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Preparation and characterization of ZnO nanometer powder①

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Abstract: Hard zinc from thermo-plating zinc factory had been treated for preparation of ZnO nano-powder by chemical precipitation. The ion-type and non-ion-type surface-active reagents were added in different steps and ultrasonic agitation was used in preparing process. TG/DTG was applied to determine thermo-decomposition temperature of the precursor as about 450 ℃. The product is light yellow, and had been characterized by XRD, S_{BET} and TEM, through which the good dispersing sphere particles with the average diameter of approximately 50－60 nm are observed, and the crystal is pure ZnO with hexahedral structure. The cost of preparing nanometer zinc oxide is low.

Key words: zinc oxide; nanoparticle; ultrasonic wave; surface-active reagent
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1 INTRODUCTION

ZnO nano-particles could be widely used in the fields of anti-bacteria and against ultraviolet cosmetic, textile industry, ceramic, glasses, rubber, paint, electrics, electromagnetics, acoustics, optics, photo-electrochemical and so on, for the properties inherent of this material[1, 2]. A lot of techniques have been used to prepare nanometer particle[3], for example, the pure organic phase gelation[4, 5], acetate-citrate gelation[6], micro-emulsion[7-9], thermal explosion[10], homogeneous precipitation[11], freeze-drying precursor[2], aerosol spray pyrolysis[12], the vaporization-condensation[13], surface-modified method[14], etc. These methods can obtain the ZnO nano-powder with sizes from 2－6 nm to 175 nm in average size and with different shape, such as coneshaped, spherical.

Zn^{2+} recycle from hard zinc containing 3%－4% Fe and small amount of Al, Si, etc and Na_2CO_3 are used for preparation of ZnO nano-particles by a modified chemical precipitation, in which, the ion-type and non-ion-type surface-active reagents are added divisionally and the ultrasonic condition is used in the reaction, washing and drying.

2 EXPERIMENTAL

Scrap zinc from thermo-plating zinc factory was used to prepare a solution containing 1.0 mol/L Zn^{2+} ions. The solution was purified first. And adding a kind of surface-active reagent, 0.05% M, and 10% ethanol to the solution under the ultrasonic conditions (ultrasonic washing Instrument SB-8500, China) and agitating for a certain period of time, adding the same reagents into the Na_2CO_3(1.0 mol/L) solution under the same conditions, mixing two aqueous solutions proportionally and agitating for 30 min under the ultrasonic action. Sequentially, adding another surface-active reagent N and agitating for 30 min again, filtering and washing several times with ethanol and distillation water alternately under the ultrasonic action. The precursor prepared was dried for 1h at 75 ℃, then roasted at 450 ℃ for 1 h to obtain ZnO nano-particles.

The obtained product was light yellow, and had been characterized by XRD (Siemens-D-500, German), S_{BET} (Monsorb-1, USA) and TEM (H-800, Japan), through which the good dispersing spherical particles with the average diameter of 50－60 nm were observed approximately, and the crystal is pure ZnO with hexahedral structure.

The nano-particles were prepared under the condition of the comparatively high concentration of zinc ions, which would provide a possibility for production in commercial scale with low cost.

3 RESULTS AND DISCUSSION

3.1 Roasted temperature

TG/DTG (TGA/SDT851/Mettler Toledo, USA) curve of the precursors are shown in Fig. 1. It can be seen from Fig. 1 that the complete decomposition of the precursor is at about 450 ℃. Based on analysis of particles size (MS-2000, Malvern Instrument, UK) and zinc content (EDTA titration) of ZnO was roasted at 300, 400, 450, 500 and 550 ℃,

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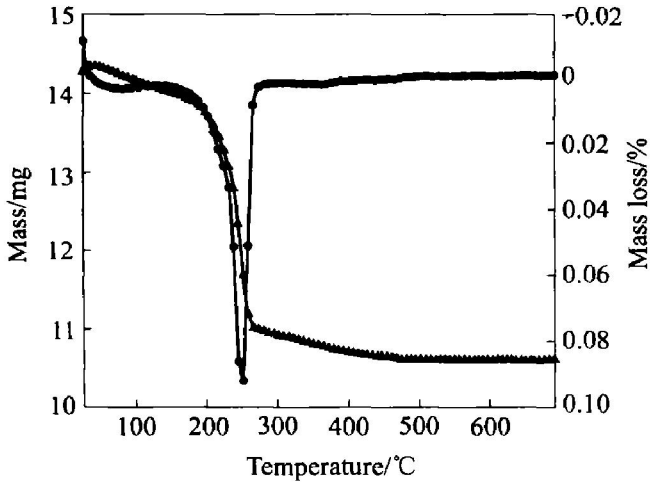

