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Preparation and characterization of ultrafine zinc oxide powder by hydrothermal method

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Abstract: With Zinc acetate and sodium hydroxide as raw materials, while polyethylene glycol employed as dispersant agent, ultrafine zinc oxide powder was synthesized by hydrothermal method. Influence of NaOH concentration on morphology of ZnO powder was studied. The as-synthesized ZnO powder looked like flower cluster and consisted of microrods with hexagonal morphologies. The crystal structure and optical property of the as-prepared powder were also characterized using XRD, UV-visible absorption spectrum and photoluminescence spectrum. The results indicate that ZnO powder is of hexagonal wurtzite structure and well crystallized with high purity. There is a strong excitation absorption peak at 300 nm in UV-visible absorption spectrum and blue shift exists obviously. The optical property of ZnO powder is excellent.

Key words: zinc oxide; hexagonal wurtzite structure; photoluminescence spectrum; optical property

1 Introduction

Different from bulk materials, ultrafine ZnO, as a new functional inorganic material, has its unique properties, such as magnetic, optical, thermal, electrical and mechanical properties[1−2]. Now, ultrafine ZnO shows significant value in many fields consisting of ceramics, chemical industry, electronics, catalyst, optics and medical chemistry. It had attracted much attention and become the focus of the researchers all over the world[3−5]. Ultrafine ZnO is able to grow with self-organizing ability. Under steady conditions, the interaction of molecules is evident, which makes molecules grow rigorously along with the epitaxial interface of crystal lattice to form homogenous structure [6−7]. Ultrafine ZnO has not only strong ability to absorb electromagnetic wave, but also shield ultraviolet ray, absorb infrared ray, disinfect, etc[8−9]. Due to its lightweight, light-color and strong wave absorption ability, ultrafine ZnO can escape detection of radar in broad frequency rang, which is significant in national defense. The ultrafine ZnO had become the research focus of radar absorbing materials[10−12]. In this work, with zinc acetate and sodium hydroxide as raw materials, while polyethylene glycol employed as dispersant agent, the ultrafine zinc oxide was synthesized through hydrothermal method at 140 ℃ in reactor with Teflon lining under high pressure. Crystal structure, morphology and optical property of the powder were characterized using XRD, SEM, UV-visible absorption spectrometry and photoluminescence spectrometry.

2 Experimental

2.1 Materials and apparatus

Zinc acetate and sodium hydroxide with analytic grade were used as raw materials. Polyethylene glycol with analytic grade was used as dispersant agent. Distilled water was obtained in laboratory.

2.2 Preparation

Preparation of ZnO involved four steps: (1) Weigh proper amount of zinc acetate and sodium hydroxide, then formulate 0.5 mol/L and 10 mol/L solution, respectively; (2) Admix isopyknic solutions of the above two to form solution A which was stirred with magnetic agitator to make the solution homogeneous; (3) Make solution B by dissolving of a certain amount of PEG in distilled water; (4) Prepare ZnO powder by mixing A and B into reaction kettle with lining teflon. Reaction temperature was controlled at 140 ℃ for 12 h, then the

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reactor was cooled-down to room temperature naturally. The as-prepared ZnO was centrifuged to solid matter and solution. The solid matter was washed firstly by distilled water repeatedly, and then twice by absolute ethanol, finally dried in vacuum drying oven. At last, the ZnO powder was successfully obtained.

2.3 Characterization

The structure of as-prepared ZnO was characterized with a Japan Rigaku X-ray powder diffractometer. The morphology and size of ZnO were observed using a Japan Shimadzu SSX-550 scanning electron microscope. The optical properties of the sample were examined on a Shimadzu UV-visible spectrometer and on a Hitachi F-4500 fluorescence spectrometer.

3 Discussion

3.1 Influence of NaOH concentration on morphology of ZnO powder

The influence of the NaOH concentration on the morphology of ZnO powder was studied, and the results are shown in Fig.1. In Fig.1, (a), (b) and (c) are corresponding to sodium hydroxide solution with concentration of 2, 5 and 10 mol/L, respectively. As shown in Fig.1, ZnO powder looked like flower cluster, and ZnO flower became obvious and the microrods of ZnO flower grew longer when the concentration of the NaOH was increased. At the same time, the size of the ZnO powder grew larger. This is because the NaOH solution is alkaline with strong polarity. The polarity was enhanced when the concentration of NaOH solution increased. It was evident that the microrods of ZnO flower were able to grow with polarity, which was enhanced when NaOH concentration was increased.

