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Ceramics International 37 (2011) 3431–3436
CERAMICS INTERNATIONAL
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A CTAB-assisted hydrothermal and solvothermal synthesis of ZnO nanopowders

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Received 13 October 2010; received in revised form 21 February 2011; accepted 28 April 2011
Available online 12 June 2011

Abstract

ZnO nanopowders were synthesized by hydrothermal and solvothermal method by using CTAB as surfactant, and the effects of CTAB on the morphologies of ZnO nanopowders were investigated. The results showed that the presence of CTAB could greatly vary the shape of the ZnO crystals. ZnO nanorods were prepared from the hydrothermal system without CTAB and flowers-like ZnO nanostructures were produced from hydrothermal system with 0.4 M and 0.5 M CTAB. Low concentration of CTAB in ethanol was conducive to the formation of ZnO nanorods, but the concentration continued to increase, the morphology of sample transformed into hexagonal bipyramid, and then transformed into spherical. The synthesis mechanism of ZnO powders with different morphologies has been presented.

Keywords: D. ZnO; Chemical preparation; Hydrothermal and solvothermal synthesis

1. Introduction

ZnO is an important semiconductor due to the wide direct band gap (3.37 eV) and large exciton-binding energy (60 meV). ZnO exhibits many interesting properties including near-UV emission, conductivity, piezoelectricity, photocatalysis, and gas sensitivity. Synthesis of size and shape controlled ZnO nanostructures is very important in controlling their physical and chemical properties, and crucial for their potential uses.Over the past decade, ZnO crystallites have been obtained by several preparation approaches including sol–gel method, evaporative decomposition of solution, wet chemical synthesis, and gas-phase reaction and hydrothermal synthesis. Among these methods, hydrothermal and solvothermal approach [1–6] have a great advantage in synthesizing ZnO crystals through relative low temperature and simple equipment, which makes these methods more suitable and economic for large-scale production. In order to control the morphology of ZnO crystals, organic additives such as ethylene diamine tetraacetic acid (EDTA) [7,8], polyethyleneglycol (PEG) [9,10] and sodium dodecyl sulfate (SDS) [11–13], were commonly introduced into the reaction system to manipulate the nucleation and growth in hydrothermal and solvothermal reactions. Recently, cetyltrimethylammonium bromide (CTAB) assisted hydrothermal technique has emerged as an attractive technique to investigate the synthesis of ZnO nanostructures [14]. Sun et al. [15] reported the synthesis of ZnO nanorods by CTAB-assisted hydrothermal technique. Ge et al. have reported a 3D ZnO nanostructure with sisal-like morphology via the assembly of CTAB [16]. Nia et al. have used a mixture of zinc acetate and CTAB to obtain ZnO rods in the presence of KOH [17]. Until recently, there exist a few reports about the preparation of ZnO nanostructures by using CTAB assisted hydrothermal and solvent thermal technique [18]. The precise effect mechanism of CTAB on the synthesis of ZnO nanopowders has not been revealed yet. Zhang H et al. considered that CTAB can interact with growth units of ZnO to generate active sites on the surface of ZnO nuclei so that sword-like ZnO nanorods are created on those sites, resulting in the formation of the flower-like ZnO nanostructures [19]. As properties of nanomaterial depend on their shape and size, the development of synthetic methods and understandings of the mechanism by which the shape and size can be easily controlled are key issues in nanoscience and nanotechnology.

CTAB is a cationic surfactant. When CTAB is dissolved in water or ethanol, it will ionize into CTA^+ and Br^-. ZnO, as a

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.04.134

polar crystal, has a polar axis and possesses a positive face and a negative face on the crystal due to the asymmetrical distribution of Zn atoms and O atoms along its polar axis, and the positive face (0 0 0 1) is occupied by Zn atoms while the negative face ($0\,0\,0\,\bar{1}$) is distributed by O atoms. So CTA^+ and Br^- will affect the morphology of ZnO by electrostatic attraction. On the other hand, CTAB can form micelles or reverse micelles, which also play a very important role in the final morphology of the ZnO nanopowders. In this work, the effects of CTAB on the morphologies of hydrothermal and solvothermal synthesis of ZnO nanopowders were investigated. Moreover, the synthesis mechanism of ZnO nanopowders with different morphologies has been presented.

