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Facile Preparation and characterization of zinc phosphate with self-assembled flower-like micro-nanostructures

Xiaoming Zhou, Hanjie Du, He Ma, Lingna Sun *, Rui Cao, Heshan Li, Peixin Zhang *

ShenZhen Key Laboratory of Functional Polymer, College of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, China

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ABSTRACT

The three-dimensional flower-like zinc phosphate [$Zn_3(PO_4)_2 \cdot 4H_2O$] micro-nanostructures was synthesized by a microwave-assisted sonochemical method in the absence of template under ambient conditions. The effects of reaction temperature of water bath and reactant concentrations on the particle size and morphology of flower-like zinc phosphate were studied. The scanning electron microscopy, transmission electron microscopy, X-ray diffraction and infrared spectroscopy were used to characterize the samples. The results showed that the three-dimensional flower-like zinc phosphate is composed of self-assembled two-dimensional nanosheets. The average thickness of two-dimensional nanosheet was 35–40 nm, and 5–12 layers of nanosheets formed a layered flower with an average thickness of 220–540 nm. The reaction temperatures of water bath and reactant concentrations are the key factors to synthesize perfect three-dimensional flower-like zinc phosphate. The self-assembly is main growth mechanism to form the flower-like zinc phosphate.

1. Introduction

The urgent need for a variety of high-tech field of inorganic functional materials, was promoting the rapid development of micro and nano materials synthetic chemistry. Some micro-nano material having excellent performance in the field of the computer storage, photoelectric communications, energy storage and superconducting materials and the biomedical materials, have been studied and development constantly [1–6]. However, the properties of materials are associated to their own particular structure, morphology, surface and interface of chemistry properties. A new open-framework zinc phosphate with 12-ring channels has been solvothermally synthesized by using the in situ generated methylviologen as the template, which exhibits multi-photoactive properties such as photochromism, photoelectricity and fluorescence [7]. Therefore, the synthesis of design and rule for micro-nano crystalline materials with different morphologies and structures has become the topics at the forefront of synthetic chemistry.

As an important inorganic functional material, zinc phosphate is widely used, such as eco-antirust paints, dental adhesives, phosphating agents for steel and iron, flame retardants, etc. [8–11]. As a good base material, zinc phosphate can also be used to synthesize inorganic or organic-inorganic luminescent materials, biomedical materials, etc. [12,13]. By using different synthesis methods, zinc phosphate micro/nano-materials with different morphologies, scales, structures, and physical and chemical properties can be prepared, which further expands the application field of zinc phosphate. In the absence of a template agent, Jung and his colleague synthesized hexagonal bipyramid zinc phosphate via disodium hydrogen phosphate-assisted sonochemical route [14]. Zinc phosphate nanoparticles with uniform in size and shape are prepared via a polyol-mediated method by Marcus Roming [15]. Xie et al. synthesized zinc phosphate with flake and spherical microstructures in template-free aqueous phase at room temperature by controlling the pH values of the solution [16]. The synthesis of lamellar zinc phosphate is mostly involving the addition of surfactants or templating agents in the reaction system [17,18]. In recent years, more concern is given to inorganic layered nano-materials because it can provide more reactive centers and facilitate the assembly of guest molecules between layers. The related new luminescent materials, catalytic materials, optoelectronic nanodevices, biosensors and many other areas have been extensively studied.

We report here the synthesis of zinc phosphate with open three-dimensional flower-like multi-layered structure by using microwave-assisted sonochemical method in the absence of template. This kind of zinc phosphate can provide a full-range three-dimensional space for intercalation and loading, and its own various properties and features are changed through structured and intercalated reactions, which can make the application potential of

* Corresponding authors. Fax: +86 755 26536141.
E-mail addresses: lindasun1999@126.com (L. Sun), pxzhang2000@163.com (P. Zhang).

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zinc phosphate more effectively developed. Moreover, the synthesis method used is simple, effective and green.

2. Experimental section

$Zn(CH_3COO)_2 \cdot 2H_2O$ and $(NH_4)_2HPO_4$ are used as precursors of zinc cation and phosphate anion, respectively. All chemicals were analytical reagents and used without further purification.

The 0.1 mol L^{-1} of zinc acetate solution and 0.1 mol L^{-1} of diammonium phosphate solution were prepared at room temperature. Firstly, 37.5 mL of zinc acetate aqueous solution was put into a conical flask, and 25 mL of diammonium phosphate solution was added dropwise with a dropping funnel with continuous stirring. Then 4 mol L^{-1} of ammonia solution was used to adjust the pH of the mixed solution (pH=8), and then a certain amount of deionized water was added to the mixed solution to a total volume of 80 mL. After stopping stirring, the conical flask with the mixed solution was put into a conventional microwave oven (Panasonic NN-S3440WF with the output power of 800 W) for microwave radiation for 2 min, and then it was cooled down. Then the conical flask was placed in the ultrasonic oscillator (ultrasonic frequency 20 kHz) for ultrasonic vibration for 20 min. Then, the flask was put into a water bath with constant preset temperature to age for 2 h. The white products were collected by centrifugation, washed with deionized water and ethanol twice, respectively, and dried at 70 °C.

