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## RESEARCH NOTE

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# CONTROLLABLE SYNTHESIS OF FLOWER-LIKE ZnO NANOSTRUCTURE WITH HYDROTHERMAL METHOD

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**Abstract** Flower-like ZnO nanostructures were synthesized by decomposing  $Zn(OH)_2$  in 1,4-butanediol at 105 °C for 36 h. Size of flower-like ZnO nanostructure can be controlled by pH of the aqueous solution. In the preparation of flower-like ZnO nanostructure, zinc nitrate was used as a precursor. The morphology and microstructure of flower-like ZnO nanostructure have been characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. The synthesized flower-like ZnO nanostructures have a hexagonal wurtzite structure. A possible growth mechanism with regard to pH solution has been proposed.

**Keywords** ZnO, Flower-Like, Nanostructure, Hydrothermal

**چکیده** نانوساختارهای گل مانند اکسید روی (ZnO) با تجزیه هیدروکسید روی ( $Zn(OH)_2$ ) در ۱،۴-بوتان دی ال در دمای ۱۰۵ درجه سانتی گراد به مدت ۳۶ ساعت سنتز شده است. اندازه نانوساختارهای گل مانند اکسید روی (ZnO) با pH محلول کنترل می شود. برای تهیه نانو ساختارهای اکسید روی (ZnO) نیترات روی به عنوان پیش ماده استفاده شده است. شکل گل مانند نانوساختارهای گل مانند اکسید روی (ZnO) با میکروسکوپ روبش الکترونی (SEM)، پراش پرتو X-تو (XRD) و طیف نوسنجی مادون قرمز (FT-IR) شناسایی شده است. نانو گل های سنتزی دارای ساختار شش گوشه بوده اند. مکانیزم احتمالی رشد کریستالی نسبت به pH محلول پیش بینی شده است.

## 1. INTRODUCTION

Zinc oxide, a semiconductor with wide band gap (3.37), high excitation binding energy (60 meV) at room temperature [1,2], has large surface area and hydrophilic nature. It has unique optical and acoustic properties as well as excellent chemical and thermal stability [3]. Different ZnO nanostructure such as nanowire [4], nanoneedles [5-7], nanopins [8], nanoflower [9, 10], nanobelts [11], nanorode [6], nanotube [12], nanowhiskers [13], nanobridge

and nanonails [14] have been fabricated. Though, the physical and physicochemical properties of nanoparticle are determined by means of size and shape of the particles [15]. Therefore, zinc oxide can be used in various applications e.g. as varistor, gas and piezoelectric sensing [11,16,17], and as transparent electrode material for solar cell [18], catalyst, pigment, display screen, photocell electrode, UV-light emitting diodes [2,19,20]. According to great function of zinc oxide, various techniques have been applied to

grow nanostructures of ZnO such as thermal evaporation [7], hydrothermal process [21], cyclic feeding chemical vapor deposition [22], chemical vapor deposition (CVD) [23], metal-organic CVD [24], sol-gel synthesis [25] and solution growth [26-28].

Wu, et al reported synthetic flower-like ZnO nano/microstructures prepared by thermal treatment of  $\text{Zn(OH)}_4^{2+}$  precursor in aqueous solvent using ammonia as the structure directing agent [29]. Zhang, et al reported synthetic ZnO with a diversity of morphology as flower, snow flake, prism, prickly sphere and rod like using decomposition  $\text{Zn(OH)}_4^{2-}$  or  $\text{Zn(NH}_3)_4^{2-}$  as precursor solutions (prepared in various solvent such as n-heptane,  $\text{H}_2\text{O}$  and ethanol) [30]. Pan, et al reported synthetic flower-like ZnO nanostructure prepared by a very simple solvothermal processing of prepared hydroxide collides  $\text{Zn(OH)}_2$  in anhydrous ethanol [31].

In this paper, different shapes of ZnO flowers were synthesized with a single precursor at relatively low temperature by employing simple solution method. The flower-like ZnO nanostructure was synthesized by variation of ammonia concentration in the preparation of ZnO fine micro-particles. The results indicated that addition of high amount of ammonia to aqueous solution of  $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$  could greatly affect the morphology and size of ZnO. Preparation of the flower-like ZnO nanostructure was examined by low temperature heat treatment of zinc hydroxide [ $\text{Zn(OH)}_2$ ] in a 1,4-butanediol solution.

