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PREPARATION AND CHARACTERIZATION OF NANO-ZnO FLAKES PREPARED BY REACTIVE ION EXCHANGE METHOD

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Nano-ZnO flakes were synthesized by calcination of the precursor of $Zn(OH)_2$ obtained via the reactive ion exchange method between an ion exchange resin and $ZnSO_4$ solution at room temperature. Scanning electron microscopy, X-ray diffraction, energy dispersive X-ray spectroscope, UV-Vis diffuse reflection spectrum and Na_2EDTA titration were used to characterize the structure features and chemical compositions of the as-prepared ZnO. The results show that the as-prepared ZnO flakes have uniform structure and high purity. Heat capacities in the temperature range of 83 to 396 K were measured. The measured heat capacities values were compared with those of coarse crystal powders and the difference between this two heat capacity curves was analyzed.

Keywords: *adiabatic calorimetry, heat capacity, nano-ZnO flakes, reactive ion exchange synthesis*

Introduction

Zinc oxide (ZnO) has received a considerable amount of attention over last few years because of many applications found in various field, such as varistor, gas sensor, catalysts and luminescent oxides [1–6]. In order to obtain high quality zinc oxide powder with a fine particle size, a narrow size distribution and a special morphology, various preparation techniques have been used. The techniques applied so far to obtain nanoparticles of zinc oxide include precipitation [7], sol–gel method [8], microemulsion [9], evaporative decomposition of solution [10], wet chemical synthesis [11], gas-phase reaction [12] and hydrothermal synthesis [13]. Among the above methods, reactive ion exchange method, belonging to the homogeneous precipitation method, has been attracting much attention. Zhang *et al.* [14] used ion exchange method to produce $Ni(OH)_2$ and NiO ultrafine particles from nickel chloride. However, up to now, this method has not been applied for the preparation of ZnO powders. Although a variety of physical properties of nano-ZnO particles were extensively studied with an eye to engineering applications, the studies of thermodynamic properties received less attention. As heat capacity of a material is directly related to the atomic structure, measurements of heat capacity as a function of temperature could indicate the structural message of nanostructured materials. This paper aims to present the results of preparation, the characterization of the structure and morphology of the obtained product, using XRD and SEM analysis, UV-Vis reflectance spectra recording and EDTA titrations. In addition, the results of low temperature heat capacity of nano-ZnO flakes are presented.

Experimental

Sample preparation and characterization

All the chemicals used in this study were of analytical grade and used without further purification. The commercial name of the exchange resin used in preparation is strong basic quaternary ammonium, 201×7 (Chemical plant of Nakai University). The main characteristics of the anion exchanger are shown in Table 1. In a typical procedure, 0.3 mol L^{-1} $ZnSO_4$ aqueous solution was mixed with a strong-basic anion-ion exchange resin with slowly stirring for 3 h at room temperature. After the reaction was completed, the precipitate was centrifuged and washed with distilled

Table 1 The main characteristics of strong basic quaternary ammonium, 201×7

Grade	201×7
Functionality	$-N^{+}(CH_3)_3$
Total exchange capacity/mmol mL^{-1}	>1.4
Pearl size/mm	0.6~1.4
Moisture content /%	42~48
True wet density/g mL^{-1}	1.06~1.11
pH range	1~14

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water. The white precursor was dried in air at 70°C for 12 h, and finally annealed at the temperature of 500°C for 3 h. The purity of ZnO was determined by Na_2EDTA titration.

Instruemental methods

X-ray diffraction measurement was performed on a JEOL JEM-200 CX X-ray diffractometer (XRD). SEM observations and energy dispersive X-ray spectroscope (EDX) measurement were made on a JSM-6360 LV Scanning electron microscope (SEM) with EDX attachment. UV-Vis diffuse reflection spectrum was recorded using a JASCO V550 spectrophotometer.