The influence of temperature and reaction time on the morphology of ZnO powder was also investigated. However, the results were not displayed because there was little change in the shape and size of ZnO powder. The influence of reaction time and temperature was less than NaOH concentration. But temperature must not be too high because ZnO flower might be damaged when temperature was excessively high.

3.2 XRD pattern of ZnO powder

The XRD pattern was obtained using X-ray diffractometer employing Cu K_{α} radiation with a voltage of 40 kV, at a scanning rate of 6 (°)/min with 2θ ranging from 10° to 80°. The XRD pattern of the as-synthesized ZnO powder is shown in Fig.2. The crystal planes of (100), (002) and (101) belonged to hexagonal system. The crystal parameters were a=0.324 9 nm and c=0.520 6 nm. All diffraction data were in good agreement with JCPDS files No.361451 (a=3.249 82 Å and c=5.206 61 Å). No other phases were detected, and the diffraction peaks were sharp. Fig.2 indicates that the ZnO flower cluster was of hexagonal wurtzite structure, and the crystal grew completely with high purity.

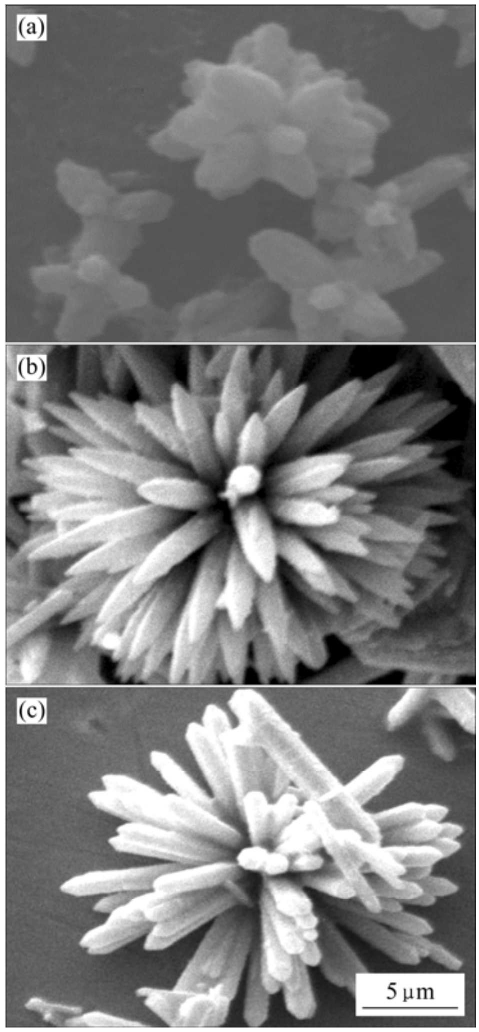

Fig.1 SEM images of ZnO powder obtained from different solutions: (a) NaOH of 2 mol/L; (b) NaOH of 5 mol/L; (c) NaOH of 10 mol/L

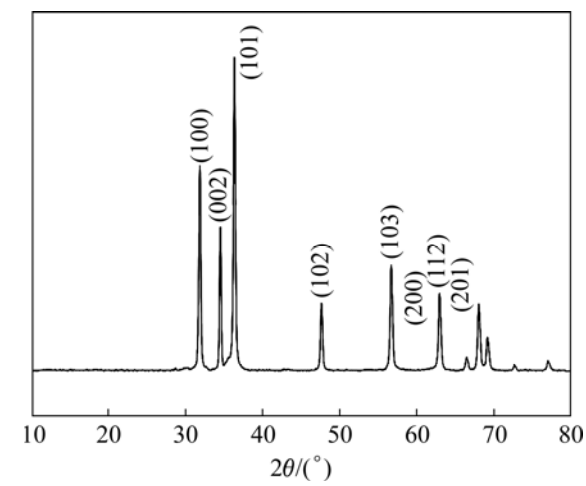

Fig.2 XRD pattern of ZnO powder

3.3 SEM image of ZnO powder

The SEM image of ZnO powder prepared from 10 mol/L NaOH solution and at 140 ℃ is shown in Fig.3. It looked like flower cluster, which was composed of microrods that were hexagon with perfect morphology. The microrods were able to grow with polarity, and the diameter and length of microrods were about 2 μm and 12 μm, respectively. In hexagonal system, the crystal plane of (001) was close-over plane. The energy was the minimum when the crystal grew along (001) plane[13], so the microrods were able to grow with directivity.

