



3D hierarchical $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and $\text{Zn}_3(\text{VO}_4)_2$ microspheres: Synthesis, characterization and photoluminescence

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ARTICLE INFO

Article history:

Received 8 August 2011

Received in revised form 10 October 2011

Accepted 18 October 2011

Available online 25 October 2011

Keywords:

- A. Inorganic compound
- B. Chemical synthesis
- C. Crystal growth
- C. X-ray diffraction
- D. Optical properties

ABSTRACT

Via a simple glycine-assisted hydrothermal route, large-scale 3D hierarchical $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ microspheres have been fabricated. Their purity, crystalline phase, morphologies and thermal stability were characterized by X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), Fourier transform IR (FTIR), scanning electron microscopy (SEM) and thermogravimetry-differential scanning calorimetry (TG-DSC). The SEM results indicate that the microspheres are self-assembled by numerous nanoflakes with mean thickness of 100 nm. Some factors influencing the morphologies of the $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ micro-/nanostructures have been systematically investigated, as well as quantity of glycine and the reaction time. The possible mechanism of the crystal growth and assembled procedure were also proposed. The as-prepared $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ can be transformed into $\text{Zn}_3(\text{VO}_4)_2$ with the similar morphologies by calcination in air at 600 °C. Furthermore, the photoluminescent properties of both $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and $\text{Zn}_3(\text{VO}_4)_2$ were studied and exhibited different spectra.

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1. Introduction

In recent years, fabrication of micro-/nanomaterials with controllable size and shape has been of great scientific and technological interest. Through nanoscale building blocks self-assembly, the synthesis of 3D hierarchical micro-/nanostructure has become a typical topic in material research fields, because the hierarchical micro-/nanostructures, compare with the bulk materials, usually exhibit improved physical and chemical properties for potential applications in, e.g., optics, electronics and catalyses [1–8]. Up to now, various 3D hierarchical micro-/nanostructures have been obtained by 2D nanoplates or nanoflakes, including Ni nanoflowers [5], $\text{Ni}(\text{OH})_2$ microflowers [6], Co_3O_4 hollow microspheres [7], etc. However, to the best of our knowledge, relatively few reports are related to the fabrication of 3D hierarchical micro-/nanostructures of the metal vanadates [8].

In the past few decades, much attention has been paid to zinc vanadates and their derivatives owing to their excellent chemical and physical properties [9–18]. However, $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ presents a novel structure that composed of alternated Zn–O layers and V–O layers. As a metastable phase, it can be used as an active starting material to prepare other new advanced zinc vanadium oxide [9–13]. Bulk $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ was firstly prepared by Zavalij via a hydrothermal process and its crystal

structure was characterized [9,10]. Yu and his co-workers [12] have prepared $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot \text{H}_2\text{O}$ nanosheets by a butylamine-assisted hydrothermal procedure, and then ZnO nanocrystals were obtained using it as a precursor. Chen et al. [13] have synthesized $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ nanodisks via CTAB-assisted hydrothermal route. Recently, Ni et al. [14,15] have prepared $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot n\text{H}_2\text{O}$ nanobelts through hydrothermal route. However, 3D hierarchical $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ micro-/nanostructures have not been reported so far. Here, we report the preparation of 3D hierarchical $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ microspheres by nanoflakes self-assembly via a facile glycine-assisted hydrothermal route at 120 °C. The effects of glycine and the reaction time on the morphologies of the final products were investigated. Furthermore, the as-prepared 3D hierarchical $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ was calcinated to form $\text{Zn}_3(\text{VO}_4)_2$ with the similar morphologies. Finally, their photoluminescent properties of $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and $\text{Zn}_3(\text{VO}_4)_2$ were studied.