Heat capacity measurements were performed using a precision automatic adiabatic calorimeter over the temperature range from T=83 to 396 K. The calorimetric apparatus has been described in detail [15–19]. Before the heat capacity measurement on the sample, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the standard material-α-Al_2O_3 (NBS SRM-720). The deviations of our calibration results from those of the smoothed curve lie within ±0.2%, while uncertainty is within ±0.3%, compared with the recommended values from the National Institute of Standards and Technology in the temperature range from 80 to 405 K.

Results and discussion

X-ray diffraction result (XRD)

Figure 1 shows the XRD pattern of the as-prepared ZnO. All of the diffraction peaks can be indexed as hexagonal phase (Wurtzite-structure) of zinc oxide by comparison with the data from JCPDS cards No. 36-1451. The strong and narrow diffraction peaks indicate that the material has a good crystallinity. No characteristic peaks from impurities such as $Zn(OH)_2$ are detected.

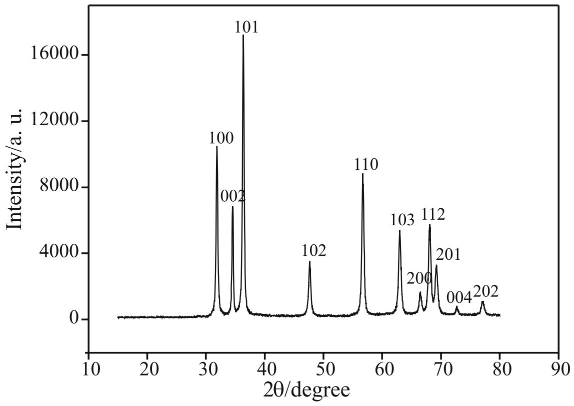

Fig. 1 XRD pattern of the as-prepared ZnO flake

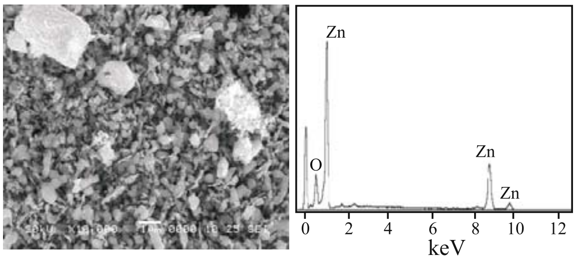

Fig. 2 a – SEM image and b – EDX pattern of the as-synthesized ZnO flake

Scanning electron microscope result (SEM) and EDX analysis

The SEM image of the as-synthesized ZnO is shown in Fig. 2a. As can be seen, the synthesized ZnO has a large quantity of uniform flake shape with a narrow size distribution. The average size of particles is about 250 nm. The EDX analysis was employed to determine the composition of as-synthesized ZnO flakes. The corresponding EDX spectrum (Fig. 2b) suggests that the as-synthesized ZnO flakes are only composed of zinc and oxygen elements and the atom ratio is 1:1, which indicates the product is high-purity ZnO. This is also in agreement with the result of the Na_2EDTA titration (99.9%)

UV-Vis diffuse reflection spectrum result

Figure 3 shows the UV-Vis diffuse reflection spectrum of the as-synthesized ZnO. From the figure, it can be seen that the absorption wavelength range of the as-synthesized ZnO is from 250 to 400 nm, which shifts towards blue with respect to that of the bulk ZnO. Such a phenomenon may be due to the pronounced quantum confinement effect in the as-synthesized ZnO. The result also indicates the size of as-obtained ZnO is nanometer scale [20].

