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Preparation and shape control of ZnO nanorods by a simple method

Kun Peng[1,2*], Anna Yue[1], Jiajun Zhu[1], Lingping Zhou[1], Deyi Li[1]

[1]College of Materials Science and Engineering, Hunan University, Changsha, 410082, (CHINA)

[2]State Key Laboratory of Powder Metallurgy, Central South University, Changsha, 410083, (CHINA)

E-mail : kpeng@hnu.cn

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ABSTRACT

One-dimension Zinc oxide (ZnO) nanorods were successfully synthesized by calcining the precursors, which were produced by a chemical precipitation method. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) results showed that the diameters of the nanorods were about 40-50 nm and the lengths up toμm scale. High-resolution transmission electron microscopy confirmed that the quadrangular ZnO nanorods had a wurtize structures and grow along the (0001) direction, and which was explained by the "lowest-energy" theory. the product transformed from long rods to rods composited of stacked nanoplates along with the increase in citrate concentration. The calcining temperature and citrate concentration were the key parameter for the morphology of the ZnO products.

KEYWORDS

Zinc oxide;
Nanorods;
Fabrication;
Layered structure.

INTRODUCTION

One-dimensional (1D) nanoscale materials have received considerable attention due to their remarkable properties and potential applications in nanodevices[1-3]. Compared with micrometer diameter whisker and fibers, these nanostructures are expected to have remarked optional, magnetic, electrical and mechanical properties. Different approaches such as the vapor-liquid-solid (VLS) growth[3-5], solution-liquid-solid (SLS) method[6], template-mediated growth method[7,8], scanning tunneling microscopy (STM) techniques[9] have been used to synthesis quasi 1D nanostructures. Exploration of novel methods for the large-scale synthesis of 1D nanostructure is a challenging research area. As n-type semiconductor materials, ZnO has received a considerable amount of attention over last fewer years because of many applications it has been found in various field, especially, ZnO nanostructure materials are expected to possess properties having applications in shock resistance, sound insulation, photosensitization, fluorescence, gas sensitization and catalysis[10]. Up to now, many methods have been developed to synthesis ZnO nanoparticles, and some method has been used to fabrication of ZnO nanorods, such as soft chemical method[11-14], thermal decomposition of precursors of ZnC_2O_4[15], gas reaction method[16], and hydrothermal synthesis[17, 18]. These methods often are faced with problems such as tedious operation procedures, templates/catalyst removal, and poisonous surface active agent. In this paper, we report a simple method for obtaining the uniformly size distributed straight ZnO nanorods and the morphology can be controlled by temperature and citrate concentration.

EXPERIMENTAL

All the chemicals used in this experimental were analytical grade reagents without further purification. 10mmol Zinc acetate was dissolved in distilled water to form solution A, and a certain amount tri-ammonium citric was dissolved in ethanol to form solution B, and then the solution B was drop wised into the solution A with magnetic stirring. The mixture solution was kept at 353K for 2 hours to obtain the white precursors. And then the precursors were calcined at different temperatures in air for removal of volatile and organic species and formation of crystalline oxides. After heat treatment, the products were cooled down to room temperature in furnace.

The samples were examined by XRD. Scanning electron microscopy (JEOL 6700F), high-resolution TEM (HRTEM) (JEOL 3010 TEM) had been taken to study the morphology of the synthesized ZnO nanorods.

