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Cavity of cyclodextrin, a useful tool for the morphological control of ZnO micro/nanostructures

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Abstract

Micro/nanostructures of ZnO with different morphologies were successfully prepared by using β-cyclodextrin (β-CD) as a crystallization modifier, at relatively mild conditions. The as-prepared products were characterized by field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). The effects of β-CD concentration, the reaction time and temperature on the final morphologies of ZnO crystals were discussed. The results showed that the β-CD concentration and reaction time played an important role for the morphological change of ZnO crystals. Additionally, the cavities of β-CD molecules were underlined in the process of ZnO crystallization. On the basis of the multiple functions of β-CD molecules, we proposed a possible mechanism for the morphological evolution of various ZnO crystals.

Keywords: A. Powders: chemical preparation; B. Microstructure-final; D. Transition metal oxides; β-Cyclodextrin

1. Introduction

Zinc oxide (ZnO), a direct wide band gap (3.37 eV) semiconductor with a large excitation binding energy (60 meV) [1], is an important multifunctional material because of its promising applications in sensors [2], solar cells [3] and photocatalysts [4,5]. These applications are related with the size, composition and morphology of ZnO. Rich morphologies of ZnO have been prepared such as nanotubes [6], nanorods [7], and core-shell microspheres [8], since the last decades. Meanwhile, various physical methods have been used including thermal evaporation, chemical vapor deposition, and electrodeposition. Nevertheless, these routes usually require high reaction temperature, complex apparatus or other rigid conditions.

Recently, varied wet chemical methods have been applied to fabricate ZnO micro/nanostructures. Accompanied solution system has the advantage of adjusting high uniformity and supersaturation degree for particle morphology control [9]. Among these techniques, addition of biomolecular templates such as proteins and DNA has received a tremendous amount of attention [10–12]. These kinds of biomolecules, however, are usually expensive and sometimes toxic. In contrast, some biopolymers, such as cyclodextrins, supply many advantages. They are abundant in the biomass and are easily accessible from various sources, such as grasses, forest products, and stalks [13]. Therefore, they might be a viable substitute of other chemical or physical methods to mediate the morphologies of inorganic materials.

As a kind of biopolymers, cyclodextrins (CDs) are cyclic oligosaccharides consisting of D-glucose units arranged in a circle, which are characterized by a hydrophilic rim and a porous-shaped structure. The former construction is made of hydroxyl groups, making the molecule water soluble, and the latter is a hydrophobic cavity, encapsulating a variety of inorganic and organic guest species through non-covalent interactions such as hydrophobic effect, hydrogen bonding and van der Waals force [14]. CDs are relatively inexpensive, easily available and chemically reactive, being idea templates to fabricate inorganic materials. Latterly, a few reports on CD-directed growth of metal oxides have appeared in literature [15,16]. Nevertheless, to the best of our knowledge, the exact mechanism of the interaction of CDs to ZnO is still unclear and further understanding of the details of the

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molecule recognition of CDs happened on the interface is needed.

Herein, we chose β-cyclodextrin (β-CD) as crystal modifier for the synthesis of ZnO with unusual surface morphology at a relatively mild temperature of 70 °C. In our system, the morphological evolution of ZnO crystals from flower-like to spherical microstructures was investigated. The effects of the reaction time and temperature on the final ZnO morphology were also explored in detail. In addition, a growth mechanism was proposed based on the coating and join effect of β-CD molecules, emphasizing the role of the cavities of β-CD in ZnO crystallization.

2. Experimental

2.1. Preparation

All chemicals were of analytical grade and used as received without further purification. Ultrapure grade water was used throughout the experiments. In a typical process, 0.06 g of β-CD (obtained from Sigma, C 4767) and 2 mmol of zinc acetate dihydrate ($Zn(Ac)_2 \cdot 2H_2O$) were dissolved in 30 ml of 50% ethanol under constant stirring. After a stirring of 10 min, 30 ml of 50% ethanol solution containing 20 mmol NaOH was added to the above solution with stirring for another 10 min. Afterwards, the vessel was sealed and kept in an oven at 70 °C for 10 h. The product was collected by centrifugation (3000 rpm, 5 min) and thoroughly rinsed with absolute alcohol, and finally dried in an oven at 70 °C for 10 h.