## 2. EXPERIMENTS

**2.1. Materials** All chemical materials (zinc nitrate, ammonia (25%), sodium hydroxide, 1,4-butanediol) were supplied by Merck. All chemical reagents were analytical grade and used without any purification.

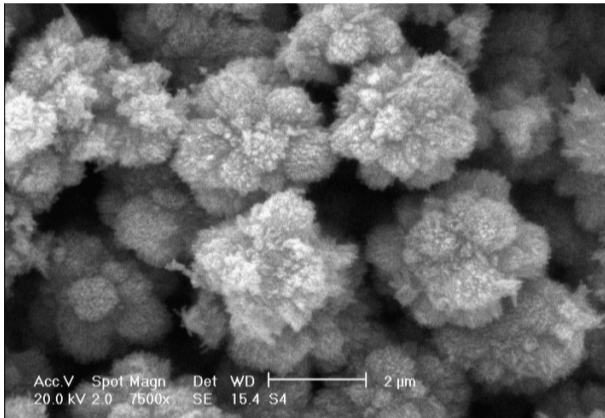
**2.2. Preparation of Flower-Like ZnO Nanostructure** The current synthetic procedure is a modified method developed by Uekawa and co-workers for formation of spherical aggregated structure of ZnO nanoparticle by heating of  $\text{Zn(OH)}_2$  in 1,4-butanediol solution [32]. The preparation of flower-like ZnO nanostructure is described as: 2.62 g

zinc nitrate hexahydrate [ $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] was dissolved into 100 ml of distilled water. Then, 100 ml of  $\text{NH}_3$  aqueous solution (3%) for solution (A) and 3 ml concentrated ammonia (25%) for solution (B) was added to an aqueous solution of zinc nitrate. Resulted  $\text{Zn(OH)}_2$  precipitate was separated by centrifugation at 3000 rpm for 5 min and then dispersed in 50 ml of 1,4-butanediol. The solution with the dispersed  $\text{Zn(OH)}_2$  was heated at  $105^\circ\text{C}$  for 36 h in a closed glass bottle. To separate the obtained particle from the sol, 100 ml  $\text{NH}_3$  solution (3%) and 3 ml  $\text{NH}_3$  (25%) were added into the samples A and B, respectively. Then, the resulting solid product was centrifuged at 3000 rpm for 5 min and washed several time with methanol to remove the remaining ions in the final product, and finally, the precipitate was dried at  $70^\circ\text{C}$  for 12h.

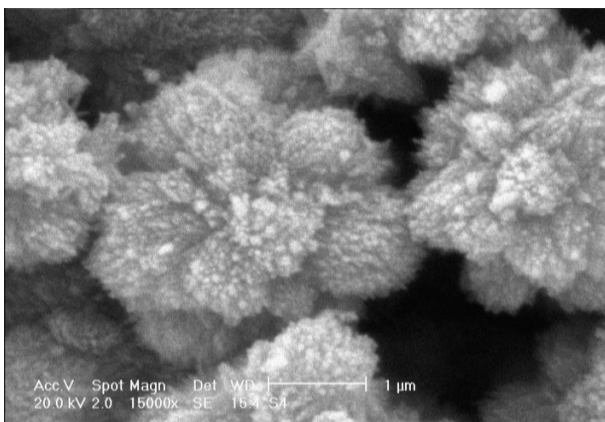
**2.3. Characterization** The crystalline structures of samples were characterized by X-ray diffraction (XRD) on a Philips (E'pert, Holland) diffractometer that was operated at an acceleration voltage of 40 kV, using Cu  $\text{K}\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ). The morphology of samples was examined by scanning electron microscopy (SEM, Phillips XL30, and Holland). The size of the ZnO particles was estimated from the SEM images. The quality and composition of the samples were characterized by Fourier transform infrared (FT-IR) spectroscopy (Shimadzo FT-IR1650 spectrophotometer, Japan) in range of  $400\text{-}4000 \text{ cm}^{-1}$ . The performance of FT-IR measurements was done with KBr pellets in the ratio of 1:100 containing same amounts of ZnO samples to monitor the variation of defect contents in them qualitatively.

