



Controlled additive-free hydrothermal synthesis and characterization of uniform hydroxyapatite nanobelts

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Abstract

Uniform hydroxyapatite (HAp) nanobelts were successfully synthesized with a facile and economic hydrothermal method for the first time. During the preparation process, without surfactants or additives were used except for three requisite cheap reactants, and the experimental procedures were very simple. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrum (EDS), inductively coupled plasma (ICP), Fourier transform infrared spectrum (FTIR), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were employed to characterize the products. Then the influences of the hydrothermal reaction time, hydrothermal temperature and dosage of NaOH on the formation of HAp nanobelts were investigated. In addition, a possible formation mechanism of the HAp nanobelts was proposed. This additive-free hydrothermal method provides a simple and controllable route to synthesize HAp nanobelts.

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1. Introduction

Hydroxyapatite (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is one of the most stable forms of calcium phosphates and consists mainly of calcium and phosphate at a molar ratio of 1.67 [1]. It is a major inorganic component of human body hard tissues such as bones and teeth, which makes up about 70% of the skeleton and 90% of the tooth enamel [2]. HAp materials, especially nanoscale HAp materials have become one of the most useful functional materials in various fields in recent years [3]. Owing to their high ion-exchange capacities [4] and strong surface adsorption abilities [5] that result from their surface groups and special chemical constitutions, HAp nanomaterials have been widely used in high-capacity drug loading [6], protein purification [7], and inorganic and organic pollutants removal from water [8,9]. Furthermore, HAp nanomaterials exhibit excellent chemical stabilities [10], bioactivities [11], biocompatibilities [12] and

high compressive strengths [13] because they have the same chemical compositions and structures as human hard tissues. Therefore, HAp nanomaterials are promising bioceramics for various clinical applications, like bone regeneration [14], oral rehabilitation [15] and cancer treatment [16]. In addition, HAp nanomaterials can be used in fluorescent materials [17], sensors [18], and paper-making engineering [19].

With the development of nanoscience and nanotechnology, more and more nanomaterials with different microstructures have been prepared, and studies have shown that the microstructures of nanomaterials have great effects on their physical and chemical properties [20]. Among various nanomaterials with different microstructures, one-dimensional (1D) nanoscale materials, such as nanorods [13], nanowires [19], nanotubes [11], and nanobelts [21] have recently stimulated considerable interests. Owing to their unique thermal [22], electronic [23], and mechanical [19] properties, 1D nanomaterials exhibit promising applications in various fields in the future [24].

As for HAp, many attempts have been made to synthesize 1D nanostructured materials, and a large number of 1D HAp

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nano-structures with excellent physical and chemical properties have been prepared in recent years [11,13,19,21,25]. However, most researches have been concentrated to investigate the fabrication of HAp nanorods [13] and nanowires [19], leaving reports about HAp nanobelts scarcely existent [21,25]. Furthermore, until now, no information has been reported concerning the synthesis of uniform HAp nanobelts.

In this paper, uniform HAp nanobelts were successfully synthesized with an additive-free hydrothermal method for the first time. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrum (EDS), inductively coupled plasma (ICP), Fourier transform infrared spectrum (FTIR), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were employed to characterize the products. Following this, the influences of the hydrothermal reaction time, hydrothermal temperature, and dosage of NaOH on the formation of HAp nanobelts were studied. Moreover, a tentative growth mechanism of the HAp nanobelts was also discussed.

2. Materials and methods

2.1. Materials

Disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), sodium hydroxide (NaOH) and ethanol absolute ($\text{C}_2\text{H}_6\text{O}$) were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All of the chemical reagents were analytical grade and used as received without further purification. Deionized (DI) water was used for rinsing and makeup of all aqueous solutions throughout the study.

