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Controllable fabrication of various ZnO micro/nanostructures from a wire-like Zn–EG–AC precursor via a facile solution-based route

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ABSTRACT

In this paper, ZnO particles with various morphologies were prepared though a facile solution-based route. The complexes Zn–EG–AC (EG: ethylene glycol; AC: CH₃COO⁻ groups) obtained by reaction of anhydrous zinc acetate and EG were used as precursors. It is found that the precursor could transform into ZnO in water with no need of assistant of additional alkali as it is sensitive to water. At the same time, it is well dispersed in reaction medium (water and ethanol). Experimental results showed that ZnO particles with various morphologies, such as the hexagonal rings, the hexagonal plates, the tubes, the prisms, and some interesting hierarchical structures, could be obtained by controlling hydrolysis of precursor in water and water/ethanol medium through finely tuning the experimental parameters. The success of shape-controllable fabrication was related intimately with the Zn–EG–AC precursor used in our synthesis.

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1. Introduction

Precise control of size and shape is current research topics in the areas of nanomaterials [1]. Especially, the control of the morphology has received special attention because of the essential effect of the morphology on surface atomic arrangement and coordination of the particles, and consequently, the performance of the materials [2,3]. Zinc oxides (ZnO), a wide band gap (3.37 eV) semiconductor, have great potential in the fields of catalysis, sensor, photoelectric transformation and piezoelectric devices [4]. The morphology plays key role on governing the property of the ZnO materials. Typically, the $(0 \ 0 \ 0 \ 1)$ and $(0 \ 0 \ 0 \ \overline{1})$ facets of the ZnO have exhibited specific adsorption activity for CO during the synthesis of methanol [5], and for photodegradation reaction of the organic contaminations [6]. Recently, the shape-related optical properties of ZnO were detailed reviewed by Djurišić et al. [7]. Furthermore, the effect of microstructures on the photo-electric transformation performance of ZnO has been analyzed by Cao et al. [8]. All of the studies showed the importance of morphology in the areas of the technological applications and fundamental studies for ZnO materials. Consequently, it is not surprising that much effort has been devoted into controllable synthesis of ZnO particles. Wang and co-workers have reported the fabrication of ZnO nanobelts by the vapor deposition technique [9]. ZnO nano-nails and nano-bridges were obtained through thermal vapor transport and condensation methods [10]. Besides, the rod-like ZnO particles were successfully prepared with the assistance of ethylenediamine and NaOH through a hydrothermal route [11]. Hexagonal ZnO single-crystal slices with predominant (0 0 0 1) and (0 0 0 1) facets were fabricated by poly(ethylene glycol)-assisted chemical bath deposition route [12]. Recently, the large arrays of hierarchical ordered crystal architectures of ZnO were designed by "sequential nucleation and growth" strategy [13,14]. In addition, ZnO nanoparticles were prepared from nanowhisker precursor through a simple solvothermal route [15]. Above analyses showed that there are already large successes in shape-controllable fabrication of ZnO micro/nanostructures. Nevertheless, it still holds intensive interest and remains a big challenge for preparing various ZnO micro/nanostructures via a facile process. Doing it real should be important for further applications of ZnO-based materials.

In this paper, we reported the fabrication of ZnO particles with a wide variety of morphologies via an effective solution chemical route (SB route) under alkali-free conditions. As known, the physical process needs usually harsh reaction conditions in company with lower yield, which are disadvantageous for the practical application of the materials. In this regards, SB routes are promising for the preparation of ZnO crystals due to their merits of low cost, mild reaction condition and potential mass production. In the route, tuning the balance of nucleation and growth process is key factor to control the microstructure of ZnO crystals [11,13,14]. Notably, the precursor to ZnO plays important role for tuning the balance based on their intrinsic ability to release Zn source [16]. The typical precursor to ZnO included zinc salts or water-soluble ZnO complex, such as Zn(CH₃COO)₂, Zn(NO₃)₂, Zn(NH₃)₄²⁺, etc.

