



From hexagonally arrayed nanorods to ordered porous film through controlling the morphology of ZnO crystals

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ABSTRACT

The macrostructure can be changed by changing the morphology of its units. In this article, we use a colloidal template route, combined with hydrothermal growth method, to get the hexagonally arrayed ZnO nanorods on the polycrystalline ZnO substrate. More significantly, through controlling the morphology of ZnO crystals by adding structure-directing agent in the precursor solution, the highly ordered porous ZnO films were obtained instead of ZnO nanorods. This templated solvent-thermal method has great potential in micro/nano-fabrication.

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1. Introduction

In this paper, we developed a low-temperature, environmentally benign, solution-based method to prepare the large-scale hexagonally arrayed ZnO nanorods and two-dimensional (2D) ordered pore arrays. Through controlling the morphology of ZnO crystals by adding structure-directing agent in the precursor solution, the highly ordered porous ZnO films were obtained instead of ZnO nanorods, which reveals that the macrostructure can be changed by changing the morphology of its units. To our knowledge, it is the first time to report the fabrication of highly ordered macroporous structure by hydrothermal method. As an important wide-band gap semiconductor, the ordered 1D or 2D structured ZnO has significant applications in optoelectronics, field emission, and gas sensor. Although the present approach was realized on the polycrystalline ZnO substrate, we have a strong faith that this kind of process can apply to the single crystal ZnO substrate, and other single crystal oxides or semiconductor film substrates.

Now, the controlled and extended growth of micro/nano-structured material is becoming a novel method for fabricating ordered structures [1–3]. Through controlling the growth conditions, such as pH, temperature, and adsorbing molecules, the researchers can vary the morphology of the crystals, and realize the epitaxial growth of single crystals structure on a substrate. Usually,

the conventional micro/nano-fabrication methods, such as electron-beam lithography (EBL) [4], nanoimprint lithography [5], were utilized to fabricate the large-area, high-resolution nanostructures. But they suffer from high cost and low efficiency. The nanospheres lithography (NSL) [6–8] method used self-assembled micro/nanospheres becomes one of the most active research areas due to its lower cost, higher output, greater flexibility, and easier implementation for large-scale and long-range periodical structures [9–11].

2D ordered porous film, with a high specific surface area and an ordered arrangement of pores, has received great attention in recent years for their unique properties and potential applications in many fields, such as high-performance catalysis [12], optoelectronic devices [13], chemical sensors [14] and biosensors [15,16]. As a II–VI compound semiconductor, ZnO has a wide band gap (3.37 eV) and a large exciton binding energy (60 meV). Because of its remarkable properties, ZnO has attracted a great deal of interest for its potential application in optical and electronic industries including blue and ultraviolet UV optical devices, such as light-emitting diodes and laser diodes [17]. The other applications include transparent ultraviolet-protection films and chemical sensors [18]. Therefore, it is of significance for the fabrication of 2D ordered porous ZnO films. In order to prepare the large-scale 2D ordered porous ZnO films, many methods were developed, such as electrochemical deposition method or solution-dipping technique with the 2D colloidal monolayer as the masks [19].

As an important method of crystal growth, hydrothermal method was developed to fabricate zinc oxide single-crystal [20],

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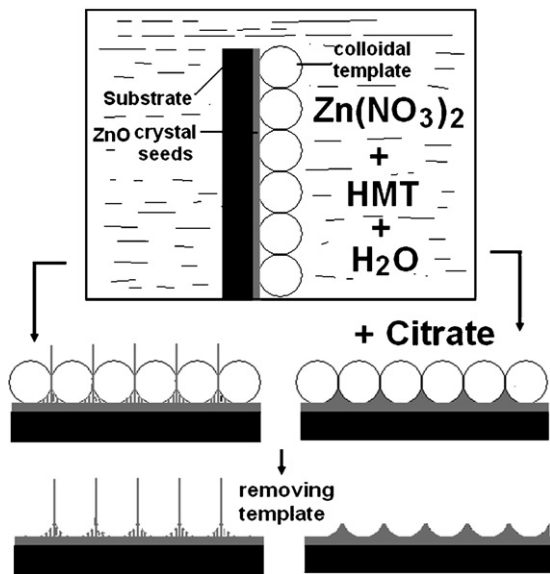


