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Synthesis of mesoporous ZnO nanowires through a simple *in situ* precipitation method

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Abstract

Mesoporous crystalline ZnO nanowires have been successfully fabricated by a simple *in situ* precipitation method combined with porous anodic alumina membranes as the templates. XRD, TEM, and HRTEM analysis shows that the as-synthesized samples are mesoporous ZnO nanowires with a hexagonal structure, which consist of ZnO nanocrystals and pores. The growth mechanism of mesoporous nanowires was discussed.

1. Introduction

One-dimensional (1D) nanostructured materials have attracted increasing attention in recent years, mainly due to their potential applications in mesoscopic physics and nanodevices. The fabrication of nanowires, nanoribbons, nanorings and nanotubes has been widely studied by different methods [1–11]. Among them the porous anodic alumina (PAA) membrane-based synthesis has been extensively used to fabricate nanostructures which are composed of different materials, such as metals, semiconductors and polymers [1, 8, 12, 13], because the PAA templates have readily controllable features, such as hexagonal porous structure, uniform pore size and high pore density [14, 15]. However, few studies have focused on the synthesis of porous nanowires [16]. Owing to their promising characteristics, such as high surface-to-volume ratio, variable framework compositions and, in most cases, high thermal stability, the porous materials could be potentially used in the fields of selective adsorption and catalysis, separation, bioengineering, environmental engineering, microelectronics, and photonic crystals [16, 17]. Thus, it is important to synthesize mesoporous nanowires through a simple method.

Zinc oxide, with a wide bandgap of 3.37 eV and large exciton binding energy (~60 meV), has been recognized as one of the most important semiconductor materials, exhibiting near-UV emission, transparent conductivity, and

piezoelectricity [18–20]. Recently, intensive research has been focused on fabricating ZnO nanostructures and revealing their growth mechanisms and optical and electronic properties. A variety of ZnO nanostructures, such as nanowires, nanobelts, nanorods and nanorings, have been synthesized [1, 5, 6, 19, 21–25]. But the preparation of porous ZnO 1D nanostructures still remains a challenge, thus the synthesis of the crystalline ZnO 1D nanomaterials with porous structure and well defined size via a facile method is significant. In this paper, we report the synthesis of mesoporous crystalline ZnO nanowires through a simple *in situ* precipitation method combined with PAA membranes as the templates.

2. Experimental details

PAA membranes used as the templates in this work were prepared by a two-step anodic oxidation process in a 0.3 M oxalic acid solution, and are similar to those described previously [12, 13]. The pore diameters were in the range of 60–80 nm. First, high purity aluminium sheet (99.999%) was anodized at 40 V in 0.3 M oxalic acid electrolyte at 12 °C for 4 h. The alumina layer produced was removed by immersing it in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at 60 °C for 6 h. The second anodization process was performed under the same conditions as the first one for 12 h. After the anodization, the bottom central aluminium substrate was removed in a saturated SnCl₄ solution, then the alumina barrier layer was dissolved in 6 wt% phosphoric acid solution

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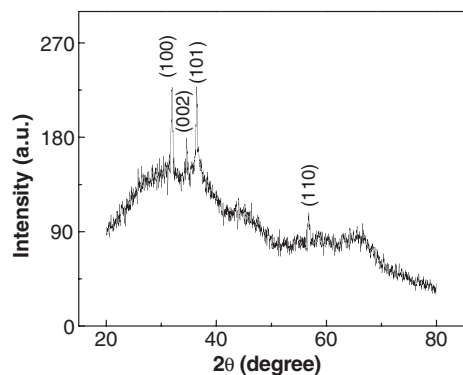


Figure 1. The x-ray diffraction pattern of as-grown mesoporous ZnO nanowires.

at 30 °C for 1.5 h to get the final PAA with the pore size in the range of 60–80 nm.