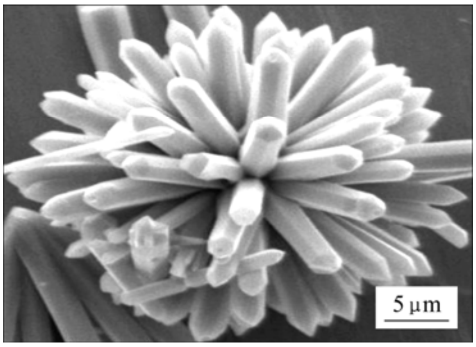

Fig.3 SEM image of ZnO powder

3.4 UV-visible absorption spectrum of ZnO powder

The UV-visible absorption spectrum of ZnO powder is shown in Fig.4. At room temperature, the sample was dispersed in absolute ethanol and ultrasonicated before the test. The deviation was compensated in baseline. The exciton absorption appeared at 300 nm. It is known from literatures that the exciton absorption of ZnO powder and bulk ZnO material appeared at 327 nm and 373 nm, respectively. By comparing the results of the experiment and those of Refs.[4−5], blue shift caused by quantum effect was generated evidently.

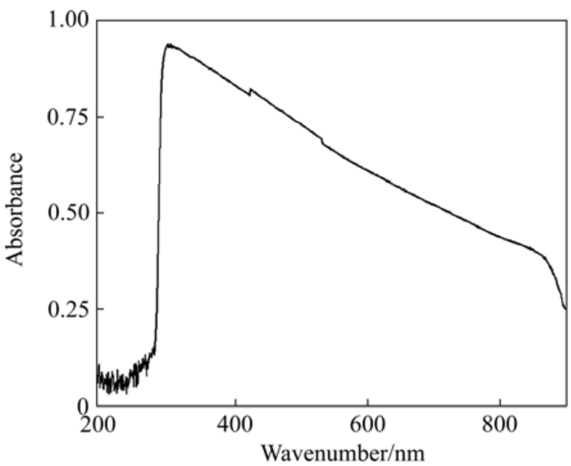

Fig.4 UV-Visible absorption spectrum of ZnO powder

3.5 Photoluminescence spectrum of ZnO powder

The photoluminescence spectrum of the ZnO powder was carried out at room temperature using a laser with 325 nm wavelength as the stimulating source, as shown in Fig.5. Two emission bands could be observed in Fig. 5. The former band near 360 nm was UV emission which was attributed to the recombination of free exciton, indicating the good crystallinity of the ZnO nanorods[14]. The latter band was situated in the visible light region with the maximum near 525 nm. This visible emission band was commonly attributed to a transition of photogenerated electrons from a shallow level close to the conduction band edge to a deeply trapped hole, which was referred to O^{2-} in the ZnO structure[15].

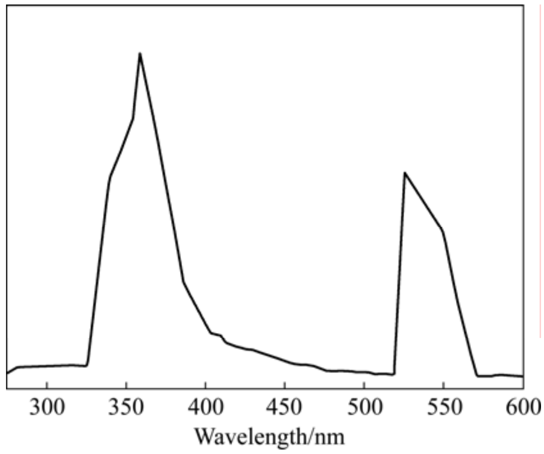

Fig.5 Photoluminescence spectrum of ZnO powder

4 Conclusions

1) The NaOH concentration has notable influence on the morphology of ZnO powder. The microrods of ZnO grow longer when the NaOH concentration increases.

2) The as-synthesized ZnO powder is of hexagon wurtzite structure with high purity, and the microrods are hexagon with nice morphology.

3) The exciton absorption appeared at 300 nm in UV-Visible spectrum, and blue shift is obvious. Photoluminescence spectrum shows that the optical property of ZnO powder is excellent.

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