RESULTS AND DISCUSSION

A typical powder XRD pattern of the products was shown in Figure 1. It was obviously that all diffraction peaks were quite similar to those of a bulk ZnO, and the diffraction data shows good agreement with those

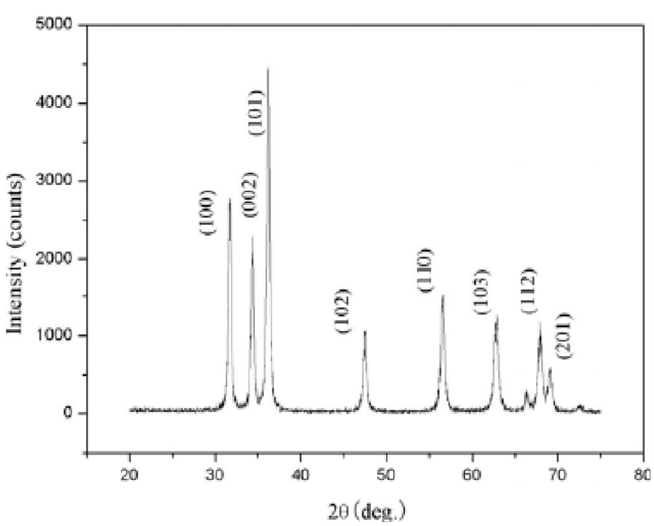
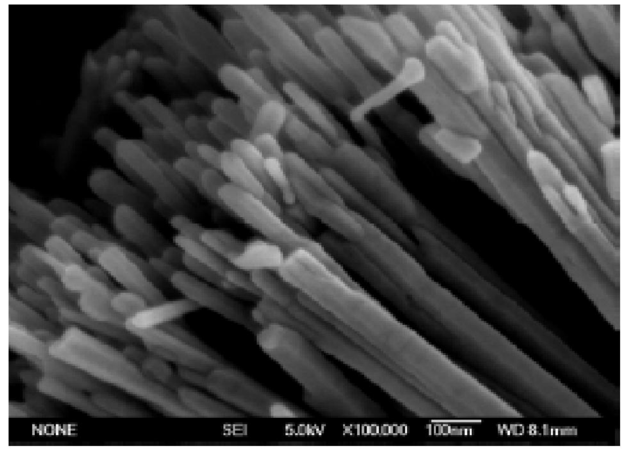
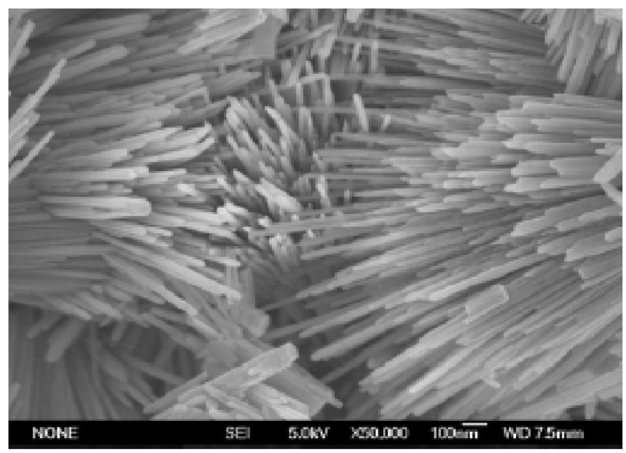


Figure 1 : XRD pattern of ZnO nanorods

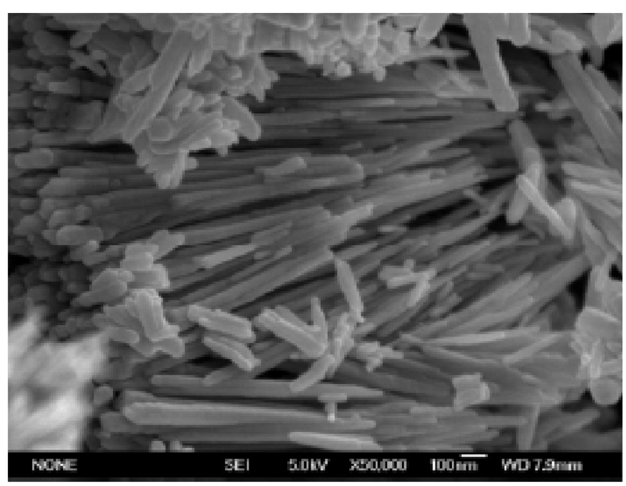
of the hexagonal ZnO with lattice constants a=0.32498nm, and c=0.52066nm. (JCPD file No. 36-1451.) No characteristic peaks of impurities were detected, which indicated that the prepared product is purity single phase hexagonal ZnO.