2.2. Characterization

The morphology of the samples was investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800). The crystalline phase of the products was characterized by X-ray diffraction measurements (XRD, Germany Bruker D8-ADVANCE, Cu Ka radiation).

3. Results and discussion

Generally, the growth of crystals is a kinetically and thermodynamically controlled process, and different shapes of products can be obtained through the manipulation of various reaction parameters. However, these material structures are sensitive to many parameters such as reaction time [17], temperature [18], concentration of inorganic additives [19], type of precursor and template [20]. In this experiment, we focused on the effects of β-CD concentration, reaction temperature, and reaction time on the final shapes of ZnO crystals.

3.1. Effect of β-CD concentration

Fig. 1 shows the FESEM images of ZnO crystals prepared in 50% ethanol solution sampled at various concentrations of β-CD at 70 °C for 10 h. Low β-CD concentration (0.5 mg/ml) yielded the flower-like ZnO crystals with hierarchical structures (Fig. 1a). We found that the as-synthesized products consisted of a large quantity of ZnO flakes with surface grafting of nanoparticles. Thus, the product was considered to be a

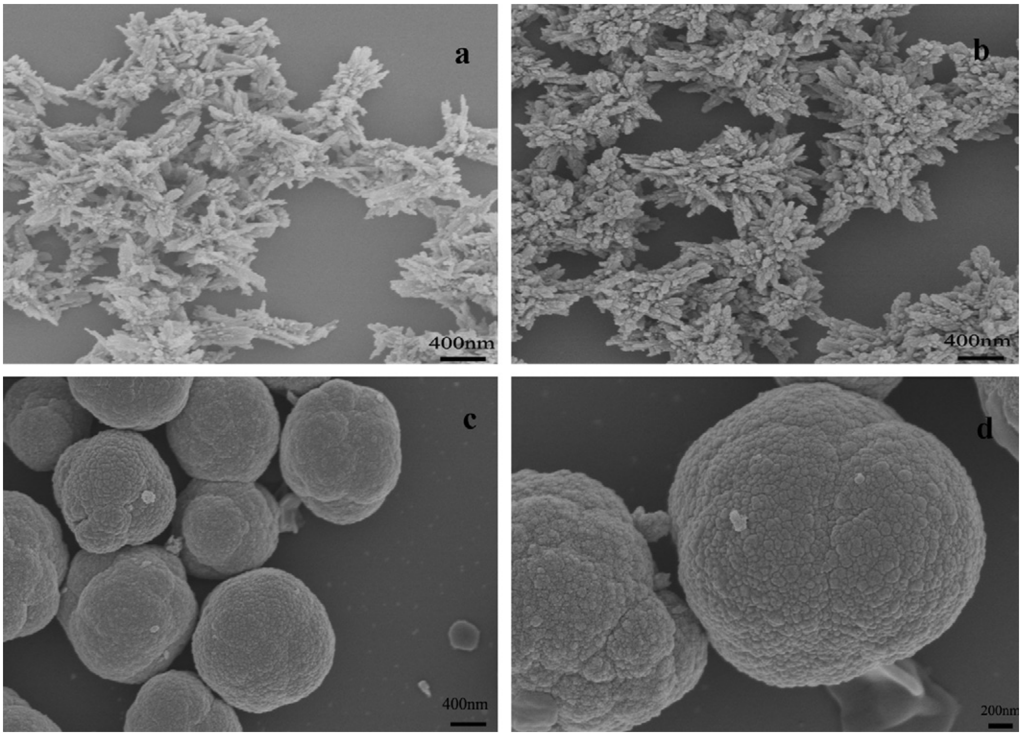

Fig. 1. FESEM images of the as-prepared ZnO grown in 50% ethanol solution at 70 °C for 10 h with different β-CD concentration: (a) 0.5 mg/ml; (b) 1 mg/ml; (c and d) 2 mg/ml.