## 3. RESULTS AND DISCUSSIONS

The shape of samples was characterized using SEM. Figures 1a,b and 2a-d show the representative SEM images of the products at different magnifications. The surface morphology of the samples with different amount of ammonia is showed in Figures 1a,b and 2a-d. A novel shape of flower-like ZnO nanostructure formed when 100 ml of 12.3 % (w/w) ammonia (3% v/v) was added into 100 ml aqueous solution of zinc nitrate hexahydrate (Figures 1a,b). The flower-like ZnO nanostructures consisted of



(a)

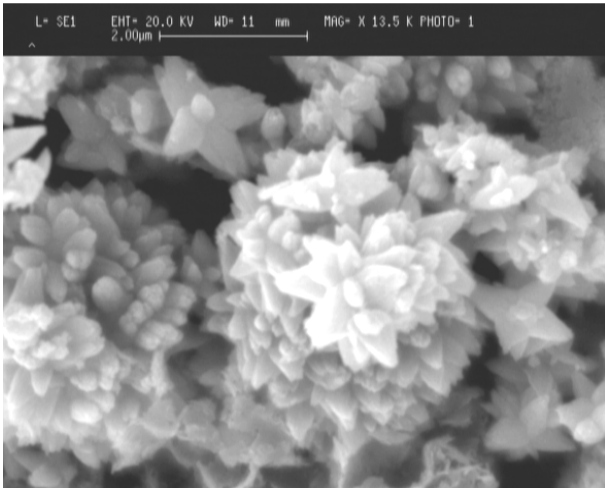


(b)

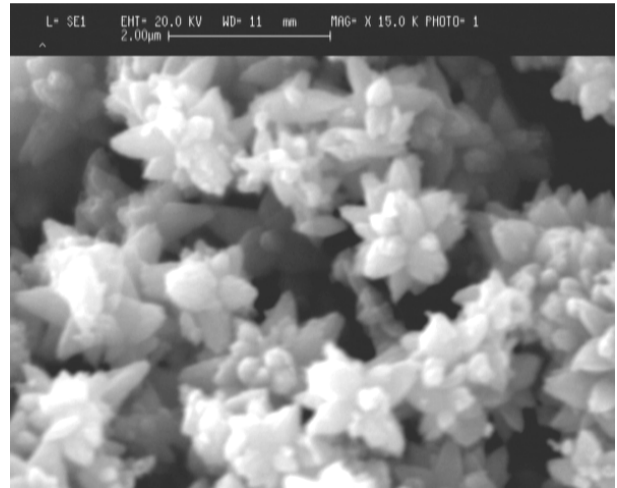
**Figure 1.** SEM image of flower-like ZnO nanostructure with a 100-ml diluted ammonia (3%, v/v); (a) low-resolution image, (b) high-resolution image.

petals, each includes several nanorods that was achieved with 3 ml (37%, w/w) concentrated ammonia into 100 ml aqueous solution of zinc nitrate hexahydrate as presented in Figures 2a-d. The obtained size of full array of a flower-like structure with diluted ammonia was in the range of 2-3  $\mu\text{m}$  (Figure 1a). However, the obtained size of full array of a flower-like structure with concentrated ammonia was found to be in the range of 1-1.7  $\mu\text{m}$  as presented in Figures 2a,b. Furthermore, the size of each petal of flower-like structure was in the range of 0.6-1.5  $\mu\text{m}$  (Figures 1a,b) and that of obtained by concentrated ammonia was ranged from 200 to 600 nm (Figures 2c,d).