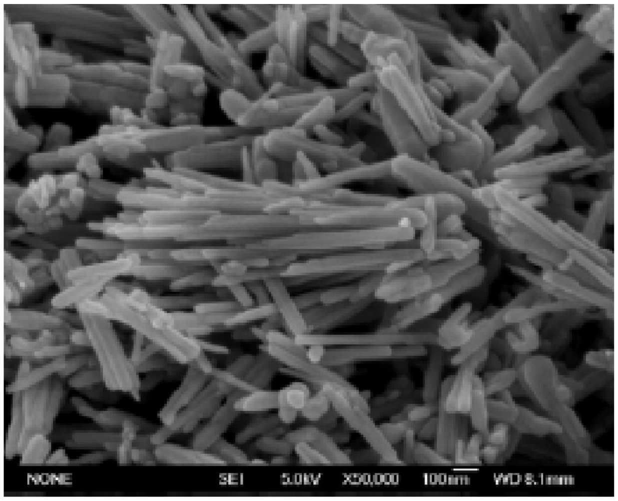
(a)



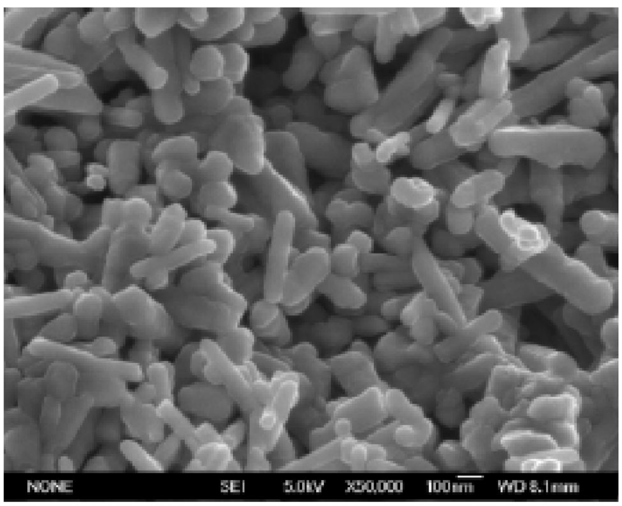
(b)



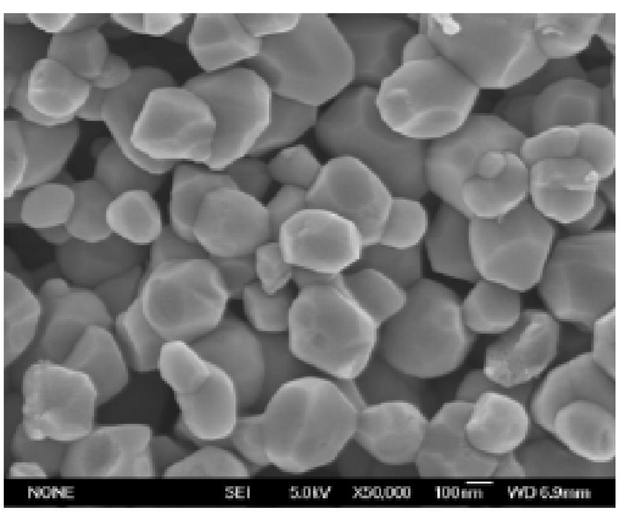
(c)



(d)



(e)



(f)

Figure 2 : The influence of calcinations temperature on the morphology of ZnO (a) 623K (b) 673K (c) 723K (d) 773K (e) 873K (f) 973K