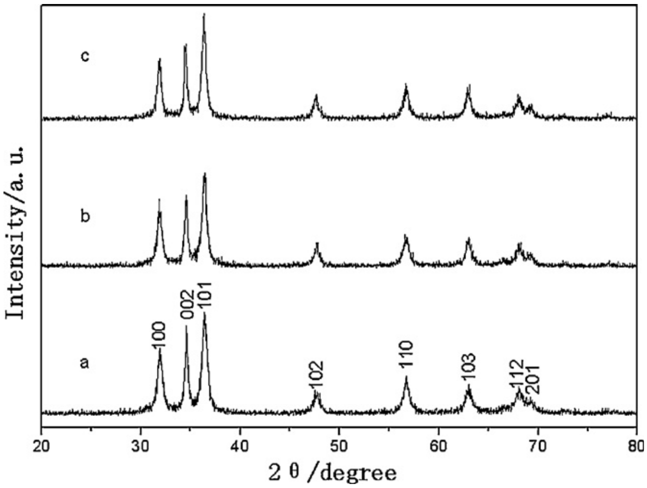

Fig. 2. XRD profiles of ZnO crystals grown in 50% ethanol solution at 70 °C for 10 h with different β-CD concentration: (a) 0.5 mg/ml; (b) 1 mg/ml; (c) 2 mg/ml.

three-dimensionally hierarchical micro/nanostructure. When the β-CD concentration was 1 mg/ml, the morphology of the sample did not change greatly, except that the structure of the product was more compactly assembled (Fig. 1b). With the increase of β-CD concentration to 2 mg/ml, the products showed a completely diverse morphology (Fig. 1c). The products were composed of spherical ZnO particles with diameters of *ca.* 1.5–2 μm. The examination of the faces of products at high magnification strongly suggested that the particles were constructed from small distinct crystalline units (Fig. 1d). These results clearly indicated that the shape and size of ZnO were strongly related to the concentration of β-CD.

Fig. 2 depicts the corresponding XRD patterns of the products mentioned above. All the products prepared in the presence of β-CD exhibited almost the same XRD characteristic as the standard data of wurtzite type ZnO (JCPDS card no. 80-0074, $a = 0.325$ nm, $c = 0.522$ nm, hexagonal, space group $P6_3mc$), except for the relative intensity ratio of diffraction peaks. In addition, the diffraction peaks were sharp, indicating the high purity and good crystalline of products. It was noticeable that the (0 0 2) peak of each sample was much stronger than that of the standard sample, indicating their preferential orientation growth along the *c*-axis [0 0 1] direction.

In the absence of β-CD, a new hierarchical structure of ZnO, which was composed of many sheet-like structures, was formed (Supporting Information, Fig.S1). The surfaces of the sheets were smoother than those of the building units of the products created using β-CD. The corresponding XRD pattern was depicted in Fig. S2. All the diffraction peaks, especially the intensity of the (0 0 2), were even stronger and sharper than those of the products determined above, indicating that the obtained product was also highly crystalline and had tendency of the preferred orientation growth along the *c*-axis [0 0 1] direction. The results indicated that β-CD was crucial in forming the as-produced structures shown in Fig. 1.

In addition, we found that the mixture of water–ethanol solution played an important role during the formation of the as-synthesized ZnO crystals. Without the addition of ethanol, ZnO crystals took on peltate morphology with length × width of 5 μm × 2 μm (Fig. S3). They showed monodispersed shape and aggregation of irregular crystal blocks, which could be identified from the cracks on the surface of each product.

3.2. *Effect of reaction temperature*

Fig. 3 shows the FESEM images of ZnO crystals grown with 1 mg/ml β-CD in 50% ethanol solution for 10 h at 30 and 90 °C. Neither of the product morphology synthesized at the two temperatures had evident different from that of the ZnO crystals fabricated at 70 °C. The result showed that the reaction temperature did not play a crucial role in the formation of ZnO crystals, suggesting a quick crystalline process.

