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The biomimetic synthesis of zinc phosphate nanoparticles

Shunpu Yan [a], Wen He [a,b,*], Caiyun Sun [c], Xudong Zhang [a], Hongshi Zhao [a], Zhengmao Li [a], Weijia Zhou [a], Xiuying Tian [a], Xianan Sun [a], Xiuxiu Han [a]

[a] *Department of Materials Science and Engineering, Shandong Institute of Light Industry, Jinan 250353, PR China*
[b] *Biomaterials Research Center, South China University of Technology, Guangzhou 510640, PR China*
[c] *State Key Lab of Microbial Technology, Shandong University, Jinan 250100, PR China*

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ABSTRACT

A generic approach, based on the basic principles of biomineralization, has been applied to the synthesis of zinc phosphate nanoparticles by chemical precipitation using yeast cells. UV, XRD, FTIR, and SEM were employed to characterize the product. The single-stage synthesis is cost-effective, easy to control and is performed at low temperature and normal pressure. The mechanism of the formation of $Zn_3(PO_4)_2$ nanoparticles was studied.

1. Introduction

The creation of nano-materials for advanced structures has led to a growing interest in the area of biomineralization. Numerous microorganisms are capable of synthesizing inorganic-based structures [1,2]. In biological systems, a large variety of organisms form organic/inorganic composites with ordered structures by the use of biopolymers such as protein and microbe cells, which have defined monomer sequences and controlled three-dimensional structures [3–5]. The process of biomineralization and the assembly of nanostructured inorganic components into hierarchical structures have led to the development of a variety of approaches that mimic the recognition and nucleation capabilities that occur in biomolecular inorganic synthesis [6–10]. Several studies have demonstrated that biomolecules identified from biological organisms can be used as enzymes or templates for material synthesis in vitro to control the nucleation and growth of the inorganic structure [11–13].

In the past decade, the crystallization of inorganic compounds on solid organic templates has attracted a great deal of attention. For example, diatoms used amorphous silica as structural materials [14], bacteria synthesized magnetite (Fe_3O_4) particles and form silver nanoparticles, and collagen, cholesterol, elastin and chitin showed significant effects on the control of $CaCO_3$ crystallization [15–18].

Inspiration for the synthesis of zinc phosphate nanoparticles described herein comes from earlier reports on the biosynthesis of silver [14,19], calcium carbonate [15–18] and other nanocrystals by bacterial cells [14] and organic macromolecules. Zinc phosphate, as a new type of non-toxic, ecological anticorrosive pigment with excellent properties, has been employed in the coating industry widely. However, owing to its low activity resulting from reunion and the dimension of big particles, it cannot replace traditional toxic anticorrosive pigments completely [20]. As a consequence, the preparation of zinc phosphate powders with mono-dispersion and narrow-size distribution is urgent so as to develop a new generation of zinc phosphate pigments of high performance. Many techniques such as hydrothermal, sol–gel technique and solid-state reactions have been employed to prepare zinc phosphate. It is evident that every method has its own shortcomings. Hydrothermal method needs high temperature and pressure [21]. It is expensive to synthesize zinc phosphate by sol–gel technique. To our best knowledge, no particles less than 1 μm were prepared by solid-state reactions [22]. Compared to the methods above, the chemical precipitation method in the presence of yeasts provides flexibility of operation and simplicity.

The object of this paper is to prepare nanoscale, easily dispersed, anticorrosive zinc phosphate using yeast templates; the reaction of zinc sulfate heptahydrate and trisodium phosphate was employed

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[*] Corresponding author. Department of Materials Science and Engineering, Shandong Institute of Light Industry, Jinan 250353, PR China. Tel./fax: +86 531 88522792.

E-mail address: hewen19602008@126.com (W. He).

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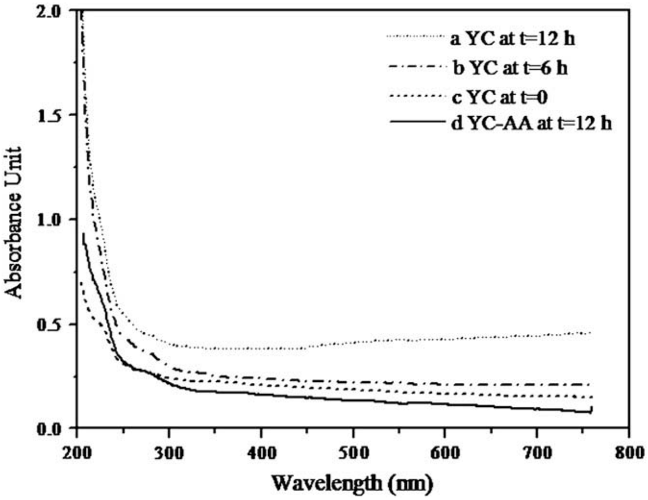

Fig. 1. UV spectra of yeast cells mixed with 0.1 M of $ZnSO_4$.

as a control. The fabrication of $Zn_3(PO_4)_2$ nanoparticles is studied, and the effects of yeasts on the formation and reunion of media are also discussed.

2. Experimental

2.1. Materials and methods

The starting materials used in this study include zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, 99.0%, Tianjin Baishi Chemical and Industry Ltd), trisodium phosphate dodecahydrate ($Na_3PO_4 \cdot 12H_2O$, 99.0%, Tianjin Baishi Chemical and Industry Ltd) and single-celled yeast microbes (Angel Yeast Co., Ltd). All chemical reagents are of analytical grade. Deionized water was used throughout the experiment.