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Recently, it was reported that the metal-ethylene glycol (metal-EG) complexes could be used as precursor to prepare corresponding oxides via solid-state pyrolysis process [17-19]. Typical samples included Sn-EG, V-EG and Zn-EG. It has been found that Zn-EG complexes were sensitive to water, that is, could hydrolyze to form ZnO in pure water with no adding additional alkali [19]. This phenomenon stimulated us think if the characteristic could be utilized to controllably synthesize corresponding oxides. Herein, we demonstrate, for the first time, the complexes obtained by reaction of anhydrous zinc acetate and EG (refereed as Zn-EG-AC in here, EG: ethylene glycol, AC: CH₃COO⁻ groups) could act as a suitable precursor for fabricating ZnO crystals with various morphologies, including typically hexagonal rings, hexagonal plates, tubes, prisms, twinned discs and some hierarchical structure. Compared to the methods reported before, present route has several obvious advantages. First, ZnO particles with a variety of morphologies and uniform shape (up to 15 kinds) were easily fabricated by simply tuning the experimental parameters. Second, no dangerous reagents (such as strong alkali NaOH and NH₃) were used in whole preparation process. The shape-controllable synthesis was related intimately with the characteristics of Zn-EG-AC precursor used in here, such as easily adjusting the hydrolysis rate by water amount and good dispersity in reaction medium.

2. Materials and methods

2.1. Chemicals

Zinc acetate dihydrate (Zn(CH₃COOH)₂·2H₂O, Zn(Ac)₂·2H₂O), ethylene glycol (EG), ethanol, cetyltriethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), polyvinyl pyrrolidone (PVP, K3O), glucose and starch were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. PEO–PPO–PEO (P123) was purchased form Sigma. All reagents were used as received without further purification.

2.2. The preparation of ZnO micro/nanostructures

The anhydrous zinc acetate was obtained by heating $Zn(CH_3COOH)_2 \cdot 2H_2O$ at 100 °C for 12 h. To prepare the precursor Zn-EG-AC, 4.0 g of anhydrous zinc acetate and 40 mL of the EG were added in a 250 mL round-bottom flask and the solution was heated at 160 °C for 1 h. After naturally cooling to room temperature, the white solids were separated by centrifugation and washed with anhydrous ethanol for 3 times. The products were saved under vacuum at 40 °C. The reaction could be scaled-up by increasing the amount of the anhydrous zinc acetate and EG.

'The ZnO micro/nanostructures were prepared by the hydrolysis of Zn–EG–AC precursor in water/ethanol solvent (or pure water). Typically, for the preparation of ZnO nanorings, 4.0 g of Zn–EG–AC precursor and 0.5 g of CTAB were added into the solvent that was composed of 20 mL of H₂O and 20 mL of ethanol. After stirring at room temperature for 1 h, the mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave. The autoclave was heated at 100 °C for 10 h. Final white products were separated by centrifugation, and purified through washing with distilled water and ethanol for several times, finally dried at 60 °C. The experimental parameters, including reaction temperature, time, kinds of surfactant and volume ratio of ethanol/water (denoted as R), were tuned to study the influence of the parameters on the morphologies of ZnO. In all experiment, 4.0 g of Zn–EG–AC precursor was used.

2.3. Characterizations

The morphology of the samples was studied by Hitachi S-4800 scanning electron microscope. X-ray diffraction pattern was

recorded on a Rigaku D/Max-2550 (40 kV, 200 mA) diffractometer using Cu K α radiation with wavelength of λ = 0.15406 nm. FT-IR spectra were recorded on a PerkinElmer Spectrum One spectrometer using KBr pellets in the range of 400–4000 cm⁻¹. Thermogravimetric analysis was performed on a TG (TA, Q600) thermal analyzer under air with a heating rate of 10 K/min. The nitrogen adsorption–desorption isotherms were measured at 77 K using an Micromeritics Tristar. Before measurement, the samples were out gassed at 150 °C for 4.5 h, the specific surface area of the materials was calculated by the Brunauer–Emmett–Teller (BET) theory.