3.3. *Effect of reaction time*

For a complete view of the formation process, time-dependent morphology experiments were investigated by intercepting intermediate products of ZnO in different reaction stages in the presence of 1 mg/ml of β-CD at 70 °C. The morphological evolution was examined by FESEM, and the results are shown in Fig. 4. Within the initial reaction process

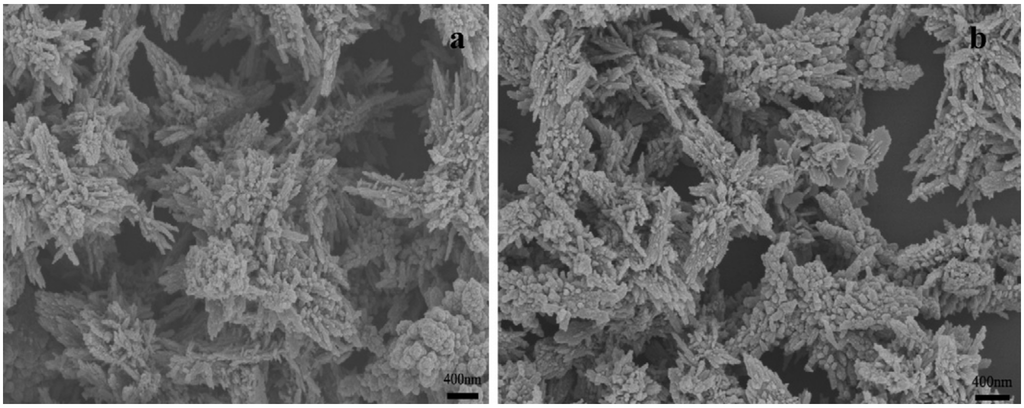

Fig. 3. FESEM images of the as-prepared ZnO grown in 50% ethanol solution with 1 mg/ml β-CD for 10 h at (a) 30 °C and (b) 90 °C.