2. Experimental

2.1. Chemicals

All chemicals were analytical grade and used as purchased without further purification. Zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$, as a zinc source), ammonium carbonate (as precipitating agent), and cetyltriethylammonium bromide (CTAB, as a cationic surfactant) and ethanol were purchased from Shanghai Chemical Reagents Company.

2.2. Experimental

ZnO nanopowders were synthesized by two steps. First, 200 mL of 1 M zinc nitrate aqueous solution was mixed with 50 mL of 1 M ammonium carbonate and the resulting mixture was stirred thoroughly. Some white precipitates (the precursor) were obtained. Then resulting white precipitate was collected and washed with deionized water several times. For hydrothermal synthesis, precursor powders (1.5 g) were added to 45.5 mL of different concentrations of CTAB aqueous solution (0.1 M, 0.5 M and 0.8 M). For solvothermal synthesis, precursor powders (1.5 g) and a certain amount of CTAB were added to graduate with a capacity of 50 mL, then ethanol was added to graduate until 45.5 mL mixed liquid was obtained. No matter be it hydrothermal synthesis or solvothermal synthesis, NaOH was introduced to adjust the pH value of

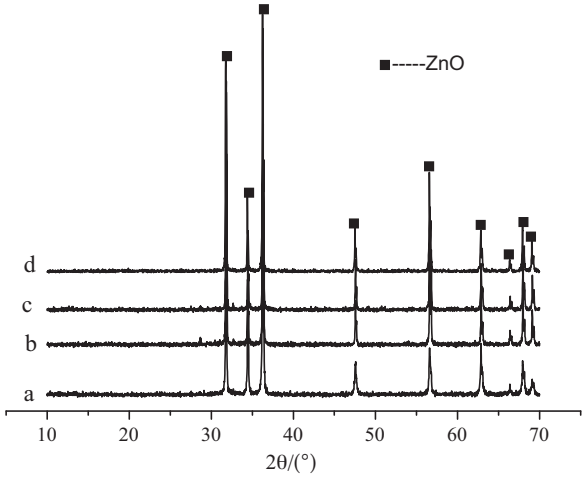

Fig. 1. XRD patterns of ZnO nanopowders with different CTAB concentrations in water: (a) without CTAB, (b) 0.1 M, (c) 0.5 M and (d) 0.8 M.

