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Simple Hydrothermal Preparation of Zinc Oxide Powders Using Thai Autoclave Unit

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Abstract

Zinc oxide powders with different morphology have been successfully prepared by adopting zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and sodium hydroxide (NaOH) as the starting precursors in the mole ratio of $Zn(NO_3)_2.6H_2O$: NaOH of 1:2 and 1:10, via the simple hydrothermal process (60 °C for 6h) using Thai autoclave unit. The shape, size, and crystalline structures of the as-prepared ZnO powders were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM) and x-ray diffraction (XRD). At the lower alkaline concentration, the prepared showed powder short prism-like shape with hexagonal phase. The average particle size was about 0.3-0.5 μm in width and 0.5-0.7 μm in length. At the higher alkaline concentration, the microstructure of ZnO powders change in turn from short prism to flower-like shapes. The particle size was about 30-80 nm in width and 0.5-1 μm in length. This preparation method provide a simple hydrothermal routes to fabricate ZnO powders using Thai autoclave Unit.

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Keywords: ZnO; Hydrothermal; Morphology.

1. Introduction

Zinc oxide (ZnO) is an n-type II-VI compound semiconductor with a wide direct-band gap of 3.3 eV. ZnO and ZnO-related materials have attracted more and more attention over the past few years because of this applications in various fields, such as filtering materials for ultraviolet (UV) light-emitters, catalysts, varistors, semiconductors, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers, gas sensor, field emission display and solar cells, etc. [1-3]. However, in order

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to obtain ZnO powders with appropriate chemical, electrical and optical properties specific for their intended applications. The purity and particle size during their synthesizing process is important factor. Up to now, different shapes of ZnO powders including prismatic [4], ellipsoidal [5], bi- pyramidal and dumbbell-like [6], flower-like [7], nanowire [8], and nanorod [9] and so forth, had been prepared via different synthesis method or under different preparation conditions. Different routes such as precipitation [10-12], spray pyrolysis [13], thermal decomposition [14] and hydrothermal process [15-19] have been utilized for preparing ZnO powders. The hydrothermal synthetic route [20-21] has advantages to obtain high-crystallized powders with narrow grain size-distribution and high purity without the expensive precursors, elaborate apparatus and and heat treatment at high temperature [21-25].

This study was aimed at the hydrothermal preparation of ZnO powders by a simple hydrothermal process using Thai autoclave unit. The effect of alkaline concentration on the morphology of as-prepared ZnO powders have been examined in detail.

2. Experimental procedure

2.1. Synthesis

Fig. 1. Teflon-lined stainless steel autoclave unit.

Analytical grade zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, 98%, Ajax Finechem, Newzealand) and sodium hydroxide (NaOH, 97%, Ajax Finechem, Newzealand) were used as the starting materials. They were dissolved in deionized water. An aqueous solution of 0.5 mol/L $Zn(NO_3)_2.6H_2O$ was mixed with the appropriate amount of 1 and 5 mol/L NaOH solution under magnetic continuous stirring to obtain the mole ratio of $Zn(NO_3)_2.6H_2O$:NaOH of 1:2 and 1:10. The final pH of the mixed solutions was highly basic with pH of 14. The mixture was put into a Teflon-lined-stainless steel autoclave unit, that was built at Rajamangala University of Technology Thanyaburi (RMUTT), Thailand (Fig. 1), with the hydrothermal reaction at 60 °C for 6h. For enhancing the reactivity and homogeneity of reacting solution, a mechanical stirrer was used. After hydrothermal reaction, the reactor was naturally cooled to room

temperature, the obtained product was filtered, washed with deionized water until the pH of final solution was 7.0 and dried at 100 °C for 12h in an oven.

2.2. Characterization

The morphology of ZnO powders was observed by scanning electron microscope (JSM-6510, JEOL, Japan) and transmission electron microscope (JEM-2100, JEOL, Japan). x-ray powder diffraction (X'Pert PRO MPD, PANalytical, Natherlands) was used to check the crystaline structure of the prepared samples.