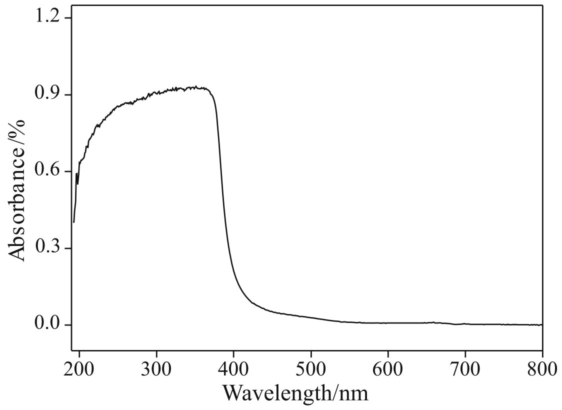

Fig. 3 UV-Vis diffuse reflection spectrum of the as-synthesized ZnO flake

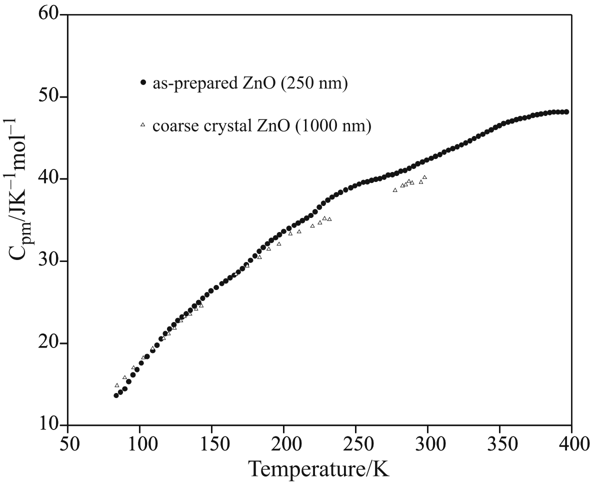

Fig. 4 C_p–T curves of as-prepared ZnO (approximate 250 nm) and coarse-grained ZnO (approximate 1000 nm) in the temperature range from 83 to 398 K

Heat capacity measurement result

The experimental data of molar heat capacity for as-obtained ZnO over the temperature range from 83 to 396 K were plotted in Fig. 4. The heat capacities data of coarse crystal ZnO in the literature [21] were also plotted in Fig. 4. The experimental molar heat capacities of the as-obtained ZnO sample were fitted to the following polynomial equation by the least square method.

$$C_{p,m}/\mathrm{J\ K^{-1}\ mol^{-1}}= \\ =32.77293+15.04199X–6.67959X^2+ \\ +2.792853X^3 \qquad (1)$$

where X is the reduced temperature, and X=[(T/K)–239.5]/156.5 and T is the absolute temperature. The correlation coefficient R^2=0.9984.

It can be seen from Fig. 4 that no phase transition or thermal anomaly appears over the investigated temperature range. The heat capacity of as-prepared ZnO is lower than that of the coarse crystal ZnO (approximate 1000 nm, purity: 99.9%) in the temperature range from 83 to 103 K and becomes higher than that of the coarse crystal ZnO. This phenomenon agrees well with those found by Yi and Yue [22, 23]. Yi and Yue think it is inbeing feature of the nano-ZnO. So it indicated that the as-prepared ZnO is nanometer scale, which is agreement with the results of UV-Vis diffuse reflection spectrum. Why does the heat capacity of nano-ZnO enhance when the temperature is higher than 103 K? As we know, the heat capacity enhancements in the nanostructured materials are usually associated with an increase in the configuration and vibrational entropy of grain boundaries. The excess heat capacity of grain boundary component would correspond to the excess volume of grain boundary, and larger specific surface materials have big excess volume, so higher C_p enhancement was exhibited. Why does the heat capacity of nano-ZnO weaken when the temperature is lower than 103 K? This question is under investigation.

Conclusions

We synthesized nano-ZnO flakes by the reactive ion exchange method at room temperature. IR spectra, XRD pattern, UV-Vis spectrum and Na_2EDTA titration indicate that the as-prepared ZnO flakes have uniform structure and high purity and the average size of particles is about 250 nm. The heat capacity of as-prepared ZnO is lower than that of the coarse crystal ZnO (approximate 1000 nm) in the temperature range from 83 to 103 K and becomes higher above 103 K than that of the coarse crystal ZnO.

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