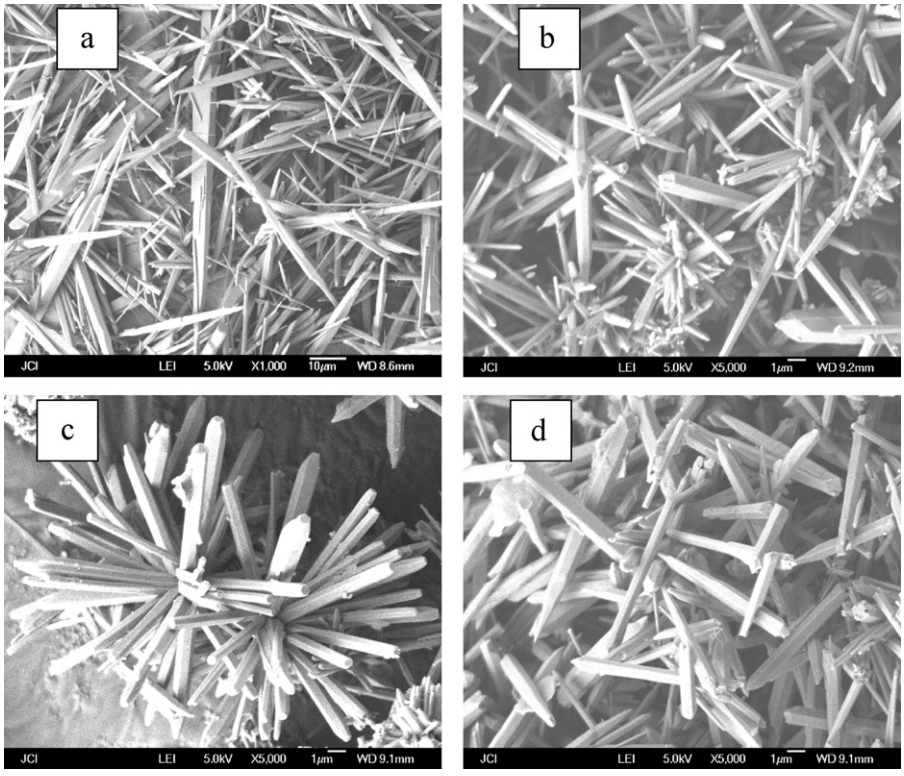

Fig. 2. FSEM photos of ZnO nanopowders prepared with different CTAB concentrations in water (a) without CTAB, (b) 0.1 M, (c) 0.5 M and (d) 0.8 M.

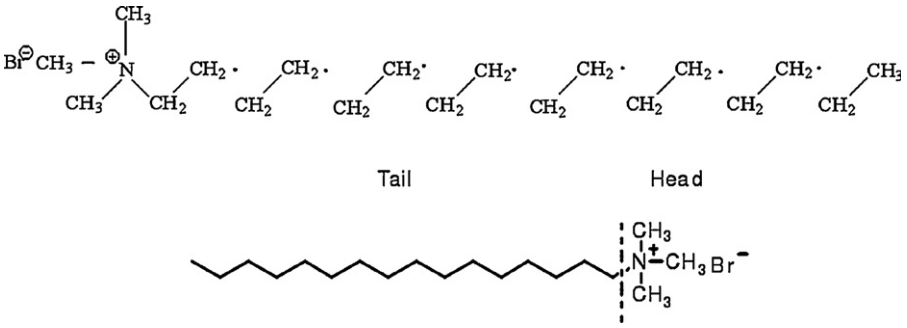

Fig. 3. The structure of the hydrophobic tail and hydrophilic head of CTAB [15].

the solution (pH 10), and the resulting solutions were stirred. Then the above 45.5 mL solution was transferred to a Teflon-lined autoclave for hydrothermal synthesis at 220 °C in an oven for 18 h. The autoclave has a capacity of 70 mL. When the reaction time was reached, the autoclave was removed and cooled to room temperature. After this process, white crystalline product was collected by centrifugation and thorough washings with ethanol and then dried at 60 °C.

2.3. Characterization

The morphology of the resulting powder was examined using JSM-6700F field emission scanning electron microscopy. X-ray diffraction patterns were taken using a Bruker D8 ADVANCE diffractometer with Cu Kα radiation.

3. Results and discussion

3.1. Structure and morphology of CTAB-assisted hydrothermal synthesis of ZnO nanopowders

Fig. 1 shows the XRD patterns of the ZnO products obtained after hydrothermal treatment in the absence and presence of CTAB. All the diffraction peaks are in good agreement with the JCPDS file for ZnO (JCPDS 36-1451, $a = 3.249$ Å, $c = 5.206$ Å), which can be indexed as the hexagonal wurtzite structure of ZnO. The sharpness of the peaks implies a high crystallinity of the as-produced samples.

Fig. 2 shows FSEM photos. It was found that flower-like assemblies can be obtained with CTAB concentration in the range of 0.1–0.5 M (Fig. 2b and c). With CTAB concentration increasing from 0.1 M to 0.5 M, the length of the nanorods increased from 3 μm to 6 μm and the diameter of the nanorods was invariant. However, only rod-like 1D structures with a length of about 8–10 μm and a width of 200–400 nm were obtained (Fig. 2a) without using CTAB. With a high concentration of CTAB (0.8 M), ZnO nanorods were obtained again.

The formation process for ZnO nanopowders under hydrothermal condition can be represented as follows: precursor of basic zinc carbonate ($Zn_4CO_3(OH)\cdot 6H_2O$) hydrolysis, which induce the forming of zinc hydroxide ($Zn(OH)_2$) hydrosol (shown in formula (1)).