The scanning electron microscope was conducted on Hitachi S-3400 N (II) and SE-70 high resolution scanning electron microscopy made in Japan. The morphology, layered structure, crystalline phase, crystallinity, and chemical composition of zinc phosphate were characterized with FEI Company Tecnai F20 transmission electron microscope (TEM) and selected area electron diffraction (SAED) (accelerating voltage of 200 kV), and Bruker D8 Advance SS 18 kW X-ray diffractometer (Cu target Kα line, wavelength 0.154178 nm) made in Germany and Shimadzu IR Affinity-1 Fourier-transformed infrared spectrometer made in Japan.

3. Results and discussion

3.1. Structure and composition of zinc phosphate

Fig. 1 shows the high-resolution SEM images of three-dimensional flower-like zinc phosphate prepared after water bath reaction at 90 °C for 2 h with microwave-assisted sonochemical method. As shown in the figure, each petal is multi-layered sheet structure composed by two-dimensional nanosheets, and numerous layered structures form the three-dimensional flower-like zinc phosphate by self-assembly. The monolayer nanosheet perpendicular to the paper was chosen to measure their average thickness, which is about 35–40 nm, and 5–12 layers of nanosheets form a petal with an average thickness of 220–540 nm.

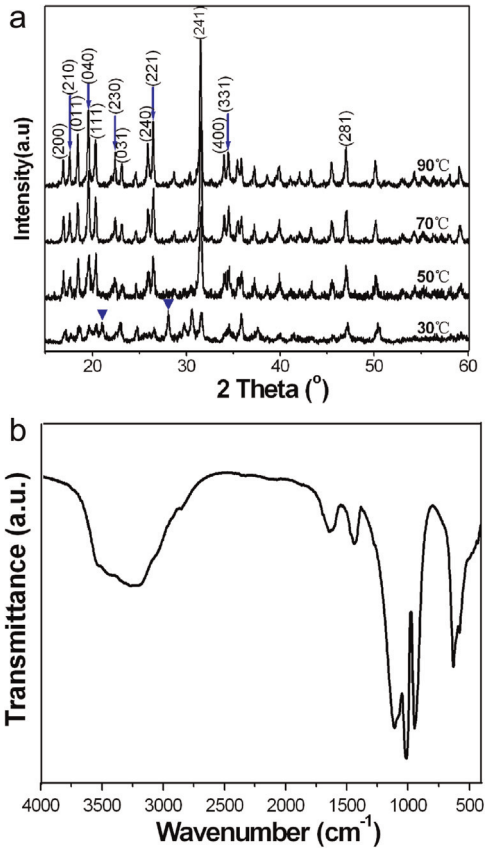

Fig. 2. (a) The XRD patterns of zinc phosphate prepared at various reaction temperature in water bath and (b) FT-IR spectra of zinc phosphate prepared at 90 °C.

Fig. 2(a) shows that, the diffraction peaks with 2θ values at 9.85°, 17.58°, 18.48°, 19.60°, 20.25°, 25.86°, 26.47°, 31.50° were from the (020), (210), (011), (040), (111), (240), (221) and (241) planes of orthorhombic zinc phosphate tetrahydrate (JCPDF 33-1474), indicating that the prepared samples are composed of single component $Zn_3(PO_4)_2 \cdot 4H_2O$. It can be considered that the as-obtained samples have a good crystallinity and no other impurities were observed in the products. The peaks of sample obtained at 90 °C are obviously more sharp than those of the other three patterns, because the crystallinity of the sample is much better with the reaction temperature increasing. The sample prepared by reaction at 30 °C in water bath shows different diffraction peaks from other samples with 2θ values at 11.32°, 20.92°, 28.11°, which should be attributed to monoclinic zinc phosphate $[Zn_3(PO_4)_2 \cdot H_2O]$ (JCPDF 37-0316). Probably at a lower temperature, a very small amount of monoclinic crystals are formed. Fig. 2 (a) also shows that the crystallinity of the samples was enhanced with increasing reaction temperature.

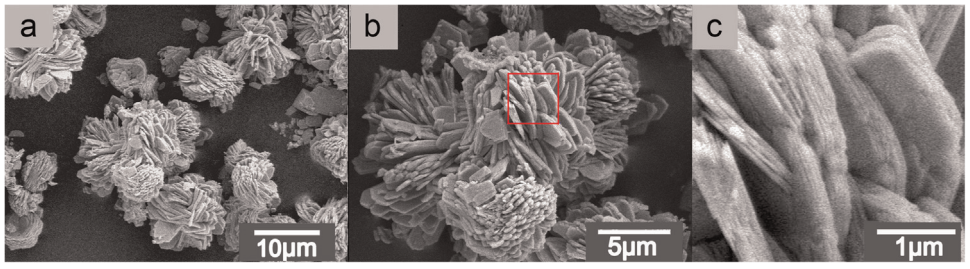

Fig. 1. (a) (b) (c) SEM images of flower-like zinc phosphate and its nano-sheet structure.