3. Results and discussion

Scheme 1 is a schematic procedure to prepare ZnO micro/nano structures. The process includes the first preparation of Zn-EG-AC precursor (Step 1), and its subsequent hydrolysis to form ZnO crystals (Step 2). The precursor was characterized by IR, TG, XRD, and SEM techniques. In IR spectra (Fig. S1), the broad peak at about 3416 cm⁻¹ is assigned to ν (O–H) from adsorbed water, while the peaks located at 2830–2960 cm⁻¹ are indexed to the vibration of C–H bands. In addition, the peaks in the range of 1000-1250 cm⁻¹ can be indexed to $\rho(CH_2)$, $\nu(C-C)$ and $\nu(C-O)$ bands. As control, IR spectra of EG is also provided. It can be seen that most peaks in IR spectra of EG and Zn-EG-AC spectra are same. The results indicate the presence of EG unit in the precursor. In addition, the two peaks at 1425 and 1561 cm⁻¹ in Zn–EG–AC precursor are ascribed to the v_{as} and v_s (0=C-O-) bands of CH₃COO⁻ groups, indicating the presence of CH₃COO⁻ in the products. TG analysis is also performed to give deep insight on structure of Zn-EG-AC precursor. As shown in Fig. S2, the loss weight before 100 °C (about 3.5%) is due to the residual ethanol in the products from the washing process. A major mass loss is observed at around 350 °C, attributing to the decomposition of the Zn-EG-AC. Final weight loss of as-prepared Zn-EG-AC within 350-600 °C is about 43%. Based on proposed structure by Zhang et al. [20], the theoretical loss weight from precursor to ZnO is about 35.13% calculated as below:

$$\text{Ratio of weight loss} = \frac{125.45 - 81.38}{125.45} \times 100\% = 35.15\%$$

where 125.45 is the theoretical molecular weight of $Zn(OCH_2-CH_2O)$, and 81.38 is that of ZnO. The value (35.13%) is very close to value tested by our TG results. The deviation between experimental (about 43%) and theoretic (35.13%) values should be due to presences of CH_3COO^- groups. Compared with $-OCH_2CH_2O^-$, the CH_3COO^- have similar molecular but with little coordination number (2:1). Thus, the ratio of ZnO will decrease in precursor. In addition, XRD pattern of the precursor shows an intensive peak at about 10° (Fig. S3), which is characteristic to M (metal)–EG composites (metal = Sn, V and Zn) [17–19]. By combination of XRD, IR, TG analyses and previous work, the proposed structure of precursor should be Zn ($OCH_2CH_2O)x(CH_3COO^-)y$, where 1 < x + y < 2. For convenience, we call the precursor as Zn–EG–AC. SEM analysis shows that the precursor are the long wire with the diameter about 500 nm and length of several tens micrometers



Scheme 1. Schematic process for fabrication of ZnO ($n \ge 15$).



Fig. 1. (a) SEM image and (b) XRD pattern of ZnO nanorings.

(Fig. S4a). Also, a magnified SEM image indicates the existence of many rumples on the wire surface (Fig. S4b).

ZnO particles were obtained by controlling the hydrolysis of Zn-EG-AC precursor in water/ethanol solvent. Fig. 1a shows SEM image of ZnO nanorings that was obtained by hydrolysis of the precursor in 20 mL ethanol + 20 mL $H_2O(R = 1)$ at 100 °C for 10 h with assistant of 0.5 g CTAB. As shown, the products are mainly composed of the hexagonal rings with thickness about 400 nm and diameter about 2 µm. In XRD pattern (Fig. 1b), the peaks located at $2\theta = 31.7^{\circ}$, 34.4° , 36.2° , 47.5° , 56.6° , 62.8° , and 67.8° are, respectively, indexed to (100), (002), (101), (102), (110), (103) and (112) diffractions of hexagonal structure ZnO (wurtzite) (JCPDS card no. 36-1451). The experimental parameters, including reaction time, CTAB and R value, have obvious effect on the microstructure of resulting ZnO crystals. Fixing the other parameters, the solid hexagonal ZnO plates with size about 2 um are obtained after performing the reaction for 1 h (Fig. 2a). With prolonging time to 5 h, the hexagonal plates with corrosive centre are main products as shown in Fig. 2b. Hollow hexagonal plates (hexagonal rings) are obtained as predominated product after performing the reaction for 10 h as depicted in Fig. 1a. Besides the reaction time, the CTAB are also important factor that affect ZnO shape. More specifically, ZnO thin plates with predominant (0001) and $(000\overline{1})$ facets [21] were gained in the absence of CTAB, as shown in Fig. 2c. The diameter of the plates is about 500 nm with thickness of 50 nm. As 0.2 g CTAB was added, ZnO hexagonal plate in company with a little of ZnO hexagonal ring are observed as shown in Fig. 2d. Increasing the dose of CTAB to 0.5 g, the hexagonal rings were formed with high yields. The effect of R value is also very obvious. Based on SEM analyses, we found that the products are composed of irregular ZnO particles as R is 9/1. While decreasing R to 0, the hexagonal prisms with diameter about