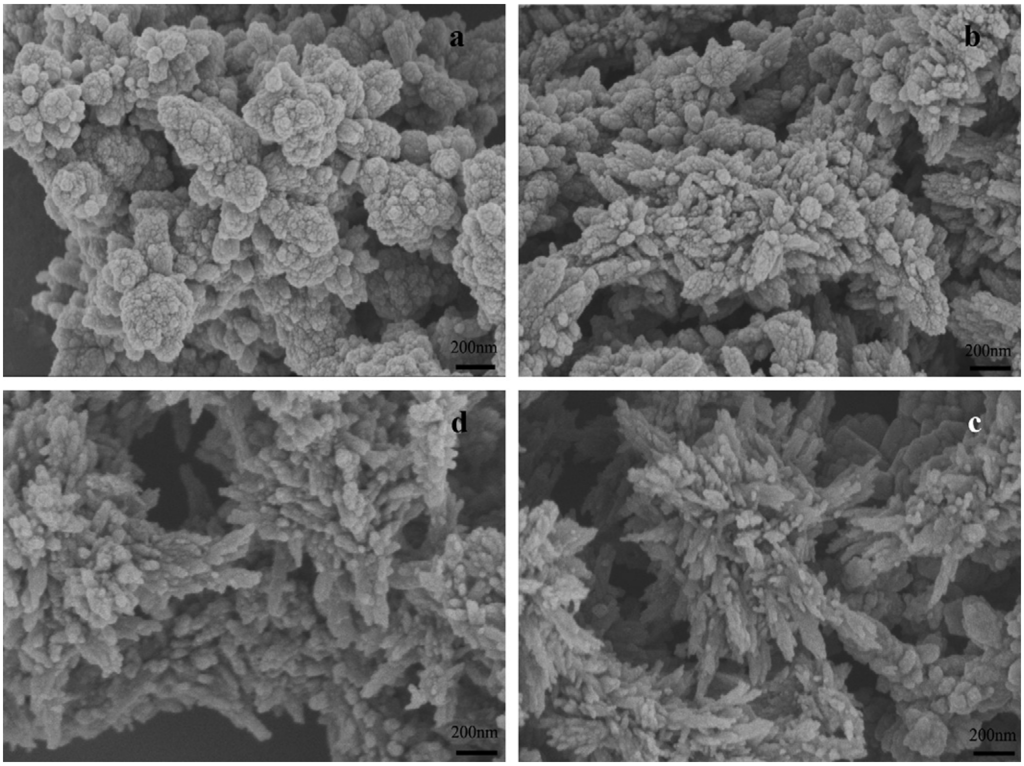

Fig. 4. FESEM images of the as-prepared ZnO grown in 50% ethanol solution with 1 mg/ml β-CD at 70 °C at different times of (a) 30 min, (b) 1 h, (c) 2 h and (d) 5 h.

for 10 min, visible precipitates were not observed. When the reaction time carried out for 30 min, irregularly shaped polycrystalline aggregates began to appear (Fig. 4a). The surfaces of the aggregates were composed of many nanoparticles. With the prolonged reaction time (1 h), slightly pointed tops of the aggregates exhibited (Fig. 4b). When the reaction time was increased to 2 h, the nanoparticles still remained but the nanosheets as building blocks began to increase, thus the products evolved toward flower-like structures (Fig. 4c). All results indicated that there was a dissolution-recrystallization process of the inorganic crystals. When the aging time was prolonged to 5 h, the morphology of the products had not evidently changed (Fig. 4d). The corresponding XRD patterns (Fig. 5) showed that all products grown at experimental time were hexagonal-phased structures (JCPDS card no. 80-0074). These results showed that the crystalline process of as-synthesized ZnO made by using our method was very fast.

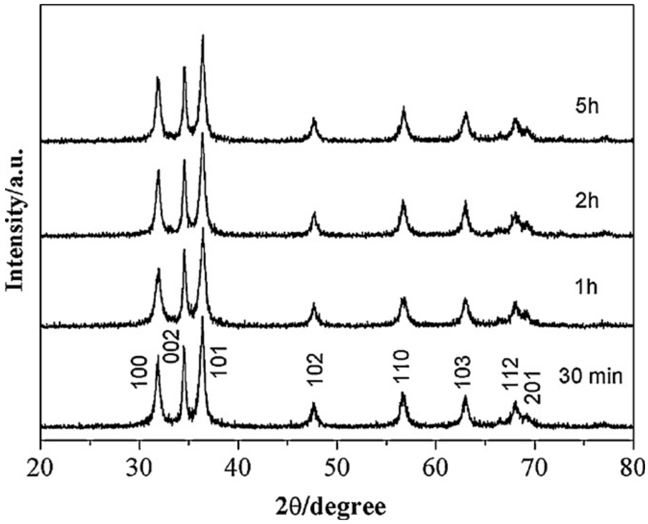

Fig. 5. XRD patterns of the samples isolated at different reaction time at 70 °C.

3.4. Growth mechanism

Fig. 6 depicts the proposed forming mechanisms. It is known that wurtzite ZnO crystal is composed of a number of alternating planes stacked along the *c*-axis direction. Since the Zn^{2+} terminated (0 0 0 1) face has the maximum surface energy and O^{2-} terminated (0 0 0 −1) has the minimum surface energy, the growth along [0 0 0 1] (+*c* axis) direction has a faster rate than other directions.

