Hydrothermal Synthesis of ZnO Long Fibers

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ZnO fibers are synthesized by hydrothermal method from $Zn(OH)_4^{2-}$ starting solution. The morphologies of obtained ZnO fibers are closely related to the hydrothermal treatment temperature and Zn^{2+}/OH^- ratio, and the bunch-like growth phenomenon is revealed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

ZnO fiber has attracted much attention recently because of its optical and sensor applications,[1–4] which then triggers a wide range of subsequent researches in the synthetic methods such as evaporation method[2,3] and hydrothermal method.[4] Though the long ZnO fibers have been popularly prepared by evaporation method, this method usually needs high temperature and catalyst which might result in contamination of the products.[2,3] Thus, the hydrothermal method is a promising way because it is the low-temperature processing to give highly crystalline materials. Up to now, few papers report the long ZnO fibers by hydrothermal method, although the rod-like ZnO particles have been easily obtained by hydrothermal treatment.[5–7] Particularly, Choy et al.[4] synthesized the long ZnO fibers under neutral conditions on thin ZnO film coated on glass substrate using hydrothermal method at 330 °C, but the high-hydrothermal temperature may cause the dissolution of glass substrate and contamination of the products. Thus, it is essential to explore a seed-free hydrothermal method at low temperature to fabricate long ZnO fibers. In this paper, we report a low-temperature hydrothermal method to obtain long ZnO fibers from $Zn(OH)_4^{2-}$ starting solution, and investigate the morphological changes under different hydrothermal conditions.

In our experiments, the starting solution of zinc was prepared by adding 0.1–1 M $ZnCl_2$ solution (100 cm^3) into 4 M NaOH solution (100 cm^3). Transparent solutions were obtained only when the concentration of zinc was less than 0.6 M, otherwise white precipitates appeared. The starting solutions were transferred into a Teflon-lined autoclave with 75% filing ratio and then hydrothermally treated at 80–220 °C for 10 h. After the reaction, the white powders were harvested by centrifugation and washing with distilled water.

The crystalline structure of obtained powders is proved to be wurtzite by XRD pattern. The results show that ZnO fibers can be obtained only from transparent starting solutions. Typically for 0.3 M zinc starting solution, the ZnO fibers can be synthesized at as low as 80 °C for 10 h. SEM observations show that the length of fibers increases from 50 to 200 μm when the temperature increases from 80 to 220 °C and all the ZnO fibers arrange in the form of bunch-like assembly (Figures 1a–1c). It is worthy noting that the ZnO fibers obtained at 80 °C for 10 h are all spear-like instead of rod-like, which indicates that the growth rate along the ⟨0001⟩ is much higher than that in other directions. The top view of the ZnO fibers shows well faceted hexagonal shape (Figure 1d) which matches the hexagonal structure of ZnO wurtzite and also proves the preferred growth along ⟨0001⟩ direction.

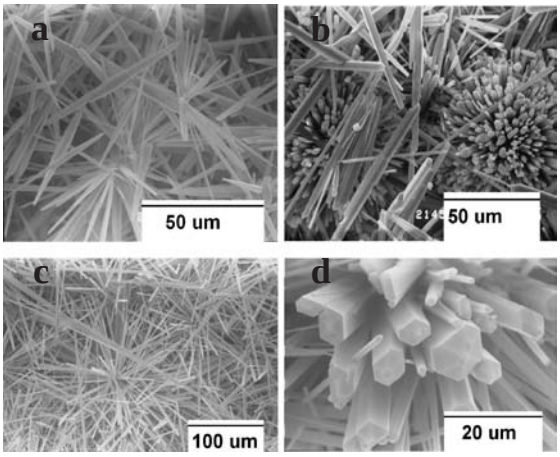

Figure 1. SEM pictures of obtained ZnO fibers (0.3 M zinc starting solution). a) 80 °C, 10 h; b) 150 °C, 10 h; c) 220 °C, 10 h; d) top view of ZnO fibers in picture c.

As Li et al.[7] suggested, the fiber-like growth is surely due to the intrinsic anisotropic growth characteristics, $V(0001) > V(01\bar{1}0) > V(000\bar{1})$. However, the hydrothermal conditions in our experiments are quite different from those of Li et al.[7] They just obtained shortened prisms in alkaline medium and rods in neutral medium while we obtained the long fibers in alkaline solution. The reasons should lie in the starting solutions. Li et al. used $Zn(OH)_2$ colloids as starting solution while we used clear zinc alkaline solution, which caused difference in nucleation. In fact, Ohshima et al.[8] also reported that the shape of ZnO crystals was strongly influenced by that of seed crystals in spite of the same precursor and solution basicity. Therefore, different nuclei morphologies can cause the different crystal shape in the alkali solution.

In strong alkaline solution, the Zn^{2+} exists in the form of $Zn(OH)_4^{2-}$ complexes instead of $Zn(OH)_2$ colloids.[5,6,9] However, if the zinc concentration in the starting solution is high enough (more than 0.6 M in our experiments), the $Zn(OH)_4^{2-}$ complexes can be saturated to precipitate. TEM shows that the as-precipitates in high concentrated solutions at room temperature are starfish-like (Figure 2a), which quite matches the obtained bunch-like ZnO fibers.