Fig. 1 TG- DTG curve of precursor at different temperatures

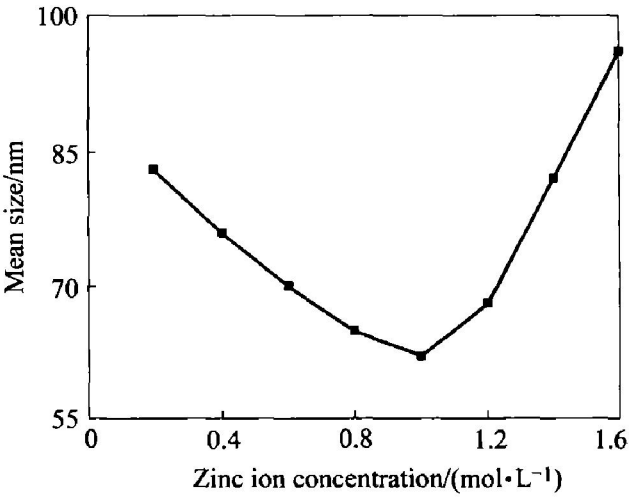

Fig. 2 Effect of concentration of zinc on size

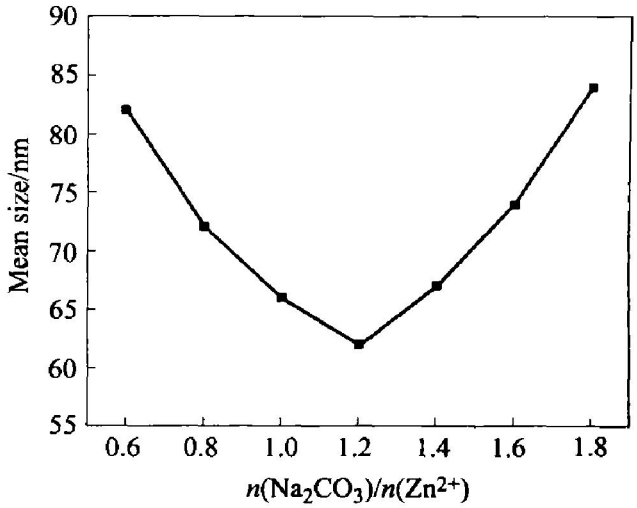

Fig. 3 Effect of ratio of reactants on size

the particle enlarged over 500 ℃, and the precursor decomposed incompletely and the product was impurity below 400 ℃. In order to lessen agglomerate and decompose completely, 450 ℃ was selected in roast.

3.2 Option of Zn^{2+} and CO_3^{2-} / Zn^{2+}

With respect to the cost in the industrial scale, Zn^{2+} ion concentration in the primary solution should be as high as possible. The effects of the concentration of zinc ions and the ratio of reactants on the size had been investigated. The results are shown in Figs. 2 and 3, from which, it is evident that there are an optimal concentration of zinc ions and an optimal ratio of reactants to be obtained the smallest particles in size. In the range of concentrations below the optimum, the growth rate of the crystal core is quicker than that of its formation as the concentration of zinc ions decreases. While in the range of concentration over the optimum, the precursor enlarging owe to colliding with each other, and aggravating agglomeration. As for the ratio of reactants, when it is low, the zinc ions could not precipitate completely and are absorbed by the precursor, and making the precursor enlarge. On the other hand, it is obvious that the colloid particles would not form in the solution with extra sodium ions. Therefore, 1.0 mol/ L Zn^{2+} and the molar ratio of CO_3^{2-} to Zn^{2+} being 1∶2 should be selected.

3.3 Surface-active reagent

The size of nano-particles prepared by chemical precipitation can be effectively controlled by the surface-active reagent. The dispersity of the precursor in solution was related with the zeta potential of it. If the surface potential changes owed to unavailable treatment, it would make the precursor agglomerate. For example , the agglomeration would occur in entirely washing process because continuous change in the zeta potential was caused by pH value of solution in the process[15]. However, the constant adjusting of pH value of the washing detergents would be inconvenient. According to the charges of precursor and surface-active reagents in the solution, firstly, added a kind of ion-type surface-active reagents M, formed a layer of compact coating on the surface of precursor due to electrostatic attracting. Then another kind of non-ion-type surface-active reagents N were added, formed a second layer of coating on the surface of precursor. Thus there was not electrostatic on the surface of precursor, keeping from agglomeration in washing and drying. It can be seen from Fig. 4 that if there exists no surface-active reagent or only ion-type one in the solution, the agglomeration will be aggravated.