2.1.1. Preparation of $Zn_2(PO_4)_3$/YCs

Firstly, 2.00 g of dry yeasts were cultivated in glucose aqueous solution (2 wt.%, 50 ml) at a temperature of 36 °C for 30 min. Then the as-prepared mixture was poured into an aqueous solution of zinc sulfate (0.1 M, 150 ml) to obtain the yeast/zinc mixture which was stirred for 24 h at room temperature. After the mixture was stirred for 24 h, Na_3PO_4 aqueous solution (0.1 M, 100 ml) was gradually added drop by drop under stirring condition, then continue stirring the mixture for 2 h and let it age for 48 h. An aqueous solution of NaOH (0.05 M) was employed to adjust the pH value of the reaction solution to 8–10 which was the range of the presence of zinc phosphate precipitation. Finally, the deposition was collected from the mixture by centrifugation at a rotation speed of 4500 rpm. The deposition was washed by distilled water until the conductivity of the filtrate was less than 2 ms/m and washed by ethanol once. The resultant powders were dried at 80 °C for 24 h.

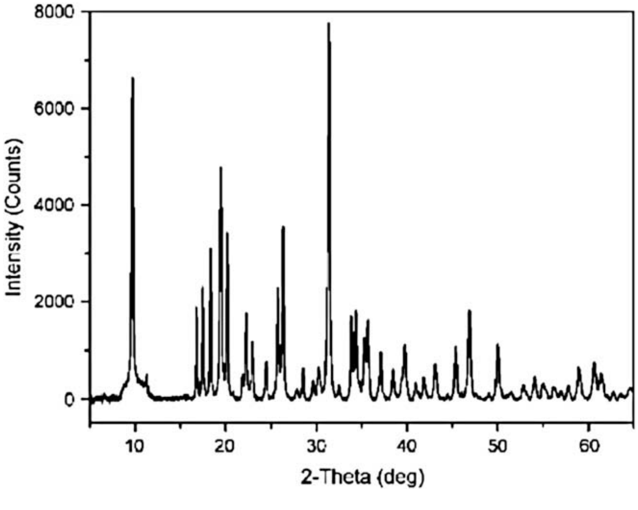

Fig. 2. XRD pattern of the as-prepared $Zn_3(PO_4)_2$ particles.

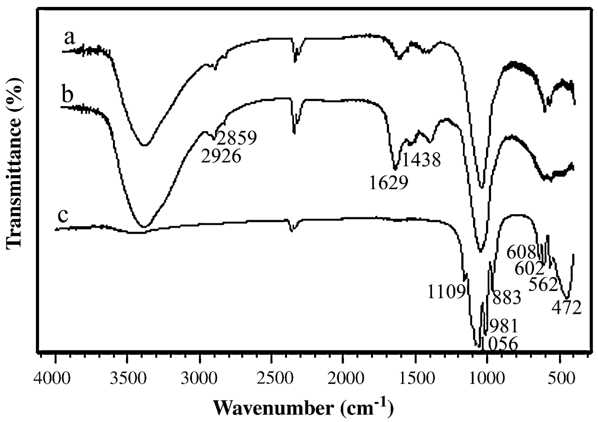

Fig. 3. FTIR spectra of $Zn_3(PO_4)_2$ without (a) and with (b) yeast cells. $Zn_3(PO_4)_2$ with yeast cells was calcined at (c) 750 °C for 2 h.

2.1.2. Preparation of yeast cells–acrylic acid (YC–AA)

An aqueous solution of 3 wt.% acrylic acid (AA) was gradually added into the as-prepared mixture of yeasts until the conductivity of the mixture got to the minimum. Then, the mixture was treated in the process of preparing $Zn_2(PO_4)_3$/YCs.

2.2. Characterization

Ultraviolet–visible spectrum (UV757, Shanghai) was used to observe the conjunction between zinc ions and functional groups. X-ray diffraction (XRD) patterns of samples were obtained on a Panalytical X'Pert PRO (PANalytical, Netherlands) using Cu Ka ($\lambda = 0.15418$ nm) radiation. The crystallite size of $Zn_3(PO_4)_2$ particles was estimated from the FWHM of XRD peaks according to Scherrer equation. Fourier transform infrared (FTIR) spectra were collected on a Nicolet Nexus spectrometer by using a KBr wafer technique in order to study the composition of the samples. The morphologies of the products were observed by scanning electron microscopy (S-4800, Hitachi).

3. Results and discussion

3.1. Ultraviolet–visible spectroscopy analysis

The ultraviolet–visible absorption profile for zinc sulfate solution mixed with yeasts and YC–AA is shown in Fig. 1. When the YCs and YC–AA were incubated in an aqueous solution of 0.1 mM zinc sulfate for 12–24 h at room temperature, series of changes were measured by ultraviolet–visible spectroscopy. Though no distinct surface plasmon characteristic absorption band at 200–800 nm was observed in our zinc sulfate solution incubated with the yeasts in the case of no developer, we found that the intensity became strong and curves a and b shift to red side along with the time. It may be imputed to the increase of homogeneous ligands around zinc ions. Unlike YC, the intensity of the UV spectrum of the YC–AA solution