2.3. Photocatalytic activity measurement

The photocatalytic activity was measured through the formation rate of I_3^- due to the oxidation photo reaction of I^- to I_2 in excess I^- conditions [28-29]. A reaction system was set up by adding 50 mg of a sample powder into 10 ml of 0.2M of potassium iodide (KI) aqueous solution then stirred and irradiated with UV light with a maximum emission at about 365 nm at room temperature. After the irradiation of 15, 30, 45, and 60 min, the suspension was withdrawn and centrifuged. After the clear supernatant was diluted 10 times, the concentration of liberated I_3^- ions was monitored by the absorbance at 288 nm, using an UV–vis spectrophotometer (Shimadzu UV 2450). The molar extinction coefficient was determined to be 4.0×10^4 (cm mol/l) $^{-1}$. For reference, The commercially available ZnO powders (Sigma-Aldrich Inc., Germany), was tested.

3. Results and Discussion

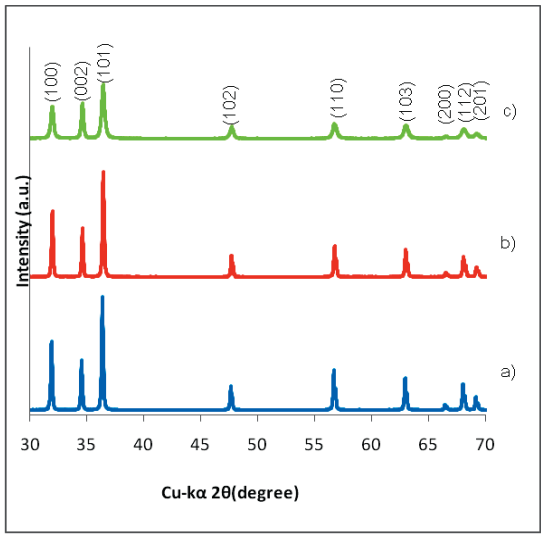

Fig. 2. X-ray diffraction patterns of (a) commercial ZnO pwders, (b) as-prepared ZnO powders at 1:2 ratio of $Zn(NO_3)_2.6H_2O$:NaOH, (c) as-prepared ZnO powders at 1:10 ratio of $Zn(NO_3)_2.6H_2O$:NaOH

The XRD patterns of the commercial ZnO powders and the prepared ZnO powders are shown in Fig. 2. The sharp diffraction peak of the ZnO powder synthesized with the ratio concentration of

$Zn(NO_3)_2.6H_2O$: NaOH 1:2 (Fig. 2(b)), imply their good crystallinity and similar to the sharp diffraction peak of commercial ZnO powders (Fig. 2(a)). All diffraction peak in the XRD patterns of as-prepared ZnO powders can be assigned to the hexagonal structure reported in JCPDS File Card No. 36-1451 [26].

