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Amino acid-assisted synthesis of ZnO twin-prisms and functional group's influence on their morphologies

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ABSTRACT

ZnO twin-prisms were prepared by a simple solvothermal process with glutamic acid as surface modification agent in ethanol. Compared with the twin-cones that were obtained when glutamic acid was absent, the ZnO twin-prisms have optimized crystallinity with high symmetry, sharp crystal edges and few defects. Probable reaction mechanism between ZnO and glutamic acid was proposed based on our experimental analysis. Then it was verified by a series of comparison experiments by employing glycine, acetic acid and ethylamine as surface modification agents. Our results indicate that both alkaline and acidic groups play an important role on the formation of ZnO twin-prisms, and when either of them was absent, twin-prism structures cannot be obtained. The photoluminescence properties of as-prepared ZnO twin-prisms and twin-cones were also studied.

1. Introduction

Zinc oxide (ZnO) is an important semiconductor with wide band gap (3.3 eV) and large exciton binding energy (60 meV) at room temperature. It has already been widely used in many fields, such as photocatalysis, optoelectronic devices, lasers, solar cells, sensors and varistors [1–6]. On the purpose to improve the electrical and optical properties of ZnO, many works on controlling the size and morphologies have been carried out. Up to now, various methods [7–13] of preparing ZnO nano/microcrystals have been reported, and plenty of self-assembled 2D and 3D ZnO nano/microstrucutures have been synthesized [14–16,21–24,17]. Recently, the synthesis of metal oxides of specific morphologies by the interactions between nanoparticles and organic molecules has attracted tremendous attentions [17–20]. Organic matters have also been involved in the crystallization of ZnO in solution. The polymer has been considered to be adsorbed to different crystalline planes of ZnO crystals and changes the crystallization habits, which result to abundant of ZnO hierarchical structures [21]. Some processes of ZnO preparations with organic matters involved have been reported to be effective in the growth of ZnO crystals. Hu et al. have prepared arrayed ZnO nanorods on glass substrates using monoethanolamine ($NH_2CH_2CH_2OH$) as additive by a two-step wet chemical process [22]. And prismlike, flowerlike and hollow ZnO have been developed using the amino acid histidine as the directing and assembling agent [23]. Mandal et al. have investigated the interaction of an essential amino acid L-tryptophan (TRP) and amino acid L-aspartic acid (ASP) to ZnO by steady state and time resolved spectroscopic technology [24]. And various zinc oxide nanostructures were prepared in different polar organic solution of NaOH via a facile self-assembly solvothermal growth process [17].

In this work, ZnO twin-prisms with optimized morphology and improved crystalline quality were synthesized by a solvothermal process employing glutamic acid as surface modification agent. Probable growth mechanism of ZnO twin-prisms was proposed based on FTIR analysis by investigating the role of functional groups of amino acid and the interactions between ZnO and amino acid. Our results indicate that both carboxyl (–COOH) and amino ($–NH_2$) groups are necessary on the formation of ZnO twin-prisms. When amino acid was replaced by organic acid or amine, no ZnO twin-prisms can be obtained. The photoluminescence properties of as-prepared ZnO twin-prisms were also discussed.

2. Experimental details

During the synthetic procedure, all the reagents and solvents were analytical grade and used without any further purifications. In a typical run, 0.4 g glutamic acid was first added to 20 ml absolute ethanol to form a saturated solution