It was experimentally found that if an amount of surface-active reagent was too small to coat the surface of precursor completely, the size of the particles was even larger than that of no surface-active reagent. It was that the linkage of the long chain of large molecules coating on the crystal cores with each

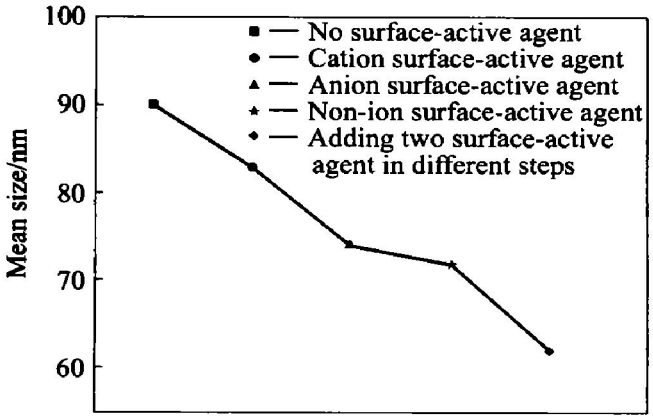

Fig. 4 Effect of surface- active agents on size

other maked them larger. If an amount of surface-active reagent was more, it could coat newly forming crystal core quickly, and also wrap more impure ions at the same time. Thus the precursor was hard to wash, and ZnO nano-particles blacked in roast as carbonization of remained organic compounds. The suitable amount of surface-active reagents is 0.05% - 0.1% (see Fig. 5).

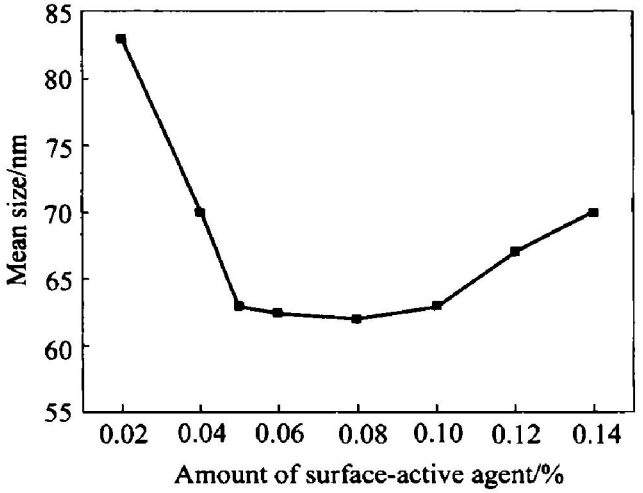

Fig. 5 Effect of amount of surface-active agents on size

It was worth mentioning that the non-ionic surface-active reagent was used to eliminate the effect of surface zeta potential and decrease causing of the agglomerate because of ionic surface-active reagent. If only non-ionic surface-active reagent was used, it was hard to form the coating on the crystal core of precursor.

3.4 Effect of ultrasonic wave

The rate of formation of the crystal core of precursor could be accelerated under ultrasonic wave action because of its effects of the power and acoustic airy hole[16], resulting from retarding the growth of core in the supersaturated state and preventing the crystals agglomeration. Compared with the traditional method, the effects of the power and acoustic airy hole make it much easy to obtain homogeneous precipitation, increase the rate of reaction, form much more cores and shear to temporary conglomerates to get small and even nano-particles.

3.5 Structure and shape characterization

Under the conditions selected, ZnO nano- particles prepared have been characterized by X-ray diffraction and TEM. The crystal is hexahedral structure(see Fig. 6). TEM photogram is shown in Fig. 7. It can be seen from Fig. 7 that the good dispersing spherical particles with the average diameter of approximately 50 - 60 nm are presented.