Fig. 1. Illustration of the whole experimental route for preparing hexagonal-patterned ZnO nanorods and 2D ordered porous ZnO film.

films [21] and nano-rods/wires [1]. However, to our knowledge, there is no report on utilizing hydrothermal crystal growth for the fabrication of relatively complex nanostructure, such as 2D ordered porous films. The hydrothermal technique has the advantages of homogeneous growth and controllable morphology by the appropriate selection of the growth conditions. It prompted the motivation of this work for the hydrothermal growth of the highly ordered macroporous ZnO film with the help of the colloidal template, where the porous structure of the film can be easily

controlled to be nanorods or ordered porous pores by the appropriate choice of hydrothermal conditions in the experiments.

Here we report a low-temperature, environmentally benign, solution-based approach for the preparation of orderly arrayed ZnO nanorods and porous ZnO films. In this paper, the citrate anions that adsorbed on the ZnO crystals were used as the structure-directing agent, and the self-assembling colloidal spheres were taken as the mask, we prepared highly ordered porous ZnO films with large area by hydrothermal growth method.

2. Experimental procedure

The experimental procedure for the preparation of the substrate was described as follows. The ZnO nanocrystals were prepared according to the method of Meulenkamp [18]. We prepare a layer of ZnO nanocrystals as seeds on the glass substrate by dip coating method. Then the substrate was annealed at 450 °C to burn out organic materials and make ZnO film crystallization.

A monolayer colloidal crystal template (the diameter of the polystyrene spheres (PSs) used in our experiments is 1 μm) was spin-coated on the substrate with ZnO crystal seeds. The colloidal template and ZnO crystal seeds coating substrate (the CT-ZnO-CSC substrate) was heated at 90 °C for 15 min to sinter the colloidal spheres before the hydrothermal growth.

Fig. 1 shows a schematic of our experiment procedure. As shown in Fig. 1, the substrate is composed of three parts: glass slide, polycrystalline ZnO film and monolayer PSs colloidal template. Usually, the polycrystalline ZnO plays the role of seed crystals in the hydrothermal process. It is well known that the $\langle 001 \rangle$ direction is the fastest growth orientation of ZnO crystals. Due to the spatially confined effect of the colloidal template, hexagonal-patterned ZnO nanorods are usually obtained in the hydrothermal experiment, which is shown schematically in the left panel of Fig. 1. As we know, citrate anions can control the crystal morphologies by adsorbing

