Synthesis and photocatalytic property of Zinc Oxide (ZnO) fine particle using flame spray pyrolysis method

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Abstract. Advance oxidation process (AOP) using photocatalysis constitute a promising technology for the treatment of wastewaters containing non-easily removable organic compound. Zinc oxide (ZnO) is one of efficient photocatalyst materials. This research reported synthesis of ZnO fine particle from zinc nitrate hexahydrate using Flame Spray Pyrolysis (FSP) method. In this method, oxygen (O₂) gas were used as oxidizer and LPG (liquid petroleum gas) were used as fuel. The effect of O₂ gas flow rate during ZnO particle fabrication to the microstructure, optical and photocatalytic properties were systematically discussed. The photocatalytic activity of ZnO was tested for the degradation of amaranth dye with initial concentration of 10 ppm under irradiation of solar simulator. The rate of decrease in amaranth concentration was measured using UV-Visible spectrophotometer. The ZnO synthesized using FSP has a hexagonal crystalline structure. Scanning electron microscope images showed that ZnO has a spherical formed which was the mixture of solid and hollow particles. The optimum condition for amaranth degradation was shown by ZnO produced at a flow rate of 1.5 L/min which able to degrade amaranth dye up to 95.3% at 75 minutes irradiation.

1. Introduction
In the current era of globalization, advances in science and technology increasing the development of industry rapidly. That condition certainly provide great benefits in the welfare of the community. In addition of positive impacts, technological progress can also cause problems for environment such as industrial waste[1].

Industrial waste such as liquid waste contaminated with paper textile residues and other industrial waste is one of the environmental problems. Nowadays, liquid batik factory waste which contaminated by textile dye was flew to the ecosystem directly without being processed at first. Of course it could be dangerous for ecosystem. Different methods has been used to overcome this problem. Advanced oxidation process (AOP) are considered a highly competitive water treatment technology for the removal of those organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability. Photocatalysis based AOP using semiconductor material had become a promising method for degradating the pollutant. One of the semiconductor material that can be used as photocatalyst is ZnO.

ZnO particles attracted the attention of many researchers due to its applications of UV absorption [2]. Gancheva. [3] also reported that zinc oxide has attracted much attention because of its property of high photosensitivity, which causes degradation of various pollutants. ZnO has potential as photocatalyst material because its property of wide band gap. Shakti [4] reported that zinc oxide is an N-type semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV.
ZnO has been produced by several methods such as hydrothermal synthesis, thermal decomposition [5], precipitation method and flame spray pyrolysis (FSP). [6] The advantages of FSP is the process carried out at atmospheric ambient, one step process and using aqueous-base salt solution for the precursor. The product is relatively uniform in size and shape, single and multicomponent and possible for doping the other materials. Thus, the present study aimed to produce pure and crystalline Zinc Oxide by the use of cost-effective process, which employs the spraying of a liquid combustible solution in a flame using LPG as a fuel source and oxygen gas as oxidator to obtain ZnO powder as well as to evaluate the photocatalytic property of ZnO powder.

2. Experimental Method

2.1. ZnO particle preparation
In the process of preparing the precursor, 20.07 g of zinc nitrate hexahydrate ((Zn(NO$_3$)$_2$). 4H$_2$O, Sigma Aldrich) was dissolved with 100 mL of aquades to obtain molarity of 0.7 M. The precursor was used for ZnO synthesis using FSP with the variation of oxygen gas flow rate of 1, 1.5, 2 and 2.5 L/min to obtain ZnO powder. Set Up of FSP can be seen on figure 1. The FSP reactor is consist of three main parts which is droplet generator using ultrasonic nebulizer, burner and particle collector. The type of burner is diffusion.

![Figure 1. The Schematic set up of FSP equipments](image)

2.2. Photocatalytic test
Amaranth (C$_{20}$H$_{11}$N$_2$Na$_3$O$_{10}$Si$_3$, Merck Germany) was used as model pollutant to evaluate the photocatalytic activity of ZnO fine particle. The photodegradation test was performed for 105 minutes with variation of sampling every 15 minutes. In the first 30 minutes was absorption process which is the sample was left in dark condition. Then the samples was irradiated using solar simulator of 1000 W/m$^3$ which equivalent to sunlight for 75 minutes to determine it’s absorbance value. The absorbance was measured at 520 nm. The concentration relative is proportional to the absorbance. The set up of photodegradation test can be seen on figure 2.
2.3. Characterization
XRD (X-ray diffraction) was performed by a Shimadzu using CuKa radiation. The crystallite size \(d_{\text{XRD}}\) was estimated by using the Scherrer equation. The particle morphology was observed using JEOL ModelJEM-2010 scanning electron microscope operated at 20 keV. The optical band gap energy \(E_{\text{gap}}\) was measured using UV-visible diffuse reflectance (UV-Vis DR) spectrophotometer (UV 2450, Shimadzu Japan). The optical band gap energy of the ZnO particle was calculated by Touch method. The UV–vis absorption spectra of the photocatalysts were obtained in the range of 200–900 nm using a UV–vis scanning spectrophotometer (Shimadzu with wave length of 520 nm).