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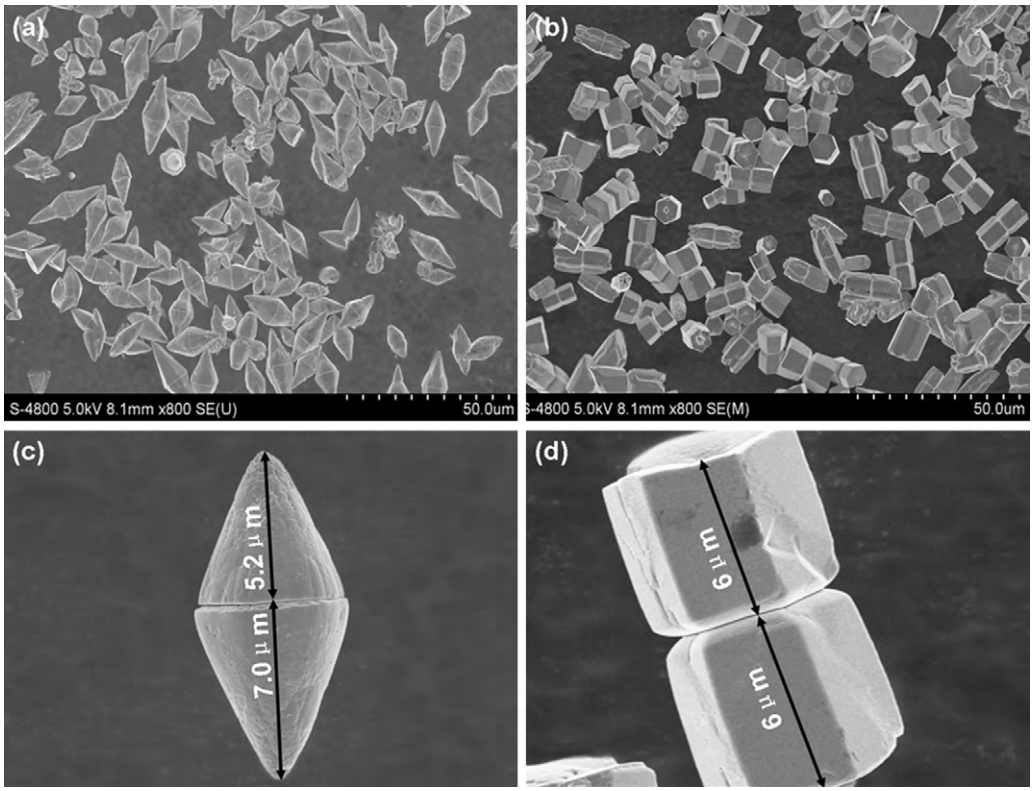

Fig. 1. SEM images of ZnO microcrystals prepared in ethanol (a) without glutamic acid and (b) with glutamic acid; zoomed-in views of a twinned cone (c) and a twinned prism (d).

under magnetic stirring. Then it was filtered and 0.595 g zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) was added. Finally, the transparent solution was transferred into a Teflon-line stainless steel autoclave and kept at 160 °C for 4 h. The final product was collected, washed with deionized water and ethanol for several times, and dried at 70 °C in air. For comparison, ZnO samples without glutamic acid were also prepared. Furthermore, in order to investigate the role of the functional groups of glutamic acid on the growth of ZnO twin-prisms, a series of experiments were carried out with different additives (i.e., glycine, acetic acid and ethylamine) under identical conditions.

The morphologies of the ZnO crystals were characterized using scanning electron microscopy (SEM, Hitachi S4800) with an accelerating voltage of 5 kV. X-ray diffraction (XRD) analysis was performed with a Bruker AXS D8 advance powder diffractometer with CuKα radiation. The FTIR spectra of the products were investigated by Fourier transform infrared (FTIR) spectroscopy (Nexus 670, Thermo Nicolet, USA) with smart iTR accessory. Photoluminescence (PL) measurements were performed at room temperature with a luminescence spectrometer (Edinbergh FLS 920) using 380 nm as the excitation wavelength.

3. Results and discussion

3.1. Morphologies of the twin-crystals obtained with and without glutamic acid

Fig. 1a and b shows the SEM images of as-prepared ZnO samples without and with glutamic acid, respectively. As we can see, the ZnO microcrystals have the morphology of twin-cones with 5–10 μm in diameter and 10–15 μm in length when glutamic acid was absent (Fig. 1a). The two cones of the twin-crystals are slightly different in size as shown in the magnified view in Fig. 1c: one cone is 5.2 μm in size and another is 7.0 μm. When glutamic acid is introduced to the synthetic procedure, there is a significant change on the morphology of the as-prepared ZnO samples (Fig. 1b and d). Strictly symmetrical twin-prisms were formed instead of twin-cones compared with the sample prepared without glutamic acid. Each prism is 5–15 μm in length and ~10 μm in diameters. It can be seen that the hexagonal ZnO prisms are well crystallized with sharp-edge and smooth surface, which indicates that amino acid plays an important role in the optimization of ZnO twin-prisms.