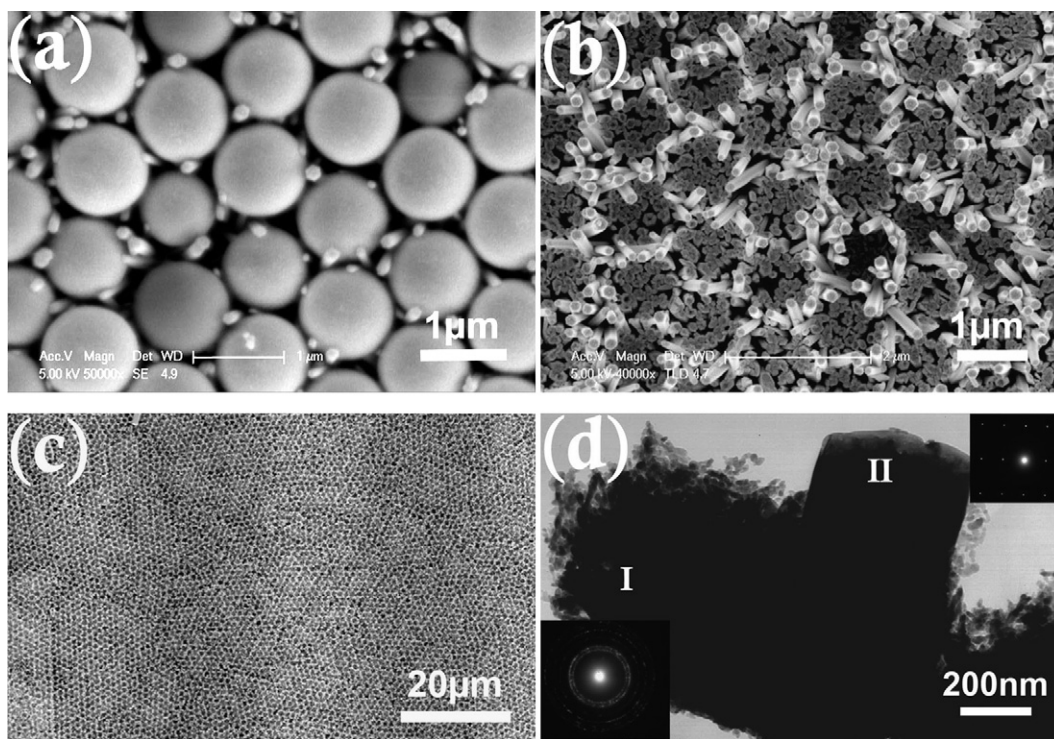


Fig. 2. (a) A typical image shows that the ZnO nanorods grew out from the space confined by the self-assembling colloidal spheres and (b) the removal of the colloidal spheres. (c) Low magnification SEM image of the hexagonal-patterned ZnO nanorods. (d) TEM image which shows clearly that the single crystal ZnO nanorod grows out from the polycrystalline ZnO seeds substrate.