500 nm and length about 1 µm are main products. The organic structure-directing agents play a key role for controlling morphology of ZnO micro/nano-sized particles. To demonstrate this, the CTAB was replaced with other capping reagent, including SDS, PVP, P123, and saccharose. Typical SEM figures are given in Fig. 3. When SDS was added, the thin ZnO nanoplates with diameter below 1 µm were obtained (Fig. 3a). Also, some large plate-like structures are observed. As PVP was used, the twinned ZnO hexagonal with unsymmetrical morphology are mainly products (Fig. 3b). At the same time, a little of hollow rings could also be observed. In the case of using P123 and saccharose, the twinned ZnO hexagonal with unsymmetrical morphology are obtained (Fig. 3c and d). However, the size and the thickness of two samples are different. The particles from saccharose have a larger size and thickness. Based on above results, one can see that the ZnO with other morphologies other than nanorinds could be obtained when CTAB was replaced by other capping agent, further demonstrating importance of CTAB in the formation of ZnO nanorings. Recently, Li's and Peng's groups reported the synthesis of ring-like ZnO particles by sodium bis(2-ethylhexyl) sulfosuccinate [22] and polyacrylamide [23] assisted routes. It was proposed that the formation of ZnO nanorings should be contributed to a selected etching process. However, the hexagonal plates with corrosive centre (that should be intermediate products) are rarely observed. In our work, we have observed the intermediates for the first time, which provided a direct evidence for the formation process of ZnO rings. Based on the above results, it was proposed that the formation of ZnO rings is relative with a CTAB-assisted etching process. Importantly, it also indicates that the microstructures of ZnO could be easily tuned as rings, plates, prisms, etc.

We found that the ZnO morphology could be easily tuned in pure water assisted by different surfactants. Specifically, with assistant of 1 g P123, ZnO prisms with the length about 2 µm and diameter about 1 µm are obtained when the synthesis was performed in 40 mL of water at 100 °C for 10 h (Fig. 4a). From the inset of Fig. 4a, we can seen that the prisms are composed of twinned hexagonal prisms that have a larger population of nonpolar $\{01\overline{1}0\}$ faces than polar $\{0001\}$ ones [4]. By replacing P123 with PVP, the ZnO microtubes are formed as shown in Fig. 4b. The tubes are twined with the diameter about $1 \,\mu m$ and length about 3 µm. The thickness of the tube wall is about 100 nm as shown in inset of Fig. 4b. In addition, the cobble-like ZnO are formed when the SDS was selected as structure-directed agents. The size of the "cobbles" is in the range of $20-100 \,\mu\text{m}$. The high magnification SEM images (inset in Fig. 4c and d) show that the cobbles are composed of the many sheets with thickness about 300 nm. Above results indicated important effect of surfactants and ratio of ethanol to water on ZnO microstructure. Notably, further experiments indicted that the ZnO particles with uniform shape and narrower size distribution could be fabricated via this facile solution-based route by tuning reaction temperature, reaction, and the kinds of capping agents (Fig. 5a-i, Fig. 5a'-i' is corresponding figure of particle size distribution). Typical samples include asymmetric hexagonal prisms (Fig. 5a), drums (Fig. 5b), twinned hexagonal prisms (Fig. 5c), yo-yo balls (Fig. 5d), hamburgers (Fig. 5e), cauliflowers-1 (Fig. 5f), hoofs (Fig. 5g), cauliflowers-2 (Fig. 5h) and acalephs (Fig. 5i). Noteworthy is that the "cauliflower" and "twinned prism" have represented different microstructures for different samples (for example, cauliflowerlike particles in Fig. 5f and h, twinned hexagonal prisms in Figs. 4b and 5b). XRD patterns of the typical samples were given in Figs. S5-S7. From the XRD patterns, we can see that the samples are crystalline ZnO with hexagonal structure (Wurtzite, JCPDS card no. 36-1451).