At the beginning of the reaction, the ZnO particle nucleates quickly, according to

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow \tag{1}$$

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

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

The morphological change of the products is correlated with a competition between the growth and erosion rates. In the erosion reaction, the excess OH– in the solution acts according to

$$ZnO + OH^- \rightarrow ZnO_2{}^{2-} + H_2O \tag{4}$$

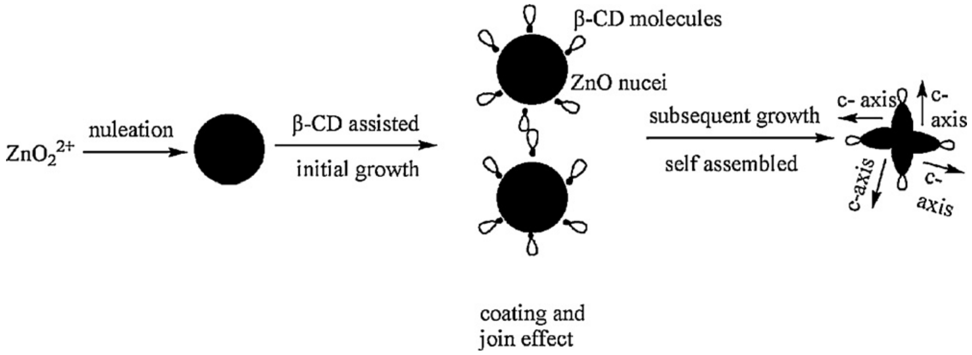

Fig. 6. Schematic illustration of the growth model.

thereby forming the flower-like ZnO structures produced in the absence of β-CD.

In the presence of β-CD, the cases have changed. We propose that β-CD molecules have multiple functions, *i.e.* adsorption, coating and join agent in the formation process of as-synthesized ZnO crystals. First, they can adsorb onto the planes of crystal preferentially. When β-CD molecules are introduced during the initial growth process of the crystals, they can adsorb onto a certain crystallographic plane more strongly because of anisotropy in adsorption stability. This process of preferential adsorption lowers the surface energy of the bound planes and suppresses the crystal growth perpendicular to this plane [21]. Second, β-CD molecules act as a coating agent to provide steric hindrance and to prevent growth and aggregation of ZnO particles. Furthermore, the interior of β-CD is a hydrophobic cavity, which can encapsulate a variety of inorganic/organic guest species through non-covalent interactions. When ZnO nuclei are just formed, each minute nucleus would be surrounded by β-CD molecules, prohibiting the agglomeration of the nucleus. When β-CD with a low concentration (for example, 0.5 or 1 mg/ml) is added into the reaction system, the coating effect of β-CD toward ZnO particles is weaker or insufficient. With the assistance of β-CD, the obtained ZnO crystals thus exhibit flake-like structure. Importantly, the surface of the products is tough and filled with the nanoparticles grafting. In this instance, join effect of β-CD might also have an effect to some extent. It has been reported that ethanol can co-crystallize with CD to form quaternary complexes of CD-guest-ethanol-hydrate [22]. As a result, consequent joining may occur among the countless ZnO nuclei that were coated in the cavities of β-CD. This effect is different from coating of β-CD, which mainly prevents the growth and aggregation of crystallites [21,23]. It is inferred that this effect might be a transitory and assistant way duo to weak chemical interaction between the β-CD molecules. In contrast, without adding β-CD, the sheet structure of the products takes on smooth surface, as shown in Fig. S1. As the crystallization is proceeding, the flakes self-assemble together along *c* axis with proper side crystal planes to reduce surface energy. Nevertheless, when β-CD is increased to 2 mg/ml, the coating and join effect among molecules are greatly enhanced. The final ZnO crystals then become spherical morphology, and the uniformity of crystallite size is simultaneously improved.

4. Conclusion

In summary, we have studied morphological change of ZnO in the presence of β-CD. In original studies, the properties of widely available biopolymers have been much less exploited for the morphological control of inorganic materials [13]. Our results showed that the adsorption, coating and join effect of β-CD were necessary in the formation of the as-synthesized ZnO crystals. Importantly, the cavities of β-CD molecules played a key role in forming the hierarchical flower-like ZnO structures. β-CD molecules as a crystal growth modifier may have general importance in the synthesis of inorganic materials with unusual morphologies. These facts help to understand the interaction and recognition of biopolymers to the surfaces of inorganic materials.

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.ceramint.2012.03.037.

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