



Ordered ZnO nanorod array film driven by ultrasonic spray pyrolysis and its optical properties

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ABSTRACT

Vertically aligned ZnO (zinc oxide) nanorod arrays with a length of approximate 10 μm were successfully prepared by ultrasonic spray pyrolysis process. The as-prepared samples were characterized by X-ray powder diffraction, field emission scanning electron microscopy, transmission electron microscopy and high-resolution transmission electron microscopy. The clear lattice fringes in the image of high-resolution transmission electron microscopy confirmed a single-crystal structure of ZnO nanorods with the growth direction along the [002] direction. A possible formation mechanism was proposed on the basis of the results of time-dependent experiments. In addition, the room temperature photoluminescence (PL) spectrum of the nanorods showed a strong UV emission peak and length-dependent green emission.

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1. Introduction

Zinc oxide (ZnO), as a well-known II–VI semiconductor oxide with a direct band gap of 3.4 eV and a large excitation binding energy of 60 meV, has attracted intensive research due to its unique properties and versatile applications in transparent electronics [1], ultraviolet (UV) light emitters [2], piezoelectric devices [3] and chemical sensors [4]. It is well known that the electronic, optical and magnetic properties of ZnO based devices are influenced significantly by its morphology, size, and structure. Many research groups have focused on controlling the morphology and size of ZnO nanostructures [5]. Currently, one-dimensional (1D) ZnO have been proved that they are the promising candidates for achieving excellent device performances due to their high surface-to-volume ratio and special physical and chemical properties. So far, various methods have been employed to synthesize 1D nanostructures, such as vapor liquid solid (VLS), hydrothermal, and electrospinning methods. Although great progress has been made on the synthesis approaches for 1D nanostructures, there still remains a great challenge to develop a facile, mild, and low cost method for the preparation of such nanostructures. In recent years, Ultrasonic spray pyrolysis (USP), a simple aerosol synthetic technique, has been extensively utilized to prepare a variety of metal [6], oxide nanoparticles [7], and porous carbon [8]. Until now, to our best

knowledge, synthesis of 1D ZnO nanostructures via USP route has been rarely reported.

Herein, we reported the growth of ordered 1D ZnO nanorod array film on quartz substrate by an ultrasonic spray pyrolysis (USP) method. This method provided an extremely facile route for the preparation of 1D ZnO nanostructures. The formation process had been investigated through the morphology evolution with different spray time, and a possible formation mechanism was speculated. Moreover, the room temperature photoluminescence of as-prepared ZnO nanorod arrays was also investigated.

2. Experimental

All chemicals in the experiment were analytical reagent grade and used without further purification. ZnO seed layer was preferentially deposited by USP method on the quartz substrate. In brief, the precursor solution was prepared by dissolving 0.9 mmol zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and 1.5 mmol hexamethylenetetramine (HMT). The precursor solution was sprayed by a general ultrasonic generator and the resistant mist was pushed forward through reaction zones with N_2 carrier gas (500 sccm), and pyrolyzed on the surface of the substrates at 300 °C for 10 min. The schematic illustration of the USP installation is shown in Fig. 1. During the growth of ZnO nanorods, the as-prepared seed layers were used as the substrates, the precursor was changed into the mixture of 10 mmol zinc chloride (ZnCl_2) and 0.1 mL monoethanolamine. The deposition time was 3 h.

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Finally, the quartz substrates with ZnO samples were treated by sintering at 500 °C for 2 h.

The structures of as-prepared samples were characterized by powder X-ray diffraction (XRD) measurement on a Rigaku D/max 2500 diffractometer with Cu K α radiation. Field emission scanning electron microscopy (FESEM) images were obtained using a JEOL JSM-7500F microscope with an acceleration voltage of 15 kV. Transmission electron microscopic (TEM), and high-resolution transmission electron microscopic (HRTEM) images were obtained on a JEOL JEM-3010 transmission electron microscope with an acceleration voltage of 200 kV. The photoluminescence spectra were recorded on SHIMADZU RF-5301PC spectrophotometer.

3. Results and discussion

Fig. 2a shows the XRD pattern of the as-prepared ZnO samples. All peaks of the samples could be indexed to hexagonal wurtzite ZnO (JCPDS card no. 75-576). No characteristic peaks from any

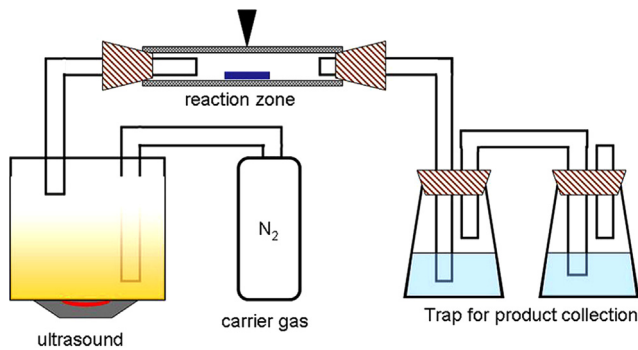


Fig. 1. Diagram of the ultrasonic spray system.