Above results indicate that Zn–EG–AC complex is a suitable precursor for the controllable fabrication of ZnO particles with



Fig. 2. SEM images of ZnO particles obtained in the case: (a) *R* = 1:1, 100 °C, 1 h, 0.5 g CTAB; (b) *R* = 1:1, 100 °C, 5 h, 0.5 g CTAB; the inset is magnified SEM image of the sample; (c) *R* = 1:1, 100 °C, 10 h, without CTAB; (d) *R* = 1:1, 100 °C, 10 h, 0.1 g CTAB; (e) *R* = 9:1, 100 °C, 10 h, 0.5 g CTAB; (f) *R* = 0, 100 °C, 10 h, 0.5 g CTAB.

either single morphological or hierarchical (assembly) structure. Although great success was done previously, it still holds intensive interest and remains a key challenge in broadly tuning ZnO microstructure. There are two obvious characteristics for our present synthesis. First, ZnO with a wide variety of microstructures could be fabricated by simply tuning the experimental parameters. Second, Zn–EG–AC precursor could transform into ZnO by using H₂O as alkali without need of using additional basic agents, such as



Fig. 3. SEM image and of ZnO structures obtained by hydrolysis of Zn–EG–AC in 20 mL H₂O + 20 mL ethanol at 100 °C for 10 h with assistance of SDS, (b) PVP, (C) P123 and (d) saccharose.



Fig. 4. SEM images of ZnO structures obtained by hydrolysis of Zn–EG–AC in 40 mL of H₂O at 100 °C for 10 h with assistance of (a) P123, (b) PVP and (c and d) SDS. The insets in Fig. 3a–c are corresponding high-magnification SEM image of the samples.

ammonia, NaOH. In contrast, the excessive alkali needs to be adopted for transformation of the precursors into ZnO in many previous works. Based on our analysis, the advantages of our method are related with the Zn-EG-AC precursor. The Zn-EG-AC complexes have a wire-like microstructure, which could acts as a "solid" precursor for ZnO. As demonstrated before, the solid precursor could act as the slow-release reagent that provides an opportunity for proper regulating balance between the rates of nucleation and growth [24]. This indicated that, by using "solid" Zn-EG-AC as precursor, we can easily tune the balance of the nucleation and growth rates in the synthesis of ZnO particles, and thus regulate ZnO shape. On the other hand, the Zn-EG-AC precursor composed of Zn²⁺ coordinated with alkoxy groups have a similar structure with the metal alkoxides (such as titanium tertbutoxide). Because H₂O is a more strong alkali than EG group, thus the precursor could transform into ZnO by using water as "alkali". In previous reports, the "solid" precursors used to prepare ZnO were composed of inorganic compounds from a precipitation reaction that have relatively high stability. For example, the precursor remained stabilization after hydrothermal treatment at 100 °C for 4 h. Thus, the excessive alkali was adapted to effectively transform the precursors into ZnO. At the same time, only several hierarchical ZnO structures were obtained in these "solid" precursor routes, including the flower-like cupped-end ZnO microrod bundles [25], the hierarchical ZnO with a bladed bundle-like architecture [26] and ring-like nanosheets standing on spindle-like rods [27].

Recently, the study by Zhang's group indicated that the wirelike precursor containing Zn and EG could transforming into the LHS-Zn under moisture [19]. Also, many study indicated that the direct medium for forming ZnO should be $Zn(OH)_4^{2-}$. In present work, we have performed serials experiments to study the transformation process of Zn–EG–AC precursor into ZnO. The reaction is too fast to be detailed monitored the phase change of the Zn–EG–AC at the higher temperature. For example, phasepure ZnO are obtained at 100 °C for only 1 h. Therefore, the hydrolysis of precursor was performed at lower reaction (70 °C) to decrease the hydrolysis rate and to monitor the phase change of Zn–EG–AC in the synthesis. As shown by XRD patterns shown in Fig. 6, Zn–EG–AC gradually transforms into the ZnO within the 8 h. At the initial step (1 h), no peaks of crystalline ZnO were

