

Preparation of tetrapod-like ZnO whiskers from waste hot dipping zinc^①

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Abstract: Large and uniform tetrapod-like ZnO whiskers (T-ZnO) were prepared from waste hot dipping zinc by vapor oxidation and examined by means of X-ray diffraction and ICP-AES analysis and scanning electron microscope. The products are pure hexagonal wurtzite crystals with tetrapod shape and edge size of center body 5 - 6 μm and needle length of 100 - 130 μm . The size and shape of ZnO particles are fully controlled by the growth conditions and T-ZnO can be obtained only at 850 - 1 000 $^{\circ}\text{C}$ and total gas flow rate ranging from 40 to 250 $\text{L} \cdot \text{h}^{-1}$ in which the size of the T-ZnO particles varies slightly with temperature. The process of the formation of T-ZnO is that T-ZnO may nucleate at the initial stage with a complete tetrapod shape and develop to the large size, but not the process of preferential growth of octahedral nuclei and subsequent growth of the needles. The experiment presents a new method to prepare T-ZnO economically by using the waste hot dipping zinc.

Key words: waste hot dipping zinc; tetrapod-like ZnO whisker; preparation; crystal morphology

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1 INTRODUCTION

Crystal whiskers are usually regarded as filamentary crystals with regular cross section and almost perfect crystallographic structure, which possess high strength approximately equal to the theoretical value of perfect crystals^[1]. Tetrapod-like ZnO (T-ZnO) is the only one with 3-dimension spatial structure among more than 100 kinds of whiskers known so far. It is because of its unique structure, that is, T-ZnO composites exhibit homogeneous microstructure and isotropic properties, which will not be expected among the others^[2-3]. In addition, T-ZnO whiskers also contribute optical, electronic, thermal and chemical properties to composite materials to satisfy special usages^[2-4]. So, more and more intensive studies have been made on T-ZnO for its great potentiality to be utilized in both functional and structural materials.

According to the pre-treating of raw material, the methods to produce T-ZnO can be classified as:

1) Pre-oxidation technique, that is to oxide the surface of Zn powders and subsequently to oxide the as-treated ZnO/Zn powders to produce T-ZnO^[5-6].

2) Direct-oxidation technique, that is to oxide Zn powders in oxygen-content atmosphere without pre-treating^[7-9].

Low yield and poor uniformity of products are expected to be solved in all these methods, in

which another disadvantage is the high cost for the strict requirements on raw materials, such as the purity of Zn more than 99.8% and particle size less than 76 μm .

Waste hot dipping zinc, exhausted from the galvanizing process to maintain good zinc coatings, with 90%-95% Zn and about 5% Fe, is now recovered by employment of distilling and smelting, which are puzzled by problems of low recovering rate, high energy consumption and environmental pollution for the high Fe-content^[10]. If it is adopted directly to prepare T-ZnO, not only will we find a simple and profitable solution to recover the wastes, but also can we broaden the raw materials and drastically reduce the production cost of T-ZnO. In this paper, the waste zinc was directly used as raw materials and turned to high purity T-ZnO under controlled reaction temperature and gaseous composition.

2 EXPERIMENTAL

2.1 Raw material

The waste zinc has approximately bulk density of 6.85 - 7.46 g/cm^3 and melting point of 700 $^{\circ}\text{C}$, and its chemical compositions are shown in Table 1. Being crashed without further sieved, it was directly used as raw material with no limitation on particle size, which varies from several micrometers to more than 1 cm.

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Table 1 Compositions of waste zine (mass fraction, %)

Specimen No.	Zn	Fe	Pb	As	Sb	Cu	Co	Ni	In
1	93.700 0	4.220 0	0.570 0	0.005 0	0.027 0	0.015 0	0.003 1	0.004 7	0.091 0
2	94.330 0	4.910 0	0.038 0	0.002 5	0.003 1	0.012 0	0.013 0	0.051 0	-

In the experiment oxygen ($w(O_2) \geq 99.98\%$) and nitrogen ($w(N_2) \geq 99.99\%$) were used.

2.2 Experimental procedure

The experimental arrangement for growing crystals consists of a zone horizontal electrical furnace (tube dimensions: 100 mm in diameter and 13.70 mm in length) with MoSi₂ heaters (GM-1800), a gas supply system, thermostats, and a reaction chamber. The furnace was pre-heated to 750–1050 °C. And the reaction chamber was placed in the furnace tube and an oxygen-nitrogen gas mixture of 0.2 MPa was supplied from one end of the tube, and exhausted from the other end with total flow rate of 20–300 L · h⁻¹. The reaction took 20–30 min.

The products were characterized with X-ray diffraction (XRD source CuK α), scanning electron microscopy (SEM JSM-5600LV), energy dispersive X-ray analysis (Vantage 4105) and ICP-AES analysis (Baird PS-6).