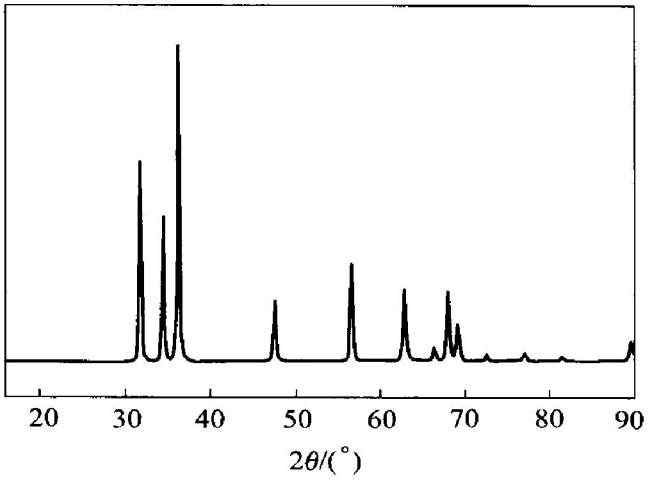

Fig. 6 X-ray diffraction pattern of nano-ZnO

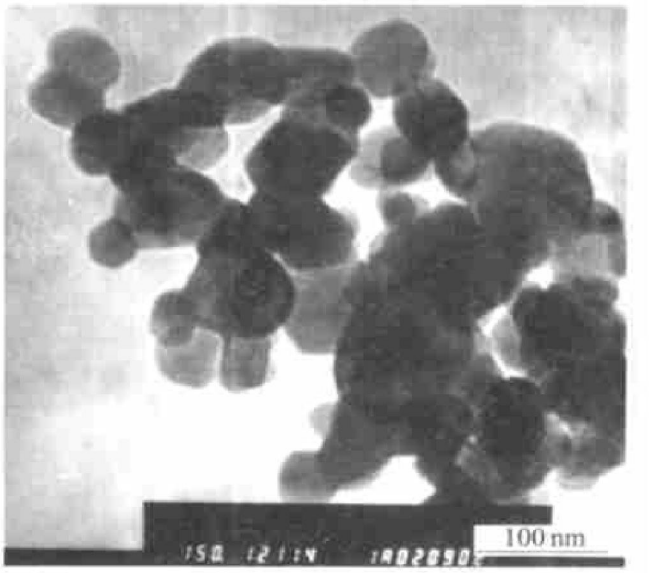

Fig. 7 TEM image of nano-ZnO

3.6 Particle size analysis

There were some methods to measure the size of nano-particles[3], such as TEM, XRD, S_{BET} and laser diffraction, each of them was imperfect on measuring the size. The size of nano- ZnO in experiment has been evaluated by TEM, XRD, S_{BET}, and laser diffraction. The size of nano-particl given by laser diffraction is about 60 nm(Fig. 8), by XRD is about

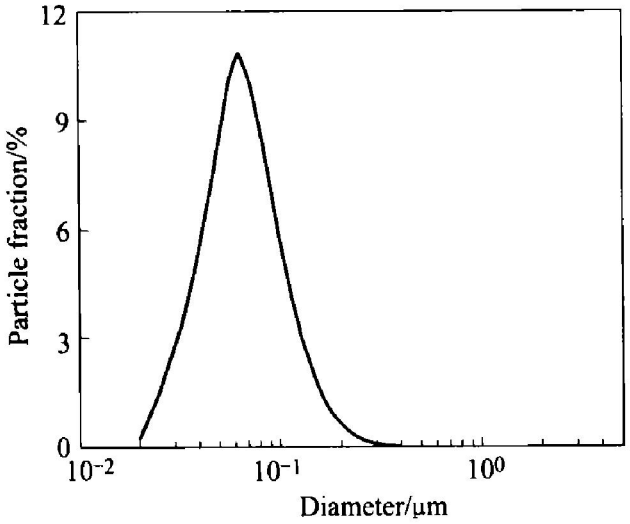

Fig. 8 Distribution of nano-ZnO particle size

30 nm, by S_{BET} is about 70 nm (d = 15.22 m^2/g), and by TEM 50 - 60 nm in average. Summarizing the results, the size of nano- ZnO is about 50 - 60 nm in average.

4 CONCLUSIONS

Hard zinc from thermo-plating zinc factory has been treated for preparation of ZnO nano-powder by a modified chemical precipitation process that the ion-type and non-ion-type surface-active reagents are added divisionally and ultrasonic agitation is used, and a followed drying and roasting treatment. The obtained light yellow product has been characterized by XRD, S_{BET} and TEM. The good dispersing sphere ZnO-particles with hexahedral structure and the diameter of about 50 - 60 nm in average is observed.

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