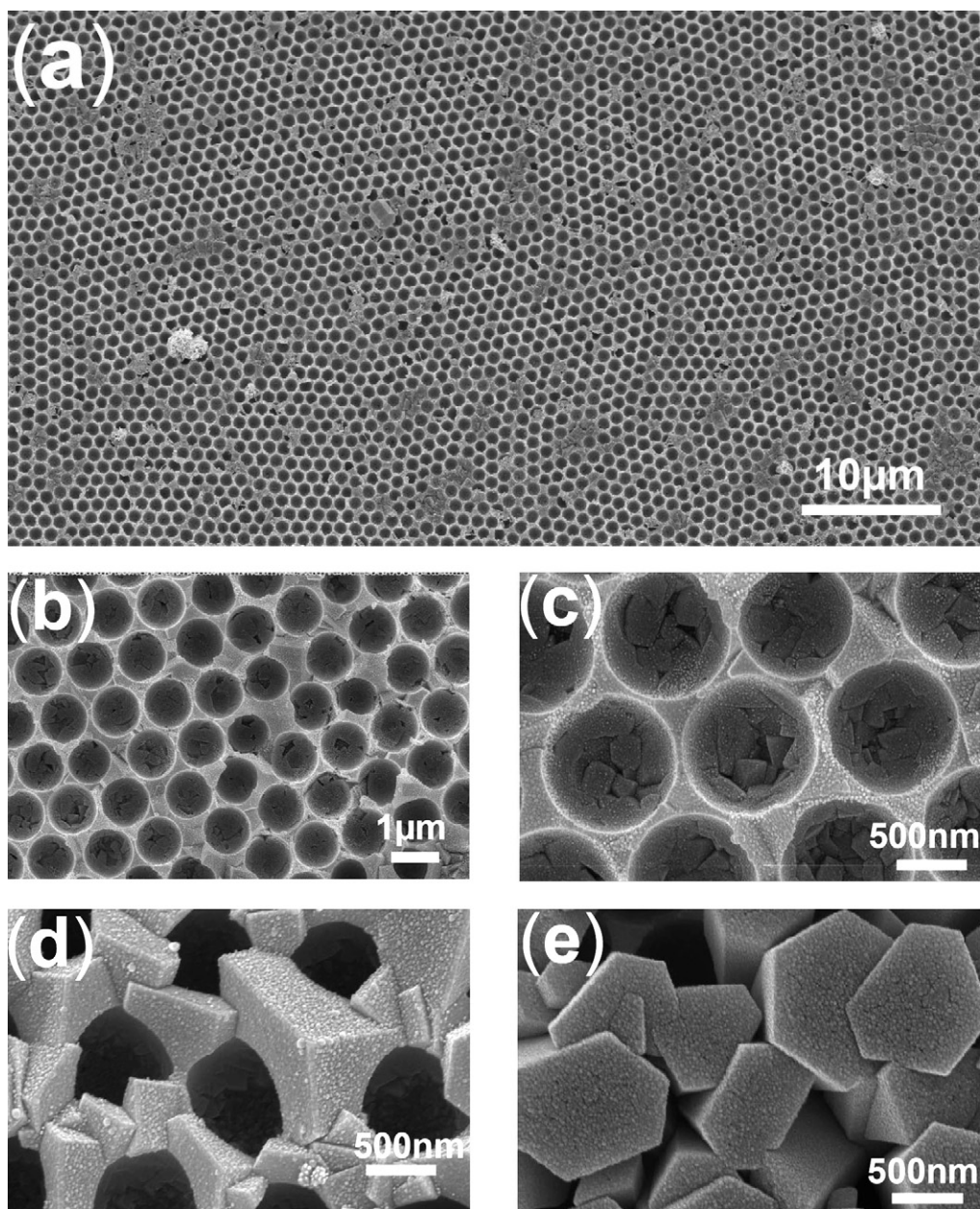


Fig. 3. (a) Low magnification of the ordered porous ZnO pattern prepared by hydrothermal colloidal template method. (b) and (c) are the high magnification of (a), and the hydrothermal growth time is 28 h. (d and e) The over-growth of the ZnO skeleton of the pore. The profiles of the ZnO crystals are shown clearly. The hydrothermal growth time is 36 and 48 h, respectively.

strongly on mineral surfaces [22] and altering the mineral growth behaviour [23]. The citrate ions are absorbed preferentially on the (001) surface of ZnO and thus inhibit the crystal growth along (001) orientations [24]. We added suitable amount of citrate in the solution to slow down the crystal growth along the (001) orientation. The growing ZnO crystallites became shorter and fatter by this modification. As a result, the crystallite began to impinge on other neighboring ones and the whole ZnO porous film was more close-grained and homogeneous than that without modification. Therefore, after removal of the template, we could get ordered porous ZnO film, as shown in the right panel of Fig. 1.

For the growth of orderly arrayed nanorods, the CT-ZnO-CSC substrate was placed vertically in a sealed Teflon cylindrical container, containing 30 ml equimolar aqueous solution (0.01 M) of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and methenamine ($\text{C}_6\text{H}_{12}\text{N}_4$). The chemical reaction procedure was described in

the literature [1]. The cylindrical container was put into a stainless autoclave and heated at 90 °C for 2 h in the muffle furnace.

For the growth of sample of ordered porous ZnO film, the CT-ZnO-CSC substrate with mask was placed vertically in a sealed Teflon cylindrical container, containing 30-ml solution of 0.3 M methenamine ($\text{C}_6\text{H}_{12}\text{N}_4$, HMT), 0.03 M zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 1.5 mg sodium citrate. The reaction temperature and time are 60 °C and 28 h, respectively.

After the hydrothermal growth, the sample was washed with distilled water and put in the oven to burn out the PSs at 450 °C in the atmosphere.

3. Results and discussion

Field-emission scanning electronic microscope (FESEM) images show the ZnO nanorods grew from the throats among the PSs, as

shown in Fig. 2a. Fig. 2b and c shows the sample after removal of the PSS. It is clearly shown that due to the confined effect of colloidal template to the growth of ZnO nanorods, the honeycomb-like arrangement of the nanorods pattern was preserved in the hydrothermal process. The nanorods aligned in circularity, and the hexagonal arrangement of the circularity can be clearly distinguished in Fig. 2b. From the TEM image (shown in Fig. 2d), the ZnO nanorod (part II) grew from the CT-ZnO-CSC substrate (part I). And the electron diffraction pattern (the right inset of Fig. 2d) reveals that nanorods are of single crystal structure.

The experimental procedure to get hexagonally porous ZnO film is similar to the above process. According to the literature [24], the addition of the citrate can control the crystal morphologies and make the ZnO crystals grow fatter and slower. Fig. 3a–c shows the ordered pore arrays. The pores are hemispherical in shape and are orderly arranged. Further experiments show that the surface morphology of the porous film depends on the hydrothermal time duration. When it prolonged to 36 h, the as-grown ZnO evolved to cover the most part of pores, which was illustrated in Fig. 3d. When the time prolonged to 48 h, the pores were completely buried beneath the ZnO submicro-rods.

