Powder Technology 210 (2011) 208–211

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Controllable synthesis and flame retardant properties of bunch-, chrysanthemum-, and plumy-like $4ZnO \cdot B_2O_3 \cdot H_2O$ nanostructures

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ARTICLE INFO

Article history:
Received 8 February 2011
Received in revised form 16 March 2011
Accepted 23 March 2011
Available online 30 March 2011

Keywords:
Nanostructures
Zinc borate
Synthesis
Characterization
Flame retardant

ABSTRACT

Three kinds of new $4ZnO \cdot B_2O_3 \cdot H_2O$ nanostructures of bunch-, chrysanthemum-, and plumy-like morphologies have been synthesized under hydrothermal conditions at 140 °C in the presence of ethanol. The as-synthesized products were characterized by the chemical analysis, TG, XRD, FT-IR, SEM and TEM. All the synthesized $4ZnO \cdot B_2O_3 \cdot H_2O$ nanostructures consist of nanoribbons. A series of control experiments confirmed that the morphologies of the products were influenced by the reaction time, temperature, and the presence of the surfactant of PEG-300. Furthermore, the flame retardant properties of the synthesized $4ZnO \cdot B_2O_3 \cdot H_2O$ nanostructures were investigated by the thermal analysis method, demonstrating that they had the better behaviors than the non-nanostructure sample.

1. Introduction

There are many kinds of zinc borates [1] found in nature as well as synthesized in the laboratory. Some of these borates have useful properties. For example, zinc borates such as $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$ and $4ZnO \cdot B_2O_3 \cdot H_2O$ are the inorganic fire retardant materials with high thermal stability, no toxicity, low cost, and good performance in particular in halogen-free systems [2–4]. As a flame retardant additive, zinc borate can be used in polymers, wood applications and textile products [5]. However, the relatively large zinc borates particles are hardly dispersed in a polymer matrix, which restrains their uses in industry. Besides the sizes, the morphologies of a fire retardant also greatly affect its fire resistance property. Therefore, much attention has been paid to the applications of nanometer particles. Recently, Yuan et al. [6,7] have reported $4ZnO \cdot B_2O_3 \cdot H_2O$ nano-/microstructures with different morphologies (rod-, wire-, and lamellar-like shapes and microspheres of nano-/microrods) prepared by a PEG-300 assisted hydrothermal method. We also reported the $4ZnO \cdot B_2O_3 \cdot H_2O$ cluster-like nanostructure and nanoribbon [8].

In this paper, three kinds of new $4ZnO \cdot B_2O_3 \cdot H_2O$ nanostructures with bunch-like(S1), chrysanthemum-like(S2), and plumy-like(S3) morphologies have been synthesized by a hydrothermal method in the presence of ethanol with the use of same source materials. In addition, we also test the flame retardant properties of as-synthesized $4ZnO \cdot B_2O_3 \cdot H_2O$ nanostructures by thermal analysis method.

2. Experimental

2.1. Synthesis of samples

All of the chemical reagents used in the experiment were of analytical grade and without any further purification. 1.90 g of borax and 0.28 g of boric acid were dissolved in 30 mL of distilled water to give solution A, and 1.43 g of $ZnSO_4 \cdot 7H_2O$ was dissolved in 20 mL of distilled water to give solution B. In addition, 4 mL of poly (ethylene glycol) 300 (PEG-300) was added to the solution B during the synthesis of S3. Both solutions were placed in ultrasonic bath and sonicated at 59 kHz for 60 min. Then the solution B was poured into the solution A slowly, forming a homogeneous mixture which was continued to be sonicated for another 30 min. After being added with 10 mL of absolute ethanol, the obtained mixture was transferred into a 100 mL Teflon-lined stainless autoclave, which was maintained at 140 °C for 20 h (7 h for S1) under autogenous pressure, and then cooled to room temperature. The resulting white precipitate was obtained by filtration, washed with distilled water and absolute ethanol 3 times respectively, and dried in air at 60 °C for 12 h.

The procedures for the control experiments were similar to those stated above.

2.2. Characterization of the samples

All samples were identified by X-ray powder diffraction (XRD; recorded on a Rigaku D/MAX-IIIC with Cu target at a scanning rate of $8° \cdot min^{-1}$ with 2θ ranging from 10° to 70°) and FT-IR spectroscopy (Nicolet NEXUS 670 FT-IR spectrometer in the range of (500–4000)

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doi:10.1016/j.powtec.2011.03.018

cm^{-1} with KBr pellets at room temperature). The chemical compositions of the sample were determined by EDTA titration for Zn^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by the mass loss in the TG curve for H_2O. The sizes and morphologies of the products were investigated by scanning electron microscope (SEM; Quanta 200, Philips-FEI; before SEM imaging, the sample was sputtered with thin layers of gold) and transmission electron microscope (TEM; Hitachi H-600).

2.3. Flame retardant evaluation

The flame retardant properties of the as-synthesized samples were studied through the thermal analysis method. Wood powder was selected as the blank sample. 20% synthesized samples and non-nanostructure sample of $4ZnO \cdot B_2O_3 \cdot H_2O$ were added into the selected wood powder, and the mixtures were stirred until homogeneous, respectively. The thermogravimetric analyses (TGA) of the obtained solid mixtures were performed on a SDT Q600 thermal analyzer under N_2 atmosphere with a heating rate of 10 °C·min^{-1}.

