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Short communication

Synthesis of nanosize single-crystal strontium hydroxyapatite via a simple sol–gel method

Wandong Zhang[a,*], Nana Cao[a], Yamin Chai[a], Xianghua Xu[a], Yonglan Wang[b]

[a]*Department of Chemistry, School of Science, Tianjin University, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China*

[b]*Stomatological Hospital, Tianjin Medical University, Tianjin 300070, China*

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Abstract

Single-crystal strontium hydroxyapatite (SrHAp) nanorods have been synthesized by a water-based low temperature sol–gel process using strontium nitrate and diammonium hydrogen phosphate as the starting materials. The SrHAp materials were characterized by powder X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy and transmission electron microscopy. The aging time was found to play a significant role in regulating the morphology of the nanoparticles and the best result was obtained for the sample aged at 60 °C for 48 h. This SrHAp sample consisted of monodipersed nanorods with lengths of 120–180 nm and diameters of around 30 nm. This synthesis strategy provides a simple pathway to obtain single-crystal SrHAp with high crystallinity and purity.

Keywords: A. Sol–gel process; B. Nanocomposite; Strontium hydroxyapatite; Aging

1. Introduction

In recent years, strontium substituted hydroxyapatite (SrHAp) has attracted much attention as a biomaterial because of its good solubility [1], antiresorptive activity [2], osteoclast apoptosis [3], osteoblast stimulation [4], and ability to treat osteoporosis [5]. Many methods have been used to synthesize strontium substituted hydroxyapatite powders, such as sol–gel [6], hydrothermal [7] and precipitation [8] methods.

The sol–gel technology is an ideal technology for the fabrication of biomaterials, which due to its ability to manipulate the structure of biomaterials at the molecular level and to carry out the reaction at low temperature. The aging time is required to complete the reaction between molecular precursors, and appropriate thermal treatment can accelerate the formation of apatite phase [9]. Furthermore, SrHAp exhibits a good thermal stability at a high temperature between 600 and 900 °C [10].

Herein, a simple strategy for the synthesis of nano-single crystals of strontium hydroxyapatite [$Sr_5(PO_4)_3OH$] via a sol–gel route is demonstrated. A simple, low temperature water based sol–gel method for the synthesis of pure nano-SrHAp was developed using $Sr(NO_3)_2$ and $(NH_4)_2HPO_4$ as the strontium and phosphorus precursors. The composition and morphology of the synthesized nano-SrHAp were investigated using X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2. Experimental

2.1. Preparation

Strontium nitrate and diammonium hydrogen phosphate were used as the strontium and phosphorous precursors, respectively. Aqueous solutions of 0.167 mol L^{-1} strontium

*Corresponding author. Tel./fax: +86 22 27403475.
E-mail address: zhangwandong@tju.edu.cn (W. Zhang).

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and 0.1 mol L^{-1} phosphate were made by dissolving the respective crystals in deionized water. The phosphate solution was then added dropwise to the strontium solution with stirring to give a stoichiometric Sr/P ratio of 1.67. To this mixture, NH_3 was added dropwise to maintain the pH of the solution at 11. A white precipitate was formed and the solution was vigorously stirred for 1 h and then aged in a water bath at 60 °C for different time periods. The precipitate aged solution was then filtered and washed repeatedly using double distilled water to remove impurities. The SrHAp filter cake was dried at 80 °C for 24 h in an oven and then the dried powder was calcined at 650 °C for 2 h using an electrical furnace in air. Based on the aging time period (24 or 48 h), batches are designated as SrHAp24 and SrHAp48, respectively. (All chemical reagents were purchased from Tianjin Guangfu Chemicals Co., Ltd., China).

2.2. Characterization

Phase analysis was performed by XRD using a BD 3000 diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å). The chemical bonding state of the synthesized samples was analyzed by FTIR spectroscopy using a Bruker ALPHA-E spectrometer. The morphology of the products was determined using SEM (Hitachi 4800-S & Hiroba EDS) and TEM (JEM-2100F).