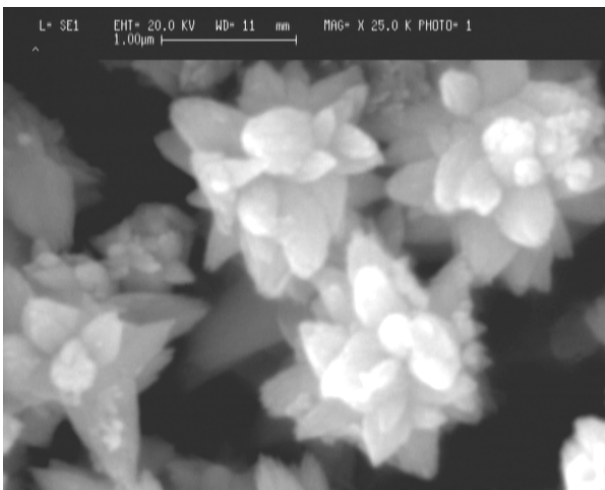
In this study, it was found that there was a relationship between ZnO structure morphology and that of  $\text{NH}_3$  which was added to aqueous solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Adding a 100 ml of diluted ammonia (3%, v/v) into 100 ml aqueous solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (sample A), the flower-like ZnO nanostructure was composed of petaloid (see Figure 1b). In this case, the solution pH was around 9 in the sample A. Furthermore, when 100 ml of 12.3 % (w/w) ammonia (3% v/v) ammonia solution was added into 100 ml of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (sample B), the flower-like nanostructure of ZnO that composed of nanorods was formed as presented in Figures 2a-d. In this case, the solution pH was around 12 in the sample B. Thus, the formation of ZnO nanostructure was greatly depended on amount of  $\text{NH}_3$ . On the other hand, solution pH was influenced the nucleation growth of flower-like ZnO nanostructure as well as size and morphology of the given crystal by participating in the nucleation and growth. It was found that at the pH about 12 in the sample B, the obtained ZnO displayed nanopetal in the flowers as SEM images presented in Figure 2d. When the rising solution pH was about 9 in the sample A, the Zn source was in form of  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ , while remaining Zn source existed in the  $\text{Zn}(\text{OH})_2$  precipitates and  $[\text{Zn}(\text{OH})_4]^{2-}$ . It seems that the stability of  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  is higher than  $[\text{Zn}(\text{OH})_4]^{2-}$  at pH 9. However, when the rising solution pH was about 12 in the sample B, the Zn source of  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  complexes was formed into  $\text{Zn}(\text{OH})_2$  precipitates by the reaction between  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  and  $\text{OH}^-$ . On the other hand, the ammonia complexes with  $\text{Zn}^{2+}$ , which increase the zinc solubility and reduce the concentration of the free  $\text{Zn}^{2+}$ . The pH is important because  $\text{Zn}^{2+}$  and  $\text{OH}^-$  form zinc hydroxo complexes that affect zinc solubility and that precipitate as ZnO via dehydration reaction in 1,4-butanediol solution at elevated temperature [33]. However, a similar result was obtained in the both pH value of the mixture solution, implying that the rate of nucleation determines the aspect ratio of the ZnO flower-like ZnO nanostructure [34]. Finally, the pH measurements show that the ammonia basicity increases zinc hydroxo complexation and that the ammonia regulation of pH is dominant mechanism controlling zinc solubility. The formation of ZnO from  $\text{Zn}(\text{OH})_2$  in a 1,4-butanediol occurred through  $\text{Zn}(\text{OH})_2$  and  $[\text{Zn}(\text{OH})_2]^{2-}$  as an intermediate [34].



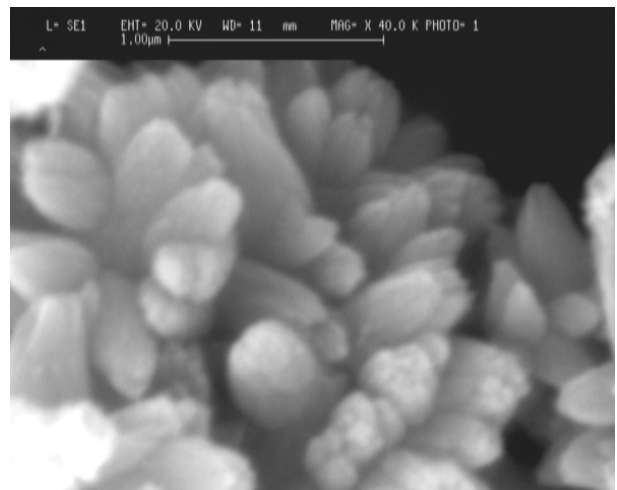
(a)



(b)



(c)

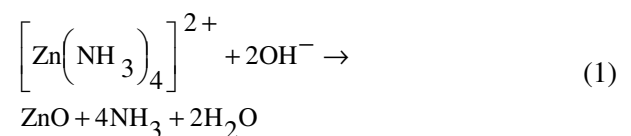


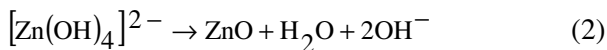
(d)

**Figure 2.** SEM image of flower-like ZnO nanostructure with a 3 ml concentrated ammonia; (25%) (a and b) low-resolution image, (c and d) high-resolution image.

