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ZnO nanowhisker clusters formed on Zn microspheres by wet chemical route

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Abstract

Urchin-like multi-dimensional ZnO nanowhisker clusters with or without void at the center of the structures have been constructed by a simple aqueous solution route to directly oxidize metallic Zn powder in concentrated NaOH solution with pre-existence of the zincate ions under various temperature conditions in a closed Teflon reactor. The morphology, size and structure of the ZnO nanowhiskers obtained under different temperature conditions have been observed in detail by field-emission scanning electron microscopy (FE-SEM). It has been found that various MD structures originate from different source and growth route. Formation mechanism of the urchin-like MD ZnO structures has been reasonably suggested on the basis of the experimental results. It is believed that the degree of supersaturation of the zincate ions in the solution plays a very important role in the process of controlling the nucleation and growth of the ZnO nanowhiskers as well as further oxidizing metallic Zn microspheres.

Keywords: Zn; ZnO; Nanowhisker; Urchin-like

1. Introduction

The design of multi-dimensional (MD) structure based on nanoscaled building units is a new challenge to realize novel nanodevices for biosensor and catalysis [1]. The material with the configuration is expected to exhibit more superior performance due to aggregation of the nanosized units without stabilizer and large ratio surface area. Although self-assembly route relying on different interactions proves highly effective to construct complex MD architectures, inevitable surface modification of the basic blocks with stabilizers can greatly minify their ability to further use for advanced applications [2].

ZnO, a kind of semiconductor with wide direct bandgap (3.37 eV) and large exciton binding energy (60 meV), represents one of the most important functional materials with unique physical and chemical properties such as electric conductivity, piezoelectricity, optical transparency, luminescence and catalysis. In the recent few years, an increasing research of ZnO has been triggered since the discovery of ultraviolet laser [3] and new photocatalysis property from ZnO nanostructures [4] at room temperature. In particular, different preparative approaches have been explored to fabricate various kinds of ZnO nanostructures including nanoparticles [5], nanowires [6], nanobelts [7], nanotube [8], nanorings [9], nanohelixes/nanosprings [10], nanobows [11], nanocombs [12], and nanocages [13], etc. Among them, several methods, for example, physical vapor deposition [14], thermal evaporation [15], metalorganic chemical vapor deposition [16], chemical vapor deposition [17], etc., have been successfully applied to synthesis ZnO nanowires with the diameter range from several tens to hundreds of nanometers. But, their assembly into two-dimensional or MD superstructure still remains difficult. Up to now, although ZnO nanowhisker aggregation with urchin-like MD structure has been realized by using thermal evaporation of metallic zinc powder [18], the control of morphology and size of the ZnO nanowwhiskers on the urchin-like structure is still a tough problem by the method. In contrast, solution chemical method may provide the opportunity for better size control and large-scale production of the MD structure with the ZnO nanowhisker aggregation. It has been well known that ZnO nanowires with a

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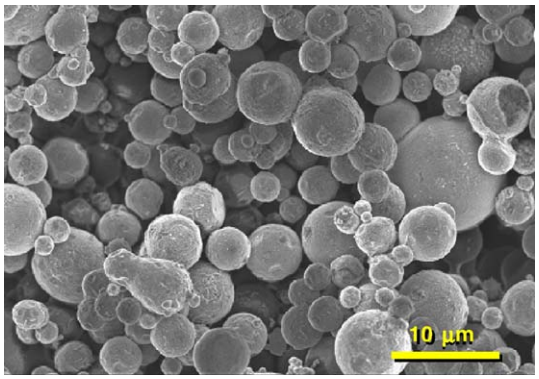

Fig. 1. A typical FE-SEM image of used metallic Zn microspheres.

single crystal structure can be synthesized by colloidal chemical route [19–21]. In this paper, we explore a simple aqueous solution route to directly synthesize ZnO nanowhisker aggregation with the urchin-like MD structure using metallic Zn powder in a closed Teflon reactor under various temperature conditions. In the process, in order to keep continuous etching of the Zn microspheres, aqueous solution with high concentrated sodium hydroxide and certain concentrated zinc nitrate have been mixed with Zn powder. ZnO nanowhiskers have been found to grow in the solution as well as on the Zn microspheres, but the diameter and length of the ZnO nanowhiskers in the solution exhibit obvious difference from those on the Zn microspheres. The morphology, size and structure of the ZnO nanowhiskers obtained under different temperature conditions have been observed in detail by field-emission scanning electron microscopy (FESEM, Hitachi S-5200). A possible mechanism has been suggested for the formation and growth of the MD ZnO nanowhiskers' aggregation with the urchin-like structure. The investigation also clearly shows that it is possible to directly control the growth of ZnO nanowhiskers on the curved surface of the metallic Zn microsphere to construct MD ZnO structure.