3. Results and discussion

Fig. 1 shows typical XRD patterns of the SrHAp powders synthesized at different aging times by the sol–gel method. All the diffraction peaks are characteristic of a pure hexagonal phase (JCPDS no. 33-1348). Moreover, no peak shifts or other phases are detected in the XRD patterns which indicate that pure SrHAp crystals were obtained by this simple method. The XRD peaks can be used to estimate the crystallite size based on Scherer's formula [11]. In addition, the lattice parameters, the d spacing and the crystallinity of the synthesized SrHAp samples from the (002) and (300) crystal faces, were obtained using the MDI Jade 6.1 software [12]. This data is given in

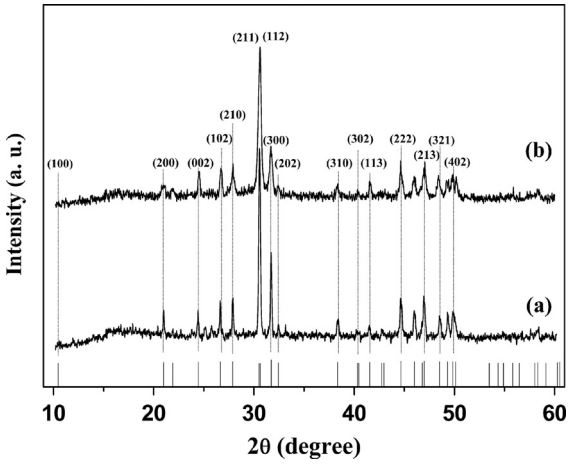

Fig. 1. XRD patterns of SrHAp samples aged for (a) 48 and (b) 24 h.

Table 1
Effects of aging time on the lattices parameter, *d* spacing, crystallinity and the crystallite size of the synthesized SrHAp samples.

Sample	Lattice parameter (nm)		*d* Spacing (nm)		Crystallinity (%)		Crystallite size (nm)	
	a_0	c_0	(002)	(300)	(002)	(300)	(002)	(300)
Reference SrHAp[a]	0.9766	0.7276	0.3638	0.2819				
SrHAp24	0.9761	0.7273	0.3633	0.2816	91.5	92.3	25.4	36.5
SrHAp48	0.9763	0.7276	0.3636	0.2819	95.3	93.3	41.0	38.5

[a]JCPDS Card no. 33-1348.

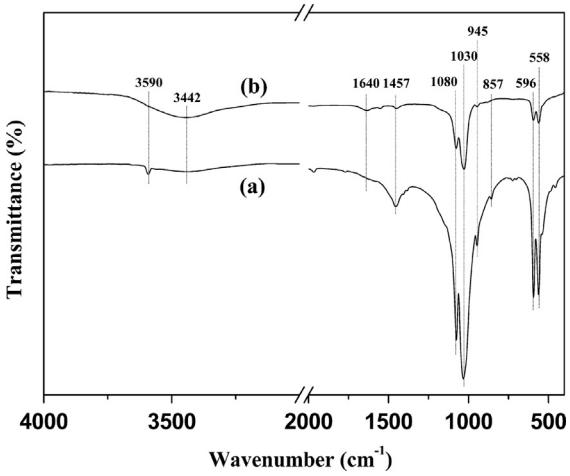

Fig. 2. FTIR spectra of (a) SrHAp48 and (b) SrHAp24.

Table 1. The refined lattice parameters and d spacing values of the SrHAp samples are in a good agreement with the SrHAp JCPDS no. 33-1348 standard.

The FTIR spectra of the synthesized SrHAp powders are shown in Fig. 2. Typical PO_4^{3-} bands are seen at 1080, 1030, 945, 596 and 558 cm^{-1} [13]. The band at 3590 cm^{-1} corresponds to OH^- groups and the bands at 3442 and 1640 cm^{-1}, to strongly adsorbed and/or bound H_2O [14]. The weak bands (centered at 1457 and 857 cm^{-1}) can be attributed to the CO_3^{2-} groups, which might be from the CO_2 in the aqueous solution or from the air used during the preparation process. From the FTIR spectra, it can be concluded that both samples show bands typical of a pure SrHAp composition, with trace CO_3^{2-} impurities.

The SEM images of the synthesized SrHAp aged at 60 °C for 24 or 48 h are shown in Fig. 3. The synthetic crystals aged at 60 °C for 24 h were agglomerations of irregular particles (Fig. 3A) whereas the crystals aged for 48 h show the presence of rod-like shapes, with diameters around 30 nm and lengths around 120–180 nm (Fig. 3B). The significant morphology difference suggests that aging time plays an important role in determining the morphology of the SrHAp products. The synthetic SrHAp48 via the simple sol–gel method in aqueous solution without using any template-directing reagents presents rod-like nanoparticles because of the preferred orientation

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