3. Result and Discussion
3.1. Crystalline property of ZnO particle
The characterization result of the ZnO particles was done by XRD. The figure showed the X-ray diffraction pattern of the powder produced by the flame based equipment with an oxygen gas flow rate variation of 1, 1.5, 2 and 2.5 L/min. Based on the pattern formed using Match! program it showed all the diffraction peaks are formed correspond to the orientation of the hexagonal crystal plane i.e (100), (002), (101), (012), (110), (013) and (200) also there’s no amorphous phase was found. It corresponds with the Crystallography Open Database on the Match! software as well as on Joint Committee on Powder Diffraction Standart (JCPDS no 36-1451). The XRD analysis showed a crystalline structure after the synthesis where hexagonal ZnO with wurzite structure can be identified. Moreover the absence of any peak of other crystalline phase confirmed that was possible to obtain the ZnO product through the one-step flame based process.

3.2. Morphological property of ZnO particle
SEM images of the samples are shown in figure 4. It can be seen that the powder was composed of primary particles of spherical shapes and also some hollow shapes. The increase of the oxygen gas flow rates affects the increase of heat in combustion. It was resulted flame profile will be higher. This caused the burning area in the reactor to be more extensive. Consequently on the higher temperature droplets possibly to experience gas-to-particle conversion which caused the formation of particles in small size. But in this study when combustion at high temperatures gas-to-particle conversion didn’t occur that causes less optimal in combustion process. So at high temperature the larger particles are formed. [7]

Particles formed at oxygen gas flow rate of 1, 1.5 and 2 L/min in the form of spherical and hollow with boundaries between the particles are distinct. The higher oxygen gas flow rates used, the larger particles are formed. In the ZnO with oxygen gas flow rates 2.5 L/min appeared nano-sized particles that smaller than the rest. This caused the particles size distribution for this sample is bimodal.
Figure 3. XRD patterns of ZnO prepared at different O\textsubscript{2} flow rate.

Figure 4. SEM images of ZnO prepared at different O\textsubscript{2} flow rate, a) 1, b) 1.5, c) 2 and d) 2.5 L/min
3.3. Particle size distribution.
Particles size distribution can be made from the morphology of ZnO particles. It’s showed that ZnO with oxygen gas flow rates 1, 1.5 and 2 L/min is monodal with each one have one peak. But ZnO with 2.5 L/min is bimodal particle distribution with 2 peaks that indicate there’s 2 average particle size.

The ZnO particle size distribution with the oxygen gas low rate variation was shown in figure 5. Based on particle size distribution histogram, the average size of ZnO particle with variations in oxygen gas flow rate obtained by 1.10 μm, 1.13μmand 1.21μm for each flow 1, 1.5, and 2. For ZnO with oxygen gas flow rate 2.5 L/min because there are 2 peaks so there are 2 average size particles. There are 0.25μm and 1.24 μm.

3.4. Optical band gap energy.

UV-vis diffuse reflectance spectra (UV-vis DR) was used to measure the bad gap of the ZnO fine particle. The energy gap of the ZnO fine particles produce by FSP method is around 3.25 eV, it showed in figure 6. The flow rate of oxidant gas did not affect the optical band gap energy of the ZnO fine particle.

Figure 5. Particle size distribution of ZnO prepared at different O₂ flow rate, a) 1, b) 1.5, c) 2 and d) 2.5 L/min.
3.5. **Photocatalytic Properties**

Spectrophotometer Uv-Vis was used to measure the rate of decrease in amaranth concentration. The decrease in amaranth concentration indicates the photocatalytic properties of ZnO. The result of the measurement was obtained ZnO absorbance value. According to the Lambert-Beer’s law the absorbance value is proportional to the concentration value of the solution so that the ZnO absorbance value is proportional to the concentration value of the amaranth solution.

Based on measurement using Spectrophotometer Uv-Vis obtained amaranth photodegradation chart using ZnO photocatalyst synthesized at different rates of oxygen gas flow rates. Figure 7 showed at the dark condition there was decreased in amaranth concentration, this is due to the process of ZnO absorption. Where as in direct irradiation conditions the decrease in amaranth concentration involves the photodecomposition process.

At direct irradiation condition it can be seen that the amaranth concentration decrease against time shown in the figure 4.5. At 105 minutes ZnO with oxygen gas flow rate of 1.5 and 2 L/min. was able to degrade the amaranth solution to reach \( \frac{C}{C_0} \) value close to 0. Whereas ZnO with oxygen gas flow rate of 1 L/min. can degrade amaranth solution up to \( \frac{C}{C_0} \) value below 0.2. whereas ZnO with oxygen gas flow rate of 2.5 can degrade amaranth solution up to \( \frac{C}{C_0} \) value 0.4.

The increasing oxygen gas flow rates causes the better photocatalytic properties but on ZnO with 2.5 L/min. oxygen gas flow rate the particle float thus the direct contact is not as effective as the other samples.
Figure 7. Photocatalytic activity of ZnO prepared by FSP at different O$_2$ flow rate, a) 1, b) 1.5, c) 2 and d) 2.5 L/min.

4. Conclusion
ZnO particles were successfully using Flame Spray Pyrolysis (FSP) method with the varieties of oxygen gas flow rate were 1, 1.5, 2 and 2.5 L/min. Increasing oxygen gas flow rates caused morphological differences that effect the photocatalytic properties. ZnO particles produced using 1.5 L/min. oxygen flow rate was able to degrade amaranth dye up to 95.3 % at 105 minutes

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