3. Results and discussion

3.1. Identification of as-synthesized samples

The chemical analytical data of sample S1 are (calcd/found,%), ZnO (78.79/79.02), B_2O_3 (16.85/16.67), H_2O (4.35/4.05), which are consistent with the theoretical values.

Fig. 1 shows the XRD patterns of the samples with different morphologies. All diffraction peaks of the samples are in agreement with those of the earlier reports [2,6,7]. No other peaks are observed, which are indicative of pure $4ZnO \cdot B_2O_3 \cdot H_2O$ obtained under the current conditions.

The FT-IR spectra of the as-synthesized samples (Fig. 2) exhibits the following absorption bands and they are assigned referring to literature[9]. The band at 3366 cm^{-1} is the stretching of O–H. The peak at 1305 cm^{-1} might be symmetric stretching of $B_{(3)}$–O. The peak at 1247 cm^{-1} is the in-plane bending of B–O–H. The peak at 716 cm^{-1} is the out-of-plane bending of $B_{(3)}$–O. The peak at 534 cm^{-1} is the in-plane bending of $B_{(3)}$–O. The peak at 1026 cm^{-1} might be the vibration of Zn–O. These assignments reveal the presence of triangle BO_3 and OH groups in this compound, which are consistent with the structure of $Zn_2(OH)BO_3$ [10].

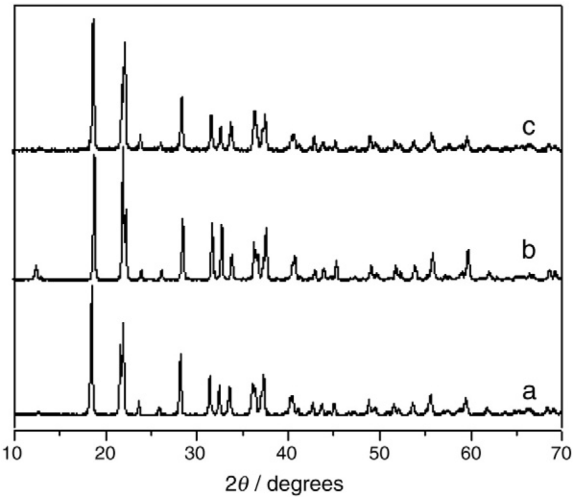

Fig. 1. XRD patterns of samples. (a) S1, (b) S2, (c) S3.

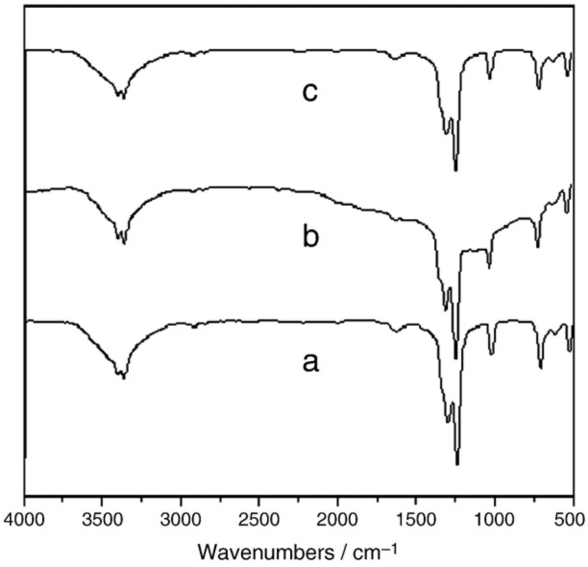

Fig. 2. The FT-IR spectra of samples. (a) S1, (b) S2, (c) S3.

3.2. Sizes and morphologies of samples

The lower magnification and higher magnification SEM images and TEM images of the three kinds of samples with different morphologies are shown in Figs. 3 and 4, respectively. As can be observed, the sample S1 was the uniform bunch-like nanostructure, which was constructed by nanoribbon with the thickness of 80–200 nm and the width of about 250–600 nm. The sample S2 was the uniform chrysanthemum-like nanostructure, which was constructed by nanoribbons with the thickness of 80–200 nm and the width of about 100–400 nm. In addition, there also existed a little shorter nanoribbons with the width of several microns in S2. The sample S3 was the uniform plume-like nanostructure, which was assembled by nanoribbons with the thickness of 80–100 nm and width of 200–500 nm.

3.3. Effect of experimental conditions on morphologies of samples

Figs. S1 and S2 in supporting information show a set of XRD patterns and typical SEM images corresponding to the samples obtained at different reaction temperatures for 20 h, respectively. As can be observed, all the products were $4ZnO \cdot B_2O_3 \cdot H_2O$. The morphologies of products, which were all different from that of S2 obtained at 140 °C, were the mixture of rod and leaf at 100 °C and 120 °C, the mixture of ribbon and bunch at 160 °C, and the uniform rod at 180 °C, respectively.

Fig. S3 in supporting information shows a set of SEM images corresponding to the samples obtained at 140 °C for different reaction times. The product was mainly the shorter bar-like morphology when the reaction proceeded for 4 h. When the reaction time was prolonged to 7 h, bunch-like nanostructure was formed as stated above. When the reaction time was prolonged to 12 h, cluster-like nanostructure was formed, which could be thought as the transitional state of S2. With the further increase of reaction time to 20 h, uniform chrysanthemum-like nanostructure was formed as stated above. When the reaction time was further extended to 68 h, the same morphology also existed, which showed that the chrysanthemum-like nanostructure was the thermodynamic phase under the present synthesizing condition.