2. Experimental

All the chemicals were analytical grade and purchased from Shanghai Chemical Reagents. In a typical process, 0.75 mmol $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.75 mmol glycine were added to 25 ml distilled water under stirring. When these reagents were dissolved, 0.5 mmol NH_4VO_3 was put into the solution. After stirring for 20 min, the obtained yellow suspension was transferred into a 30 ml-tesflonlined autoclave. The autoclave was sealed and heated at 120 °C for 12 h, then cooled to room temperature naturally. The solid products were

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precipitated by centrifugation, washed with distilled water and ethanol and finally dried under vacuum at 60 °C for 4 h.

The crystalline phases of the products were analyzed on a Shimadzu XRD-6000 powder X-ray diffractometer (Cu K α radiation $\lambda = 0.15418$ nm). The sizes and morphologies of the products were characterized by SEM on Hitachi S-4800. The XPS were collected on an ESCALAB MK II X-ray photoelectron spectrometer, using non-monochromatized Mg K X-ray as the excitation source. The FTIR spectrum was recorded between 4000 and 450 cm^{-1} on a Nicolet AVATAR 370 instrument. The luminescent spectra of the samples were recorded on HITACHI F-4600 spectrophotometer at room temperature. The thermogravimetric analysis was performed on PerkinElmer-DTA7.

3. Results and discussion

XRD was used to characterize the crystalline phase and purity of the samples. Fig. 1a shows the XRD pattern of the samples prepared in the typical procedure. All diffraction peaks of the samples are perfectly indexed to the hexagonal phase of $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, which are in agreement with the literature value (JCPDS file No.50-0570). No peaks of impurities were observed. The strong and narrow diffraction peaks indicate that the samples are well crystallized. While other reaction conditions are kept identical, the XRD patterns of the products prepared in the absence of glycine are shown in Fig. 1b. The products are still in the hexagonal phase of $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, indicating that the glycine has no obvious effect on the crystalline phase. In this work, all samples were characterized as pure hexagonal phased $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. Limited by space, we only take the two typical examples to explain the crystalline phase of the products (Fig. S1 and S2, Supporting Information).

The characteristic peaks in the FTIR spectrum are shown in Fig. 2. Two peaks at 935 and 503 cm^{-1} were assigned to $\nu_s \text{V(T)-O-Zn(O)}$ and $\nu_s \text{V(T)-O-V(T)}$. The letters T and O stand for the tetrahedral and octahedral coordination. The peak at 802 cm^{-1} can be ascribed to the corresponding asymmetric vibrations $\nu_{as} \text{V(T)-O-Zn(O)}$ and $\nu_{as} \text{V(T)-O-V(T)}$. The peaks at 3470 and 1620 cm^{-1} can be assigned to the symmetric stretching vibration and bending vibration of H–O–H in H_2O , respectively. The other strong and broad peak at 3170 cm^{-1} can be ascribed to the OH⁻ group in the framework. These data are consistent with the previous reports [11,13,16,17].

The $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ prepared by the typical procedure was also characterized by XPS (Fig. 3) for the evaluation of its

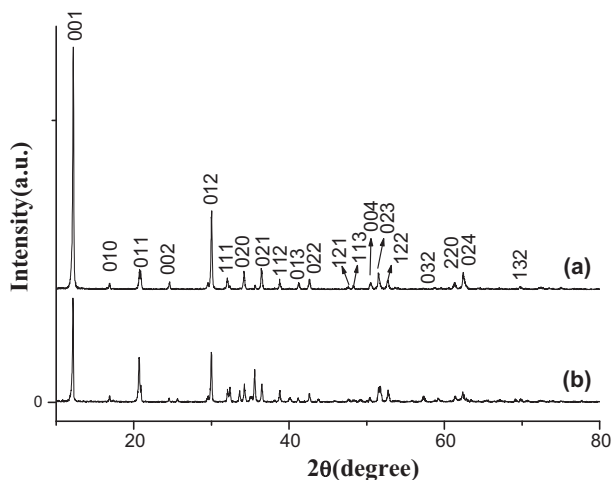


Fig. 1. XRD patterns of the products prepared from different conditions. (a) In the typical procedure and (b) in the absence of glycine.