Fig. 4a shows the XRD pattern for the ordered porous film (sample shown in Fig. 3a). All diffraction peaks can be identified as diffractions from hexagonal wurtzite ZnO. The highly enhanced (0 0 2) peaks can be seen as a result of the vertical orientation of the porous ZnO film. The room-temperature photoluminescence

spectrum of the ordered porous film was shown in Fig. 4b. A sharp peak can be observed at 382 nm (3.25 eV), which can be attributed to the exciton transition. The deep level emission, known to be related to the structure defects, centered at 567.2 nm, was quite weak, which indicates that the porous ZnO film has low defect density. Previous studies show that this kind of visible emission originated from the structure defects of oxygen [25]. The XRD pattern and PL spectrum reveal that the ordered porous ZnO film has perfect properties in crystallography and photoelectricity.

In this paper, we need to understand the effect of citrate anions. When we prepared the hexagonally patterned ZnO nanorods, only one or two nanorods grew out of the throat confined by the colloidal spheres. One reason is the spheres block the growth of ZnO nanorods underneath, but we need to give an attention to the diffusion of the precursor solution in the interstitial space confined by PSSs. Because the region just under the throat (part I) that enclosed by three colloidal spheres exposes to solution directly, the solution diffuses in part I is easier than other parts of the interstitial space confined by PSSs (part II). So the growth of ZnO crystals under throat will be preferential, which is induced by the easier diffusion in part I. When the nanorod grows out of the throat, the diffusion of precursor solution to part II is prohibited completely.

When we add structure-directing agent-citrate, the growing ZnO crystallites become shorter and fatter, in the meanwhile the growth rate of ZnO crystallite is lowered down in order to make the precursor solution diffuse into part II more completely. So, the ZnO crystallite can get closer and make the film denser. This is the key to get ordered porous ZnO film by hydrothermal method.

4. Conclusions

In summary, we developed a low-temperature, environmentally benign, solution-based method to prepare the large-scale hexagonal arrayed ZnO nanorods and 2D ordered pore arrays. In our knowledge, it is for the first time to report the fabrication of highly ordered macroporous structure by hydrothermal method. As an important wide-band gap semiconductor, the ordered 1D or 2D structured ZnO has significant applications in optoelectronics, field emission, and gas sensor. Although the present approach was realized on the polycrystalline ZnO substrate, we have a strong faith that this kind of process can apply to the single crystal ZnO substrate, and other single crystal oxides or semiconductor film substrates.

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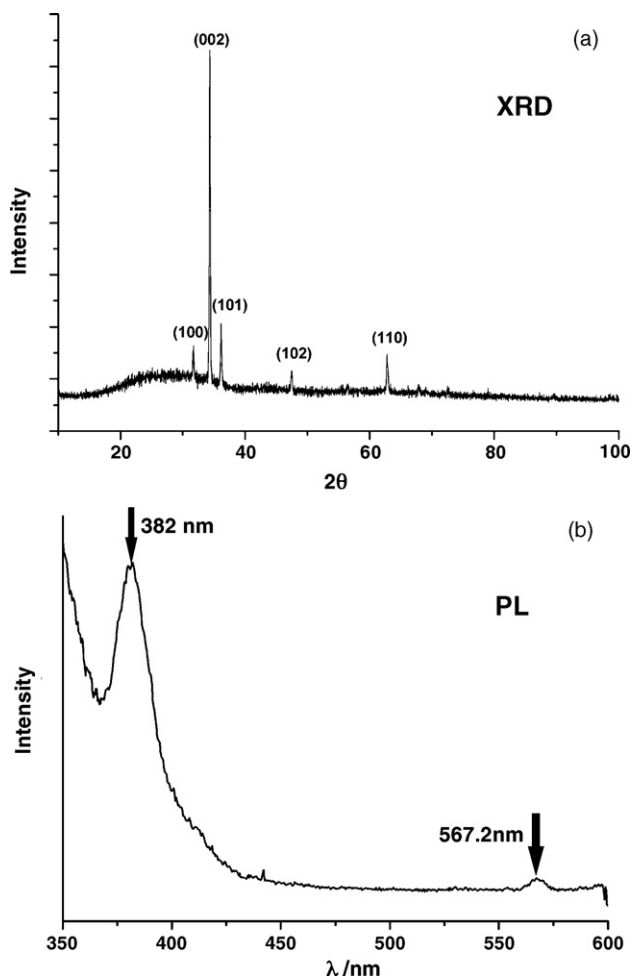


Fig. 4. (a) The XRD pattern of the ZnO ordered porous film. (b) PL spectrum of the ZnO ordered porous film. A sharp peak lies at 382 nm and a visible emission is shown in 567.2 nm.

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