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Self-assembled urchin-like ZnO nanostructures fabricated by electrodeposition-hydrothermal method

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ABSTRACT

We report the urchin-like ZnO nanostructures composed of self-assembled cone-shaped ZnO nanorods grown on the Zn-deposited Cu substrate fabricated by electrodeposition-hydrothermal method. In the FESEM images, the cone-shaped ZnO nanorods radiate from the center of the nanostructure forming a spherical urchin-like shape with a diameter of 5 μm–10 μm, the average diameter and the length of the cone-shaped ZnO nanorods can be identified as 0.1 μm–1 μm and 3 μm–5 μm, respectively. The SAED of the diffraction ring suggests that this ZnO nanorod was polycrystalline with the wurtzite hexagonal phase. The measured optical band gap Eg values are 3.12 eV, 2.98 eV, 3.04 eV and 3.10 eV respectively with the increasing pH values. In the as-prepared condition, the photoluminescence (PL) spectra of the urchin-like ZnO nanostructures are composed of a violet emission band at about 393 nm and two blue emission bands at about 446 nm and 463 nm at room temperature. With an increase in the pH value of hydrothermal solution, the intensity of PL spectra increases, while the forbidden gaps of four samples become narrower. Finally, a possible growth mechanism of the urchin-like ZnO nanostructures has been discussed.

1. Introduction

ZnO is a semiconductor with a wide band gap (3.37 eV) and a large excitation binding energy (60 meV). It possesses nontoxicity, thermal stability, high porosity, large specific surface-to-volume ratio. These versatile properties provide an opportunity to facilitate ZnO use as one of the most multifunctional materials. Therefore, ZnO nanostructures have been successfully used in the production of optoelectronic devices [1,2], solar energy [3–5], photo catalysts [6–8], sensors [9,10], etc. ZnO nanostructures have exhibited both technological and fundamental interest because of a wide range of magnetic, electrical and optical properties. When it comes down to nanostructures, the most important requirements are shape and size control [11]. Fabricating it into various kinds of nanostructures is an attempt to exploit its potential application, and it is also helpful for investigating their shape-property relationships at nanoscale [12].

Hitherto, a diverse group of ZnO nanostructures were synthesized by numerous fabrication methods, such as nanosheets [13], nanowires [14–16], nanotubes [17–19], nanodisks [20], nanospikes [21], nanobelts [22], nanospheres [23] and nanorods [24–27]. The design and rational control of the synthesis of well-defined ZnO nanostructures with different various morphologies is the cornerstone for further utilizing nanoscale materials for multifunctional nanodevice. It is demonstrated that a precise control and suitable design of the experimental parameters and preparation method can be an efficient way to fabricate well-defined ZnO nanostructures with enhanced performance and functionality [28]. It is well known that the shape and size of nanostructures can influence their properties significantly. Therefore, the ability to tune the shape and size of nanostructures is directly related to the ability to tune their properties. Self-aggregated nanostructures with novel properties and specific morphology in the nanoscale are of great attention [29]. As a novel kind of one-dimensional nanostructure, cone-shaped ZnO nanorods are of particular interest because they have a high spatial resolution in both horizontal and vertical dimensions. Therefore, the controllable synthesis of 1D ZnO nanostructures in terms of size and shape is very important for practical device applications [30].

Here, we report a simple electrodeposition-hydrothermal approach for the synthesis of urchin-like ZnO nanostructures. The

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morphology control and formation mechanism of the urchin-like ZnO nanostructures have been discussed. Meanwhile, the influence of pH value of hydrothermal solution on the structure, morphology and photoluminescence of the ZnO nanostructures has been investigated.

2. Experiment

2.1. Experimental procedure

2.1.1. Materials

$ZnCl_2$, KCl, HBO_3, $Zn(NO_3)_2 \cdot 6H_2O$, $NH_3 \cdot H_2O$, HCl, acetone, isopropyl alcohol, gelatin (AR; Sino-Pharm Chemical Reagent Co., Ltd., China), high purity (99.99%) Zn foil and Cu foil. All chemicals used in this work were of analytical reagent grade and used as received without further purification.

2.1.2. Preparation of Zn nanostructures

For the synthesis of Zn nanostructures, a Cu foil and a Zn foil (with dimensions of 4 cm × 2 cm × 0.01 cm) was polished by using a sanding process to increase the wet ability among foil and the electrolyte, favoring the homogeneous growth of Zn nanostructures at the surface of Cu foil. Then, the Cu foil was washed with dilute hydrochloric acid, acetone, and successively deionized water in the ultrasonic cleaner for 10 min to remove impurities. And the Zn foil was washed with acetone, isopropyl alcohol and successively deionized water in the ultrasonic cleaner for 10 min. A two-electrode cell was used for electrochemical deposition, where a Cu foil and a Zn foil were taken as the cathode and the anode respectively. The electrolyte consists of 0.40 M HBO_3, 2.55 M KCl, 0.44 M $ZnCl_2$ and 2 g/L gelatin. The electrochemical deposition of Zn nanostructures was performed at room temperature under a constant cell voltage of 1.2 V for 30 min.

