 nm wavelength. The MB concentration is directly proportional to the measured absorbance. Therefore, the degradation efficiency of MB can be calculated using the following equation:

\[
\text{Degradation rate (\%)} = \left( \frac{C_0 - C}{C_0} \right) \times 100\% = \left( \frac{A_0 - A}{A_0} \right) \times 100\%
\]

Where \(C_0\) represents the initial concentration, \(C\) is the concentration at definite time, \(A_0\) is the initial absorbance, and \(A\) is the absorbance at definite time.

3. Results and Discussion
In the electrospray process, the applied voltage is the key essential to determine the particle characteristics and morphology [22]. In addition, it also affected by the charged current mode (positive or negative) of the spray droplet. Its proven by the SEM results in Figure 2 of the samples using both positive and negative charged mode. Figure 2(a) shows the prepared particles from negative colloidal precursor sprayed by negative charge current. An agglomerated particle is observed, which indicate that the particles still in the fission process right before it deposited in the collector [21]. This phenomenon occurred due to the application of charge current which has similar polarity with the zeta potential of particle. Table 1 shows that all the colloidal solution which contains pure and composite particle has a negative zeta potential value.

In contrast, the negative colloidal samples which sprayed using positive charge current, free-agglomerate particles are obtained as shown in Figure 2(b). Application of the opposite polarity between the charge current and the zeta potential would reduce the fission tendency. As the result, free agglomeration particle in a spherical shape can be obtained. This result proved that in the electrospray process, the change in voltage polarity strongly affected the particle morphologies in terms of agglomerated particles. This result can be used as supporting evidence that at the same polarity, the produced particles tend to repel each other. Agglomerate particles should be hindered for the photocatalytic application which required a particle with high surface area. According to this result, a positive current charge was applied for all variables in this experiment.
Figure 2. SEM image of pure ZnO prepared by electro spray method at negative (-) and positive (+) induce charge

Figure 3. SEM image of pure ZnO and pure Silica prepared by electro spraying the colloidal solution using positive current mode

To understand the effect of silica addition to the composite morphology, the pure ZnO and ZS particle are compared which the SEM image is depicted in Figure 3. The growth of pure ZnO clearly observed in Figure 3(a) with 1 μm in average size. In the colloidal solution, individual ZnO tends to agglomerate each other [11]. As a result, the pure ZnO has a bigger average particle size compared to the composite. On the other hand, spherical composite particle has a primary particle size around 0.5 μm. This result confirm that the addition of silica led to the inhibition of ZnO growth. The particle formation mechanism seems to follow one-droplet-to-one-particle that is common in spray process. It was reported that to achieve free-agglomerate composite particle using spray process, several parameters such as colloidal composition and condition operation have to be adjusted. Especially in electrospray process, the applied voltage has an essential in controlling the particle morphology.

The successfully synthesize of pure ZnO and ZS composite was characterized using XRD and FTIR analysis as shown in Figure 4(a). The XRD patterns of pure ZnO shows the characteristic peaks of wurtzite phase of ZnO which well matched with JCPDS card number 36-1451. No diffraction peaks of other ZnO phase were observed. For the ZS composite particle, the ZnO peaks are still exist in the XRD spectra but with lower intensities. No additional peaks correspond to the silica peak which indicate the silica is most likely in amorphous phase. This result implied that the addition of silica particle does not change the crystalline structure of ZnO particle.

The FTIR spectra was strongly support the composite formation as shown in Figure 4(b). The FTIR spectrum of pure ZnO showed the presence of bands at around 819 cm\(^{-1}\), 1310 cm\(^{-1}\), and 1456 cm\(^{-1}\) which correspond to the Zn-O bridging bonds. For the ZS composite spectra, an additional sharp band clearly observed at 954 cm\(^{-1}\) and 1105 cm\(^{-1}\) corresponding to the asymmetric vibration of the Si-OH and Si-O-Si, respectively. This result confirming the presence of the silica coating in the ZS composite particle. Correspond with the XRD and FTIR results, the ZS composite was successfully synthesized through electrospray process.
Figure 4. (a) XRD and (b) FTIR spectra of pure ZnO and ZS composite

SEM micrography for the composite samples sprayed at different applied voltage (6-10 kV) presented in Figure 5. The applied voltage related to the particle interaction either in the droplet or among the particle. Agglomerate particles seem generated at 6 kV. This is due to this voltage is inadequate to break the repelling particle. In the case of higher voltage 10 kV, free-agglomerate spherical particles are observed, which indicates that the high voltage provide higher surface charge. It accommodates higher repelling between droplet and lead to the free-agglomerate composite particles. An increase in the applied voltage beyond the critical value has a role in the formation of spherical particle. According to these results, the applied voltage was fixed at 10 kV for the synthesis of ZS composite.