If the pH value in the aqueous solution is about 10, $Zn(OH)_2$ is the main composition. During the hydrothermal process, part of the $Zn(OH)_2$ colloids dissolves into Zn^{2+} and OH^- according to reaction (2). When the concentration of Zn^{2+} and OH^- reaches the supersaturation degree of ZnO; according to reaction (3), ZnO nuclei is formed. The growth units of $[Zn(OH)_4]^{2-}$ (according to reaction (4)) have a tetrahedron geometry. The reaction in the solution can be shown below [20–23]:

$$Zn_4CO_3(OH)_6\cdot H_2O + 2OH^- \rightarrow 4Zn(OH)_2 + CO_3^{2-} + H_2O \quad (1)$$

$$Zn(OH)_2 \rightarrow Zn^{2+} + 2OH^- \quad (2)$$

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

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-} \quad (4)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^- \quad (5)$$

CTAB is a cationic surfactant which ionizes completely in water. CTA^+ is positively charged with a tetrahedral head and a long hydrophobic tail. The resulted cation is also a tetrahedron

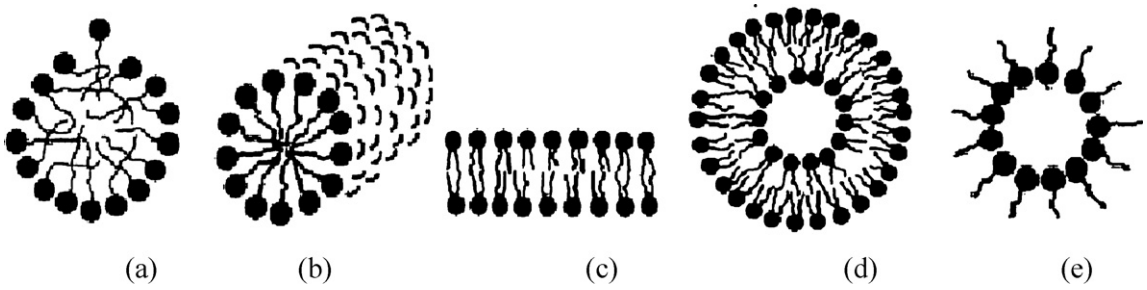

Fig. 4. Typical aggregate morphology of surfactants in solution: (a) spherical micelle, (b) worm-like micelle, (c) bilayer phase, (d) vesicle and (e) inverted micelle.

with a long hydrophobic tail (seen in Fig. 3). Therefore, ion-pairs between $Zn(OH)_4^{2-}$ and CTA^+ could form due to the electrostatic interaction. In the crystallization process, CTAB serves not only as an ionic carrier but also as a soft template. CTAB critical micelle concentration (CMC) at 25 °C in pure aqueous solution is 0.0009 mol/L, when the concentrations of CTAB are 0.1 M and 0.5 M, CTAB aggregation in aqueous solution will form spherical micelles, as shown in Fig. 4a. As the micelles in aqueous solutions are also in a dynamic balance, ion-pairs of $Zn(OH)_4^{2-}$ and CTA^+ were constantly adsorbed and detached from the surface of the formed micelle. The complementarity between CTA^+ and $Zn(OH)_4^{2-}$endows the surfactant with a capability to act as an ionic carrier. But when the concentration of CTAB is 0.8 M, CTAB aggregation in aqueous solution will form rod-like micelles which served as soft templates, so flower-like ZnO nanopowders were obtained with 0.1 M and 0.5 M CTAB, and ZnO nanorods were obtained with 0.8 M CTAB.

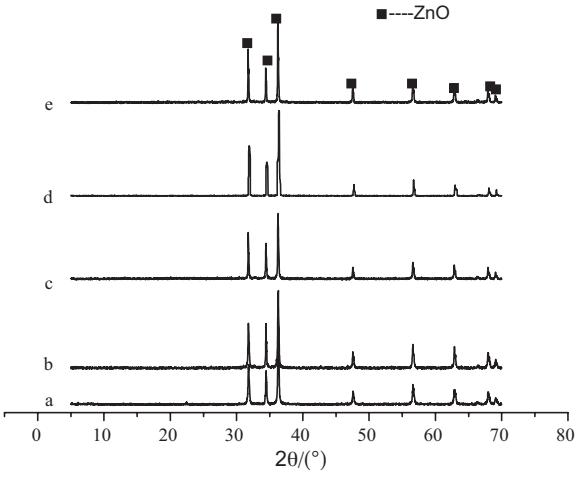

Fig. 5. XRD patterns of ZnO nanopowders prepared with different concentrations of CTAB in ethanol (a) without CTAB, (b) 0.1 M, (c) 0.4 M, (d) 0.5 M and (e) 0.8 M.