2. Experimental

In a typical synthesis, 1.3 g metallic zinc (Zn) powder was put into 10 ml deionized water with continuous stirring at room temperature. After that, 20 ml zincate ion (ZnO_2^{2-}) solution (0.5 M $Zn(NO_3)_2$ + 5.0 M NaOH) was added into the mixture. Finally, the mixed solution was transferred in a Teflon vessel (50 ml capacity) sealed in a stainless-steel bomb. The whole container was heated and maintained in an oven at 200 °C for 2 h. After that, the container was cooled to room temperature naturally. Thus-obtained white product was rinsed copiously with deionized water and ethanol, finally was collected by self-sedimentation. For further characterizations, the sample was dried in vacuum. The crystal phase of the product was analyzed with powder X-ray diffraction (XRD, Rigaku D/MAX2000 X-ray diffractometer with CuKα (λ = 1.5418 Å) radiation operating at 40 kV and 20 mA). The morphology and structure of the products were characterized by a scanning electron microscope (SEM, Philips XL30 S-FEG) and a transmission electron microscopy (TEM, with an accelerating voltage of 90 kV). Samples for SEM and TEM observations were prepared on n-Si (100) slides and carbon-coated copper grids, respectively. Reaction procedures under other temperature conditions are the same as that at 200 °C except room temperature. In the case of room temperature, the mixed solution was first transferred to a 50 ml Teflon cell with stirring for 2 h, and then, the whole system was closed and placed for 10 h without stirring at room temperature.

3. Results and discussion

Fig. 1 demonstrates a typical FE-SEM image of used metallic zinc (Zn) powder, which is composed of spherical-shaped Zn particles with the average size of several micrometers. Fig. 2 provides powder X-ray diffraction (XRD) patterns for thus-obtained white products under various reaction temperature conditions. All of the diffraction peaks marked can be well indexed to the pure phase wurtzite-type ZnO (Joint Committee on Powder Diffraction Standards [JCPDS] Card No. 89-1397). In comparison with the standard XRD pattern for bulk ZnO, the enhanced (0002) reflections may be originated from the oriented growth of the constituent nanowhiskers along the polar axis.

Fig. 3a shows a low resolution SEM image of thus-obtained product at 200 °C. It can be seen that a large number of urchin-like microspheres with the size range from 10 to 15 μm exist on Si substrate. The higher resolution SEM images reveal three typical kinds of different morphologies of the urchin-like microspheres. The first one (see Fig. 3b–c) exhibits a hollow crust structure, which is composed of short ZnO nanowhiskers radially oriented with their growth axes pointing to the center of the microsphere. The ZnO nanowhiskers have the length and diameter ranging from 1–2 μm to 100–500 nm, respectively. Apparently, the hollow microsphere with the ZnO shell is formed due to the etching of the metallic Zn microsphere by strong alkali. The second has a smaller hollow at the center with uniform radial ZnO nanowhiskers. The ZnO nanowhiskers are about 7 μm long and 700 nm wide, much longer and thicker than those of first one (see Fig. 3d–e). The structure may be produced by the oxidation of smaller Zn microsphere and subsequent growth of the ZnO nanowhiskers. The

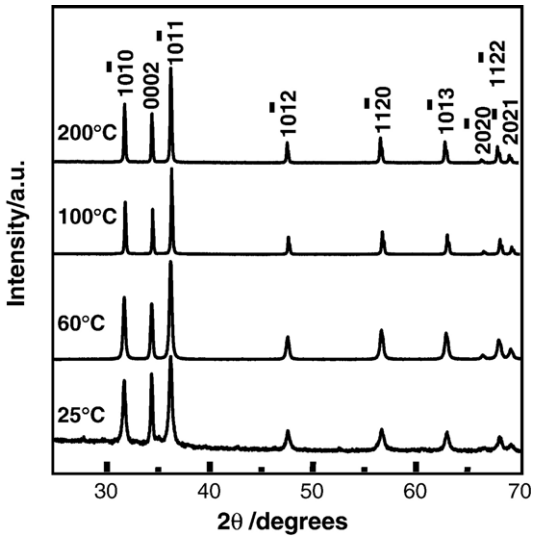

Fig. 2. XRD patterns of the ZnO products obtained under different temperature conditions.