The zinc nitrate hexahydrate and ammonia used in this experiment were A.R. grade. Firstly, the PAA template was immersed in a 0.05 M $\text{Zn}(\text{NO}_3)_2$ solution for 30 min and taken out. Thus the pores of the PAA membrane were filled with the $\text{Zn}(\text{NO}_3)_2$ solution due to capillary interactions. Secondly, the $\text{Zn}(\text{NO}_3)_2$ -filled template was placed horizontally on the outlet of a conical flask, which contained an appropriate amount of ammonia solution after the excess $\text{Zn}(\text{NO}_3)_2$ solution on the membrane surfaces had been removed by wiping with filter paper and blowing with nitrogen gas, and then a small quantity of the above-mentioned $\text{Zn}(\text{NO}_3)_2$ solution was dropped on the top surface of the template. Lastly, the PAA template was taken off after one hour, and then put into a tube furnace after the superfluous $\text{Zn}(\text{NO}_3)_2$ solution on the top surface of the template was removed. The temperature of the tube furnace was increased to 150 °C and kept constant for 1 h, then increased to 450 °C for 10 h, and finally cooled down to room temperature. The mesoporous ZnO nanowires within the pores of PAA template were obtained.

The as-synthesized sample was examined by x-ray diffraction (XRD) measurements on a Philips X'pert PRO diffractometer with $\text{Cu K}\alpha$ radiation. The investigation of morphologies and microstructures of the products were carried out by field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6700F), transmission electron microscopy (TEM) (Hitachi H-800), and the high-resolution TEM (HRTEM) (JEOL 2010, operated at 200 kV).

3. Results and discussion

The diffraction peaks of as-synthesized products can be indexed to a hexagonal structured ZnO phase (JCPDS file No 89-0511), as shown in figure 1. Figure 2(a) illustrates the side and top surface image of the ZnO nanowire array grown within a PAA template. It is found that almost all of the pores in PAA templates are filled with ZnO nanowires. The nanowires are roughly parallel to each other, vertically oriented on the PAA template to form an array, and the diameters of these nanowires are about 60–80 nm, corresponding to the pore size of the PAA template. Obviously, the diameter and the length of these nanowires are tunable by controlling the diameter and the height of the channels in the PAA templates. According

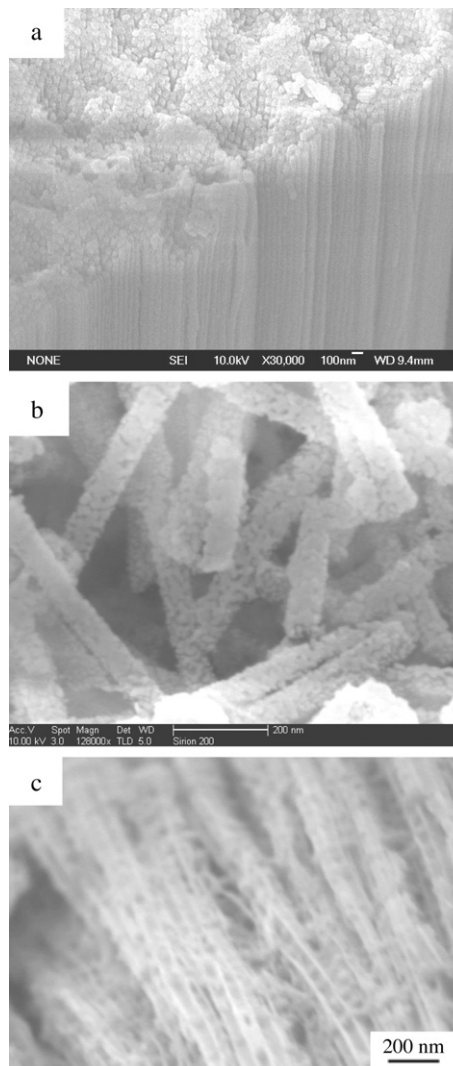


Figure 2. The typical SEM micrographs of mesoporous crystalline ZnO nanowire arrays: (a) in the PAA template; (b) released from the PAA template; (c) ZnO nanoparticles in channels of the PAA template.