The structures of the as-prepared samples were further characterized by XRD. Fig. 2 shows the XRD patterns of the samples obtained with and without glutamic acid. In this figure, we can clearly see that all our samples are well crystallized without any other impurities, and all peaks can be indexed to the hexagonal wurtzite ZnO (JCPDS no. 36-1451). For a closer observation, the sample (curve a) prepared with glutamic acid shows a markedly stronger intensity along (1 0 0) plane than the sample (curve b)

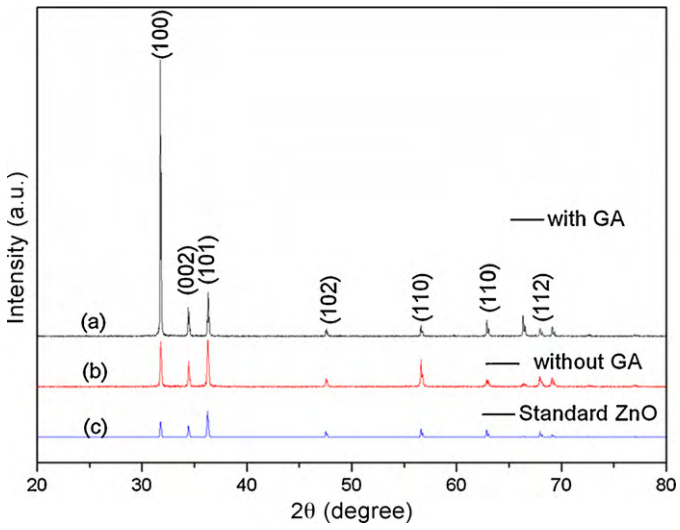

Fig. 2. XRD patterns of the ZnO samples obtained (a) with and (b) without glutamic acid. The standard diffraction pattern for wurtzite ZnO was also shown in (c) taken from JCPDS file (No. 36-1451).

without glutamic acid. That means more (1 0 0) planes would be present when glutamic acid was added during the synthetic process. This implication is consistent with the observation of twin-prisms in Fig. 1.

3.2. Probable growth mechanisms

In order to investigate the functionalization process of glutamic acid, FTIR spectra of the as-prepared ZnO samples were examined. Fig. 3 shows the FTIR spectra of non-functionalized ZnO (curve a) and glutamic acid functionalized ZnO (curve b). Comparing the two curves, the peaks around 3350 cm^{-1} and 1600 cm^{-1} can be assigned to the –OH stretching vibrations and deformation vibrations, respectively. The –OH derives from air moisture and residual water. Besides that, the peaks at ~1330 cm^{-1} and ~1044 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of $–NO_3$, which can be observed in both curves a and b. Meaning while, the broad absorption peaks consisted of multiple peaks in the range of 3100–2800 cm^{-1} and the peak at ~1086 cm^{-1} can only be detected in curve b. And according to the literature, the broad absorption in the range of 3100–2800 cm^{-1} was assigned to the NH^{3+} stretching frequencies of glutamic acid derived from the zwitterion nature of amino acids [25]. And the peak at 1086 cm^{-1} is attributed to the stretching vibrations of C–N from glutamic acid. This result further indicated that glutamic acid molecules were adsorbed to the surface of ZnO twin-prisms and may play an important role on the formation of the ZnO twin-prism structures.

Based on the experimental results, the probable reaction mechanism between amino acid and ZnO could be speculated as follows.

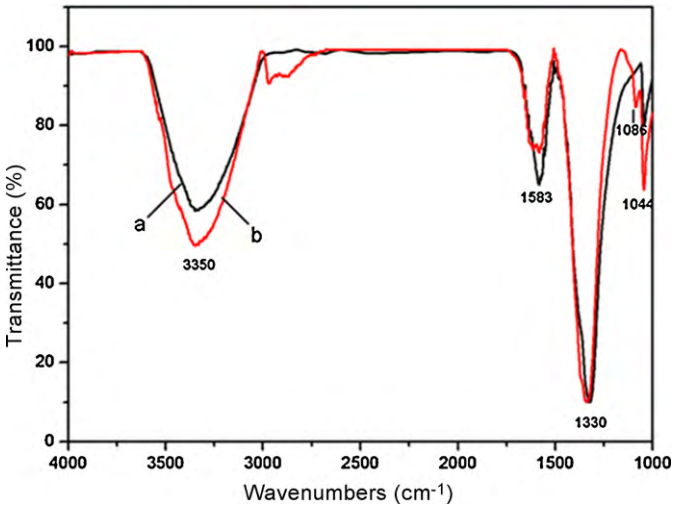

Fig. 3. FTIR spectra of the ZnO twins: (a) non-functionalized ZnO and (b) glutamic acid functionalized ZnO.