observed (Fig. 6, curve a). However, we can see that the XRD patterns of the product are different with origin Zn-EG-AC. Two typical new peaks located at about 5° and 13° indicate formation of lavered hydroxide zinc acetate (LHS-Zn) based on the previous reports of Zhang's and Jouini's groups [20,28]. As no additional acetate was used in the synthesis, the acetate in LHS-Zn should be from precursor. This further indicated presence of acetate groups in the Zn-EG-AC precursor. This observation further sustains the results obtained by TG and IR analyses. When the time prolonged to 2 h, the peaks corresponding to ZnO and LHS-Zn could be observed simultaneously (Fig. 6, curve b). The intensity ratio of ZnO phase to LHS-Zn phase gradually increased as the increase of reaction time (Fig. 6, curve c). Finally, the phase pure ZnO were obtained after 8 h of hydrolysis reaction (Fig. 6, curve d). In general, the more direct medium proposed in the formation of ZnO are $Zn(OH)_4^{2-}$. To demonstrate this speculation, the followed experiments were performed. The reaction was firstly performed at 70 °C for 1 h. After centrifugation, the supernatant (colorless, transparent) was collected followed by heating at 100 °C for 1 h. The solution became turbid and finally white precipitation (ZnO) was obtained. The results showed that the existence of $Zn(OH)_4^{2-}$ in the supernatant, implying further that the direct medium should be $Zn(OH)_4^{2-}$ in present synthesis.

Based on above analysis, we proposed that, in our synthesis, ZnO was formed through three steps as follows:

 $Zn-EG-AC \rightarrow LHS-Zn \rightarrow Zn(OH)_4^{2-} \rightarrow ZnO$

One of main characteristics of Zn–EG–AC precursor is its welldispersion in reaction medium (both water and ethanol, Fig. S8). This characteristic should be favorable for a heterogeneous nucleation process. Both of the characteristics have contributed into the fine and wide adjusting of the ZnO morphology. Zn–EG–AC precursor is sensitive to water and stable to ethanol. Therefore, by changing the ratio of water to ethanol, the nucleation and growth rate of ZnO could be tuned. The function of organic structuredirecting agents is relative with their ability to selected adsorption on certain crystal plane of ZnO, and to assemble ZnO crystals to superstructures [29,30]. Therefore, ZnO morphology could be easily regulated by changing the reaction parameters. As a particle



Fig. 5. SEM images of ZnO with different microstructures and their corresponding preparation parameters: (a) asymmetric hexagonal prism-like ($R = 0, 100 \degree C, 5 h, 0.5 g$ saccharose); (b) drum-like ($R = 0, 100 \degree C, 5 h, 0.5 g$ starch); (c) twinned hexagonal plate-like ($R = 0, 120 \degree C, 5 h, 0.5 g$ SDS); (d) twinned disk-like ($R = 0, 100 \degree C, 5 h, 0.5 g$ SDS); (e) hamburger-like ($R = 19/1, 120 \degree C, 15 h, 0.5 g$ SDS); (f) cauliflower-like ($R = 19/1, 120 \degree C, 10 h, 0.1 g$ SDS); (g) hoof-like ($R = 19/1, 140 \degree C, 10 h, 1 g$ PVP); (h) cauliflower-like ($R = 19/1, 140 \degree C, 15 h, 1 g$ PVP); (i) acaleph-like ($R = 19/1, 100 \degree C, 15 h, 0.1 g$ of PVP). The insets in each figure are corresponding high-magnification SEM image. The (a'-f') are particle size distribution corresponding to (a-f).

material, the specific surface area (SSA) is a very important parameter. The SSA of typical samples was determined and the results are listed in Table S1. From the results, we can see that the specific surface area of all samples is relative small as no obvious micro- or meso-pore in as-prepared samples. However, one can see that the assemble structures composed of small particles (Fig. 5i) and tube-like structure (Fig. 4b) have a higher BET specific surface area than other single morphological particles generally. As known, the higher BET specific surface area is important for practical application of materials in certain areas. In our further work, we will focus attention on preparing these kinds of materials by elaborately tuning synthesis parameters.



Fig. 6. XRD patterns of the solids obtained after hydrolysis of the Zn–EG–AC precursor in water at 70 $^\circ$ C for (a) 1 h; (b) 2 h; (c) 4 h; (d) 8 h.

4. Conclusions

Zn–EG–AC complex obtained from reaction of anhydrous zinc acetate and EG could as a suitable precursor for ZnO fabrication. By controlling hydrolysis of Zn–EG–AC precursor, ZnO with a wide variety of the morphologies were successfully fabricated by using water as "alkali" source. The success of shape-controlled synthesis was related intimately with the special structure of Zn–EG–AC precursor used in here. The controllable fabrication also provides a chance for studying the morphology- and/or face-dependent properties of ZnO micro/nanocrystals. Further work about these is under way.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.materresbull.2011.03.030.

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