A closer observation at the root of the ZnO bunches (Figure 2b) shows that the bunched fibers grow from one site which is believed to be the seed nucleus. However, the random growth of fibers around the nucleus is in contradiction with the anisotropic growth of ZnO, which implicates that the original nuclei may be amorphous or isotropic. This is possible since

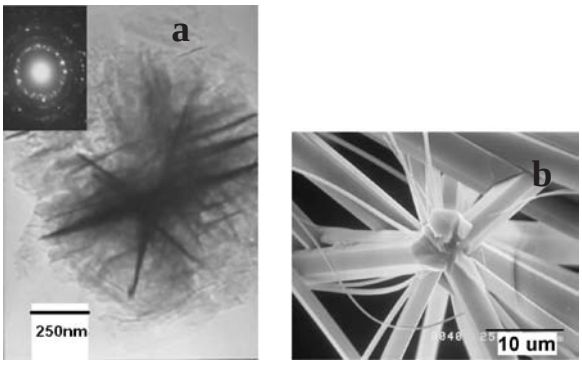

Figure 2. a) TEM photos of ZnO precipitates by adding 0.7 M 100 mL of $ZnCl_2$ solution into the 0.4 M 100 mL of NaOH solution; b) Close view of the root of the ZnO bunch in Figure 1c.

the nuclei of ZnO come from the condensation of soluble $Zn(OH)_4^{2-}$ clusters. Hence, if the precipitation rate is quick enough, the *c* axis oriented growth can happen in any directions around the condensed clusters before they are completely crystallized.

In order to investigate the effects of Zn^{2+}/OH^- ratio on ZnO morphologies, the concentration of $ZnCl_2$ starting solution was changed from 0.1 to 1 M while the concentration of NaOH maintained 4 M and the hydrothermal conditions kept at 220 °C for 10 h. When the concentration of Zn^{2+} was less than 0.1 M, no solid product was obtained. When the concentration of Zn^{2+} is between 0.2 and 0.6 M, the starting solution was clear and the obtained ZnO powders were all fibers. However, the aspect ratio of the ZnO fibers dramatically decreased with the increase in starting Zn^{2+} concentration (Figure 3a and 3b). When the concentration of Zn^{2+} was higher than 0.7 M, white precipitates which were proved to be ZnO by XRD appeared in the starting solution and the obtained ZnO powders after the hydrothermal treatment were fine particles with some big rods (Figures 3c and 3d).

The above results show that the Zn^{2+}/OH^- ratio has important effects on the morphologies of ZnO fibers and low Zn^{2+}/OH^- ratio is favorable for ZnO fibers with large aspect ratio. From the clear zinc starting solutions (0.2–0.6 M), both nucleation and growth of ZnO fibers come from condensation of $Zn(OH)_4^{2-}$ clusters through a dehydration reaction[6,7] which finally leads to the intrinsic *c* axis-oriented growth. However, the fast condensation process caused by high zinc concentration can balance the growth rate in the different directions and finally decrease the aspect ratio of obtained ZnO fibers. Thus, low zinc concentration (0.2–0.3 M) is favorable for the long ZnO fibers in our experiments. When the zinc concentration is higher than 0.7 M, precipitation occurs because of high supersaturation even at room temperature and finally the precipitates grow to the big rods by hydrothermal treatment. In the case of concentrated starting solutions, fine particles are formed by hydrothermal treatment and it should be noted that the morphologies of the fine

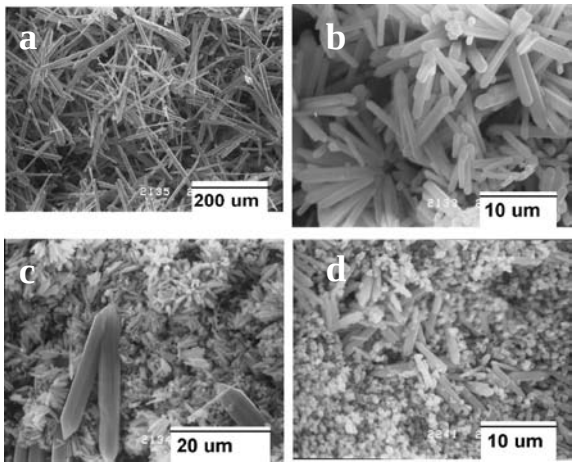

Figure 3. Products obtained at 220 °C for 10 h from different Zn concentration: a) 0.2 M; b) 0.5 M; c) 0.7 M; d) 1 M.

particles are different, i.e., rod-like particles for 0.7 M zinc solution and round particles for 1 M zinc solution. The round particles from 1 M zinc solution can be ascribed to the very fast condensation rate of $Zn(OH)_4^{2-}$ complexes.

In summary, long ZnO fibers are successfully synthesized using clear alkaline zinc solution. The obtained fibers are well hexagonal faceted and reach the length of about 200 μm. SEM shows that ZnO fibers grow from one seed nucleus and in the form of bunch-like assembly. The aspect ratio of obtained ZnO fibers is closely related to the Zn^{2+}/OH^- ratio in the starting solution, and in order to synthesize long ZnO fibers low Zn^{2+}/OH^- ratio should be adopted. The clear alkaline zinc solution is proved to be critical for the fabrication of long ZnO fibers. Furthermore, it should be noted that beside $ZnCl_2$, other zinc sources, such as $Zn(NO_3)_2$, $ZnSO_4$, and $Zn(CH_3COO)_2$, can also be used.

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