The appearance of the six (1 0 0) side-planes of a twin-prism indicates that the (1 0 0) family of planes have a low growth speed, i.e., glutamic acid restrains the growth of the (1 0 0) planes. The possible reason is the complexation between ZnO and glutamic acid. Glutamic acid has both alkaline groups ($–NH_2$) and acidic groups (–COOH). And $–NH^{3+}$ could be formed by a neutralizing reaction during the solvothermal process, which could later form N–H···O

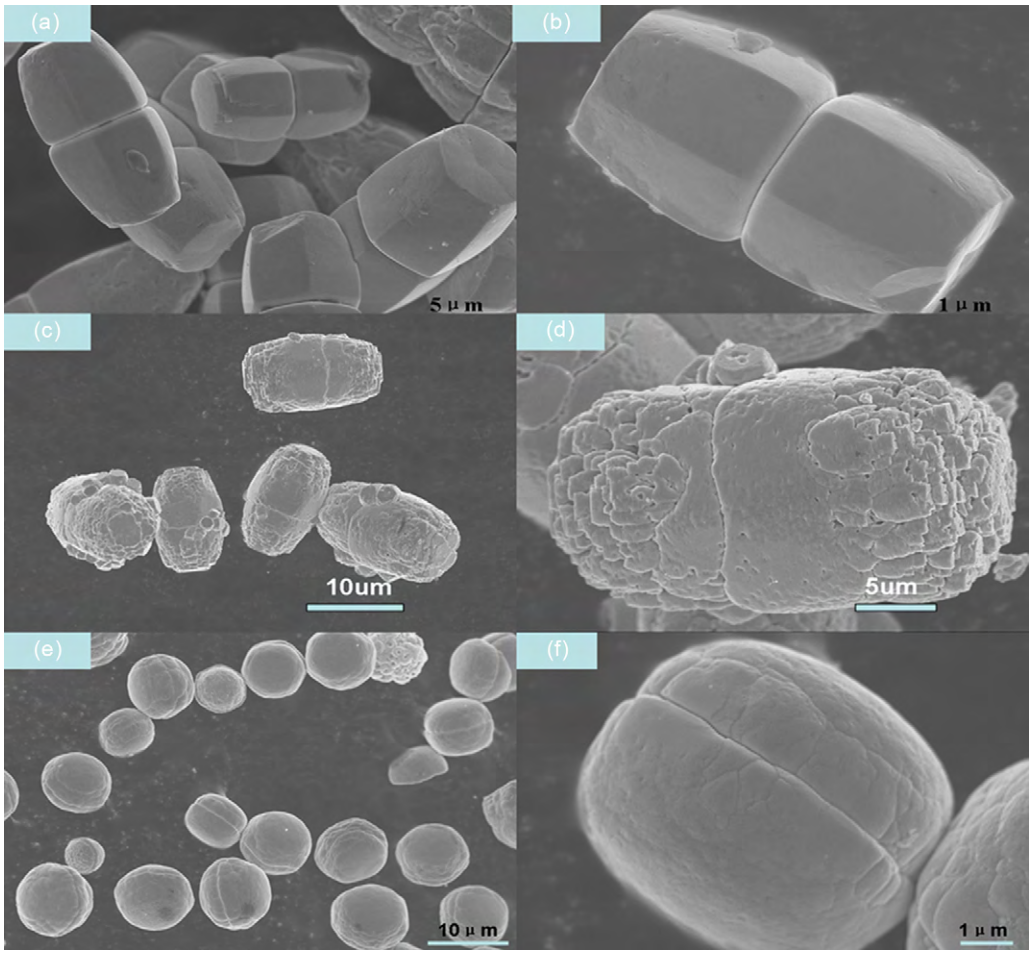

Fig. 4. The SEM images of ZnO microcrystals prepared with (a) glycine; (c) acetic acid; (e) ethylamine. The right row is the enlarged views of the left one.

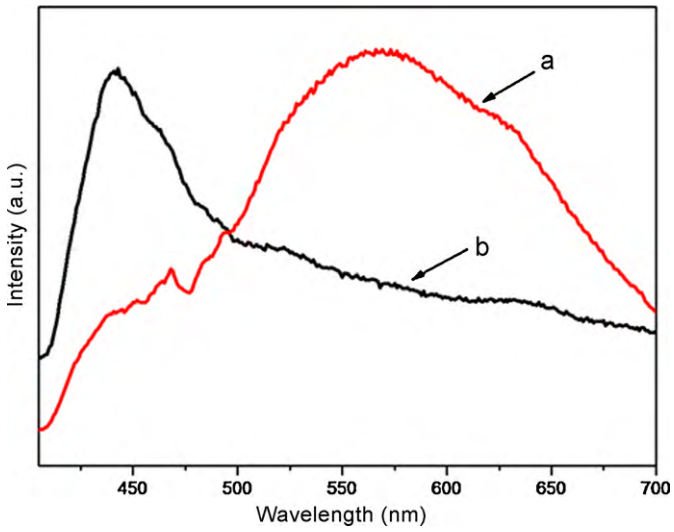

Fig. 5. PL spectra of (a) ZnO twin-cones and (b) ZnO twin-prisms.

