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Growth Mechanism and Properties of Multibranched ZnO Nano/Microstructure

FANG FANG,^{1,2,*} SHANSHAN LV,² XUAN FANG,² HAIFENG ZHAO,³ JINHUA LI,² XUEYING CHU,² ZHIPENG WEI,² DAN FANG,² AND XIAOHUA WANG²

¹Nanchang University, No. 235 East Nanjing Road, Jiangxi Province, Nanchang 330047, PR China

²Changchun University of Science and Technology, Changchun, 130022, PR China

³State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, 130033, PR China

Without any catalysts-assisted, homobranched ZnO nano/microstructure had been synthesized via a simple low temperature water bath method. Such nano/microstructure which consists of shuttle-like nano/microrod backbone was surrounded by six radial oriented branches. The length of the shuttle-like ZnO nano/microrods is about 5–10 μm . The diameter of the single shuttle-like nano/microrods is 1–2.5 μm at the stem and 10–50 nm at the tip while the branches size from top to bottom is 10–50 nm to 0.5–1 μm . A strong ultraviolet emission and weak deep level emission reflect the high optical quality. In addition, a detailed discussion regarding the probable growth mechanism is presented in this work.

Keywords Multibranched; ZnO; nano/microstructure; water bath

1. Introduction

In the last decade, nanostructured materials have sparked a worldwide interest due to their fascinating electrical and optical properties endowed by confining the dimensions of such materials [1–3]. Among these, ZnO nanostructures have attracted particular attention because of their unique properties (a direct band gap of 3.37 eV and a large excitation binding energy of 60 meV at room temperature) and diverse nanostructures. The latter relies on the anisotropic structure of ZnO and variation of growth rate on different facets [4, 5]. Various low dimensional ZnO nanostructures, such as the nanoparticles, nanowires, nanobelts and nanotubes, have exhibited outstanding properties and have been enabled to serve as fundamental building blocks in various advanced applications [6–9]. Compared with 0D nanoparticles and 1D nanowire, 3D branched nanowires possess advantages including structural hierarchy, high surface areas and direct electron transport pathways,

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*Corresponding author.; E-mail: fang_fang0131@126.com, Fangxuan110@hotmail.com

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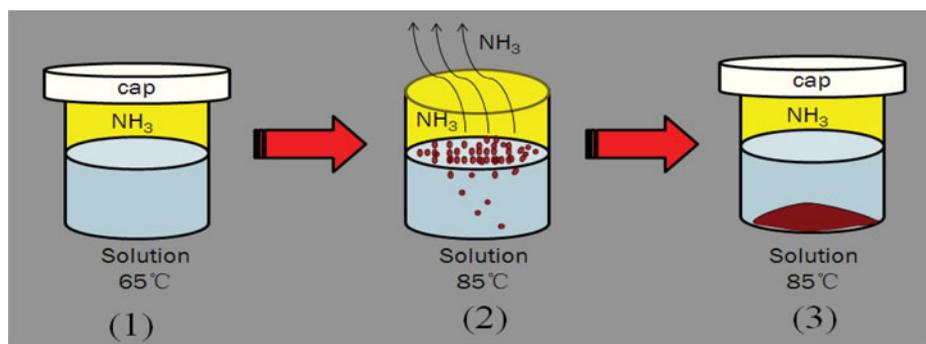


Figure 1. Schematic illustration of water bath process.

which are beneficial to energy harvesting, conversion and storage technologies application [10]. Therefore, these fascinating properties of 3D branched nanostructures have stimulated widespread interests in fabricating them. In this paper, we fabricate the 3D multibranching ZnO nano/microstructure with the side branches form a 6-fold symmetry with the trunk. Similar structures are available in previous literatures. The methods used in early reports on such branched nanostructure usually involve a sequential Sn catalyst-assisted vapour–liquid–solid growth [4], or hetero-branched structures with In_2O_3 as core [11]. Herein, we report a facile low temperature water bath approach for fabricating 3D homo-branched ZnO nano/microstructure and its structural and optical properties. Furthermore, a detailed understanding about the probable growth mechanisms of the multibranching structure is discussed.