When  $\text{Zn}(\text{OH})_2$  was heated in the sample A at  $105^\circ\text{C}$  for 36 h, flower-like ZnO nanostructure was obtained. This nucleation and growth led to the flower-like ZnO nanostructure in the 1,4-butanediol solution. Therefore, it could be concluded that the percentage of ammonia was influenced by size and morphology of flower-like ZnO nanostructures [35]. Moreover, by employing higher percentage of ammonia, the size of nanoflower decreased [36]. From this aspect, ZnO nuclei may be formed via decomposition of the

precursors; and mainly from  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  and remaining  $\text{Zn}(\text{OH})_2$  precipitates  $[\text{Zn}(\text{OH})_4]^{2-}$  at pH 9 while mainly from  $[\text{Zn}(\text{OH})_4]^{2-}$  and remaining  $\text{Zn}(\text{OH})_2$  precipitates and  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  at pH 12, in the 1,4-butanediol sample as presented in the following equations [37]:



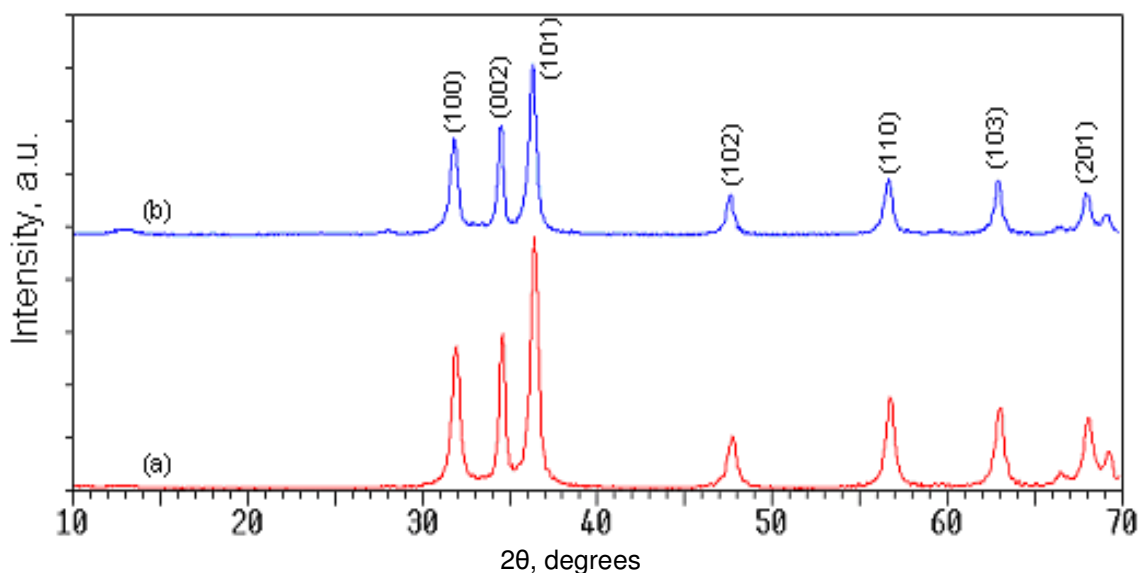


Moreover, to obtain ZnO from petal nanoflower morphology, the precursors  $[\text{Zn}(\text{OH})_4]^{2-}$  and  $\text{Zn}(\text{OH})_2$  can be adapted by adjusting the solution pH. As observed in the present study, the morphology of nanoflower-like in the sample A was reformed due to the weak basicity of ammonia and  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  cation, which may counteract the morphology of the growth. According to hydrothermal method, the effect on pH was important as  $\text{Zn}^{2+}$  and  $\text{OH}^-$  form the precursors  $\text{Zn}(\text{OH})_2$  and  $[\text{Zn}(\text{OH})_4]^{2-}$  complexes that increasing the concentration of free  $\text{Zn}^{2+}$ , thus reduces ZnO solubility. On the other hand, effect of pH on the sample A was dominated in complexation of ammonia with free  $\text{Zn}^{2+}$  which reduced the free  $\text{Zn}^{2+}$  and increased the solubility of ZnO.