other impurities could be detected. Furthermore, the strong and sharp diffraction peaks suggested that the products had high crystallinity. The significantly higher intensity of the [002] diffraction peak indicated that the ZnO nanorod arrays were preferentially oriented in the *c*-axis direction. The typical SEM and TEM images (Figs. 2b, d) of the obtained ZnO samples revealed that the samples were rod-like nanostructures and contained very developed grain boundaries, with an average length of about 9 μm . Fig. 2c shows the 45°-sectional SEM image of the synthesized ZnO nanorods grown for 3 h. No other morphologies could be detected, indicating a high yield of these nanostructures. The HR-TEM image (Fig. 2e) shows that the ZnO nanorods had a single crystal hexagonal structure and the spacing between two lattice planes was 0.26 nm, which was consistent with the (002) plane of wurtzite ZnO phase.

To reveal the growth process and possible growth mechanism of ZnO nanorods, the morphology evolution of products obtained at different reaction durations had been investigated in detail. Fig. 3a shows the SEM image of seed layer prepared in the first process. It can be seen that the as-deposited seed layer was a compact, continuous, and featureless particle film. After one-hour growth, most of the nanorods were aligned along the surface of the seed layer and the length was about 2 μm (Fig. 3b). As the reaction time was prolonged to 2 h, SEM image (Fig. 3c) shows that the length and diameter of nanorods greatly increased to around 7 μm and 1 μm , respectively. With the reaction time increasing to 3 h, the length of nanorods was further increased to about 9 μm (Fig. 3d). The detailed characteristics of them were described previously.

On the basis of above results, the possible formation mechanism of ZnO nanorod arrays had been proposed, as shown in Fig. 3e. It is well known that wurtzite ZnO can be described as the hexagonal close packing of zinc and oxygen atoms, the ZnO crystal structure consists of many crystal planes with different polarity: a positive

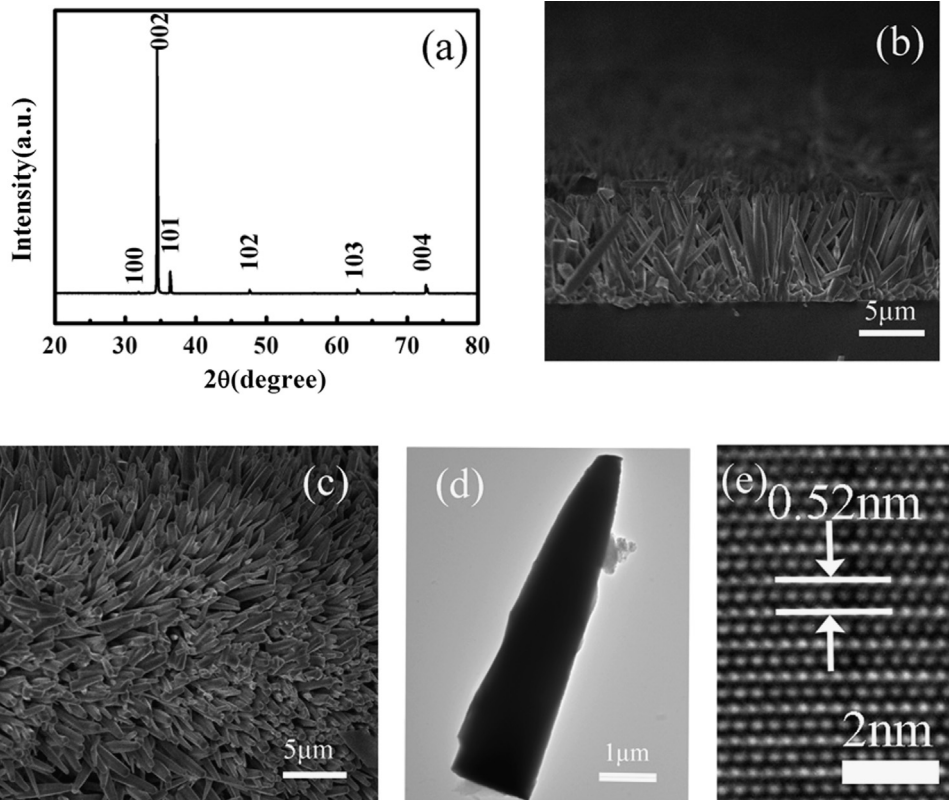


Fig. 2. (a) XRD pattern and (b) Cross-sectional and (c) 45°-sectional SEM image of as-synthesized ZnO nanorods.