2. Experiments

2.1. Synthesis of ZnO Nano/Microstructure

ZnO samples were grown by a simple water bath method. Zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, hexamethylenetetramine HMT and ammonia were employed as the precursors. 4 ml of ammonia, 0.05 M of zinc nitrate hexahydrate and 0.025 M of HMT were dissolved in 50 ml of deionized water followed by adequately stirring for 30min, when the beaker was covered by a cap in order to prevent the ammonia volatilization. When the temperature of the water bath reached to 65°C the beaker was placed on water bath. The liquid level outside the beaker was higher than it in the beaker (Fig. 1(a)); When the temperature reached to 85°C , we remove the cap about 10min waiting for ammonia probably release thoroughly (Fig. 1(b)); Then, the beaker was covered by the cap again and then react for 2 h at 85°C (Fig. 1(c)). After the reaction, the white precipitates were collected by centrifuge and washed with absolute alcohol, distilled water three times and dried in the oven.

2.2. Characterization

The samples were investigated by field-emission scanning electron microscopy (FESEM, Hitachi-4800), and a D/max-RA X-ray spectrometer (Rigaku). Photoluminescence (PL) measurements were performed using a He–Cd laser line of 325 nm as the excitation source.

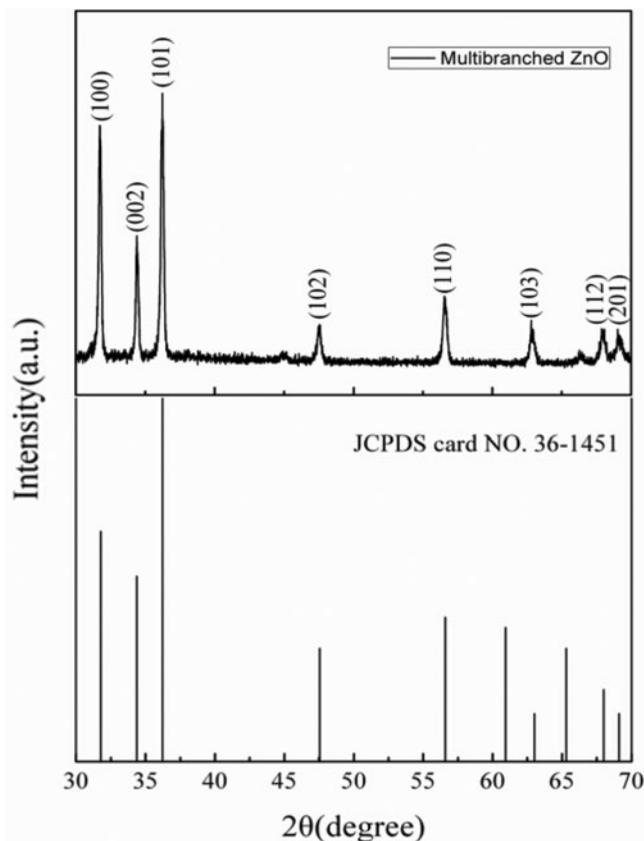


Figure 2. X-ray diffraction patterns of as-synthesized ZnO sample.

3. Results and Discussion

The structure of the ZnO samples was first characterized by XRD as shown in Fig. 2 all reflection peaks of the XRD pattern can be indexed to hexagonal wurtzite ZnO (JCPDS card no. 36-1451), indicating high purity and crystallinity of the as-synthesized products.

Fig. 3 shows the panorama of the ZnO crystals, which consists of shuttle-like nano/microrod backbone surrounded by radial oriented branches. The shuttle-like ZnO nano/microrods exhibit the length ranging from $5\ \mu\text{m}$ to $10\ \mu\text{m}$. Both backbones and branches were tower-like structure, as the inset showed in Fig. 3(b). The diameters of a single shuttle-like nano/microrods gradually decrease from the stem of $1\text{--}2.5\ \mu\text{m}$ to the tip of only $10\text{--}50\text{nm}$. The branches' size from top to bottom is $10\text{--}50\text{nm}$ to $0.5\text{--}1\ \mu\text{m}$. From the high magnification image shown in Fig. 3(b), we could see that the ZnO sample which has a fascinating structure and symmetry. Each shuttle-like ZnO nano/microrod with abundant oriented nanobranches on its six symmetrically grown surfaces (the angle between each branch is 60°). The probable explanation will be given below.