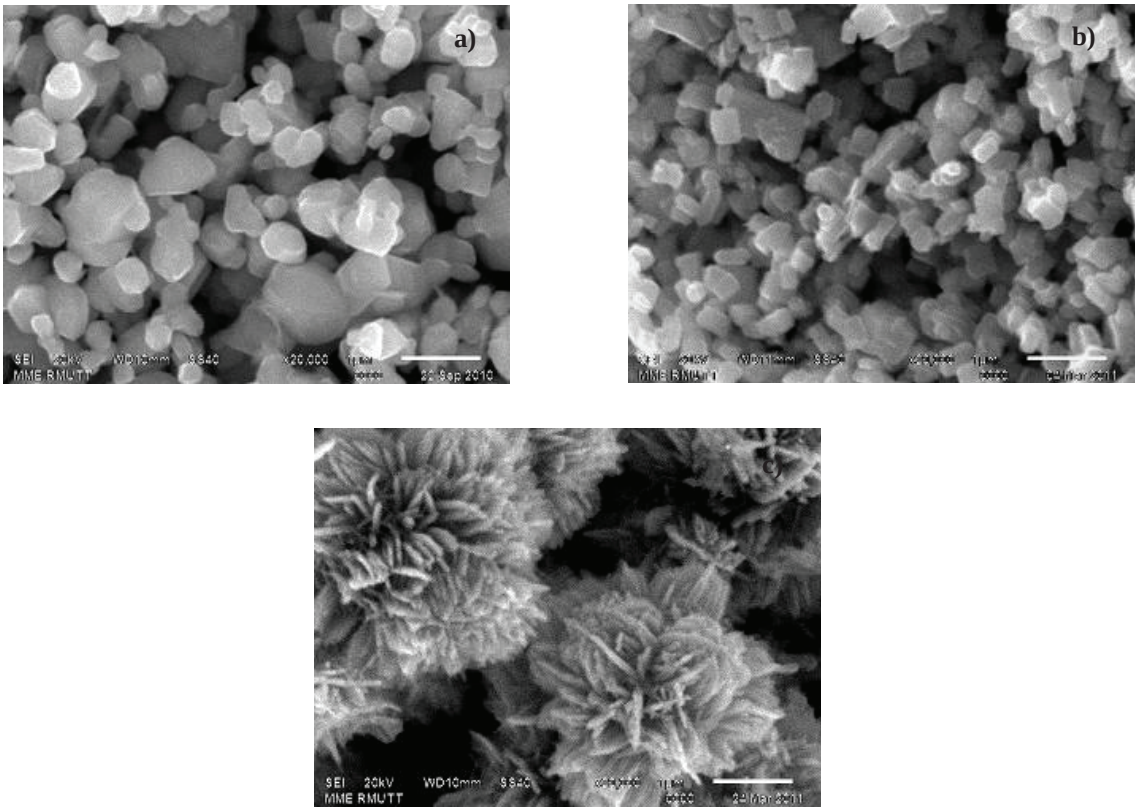

Fig. 3. SEM images at 20,000 magnified of (a) commercial ZnO pwders, (b) as-prepared ZnO powders at 1:2 ratio of $Zn(NO_3)_2.6H_2O$:NaOH, (c) as-prepared ZnO powders at 1:10 ratio of $Zn(NO_3)_2.6H_2O$:NaOH
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The SEM image of the commercial ZnO powders is shown in Fig. 3(a). The shape of the commercial ZnO is short prism-like shape. Fig. 3(b-c) shows the SEM images of ZnO powders synthesized by simple hydrothermal process at 60 °C for 6h. At the lower alkaline concentration (Fig. 3(b)), the powder is short prism-like shape similar to commercial ZnO powders (Fig. 3(a)). At the higher alkaline concentration, the powder are flower-like shape. The TEM images of the as-prepared ZnO powders are shown in Fig. 4(a-b). It was observed clearly that the particle size at the lower alkaline concentration was about 0.3-0.5 μm in width and 0.5-0.7 μm in length (Fig. 4(a)). At the higher alkaline concentration, the particle size was about 30-80 nm in width and 0.5-1.0 μm in length (Fig. 4(b)).

The particle size of ZnO powders was increased with increasing of alkaline concentration. The zinc nitrate may convert into $Zn(OH)_2$ colloids firstly under alkali solution, as shown in reaction 1. During the hydrothermal process, the part of the $Zn(OH)_2$ colloids dissolves into $Zn2^+$ and OH^- according to reaction 2. When the concentration of $Zn2^+$ and OH^- reaches the supersaturation degree of ZnO, ZnO nuclei will form according to reaction 3 [27]. The possible reaction process and sketch can be expressed as follows:

$$Zn(NO_3)_2.\,6H_2O + 2NaOH = Zn(OH)_2\,(gel) + 2NaNO_3 + 6H_2O \quad (1)$$

$$Zn(OH)_2\,(gel) + 2H_2O = Zn^{2+} + 2OH^- + 2H_2O = Zn(OH)^{2-}_4 + 2H^+ \quad (2)$$