3 RESULTS AND DISCUSSION

3.1 Characterization of products

A large amount of white, fluffy products were obtained in the reaction chamber after the reaction was finished. The yield of the products is estimated to be more than 92% for every batch. The products are verified by XRD and the spectrum is shown in Fig. 1, where the reflection peaks of ZnO are sharp and with narrow half-width and no peaks of other impurity phase are found. It is obvious that the products can be identified as perfect hexagonal wurtzite structure in crystallography according to the JCPDS data. ICP-AES analysis results reveal that the products are very pure in quality and the impurities corresponding to Table 1 are extremely low, as shown in Table 2. This results from the huge discrepancies of vapor pressure among Zn, Fe and Pb at the same temperature.

Table 2 Impurities contents in T-ZnO ($\mu\text{g} \cdot \text{g}^{-1}$)

Specimen No.	Fe	Pb	As	Sb	Cu	Co	Ni	In
1	44.5	560.4	7.7	230.8	0.9	9.5	14.8	-
2	32.9	302.2	8.6	237.4	1.1	8.4	13.4	-

Fig. 2 shows the morphologies of the products observed by SEM. It is clear that the products are large and uniform tetrapod-like ZnO whiskers. With smooth surface, the needle crystals are of hexagonal pyramid. The arrangement of the needles is that the four needle crystals extrude in different spatial angles from a common juncture and the angle between any two needles is approximately 109°. No spherical ZnO particles and secondary

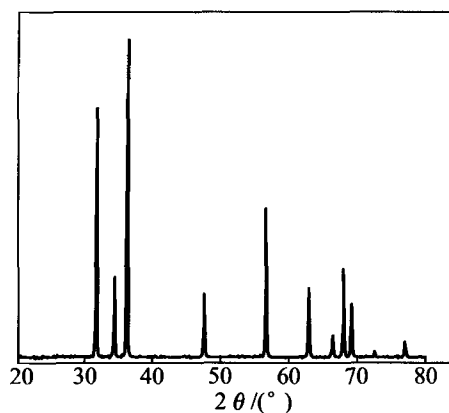


Fig. 1 XRD pattern of ZnO

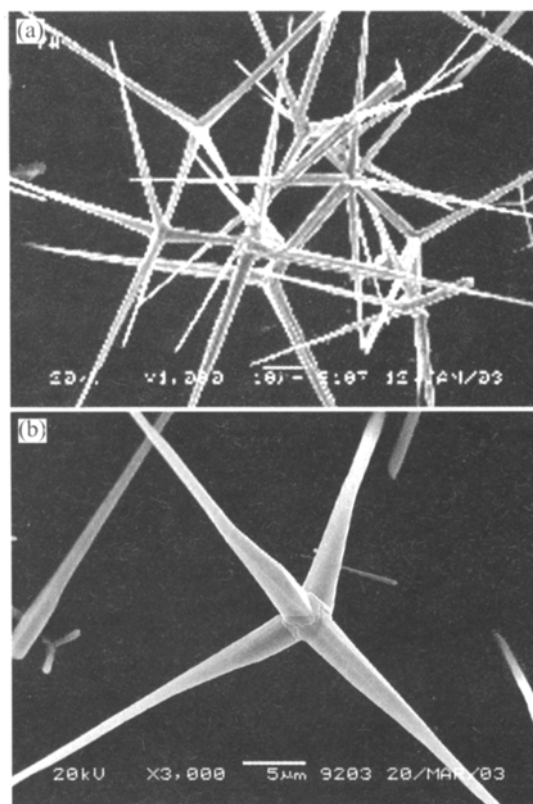


Fig. 2 SEM images of T-ZnO (a)—General image; (b)—Magnified image

growing platelets bridging between needles are observed in the products^[11], showing that the as-grown products are of uniform dimensions and perfect T-ZnO.

3.2 Variation of crystal size

The size and shape of ZnO particles were controlled by the corresponding growth conditions. T-ZnO can be obtained only at the temperature ranging from 850 to 1 000 °C. The influence of the total flow rate of O₂ and N₂ at 850, 950 °C, and constant oxygen flow is shown in Fig. 3. The mean ratio of needle length to the base diameter (l/d), is determined by the formula below:

$$l/d = \sum (l/d)_i / n$$

where $(l/d)_i$ is the needle length to the base diameter of an arbitrary T-ZnO particle, n is the number of T-ZnO particles counted for statistics.