to the aspect ratio of the channels, the maximal aspect ratio of these nanowires can reach 1000. From figure 2(b), it can be seen that the ZnO nanowires consist of ZnO nanoparticles and pores with sizes of about 5–10 nm, and that the stack of nanocrystals is disordered. Figure 2(c) shows that the products are nanoparticles, which are obtained during a reaction time of 30 min. A typical TEM image of ZnO nanowires taken out from the templates is depicted in figure 3(a). It can be observed that large-scale ZnO nanowires are obtained and that the nanowires are composed of ZnO nanoparticles and pores. The diameters of the ZnO nanowires are in the range of 60–80 nm with their shapes clearly replicating the pore structure of PAA templates. Figure 3(b) shows a typical high-magnification image and selected area electron diffraction (SEAD) pattern of an individual ZnO mesoporous nanowire with a diameter of about 80 nm, which clearly evidences the porous morphology and the polycrystalline character of the ZnO nanowires. The HRTEM image of a typical mesoporous ZnO nanowire shown in figure 3(c) further illustrates the microstructure of an individual ZnO nanowire. It can be seen

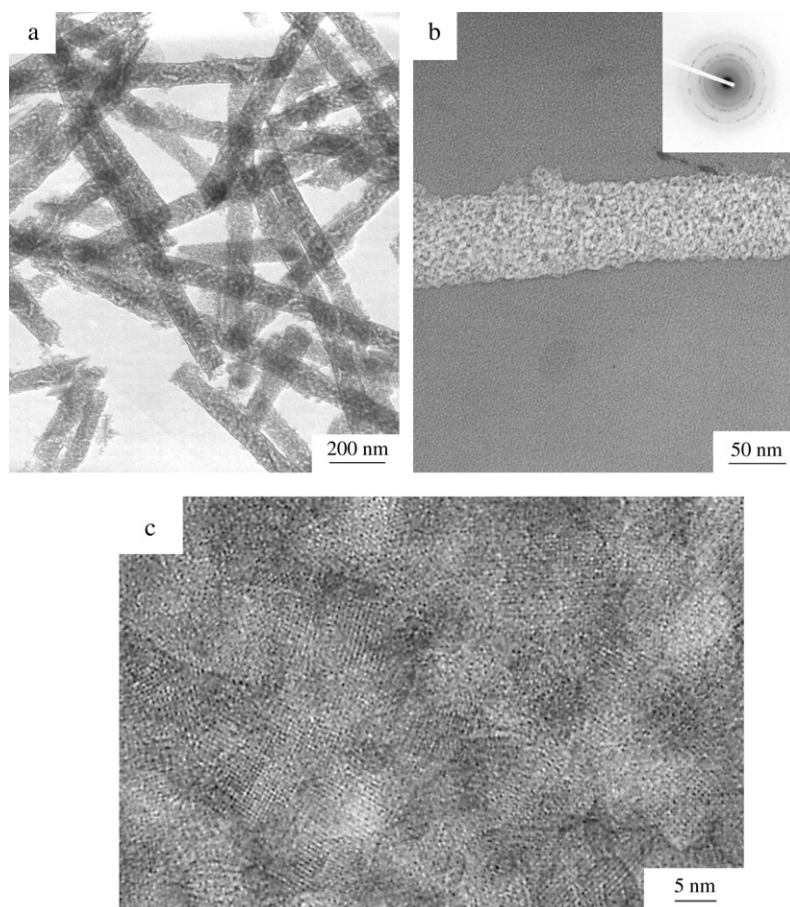
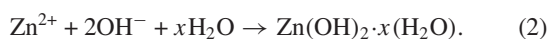
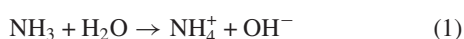


Figure 3. (a) The typical TEM images of as-synthesized ZnO nanowires. (b) A typical high-magnification TEM image of a mesoporous ZnO nanowire and its corresponding SAED pattern (inset). (c) The HRTEM image of a typical mesoporous crystalline ZnO nanowires.

that both the sizes of the nanocrystals and the pores in the nanowire are about 5–10 nm, and that the stack of nanocrystals is disordered, which is consistent with the conclusions obtained from SEM. Thus the products are mesoporous crystalline ZnO nanowires.