In order to investigate the effect of the calcined temperature on the morphology of ZnO products, samples were calcined at different temperature in air, ranging from 623K to 973K and the heating rate is kept constant at 15K/min. All these samples are treated isothermally for 2 hours at these elevated temperatures. For SEM measurement, the samples were scattered on the carbon conductive tape, and a thin layer amorphous carbon was sputtered on to them. Figure 2 shows the influence of the calcined temperature on the morphology of ZnO products. It can be seen that most of the rods have a diameter of about 40-50nm and they are parallel arranged when the precursors were calcined at lower temperature (623K and 673K), and it also can found that the diameter of ZnO nanorods increased and the length of ZnO nanorods decreased with the increase of calcined temperature. However, the products will changed into hexagonal particles when the temperature up to 973K. It implies that formation and the dimensions of ZnO nanorods strongly depend on the calcined temperatures.

In order to further characterize the ZnO nanorods, TEM was employed to observe the microstructure of ZnO nanorods. To prepare TEM samples, some products were dispersed in ethanol and immersed in an ultrasonic bath for 10 minutes, and then a few drops of the resulting suspension were placed onto a copper grid coated with a layer of amorphous carbon. Figure 3 shows the TEM images of ZnO nanorods obtained at low citrate concentration (molar ratio of citrate to Zn ion is 0.03) by calcined at 673K for 2 hours. It is clearly that ZnO nanorod were smooth in surface and straight with diameters about 50nm and length up to several μm. It also can be known from Figure 3(b) that the end of the nanorods is a hemisphere. The atomic structure detail of the nanorods was revealed using HRTEM as shown in Figure 3(c). It shows that the nanorod is structurally uniform. The lattice amounts to 0.26nm corresponding to the (0001) planes of the hexagonal structure, indicating the nanorods grows along the [0001] direction.

Figure 4 is the ZnO nanorods obtained at high citrate concentration (molar ratio of citrate to Zn ion is 0.05) by calcined at 673K for 2 hours, the length of ZnO nanorod is inequable, there are a lot of relative short nanorods. Figure 4(b) clearly shows a layered