2.1.3. Preparation of urchin-like ZnO nanostructures

Urchin-like ZnO nanostructures were synthesized via a typical hydrothermal method. The Zn-deposited Cu foil was loaded into a Teflon lined stainless steel autoclave containing 40 mL of 0.03 M $Zn(NO_3)_2 \cdot 6H_2O$ solution, of which the pH was adjusted to 8.0, 9.0, 10.0 and 11.0 by adding ammonia, and the corresponding samples were signed as (a), (b), (c) and (d), respectively. Afterwards, the Teflon lined stainless steel autoclave was sealed and maintained at 90 °C for 4 h. After cooling the autoclave to room temperature naturally, the Cu foil covered with gray products was taken out from the solution and washed with both deionized water and ethanol sufficiently to remove the presence of any ions and then dried at 80 °C for 10 h under vacuum.

2.2. Characterization

The morphology of the sample was characterized by using a field emission scanning electron microscope (FESEM) (SU8010, Hitachi). The microstructure of the sample was characterized by using a transmission electron microscope (TEM) (CM12, Philips). The crystal structure was measured by using Powder X-ray diffraction (XRD) (D8 Advanced XRD, Bruker AXS). The UV–vis absorption spectrum was measured by a UV–vis spectrophotometer (UV-2550, Shimadzu, Japan). The surface area of the sample was calculated using the Brunauer Emmett Teller (BET) (ASAP2020, Micromeritics) method and the nitrogen adsorption–desorption isotherms were obtained at a liquid nitrogen temperature. And the photoluminescent (PL) spectrum of the sample was obtained using spectrophotometer at an excitation wavelength of 325 nm.

3. Results and discussion

3.1. FESEM images

To substantially investigate the effect of pH values of hydrothermal solution on the formation of urchin-like ZnO nanostructures, we have systematically researched the growth mechanism by analyzing the samples prepared at different pH values of hydrothermal solution. Fig. 1 gives a typical view and exhibits the general morphologies of the urchin-like ZnO nanostructures grown on the Zn-deposited Cu substrate placed in different pH values of hydrothermal solution. It is found that the pH

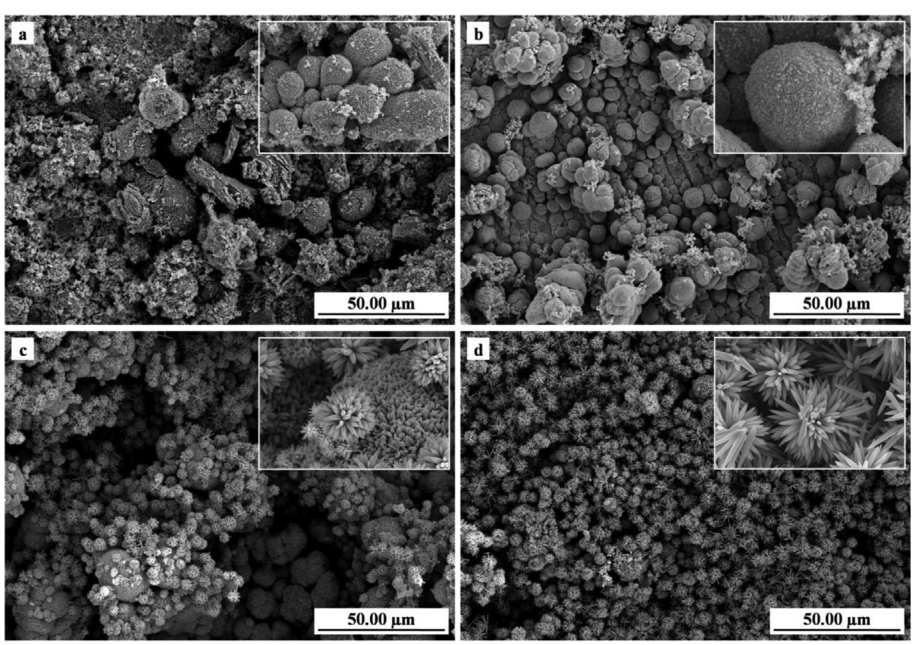

Fig. 1. FESEM images of ZnO nanostructures prepared under different pH values of hydrothermal solution: (a) 8.0, (b) 9.0, (c) 10.0, (d) 11.0.