Fig. 4 is the schematic illustration of the synthesis of multibrached ZnO nano/microstructure what we had drawn on the basis of our following analysis. We can describe the growth in two parts: Step 1, nucleation and Step 2, grow up. Ammonia is known to suppress the homogenous reactions in the solution [12]. In the initial period, the

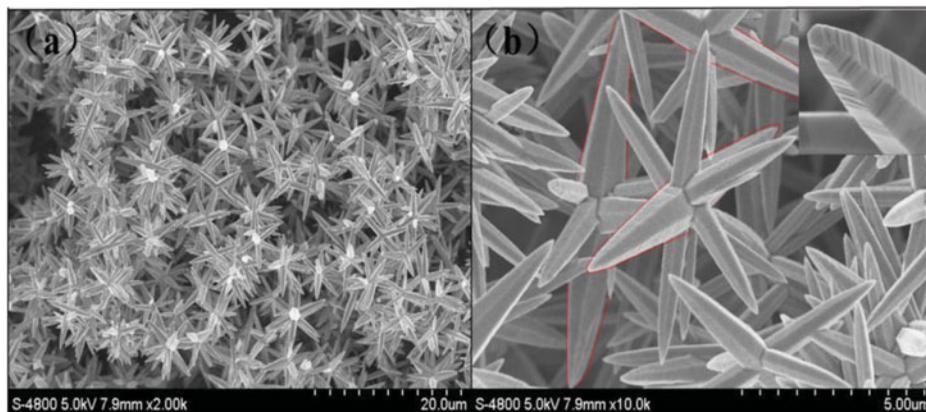


Figure 3. SEM images of multibranched ZnO nano/microstructure with (a) low, (b) high magnifications. Inset is the enlarged image.

solution remains clear and some of the ammonia evaporates from the solution to a confined space and reaches vapor liquid equilibrium in the solution headspace (Fig. 1 (a)). However, once the cover is removed (Fig. 1 (b)), a dramatic drop in ammonia concentration near the solution surface since the diffusion of ammonia. Such equilibrium is disturbed, which is believed to be the key to the formation of ZnO nuclei. Without the suppression effect of ammonia, surface reactions start immediately, forming a layer of ZnO nuclei. The wurtzite structure, which is a typical structure of ZnO, is more favoured at smaller nanoscale size and more stable in bulk phase (Fig. 5). Therefore, in the nucleation step, the initial ZnO first nucleate with hexagonal wurtzite core (as the $\pm (0001)$ facets own a high growth rate). When the core reaches a certain critical size, six lateral spines will develop along their own $[001]$ directions [13]. In the subsequent growth stages (Step 2), both backbone and those spines are able to grow unconstrained under water bath conditions. For the moment, however, we want to emphasize that the cover needs to be replaced to prevent further evaporation of water and ammonia which may otherwise change the concentration of the solution (Fig. 1 (c)). After two hour growths, multibranched ZnO structure includes a backbone with

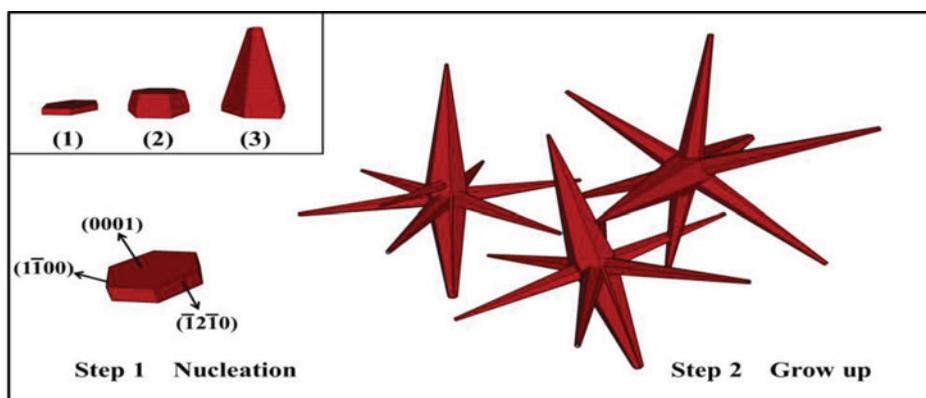


Figure 4. Schematic illustration of the synthesis of multibranched ZnO nano/microstructure.

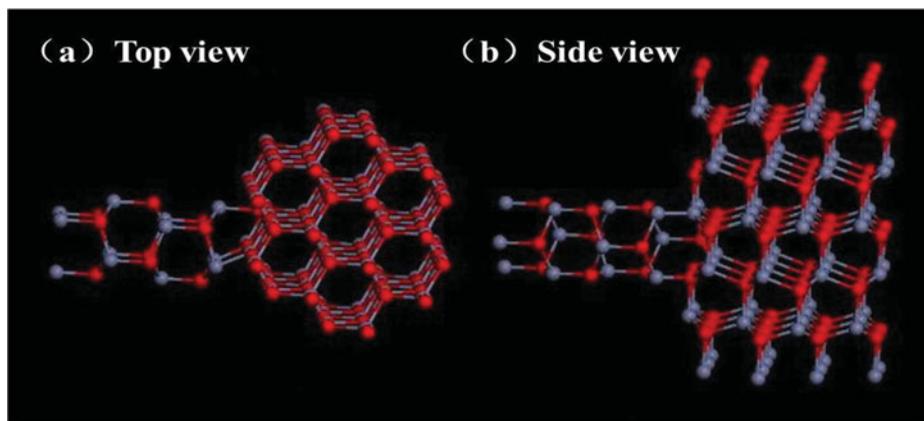
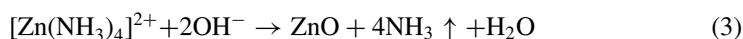