3.2. Structure and morphology of CTAB-assisted solvothermal synthesis of ZnO nanopowders

To confirm the effect of CTAB on the final ZnO nanostructures, 0.1 M, 0.2 M, 0.4 M, 0.5 M and 0.8 M CTAB were used in ethanol, respectively. Fig. 5 shows the XRD patterns of the products. All of the diffraction peaks can be indexed as hexagonal ZnO phase (wurtzite structure) by comparison with the data from JCPDS cards No.36-1451.

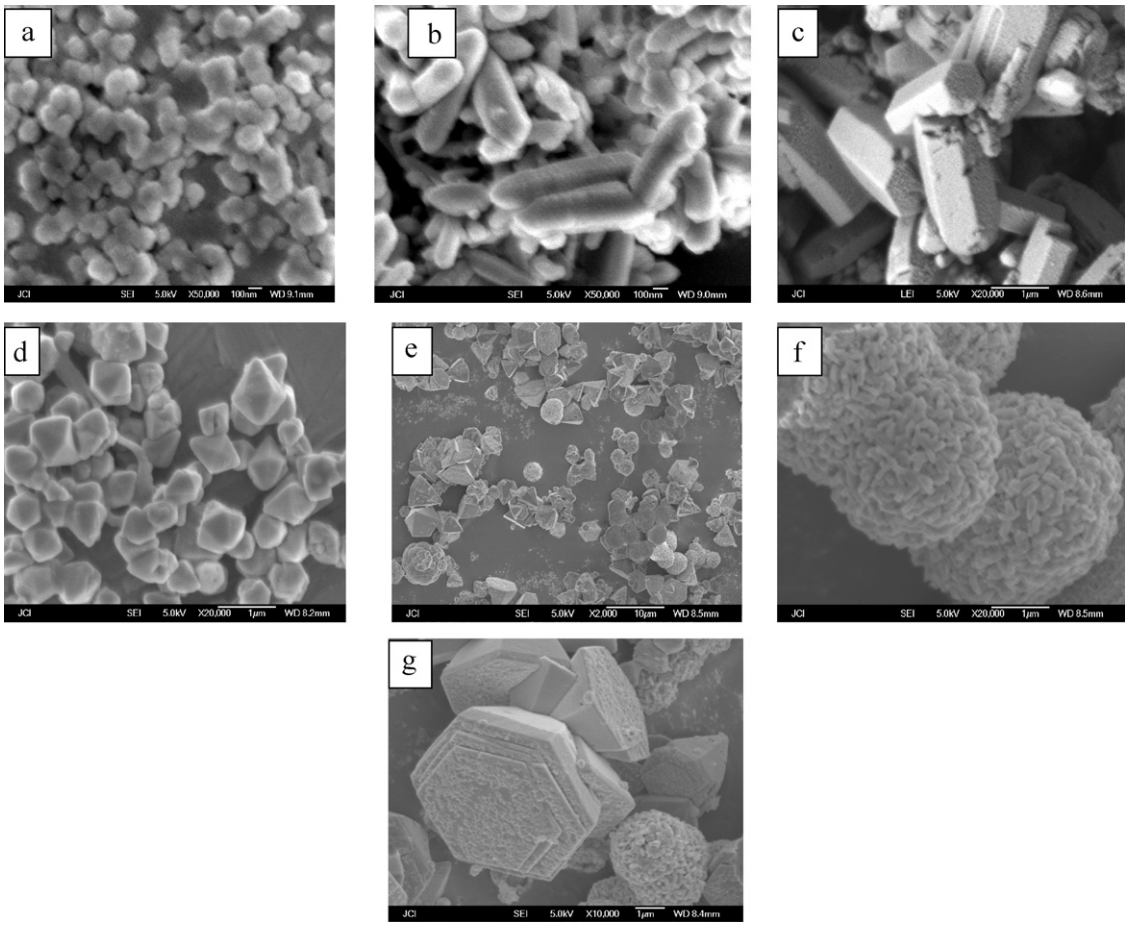

Fig. 6. FESEM photos of ZnO nanopowders prepared with different concentrations of CTAB in ethanol: (a) without CTAB, (b) 0.1 M, (c) 0.4 M, (d) 0.5 M, and (e–g) 0.8 M.