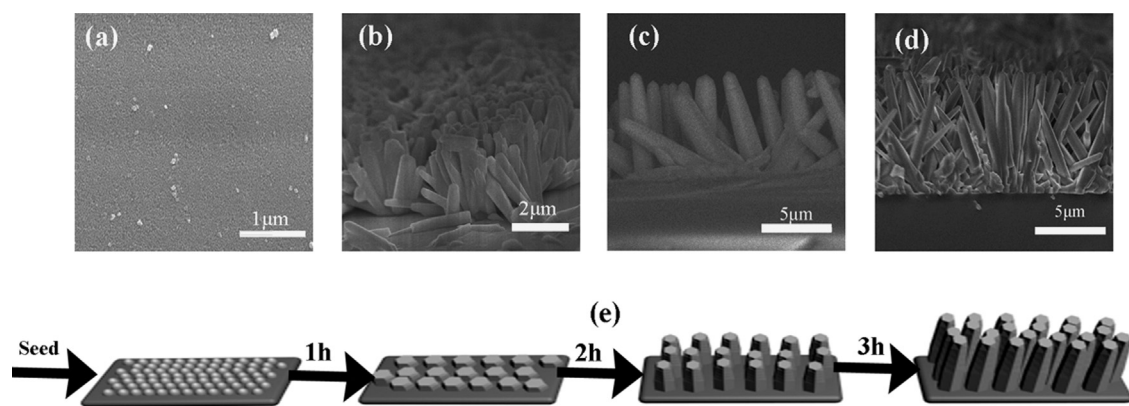


Fig. 3. (a) SEM images of the seed layer and the ZnO nanorods grown at different time: (b) 1 h, (c) 2 h and (d) 3 h, (e) Schematic illustration of the formation process of ZnO nanorod arrays.

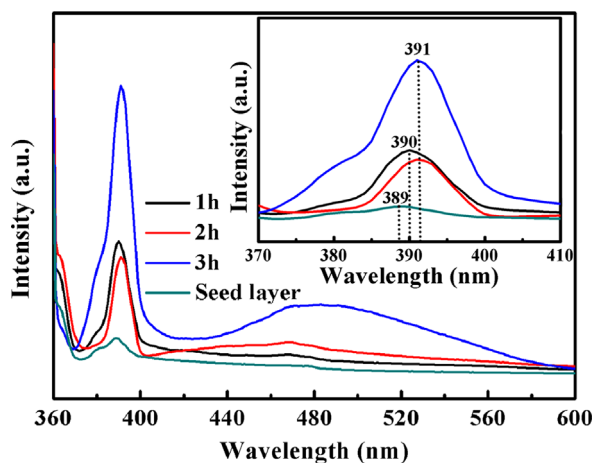


Fig. 4. PL spectrum of ZnO nanorods with different spray time.

polar zinc [0001] plane, six symmetric nanopolar $\{10\bar{1}0\}$ planes parallel to the [0001] direction (*c*-axis), and a negative polar oxygen plane $\{000\bar{1}\}$ [9,10]. Compared with the polar zinc [0001] surface, the nonpolar $\{10\bar{1}0\}$ planes possess lower surface energy and higher stability [11,12]. Since the system has a tendency to minimize the overall surface energy, the ZnO crystals grow preferentially along the [0001] direction. Moreover, the seeded layer on substrates could further lower the *c*-ZnO/substrate interface energy barrier.

The PL spectra of the ZnO samples under different spray time shown in Fig. 4 were measured from 360 nm to 600 nm at room temperature by a 364 nm excitation. The PL spectra of all samples showed a near band edge UV emission accompanied by a broad green emission. A strong UV emission around 391 nm displayed a red shift with increasing spray time, which could be ascribed to the increasing of the length of ZnO nanorods. The green light emission appeared at a range from 480 to 600 nm, which could be ascribed to the oxygen vacancy [13] and grain boundaries in the ZnO nanostructures [14]. With the increase of the rod length, the emission intensity of green light was gradual increased, which indicated that there was a greater defects density in the longer nanorods. Large crystallites own the reduction grain boundaries [15], so the green light emission can be ascribed to the recombination of a photogenerated hole with an electron occupying the oxygen vacancy [13]. Accordingly, a higher concentration of electron could be obtained through extending the length of ZnO nanorods. Because of its strong UV emission at room temperature and high electron concentration, the as-prepared ultralong ZnO nanorods have potential application in light emitting diode and dye-sensitized solar cell.

4. Conclusions

In summary, we present a simple USP method for the synthesis of well-aligned ZnO nanorod arrays. FESEM results revealed that these rod-like nanostructures with the lengths of about 9 μm were grown on the seed layer substrates. The spray time played an important role in extending the length of the ZnO nanorods. On the basis of the results of the morphology evolution with different spray time, a possible formation mechanism was proposed. This method would provide an extremely facile route for the preparation of 1D ZnO nanostructures due to its simplicity and low cost. Room-temperature photoluminescence spectra of the nanorods showed the near band-edge emission and the deep-level green light emission.

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