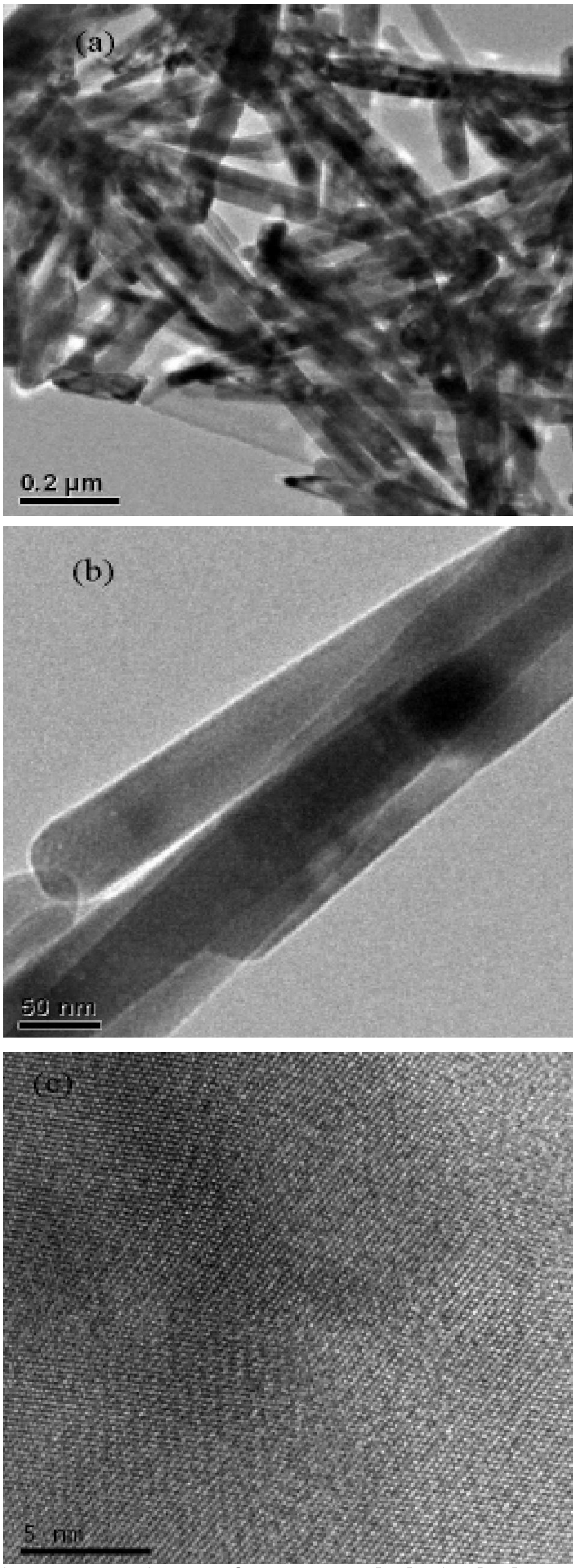
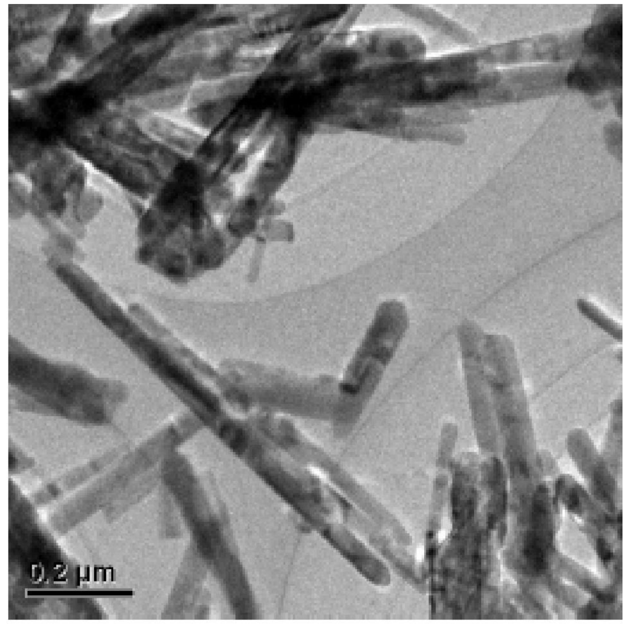
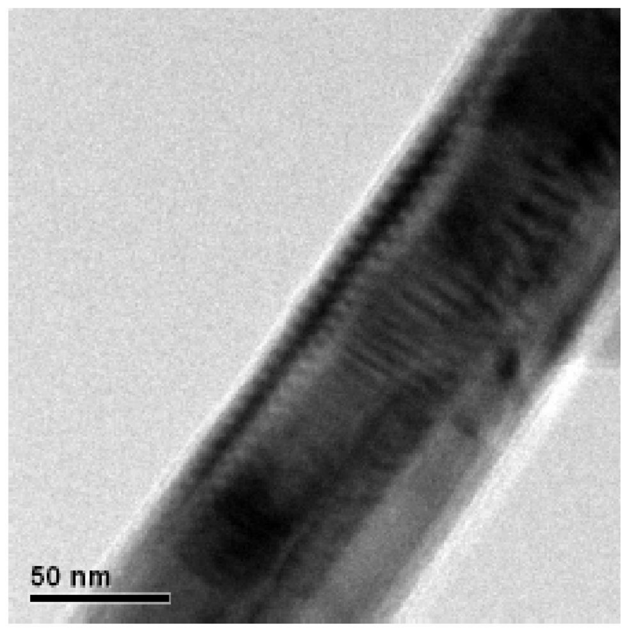


Figure 3 : TEM images of ZnO nanorods obtained at low citrate concentration (a) low magnification (b) high magnification (c) high resolution TEM



(a)



(b)

Figure 4 : TEM images of ZnO nanorods obtained at high citrate concentration (a) low magnification (b) high magnification

structure of ZnO nanorods with an interlayer spacing of about 5.2nm, which suggesting that the crystal growth along c-axial orientation was suppressed under these conditions that the crystals were still able to grow to a certain thickness to form thin platelets. The transition from long hexagonal rods to short hexagonal crystals, and then to hexagonal crystals containing stacked nanoplates along with the increase in citrate concentration.