Figure 5. The effect of voltage to the ZS composite morphology prepared using electrospray method

The amount of silica in the composite particle at different ZnO to silica ratio was analyzed by SEM and the results are shown in Figure 6. It was observed that the smaller composite particle obtained at the ratio 1:1. Increasing the silica ratio become 1:4, higher composite particle size was obtained as shown in Figure 6(b). Addition of silica particle is effective to reduce the growth tendency of ZnO particle. In addition, the presence of higher silica ratio will increase the composite average size due to the higher silica particle on the ZnO surface. In the case of agglomerated particles are observed in the higher ZnO to silica ratio 4:1, which indicate that the silica is not enough to inhibit the ZnO growth. Therefore, the uncoated ZnO continue to grow and repel each other.

In order to examine the distribution of ZnO and silica in the composite particle, elemental mapping of Zn, Si, and O by EDX analysis was done as shown in Figure 7 in the case of 4:1 ZnO to Silica ratio. The result confirmed that both ZnO and silica were well dispersed among the others. The ZnO particle size in the composite is smaller than that in the pure condition. It is also confirmed that the silica particle can inhibited the growth of ZnO particle. Through electrospray process, the negative particle surface charge and the positive current mode contributed to the agglomerate-free composite particle. Even the
repulsive charge exists between ZnO and silica, the value is too small so it can be attenuated by the 10kV positive charge current produced by the high voltage.

Figure 6. SEM image of the composite particle at different ZnO to Silica ratio (a) 4:1, (b) 1:1, (c) 1:4

Figure 7. Elemental mapping of Si, Zn, and O of ZS composite at ZnO to Silica ratio 4:1

The ZnO particle morphology strongly affected the photocatalytic activity as shown in Figure 8(a). The results were taken after achievement of the adsorption equilibrium in the dark place. The spherical ZnO particle as synthesized using positive charge showed a higher photocatalytic activity which shown by the higher degradation rate. In contrast, the aggregate ZnO particle produce using negative charge showed a lower degradation rate. This result confirmed that the agglomerate particle has lower surface area which decreased the active surface photocatalyst of ZnO. In addition, the composite particle also has a lower photocatalytic activity due to the presence of silica particle.

To understand the effect of silica addition on the photocatalytic activity of ZS composite, photocatalytic decomposition of the MB was carried out in this research at room temperature. Figure 8(b) shows the photocatalytic activity of pure ZnO and ZS composite at different molar ratio which takes in a regular interval time. For two hours sunlight irradiation, the degradation rate of MB by pure ZnO was around 90%. Compare with the photocatalytic activity of ZS composite, the result indicate that the silica effectively suppressed the photocatalytic activity of ZS composite [15]. The photocatalytic inhibition trend was consistent with the amount of silica in the ZS composite. The evident showed by the sample at ZnO to silica ratio 1:4, the photocatalytic activity decreased to 43% compare with 60% for the sample with the ratio 1:1. For the sample at higher amount of ZnO ratio 4:1, the highest photocatalytic activity achieved at 80% which have been due to the silica is not enough to cover the ZnO particle. These results confirmed that the silica could lowered the degradation rate which acted as a layer to inhibit the migration of active photocatalyst of ZnO to the surface. Silica acted as an inert material which lowered the degradation rate.
Figure 8. (a) the effect of ZnO morphology to photocatalytic activity and (b) Photocatalytic activity of pure ZnO and ZS composite at various ratio

4. Conclusion
A new and rapid method based on electrospray process has been successfully developed for pure ZnO and ZS spherical composite particles. The particle morphology found to be strongly affected by the applied voltage and the charge current mode (positive or negative). Agglomerate to spherical composite particle obtained by increasing the applied voltage from 6 to 10 kV. The agglomerate particle was hindered in photocatalytic application. The silica particle had a strongly influenced on the formation of free-agglomerate composite particle. By taking an advantage of the electrospray method which provide one-step process, free-agglomerate ZS composite can be produced. Furthermore, it also effectively suppressed the photocatalytic activity of pure ZnO. The crystalline phase of the ZS composites are still in accordance with pure ZnO revealed that the silica does not change the crystalline phase of the composite.

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