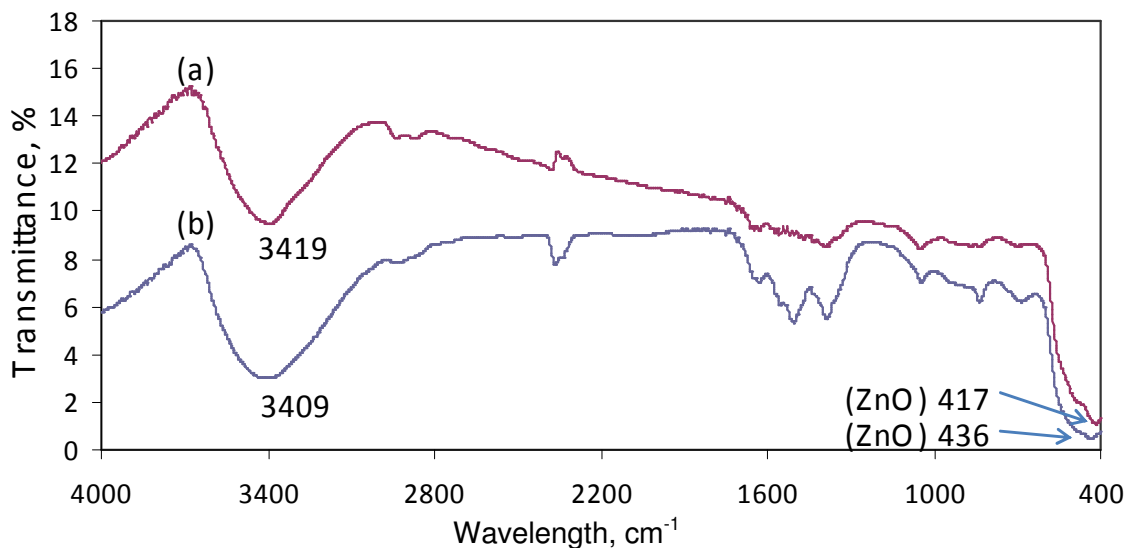
XRD was used to determine the through structure and phase purity. Figures 3a,b present the XRD patterns of powders synthesized by heating  $\text{Zn}(\text{OH})_2$  in heated 1,4-butandiol. The diffraction peaks of each sample were quite consistent with bulk ZnO, which could be indexed as the

hexagonal wurtzite structure ZnO and diffraction data were in agreement with JCPDS (36-1451) of ZnO. The sharp diffraction peaks indicated the good crystallinity of the prepared crystal and lack of any other peaks other than ZnO. All peaks of the nanoflower were corresponding to ZnO crystal faces and c-axis growth of nanopetals.

The composition and quality of the ZnO samples were also examined by the FT-IR spectroscopy. The FT-IR spectra of the flower-like ZnO nanostructures are presented in Figure 4, which was taken in a series transmittance peaks from 400 to 4000  $\text{cm}^{-1}$ . Spectra (a) and (b) represent the FT-IR of samples A and B, respectively (Figure 4). Two bands of 417 and 437  $\text{cm}^{-1}$  associate with stretching vibration of crystalline hexagonal zinc oxide (Zn-O stretching vibration), reference spectra of ZnO often show two bands at around 512 and 406  $\text{cm}^{-1}$  [38]. Observed shifts in both spectra sample (a) and (b) may attribute to thermal stress in the layers. The broad absorption at 3200-3600  $\text{cm}^{-1}$  corresponds to the existence of hydroxyl mode of vibration on the surface of the ZnO samples. The peaks position centered at 1628, 1505, 1395, 1046, 834 and 683 could not be identified. The FT-IR observations support the X-ray diffraction results.



**Figure 3.** XRD patterns of ZnO nanostructures changed with amount of  $\text{NH}_3$  added to aqueous solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; (a) 100 ml (3%, v/v) of diluted ammonia solution, (b) 3 ml concentrated ammonia (25%).



**Figure 4.** FTIR spectrum of flower-like ZnO nanostructure; (a) sample A and (b) sample B.

#### 4. CONCLUSION

In conclusion, the growth of flower-like ZnO nanostructure was demonstrated via heating of  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Zn}(\text{OH})_4]^{2-}$  and  $\text{Zn}(\text{OH})_2$  in a 1,4-butanediol solution, using zinc nitrate and ammonia. In the growth process, hydrothermal reduction of ZnO was applied at  $105^\circ\text{C}$  for 36 h. The SEM images revealed that the amount of  $\text{NH}_3$  to aqueous solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  affects the morphology and size of ZnO nanostructure. The sizes of nanoflowers were in the range of 1-1.7  $\mu\text{m}$  and 2-3  $\mu\text{m}$ . Furthermore, XRD demonstrated that ZnO flower are made up of c-axis of growth of flower-like ZnO nanostructure. The FT-IR characterization of the structural and the chemical features of the flower-like ZnO nanostructure were in agreement with X-ray diffraction results. By controlling the concentration of ammonia and pH value of mixture solution, the formation of flower-like ZnO nanostructure at a large scale and low cost for practical applications is possible.

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