A schematic diagram of the possible formation process of mesoporous crystalline ZnO nanowires is shown in figure 4. In our experiments, the templates were dipped into the solution containing zinc nitrate. The viscosity of the solution was so low that it easily filled the pores of the templates. When the $\text{Zn}(\text{NO}_3)_2$ -filled PAA template was placed on the outlet of a conical flask, NH_3 gradually dissolved in the solution loaded in the pores of the PAA template. At the same time, OH^- forms through the reaction of NH_3 with H_2O , as shown in expression (1). Then the OH^- ions combined with Zn^{2+} ions to form $\text{Zn}(\text{OH})_2 \cdot x(\text{H}_2\text{O})$ sol (see expression (2)). Due to the high solubility of NH_3 in water, the concentration of OH^- was high enough to facilitate the precipitation of $\text{Zn}(\text{OH})_2 \cdot x(\text{H}_2\text{O})$ from the solution, and simultaneous homogeneous nucleation and growth.



Because of the confinement of the channels of the PAA membrane, mesoporous nanowires were synthesized by the assemblies of $\text{Zn}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ colloidal nanoparticles.

After the annealing process, the mesoporous crystalline ZnO nanowire arrays were obtained. To further illustrate the formation mechanism, we changed the experimental conditions. First, the time of the precipitation stage was varied. When the time of this process was less than one hour, the products prepared were not porous structured nanowires but nanoparticles in the pores of PAA template (figure 2(c)). The main reason was that not enough nanoparticles were formed and they could not form nanowires during a shorter reaction time. Secondly, the $\text{Zn}(\text{NO}_3)_2$ solution was not added on the top surface of the template before the stage of precipitation. The results showed that the mesoporous nanowires could not be obtained and only the ZnO nanoparticles could be obtained, because the Zn^{2+} ions were not enough and ZnO nanoparticles obtained were not enough to form mesoporous nanowires. Therefore, to keep the concentration of the Zn^{2+} ions constant in the formation stage of the mesoporous nanowires, $\text{Zn}(\text{NO}_3)_2$ solution added on the top surface of the template is necessary.

4. Conclusion

In summary, we have demonstrated, for the first time, that large-scale aligned mesoporous crystalline ZnO nanowire arrays can be prepared by a simple *in situ* precipitation method using $\text{Zn}(\text{NO}_3)_2$ and ammonia as sources and PAA membranes as templates. The as-synthesized samples are mesoporous ZnO

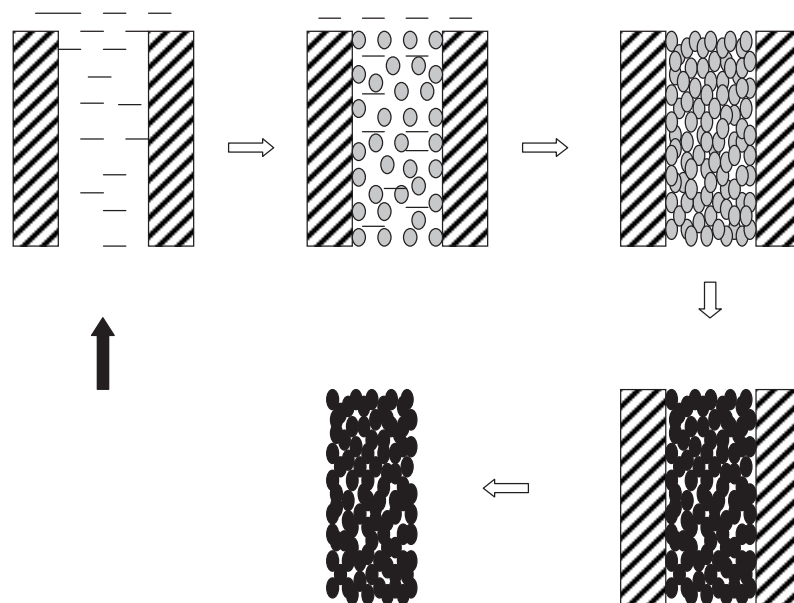


Figure 4. Schematic illustration of the *in situ* precipitation method for making mesoporous crystalline ZnO nanowires.

nanowires with a hexagonal structure, which are composed of ZnO nanocrystals and pores. These mesopores within the nanowires can be incorporated with functional materials forming 1D hierarchical nanocomposites. Therefore, the method presented here could be used for potential applications in catalysis and chemical sensors for pollutant gas species, biomolecules and photonic crystals.

Acknowledgment

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