hydrogen bonds with oxygen atoms on ZnO surfaces. Because the atomic density on the low-index facets is greater than that on the high-index facets, glutamic acid prefers to adsorb to the lower-index facets where there are more oxygen atoms through more N–H···O hydrogen bonds. In this way, the growth of lower-index facets can be restrained. In addition the growth speed of different crystal planes are usually different. Kar et al. reported that, of all planes, the family of (1 0 0) planes have the slowest growth rate in solutions [26]. Therefore, the six (1 0 0) planes finally appeared in the ZnO twin-prisms owning to the slow growth rate in solutions as observed in the SEM images and XRD patterns.

To support our viewpoints, glycine (amino acetic acid) which has both carboxyl and amino groups likewise was employed as surface modification agent instead of glutamic acid. As shown in Fig. 4a and b, the morphology of the as-prepared ZnO samples is similar to that with glutamic acid, which has a twin-prism structure with smooth surface, sharp prism and symmetrical sections. The only difference is that the two ends of the twin-prisms are a little slight, which could be attributed to the length of amino acid's carbochain. On the other hand, when amino acid was replaced by other organics with only carboxyl or amino groups, such as acetic acid or ethylamine, the morphologies of the as-prepared samples are quite different. As shown in Fig. 4c–f, the sample with acetic acid (Fig. 4c and d) exhibits twin-prism structure with weak symmetry and crude surfaces, and the sample with ethylamine (Fig. 4e and f) has morphology of spheres made up of two hemispheres. Therefore, both carboxyl and amino groups play an important role in the formation of ZnO twin-prism structures. Generally speaking, carboxyl group promotes the transformation of ZnO from twin-cones to twin-prisms, and amino group plays an important role in the formation of ZnO smooth surface and two equal parts.

The study on photoluminescence (PL) properties of ZnO is an effective way to evaluate its defects and optical properties. Fig. 5 shows the room temperature PL spectra of as-prepared ZnO twin-cones and twin-prisms. As we can see in this figure, the ZnO twin-cones display a broad emission with the central peak around 565 nm, which was commonly assigned to the intrinsic point defects of ZnO (e.g., V_o, O_i, V_{Zn}, and Zn_i) [26–30]. While, for ZnO twin-prisms, only a peak at 440 nm can be observed. The absence of the green emissions around 565 nm in ZnO twin-prisms indicates that few point defects are existed in twin-prisms. The emission around 440 nm is likely associated with the recombination of the electrons on the impurity level beneath the ZnO conduction band, which is formed by the adsorbed organic groups from glutamic acid, and lead to the red-shift of the intrinsic emission at 380 nm [31–34]. Additionally, the large size of the ZnO twin-prisms may also lead to the red-shift of the intrinsic emission [35,36].

4. Conclusions

ZnO twin-prisms have been synthesized by solvothermal method in ethanol with glutamic acid as surface modification agent. Different from the twin-cones obtained with glutamic acid absent, the ZnO twin-prisms have smooth surfaces, high symmetry, sharp crystal edges and few defects. Based on the experimental analysis, probable reaction mechanism between ZnO and glutamic acid was proposed. It was regarded that $-NH_3$, formed by the neutralizing reaction between alkaline groups and acidic groups, could react with the oxygen atoms on ZnO surfaces to form hydrogen bonds, which could finally restrain the crystal growth on (1 0 0) plane to form twin-prism structures. This interpretation was further verified by a series of comparison experiments by employing glycine, acetic acid and ethylamine as surface modification agents. Both carboxyl and amino groups play an important role on the formation of ZnO twin-prisms, and if one of them was absent, the twin-prism structures could not be obtained. Photoluminescence properties of as-prepared ZnO twin-prisms and twin-cones were also studied. The absence of green emissions in ZnO twin-prisms indicates that glutamic acid could also improve the crystallinity of ZnO samples.

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