As a rule, the chemical route direct, often very simple, chemical reactions to fabricate products in powder form. These techniques have in common the fact that they do not offer underlying of physical or chemical principle. Thus, the generalization of the processes involved must require the understanding of the formation mechanism of nanorods. From the experimental facts mentioned above, it is obvious that the calcined temperature is one of the primary factors affecting the growth of ZnO nanorods. And the existence of citric acid radical is another important factor affecting the formation of ZnO nanorods, according to our experimental result, without addition of citric acid radical ion during the process, only ZnO particle can be obtained (the results are not shown here). For the existence of the citric acid radical, the surface tension of solution is reduced, which lower the energy needed to form a new phase, and ZnO crystal could form in a lower supersaturation. In addition, through two carboxyls and one hydroxyl, the citric acid radical ion and the zinc ion form two chelate rings, i.e. a pentabasic ring and a hexahydric ring. Because the two chelate rings occur, the spatial volume of growing units is expanded. It has been known that the adsorption of growth units on crystal surfaces strongly affects the growth speed and orientation of crystal[19]. When the precursors are calcined, the molecules of complex compound tend to be perpendicular to absorbed surface, the growth units would tend to face-land onto the growing interface. Since this kind of landing and dehydration will results in three Zn-O-Zn bonds, which make the face-land of growing units on axial energetically preferable to both vertex and edge-land along the radial direction. ZnO crystal plane would grow preferentially the [0001] direction as the kind of face-land on [0001] crystal face. For the different growth rate of crystal plane, ZnO growth units further grow to rod-shape structure. For the growth process of the as-producted crystals, the calcined temperature also play a key role on the morphology and dimension of ZnO products, which can be explained by "lowest-energy" arguments resulting in rodlike crystals[20, 21]. The experimental processes illustrated that the precursor were calcined at a temperature above the melting point of the salt to form a flux of the salt composition, and thus to make mobility of the components in the flux easier, i.e, to provide a favorable liquid environment for the growth of nanorods. At this temperature the oxide were rearranged and the diffused rapidly in a liquid state of the salt. In the heating process, the ZnO nanorods were formed through the nucleation and growth process. Since the (0001) faces have higher-symmetry than the other faces, growing along c-axis is the typical crystal habit and growth in form of ZnO wurtzite. In other words, it was the "lowest-energy" theory that decided the preferential growing plane. The rule is obeyed strictly throughout the process and no branching was observed in single nanorods. However, higher calcined temperature could provide high driving-force for the nucleation and growth process, which lead to the formation of large number of nucleation and they will grown quickly in all directions, then lead to the formation of ZnO particle. Therefore, the calcined temperature plays a key role on the morphology and dimension of ZnO products, the citric acid radical is helpful for reduce of the surface tension of solution which lower the energy needed to form a new phase and the "lowest-energy" theory decided that ZnO crystal will grow along the preferential growing plane.

CONCLUSION

In summary, ZnO nanorods have been successfully synthesized by a two-step method. The citric acid radical is helpful for reduce of the surface tension of solution which lower the energy needed to form ZnO crystal and the citrate concentration affect the morphology of nanorods obviously. The results show that c-axis is the fast growth direction and which can be explained by the lowest-energy theory. The calcined temperature is a key factor to decide the morphology of ZnO products.

ACKNOWLEDGEMENTS

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