$$Zn(OH)^{2-}_4 = ZnO + H_2O + 2OH^- \quad (3)$$

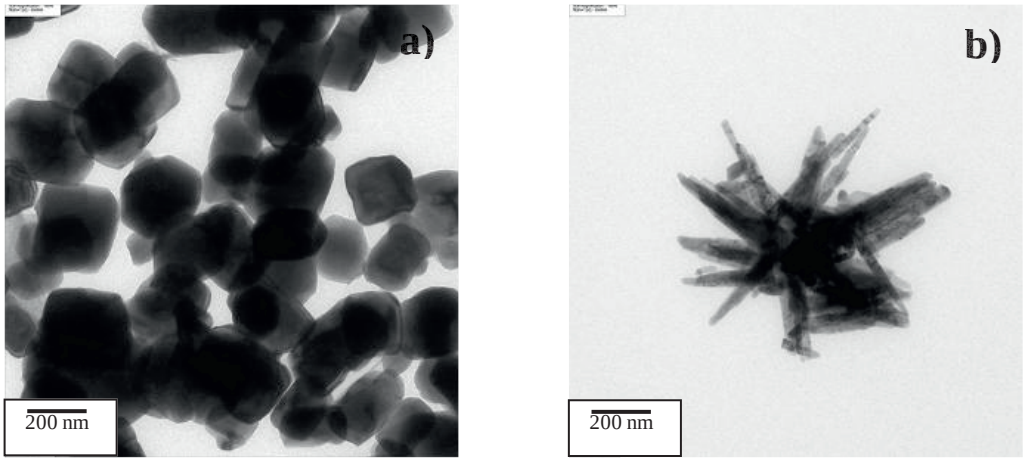

Fig. 4. TEM images at 10,000 magnified of as-prepared ZnO powders at (a) 1:2 ratio of $Zn(NO_3)_2.6H_2O$:NaOH, (b) 1:10 ratio of $Zn(NO_3)_2.6H_2O$:NaOH

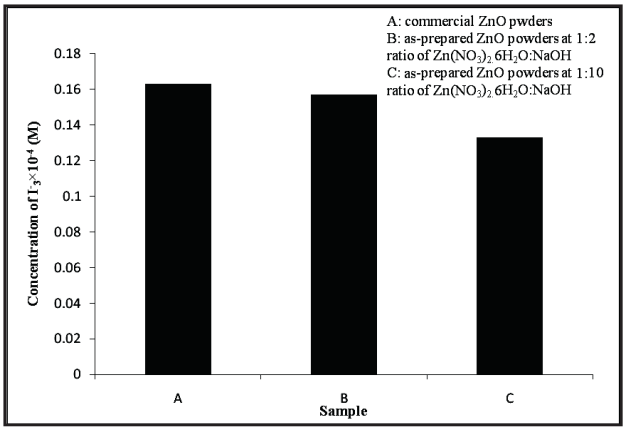

Fig. 5. Photocatalytic activity (I^-_3 concentration) of the commercial ZnO pwders, the as-prepared ZnO powders at 1:2 ratio of $Zn(NO_3)_2.6H_2O$:NaOH, and the as-prepared ZnO powders at 1:10 ratio of $Zn(NO_3)_2.6H_2O$:NaOH

The photocatalytic activity (I^-_3 concentration) of the as-prepared ZnO powders at 1:2 ratio of $Zn(NO_3)_2.6H_2O$:NaOH, as-prepared ZnO powders at 1:10 ratio of $Zn(NO_3)_2.6H_2O$:NaOH and commercially grade ZnO powders are shown in Fig. 5. It was found that the photocatalytic activity of the as-prepared ZnO powders at 1:2 ratio of $Zn(NO_3)_2.6H_2O$:NaOH almost equal to commercially grade ZnO powder but higher than as-prepared ZnO powders at 1:10 ratio of $Zn(NO_3)_2.6H_2O$:NaOH, because the crystallinity of as-prepared ZnO powders at 1:2 ratio of $Zn(NO_3)_2.6H_2O$:NaOH almost equal to commercially grade ZnO powder and higher than the as-prepared ZnO powders at 1:10 ratio of $Zn(NO_3)_2.6H_2O$:NaOH. However, as mentioned above, the prepared ZnO powders exhibit an obvious

difference in particle morphology. This decisive difference in morphology probably influences the photocatalytic activity because the exposed crystal faces or the ratios among exposed crystal faces are noticeably different for the ZnO particles composed with different crystallite forms [30-31]. The photocatalytic activity of ZnO powder depends on crystalinity and particle morphology [32].

4. Conclusion

In summary, well-crystallized ZnO powders with different morphology have been successfully prepared by the simple hydrothermal process using thai autoclave unit at 60 °C for 6h. The XRD results revealed that a hexagonal structure of ZnO powders was obtained. The SEM and TEM investigation showed that at the lower alkaline concentration the microstructure of ZnO powders was short prism-like shapes. At the higher alkaline concentration the microstructure of ZnO powders changes in turn from shot prism to flower-like shapes. The particle size of ZnO powders was increased with increasing alkaline concentration. The high crystalinity ZnO powders may show utility as a novel photocatalyst material for filtering materials for ultraviolet (UV) light-emitters, catalysts, varistors, semiconductors, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers, gas sensor, field emission display and solar cells.

Acknowledgements

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