Figure 5. Proposed atomic structural model of a multibranching ZnO nano/microstructure (a) top view; (b) side view (Zn atoms are grey, O atoms are red).

six equivalent directions branched nano/microrods form resulting geometry. The overall growth mechanism has been well documented, which can be expressed by the following reactions [12]:



Due to a large number of consumption in the process of nucleation and Zn^{+} and OH^{-} were not added any more, plenty of crystal nucleus formation made each crystal nucleus consume less raw material by the time which leading to the growth of ZnO presents smaller at the top of the tower structure. An enlarged view of the tip of multibranching ZnO structure was showed in the inset of Fig. 2 (a), and it's clearly seen that the ZnO nanomaterial contains a great many growth steps [14]. These steps caused the ZnO along the length direction of the width change is more apparent [15] so the ZnO nano/micromaterial form the tower structure of nanorods through constant superimposed growth. And because the rapid growth of the early stage, which led the dynamics stacking on polar and nonpolar surfaces of ZnO material, the tower structure was also easy to form. From what has been discussed above, multibranching ZnO structure with the tower structure tip is obtained.

To characterize and analysis the optical properties of as-prepared multibranching ZnO nano/microstructure, photoluminescence (PL) spectrum was measured under room temperature. And linksys 32 spectrometer with a He-Cd laser line of 325 nm was employed as the excitation source. From PL spectrum of ZnO nano/microstructure in Fig. 6, a strong sharp ultraviolet (UV) emission centered at 400 nm. The PL signal at 400 nm is a typical ZnO near-band-edge (NBE) ultraviolet (UV) emission, which indicates a direct recombination of excitons through an exciton-exciton collision process [16, 17]. Compared with ZnO nanorods that has a short wavelength region with a sharp band (380 nm) located at ultraviolet region reported by our previous literature [18], the multibranching ZnO nano/microstructure exhibits a red-shift which may be ascribed to size effect, their unique morphology, and the special growth condition [19–20]. Meanwhile, the deep level green emission is very weak

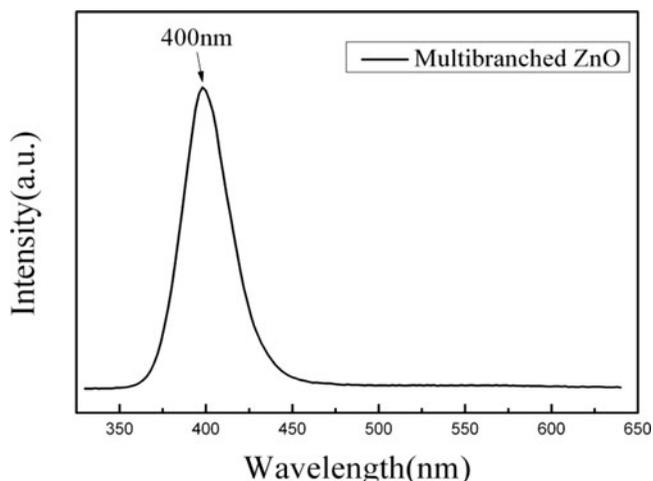


Figure 6. Photoluminescence spectrum of multibranched ZnO nano/microstructure.

compared with the UV peak. The excellent optical properties, evident in strong and sharp excitonic emission and low deep level emission, indicate that the multibranched ZnO nano/microstructures are of high optical quality.

4. Conclusions

In summary, well-crystallized 3D multibranched ZnO nano/microstructure was successfully synthesized based on a simple water bath process at 85°C for 2h. ZnO nano/microstructure relies on the spontaneous formation of a ZnO nuclei layer on the liquid-air interface of the growth solution due to a sudden drop in ammonia concentration, which facilitating the resulting growth of multibranched structure. Moreover, the synthesized nano/microstructure has high crystalline and excellent photoluminescent properties. We believe such multibranched ZnO nano/microstructure with high surface area and direct transport pathway for charge carriers are especially attractive in solar energy harvesting application.

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