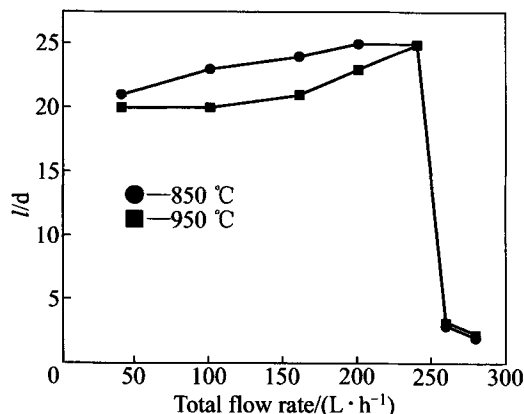


Fig. 3 Crystal size vs flow rate of gas

From Fig. 3, it can be seen that the mean value of l/d increases very slowly (from 20 to 25) with increasing the total flow rate ranging from 40 – 250 L · h⁻¹ but rapidly decreases to 2 – 3 when the total flow rate is over 250 L · h⁻¹. No T-ZnO particles are obtained when the total flow rate is over 280 L · h⁻¹, indicating that T-ZnO embryos can not develop at very low supersaturation of ZnO at high total gas flow rate. If the reaction is performed at 950 °C, the l/d is slightly lower than that at 850 °C and 50 – 250 L · h⁻¹ of the total flow rate, and when the total flow rate is over 250 L · h⁻¹, the l/d has almost the same value with data at 850 °C, irrespective of the great difference in temperature. This phenomenon reveals that the size of the T-ZnO particles varies slightly with temperature in preparation.

3.3 Formation of T-ZnO

Very tiny and complete T-ZnO crystals with length less than 1 μm are observed at centers of

some T-ZnO crystals, as shown in Fig. 4, reflecting that T-ZnO crystals may be nucleated at the initial stage with a complete tetrapod shape and develop to the large size by acquiring or coalescing more atoms. Fig. 5 shows a developing T-ZnO crystal, with four needles extruding from the inside of the center body which is not yet fully shaped. It can be inferred that the nucleation and growth of T-ZnO crystals occur simultaneously other than taking place step by step. That is, at the initial stage of nucleation the crystals grow according to undetermined twinning relations, being growth twin crystals, different from the early speculations that the needles were subsequently grown on the octa-nuclei preferentially developed^[5, 6, 11], and that the T-ZnO crystal was a octa-twinning combination^[12-13]. Recently, nanosized T-ZnO particles have been observed by other researchers^[14]. In experimental, no single and discrete octahedral nuclear crystal from which no needles grow^[11], was observed, which also supports that the growth of T-ZnO can not be divided as the preferential growth of octahedral nuclei and subsequent growth of the needles.

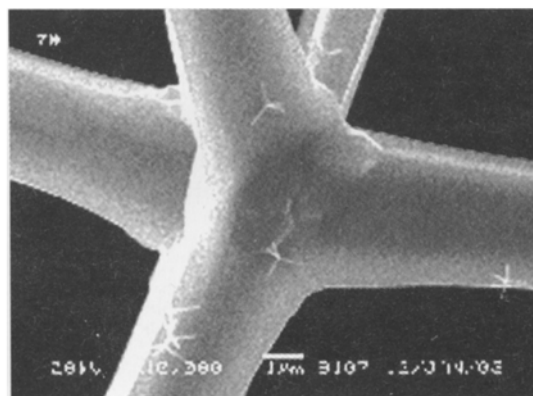


Fig. 4 Base portion of T-ZnO

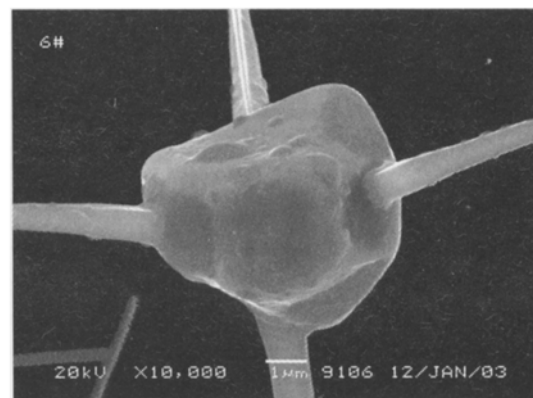


Fig. 5 Intermediate of T-ZnO growth

4 CONCLUSIONS

1) Waste hot dipping zinc can be directly used as raw material to prepare T-ZnO with high quality

at temperature 850 – 1 000 °C, total flow rates of O₂ and N₂ mixture gas 40 – 250 L · h⁻¹, gaseous pressure 0.2 MPa, reaction time 20 – 30 min. The experiment presents an economical way to produce T-ZnO.

2) The growth of T-ZnO whiskers is fully dependent on the growth condition and the size of T-ZnO has slight relation with temperature in their growth. The process of the formation of T-ZnO is that T-ZnO may nucleate at the initial stage with a complete tetrapod shape and develop to the large size, but not the process of preferential growth of octahedral nuclei and subsequent growth of the needles.

3) T-ZnO may be growth twin crystals whose nucleation and growth mechanism need to be further studied.

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