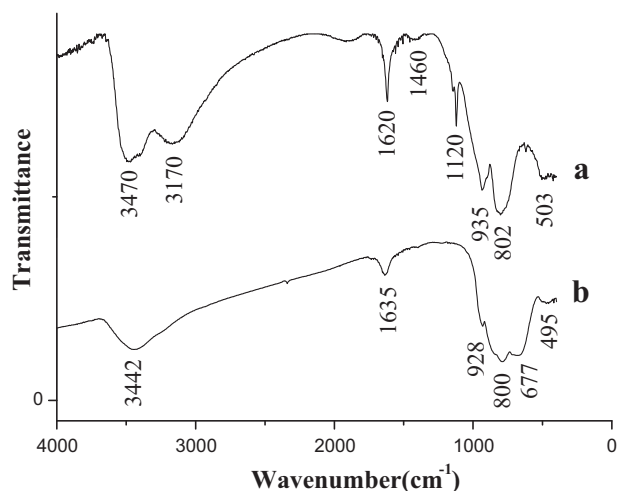


Fig. 2. FTIR spectra of (a) $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and (b) $\text{Zn}_3(\text{VO}_4)_2$.

composition on the particle surface. The binding energies in the high-resolution XPS spectra were all calibrated using that of C 1s (284.6 eV). The two strong peaks in region of 1045.3 eV and 1022.4 eV are assigned to Zn 2p_{1/2} and Zn 2p_{3/2}, as shown in Fig. 3a. The peaks located at 524.4 eV and 516.8 eV are assigned to V 2p_{1/2} and V 2p_{3/2}, respectively. The peak located at 529.8 eV is

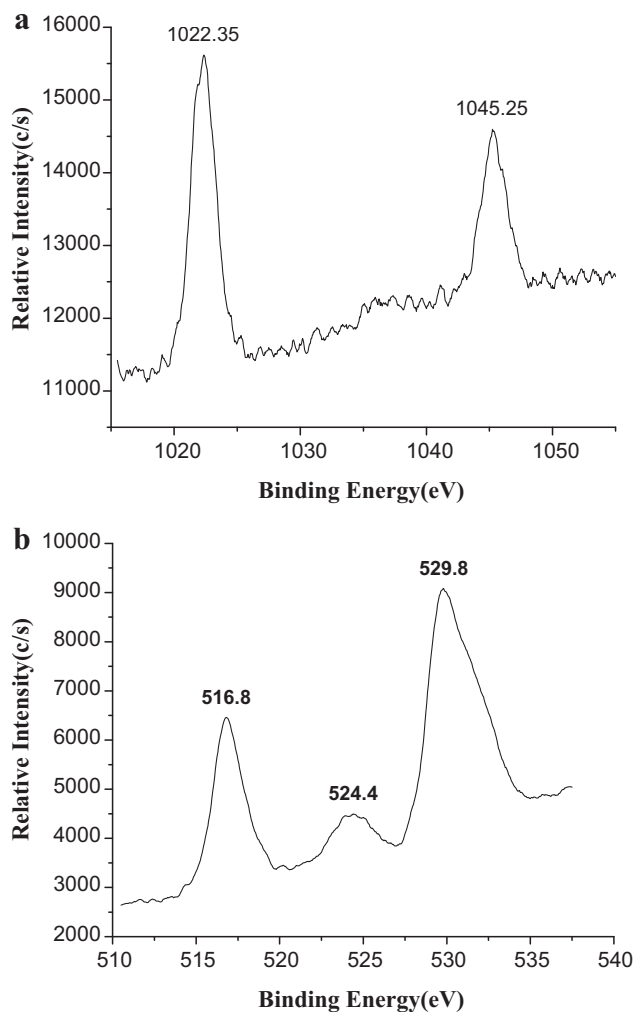


Fig. 3. XPS spectra of $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ prepared in the typical procedure.

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