FSEM photos are shown in Fig. 6. CTAB concentration was 0.1 M, ZnO nanorods with a length of about 800 nm, a diameter of about 200 nm and aspect ratio of 4:1, were obtained. With the CTAB concentration increasing from 0.1 M to 0.4 M, the diameter of the nanorod broadens noticeably from 200 nm up to 500 nm and the length of the nanorod increases from 800 nm to 1000 nm. When the CTAB concentration was increased to 0.5 M, the resulting ZnO nanopowders with uniform particle size appeared as hexagonal bipyramid. When the concentration of CTAB was 0.8 M, some stepped hexagonal crystals and small microspheres coexisted in the product (see Fig. 6e–g). Detailed views on the shell structure indicate that the ZnO microspheres are comprised of numerous building units. Fig. 6 f shows an individual ZnO microsphere, which was assembled by hundreds of uniform nanorods, in which the length and diameter of an individual nanorod were around 300 nm and 100 nm, respectively.

There are few papers about the study on solubility of CTAB in ethanol. Ethanol is a weak polar substance. When CTAB concentration in ethanol is over the critical micelle concentration, CTAB can form reverse micelles. Conformational energy difference of n-hexadecane and ethanol is −170.736 kJ/mol and conformational energy difference of n-hexadecane and aqueous solution is −73.298 kJ/mol, which shows strong interaction between ethanol molecules and hexadecane molecules. So, it is difficult for CTAB molecules to form micelles in ethanol. The critical micelle concentration of CTAB in aqueous solution is 0.0009 mol/L, whereas that of CTAB in ethanol is 0.24 mol/L at 25 °C [24].

The critical micelle concentration of CTAB increases with the increase of temperature. When the concentrations of CTAB were 0.1 M, 0.4 M and 0.5 M, CTAB cannot form effective reverse micelles, and CTAB was dissolved in ethanol to form CTA^+ and Br^-. The complementarity between CTA^+ and $Zn(OH)_4^{2-}$endows the surfactant with a capability to act as an ionic carrier, so the concentrations of CTAB were 0.1 M and 0.4 M, ZnO nanorods were obtained. ZnO, as a polar crystal, has a polar axis and possesses a positive face and a negative face on the crystal due to the asymmetrical distribution of Zn atoms and O atoms along its polar axis, and the positive face (0 0 0 1) is occupied by Zn atoms while the negative face $(000\overline{1})$ is distributed by O atoms. When the concentration of CTAB was 0.5 M, the adsorption of CTA^+ and Br^- in the negative and positive side led to lower crystal growth rate of the positive and negative face,which induce the forming of hexagonal bipyramid ZnO nanopowders. When the concentration was increased to 0.8 M, spherical or layered reverse micelles formed in ethanol. Reactants will be wrapped through CTAB template, and CTAB serves as a soft template to control the growth of ZnO. So, some stepped hexagonal ZnO crystals and small microspheres ZnO coexisted in the products.

4. Conclusion

On the basis of the information we have gathered, we think that the shapes of the micelles or reverse micelles play a very important role in the final morphology formation of the ZnO nanopowders. The shape of micelles or reverse micelles can be regulated by the concentration of CTAB and type of reaction medium. By changing CTAB concentration and reaction medium, ZnO nanorods, ZnO nano-flowers, hexagonal bipyramid ZnO and ZnO microspheres can be obtained. Low concentration of CTAB in ethanol is conducive to the formation of ZnO nanorods, but the concentration continued to increase, the morphology of the sample transformed into hexagonal bipyramid, and then transformed into spherical.

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