2.2. Methods

Typical procedures for preparing the HAp nanobelts are described as follows: 50 mL of Na_2HPO_4 solution was prepared by dissolving 2.145 g of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ in DI water, and the pH value of the solution was adjusted to 11.5 using 1 mol/L NaOH solution. Then, 30 mL solution containing 2.360 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was added dropwise to the above Na_2HPO_4 solution under magnetic stirring. After the addition of $\text{Ca}(\text{NO}_3)_2$ solution, the resulting white milky suspension was transferred into a Teflon-lined stainless-steel autoclave (100 mL capacity) and sealed. After being heated at 200 °C for 8 h, the autoclave was taken out and cooled to room temperature. The obtained HAp nanobelts were separated and collected by centrifugation, washed several times with DI water and ethanol, and then dried at 100 °C for 6 h.

To investigate the influences of the hydrothermal reaction time, hydrothermal temperature and dosage of NaOH on the formation of HAp nanobelts, the experimental conditions were changed during the synthesis process, and various HAp samples were acquired and characterized. Specifically, the hydrothermal reaction time varied from 0 to 24 h, the hydrothermal temperature varied from 100 to 200 °C, and the pH value of the Na_2HPO_4 solution varied from 10.5 to 12.5.

2.3. Characterizations

In order to determine the crystal structures of the samples, XRD patterns were recorded on a diffractometer (D8 Advance, Bruker, Germany) using $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation in the 2θ ranging from 20 to 60°. The morphologies of the samples were observed by a scanning electron microscopy (Nova 400, FEI, America), and EDS spectrum was recorded with an energy dispersive spectrometer (Inca IE 350 Penta FET X-3, Oxford, England) equipped on the SEM. The contents of Ca and P elements were determined by the ICP method using a ICP spectrometer (IRIS Advantage ER/S, Thermo Elemental, America). The constituents of the samples were examined by FTIR, and the spectra were collected with a FTIR spectrometer (Vertex 70, Bruker, Germany) in the region of 4000–400 cm^{-1} using the KBr pellets. TEM micrographs, HRTEM micrographs, and SAED patterns were taken by a transmission electron microscope (JEM 2100, JEOL, Japan).

3. Results and discussion

3.1. Characteristics of HAp nanobelts

In order to confirm the crystalline structures of HAp nanobelts obtained via the hydrothermal process, the XRD study was carried out. Fig. 1 shows the XRD pattern of the as-prepared product and the standard pattern of HAp (JCPDS card No. 09-0432). As indicated, this sample is crystallized well and could be defined as HAp because all of the diffraction peaks agree well with the standard HAp pattern. The eight main peaks located at 25.9, 31.8, 32.2, 32.9, 34.0, 39.8, 46.7 and 49.5° 2θ could be indexed to (0 0 2), (2 1 1), (1 1 2), (3 0 0), (2 0 2), (3 1 0), (2 2 2) and (2 1 3) lattice planes of the hexagonal HAp, respectively. Furthermore, it is worthwhile to note that the relative intensity ratios of the (3 0 0)/(1 1 2) and (3 0 0)/(2 0 2) reflections are larger than the standard values, indicating preferential orientation growth in the (3 0 0) direction [26]. No peaks attributed to other impurities are observed in the pattern of the product, revealing that almost no impurity was generated during the preparation processes.

The sample was further investigated by FTIR, and the results are shown in Fig. 2. It can be observed that most of the characteristic adsorption peaks in the spectrum could be attributed to the apatite hydroxyl bond and phosphate radical, which further confirms the successful synthesis of HAp. Specifically, the absorption peaks assigned to apatite hydroxyl bond are observed at 3742 and 3574 cm^{-1} , which are commonly observed for HAp [27,28]. The FTIR bands at about 966 and 467 cm^{-1} are ascribed to PO_4^{3-} (ν_1) and PO_4^{3-} (ν_2), respectively. While the bands around 1101 and 1031 cm^{-1} are due to PO_4^{3-} (ν_3), and the three adsorption peaks at 637, 604 and 565 cm^{-1} can be reasonably assigned to PO_4^{3-} (ν_4) [27–29]. Also, two peaks around 3443 and 1646 cm^{-1} are due to water molecules, which are adsorbed on the surface of HAp [27–29]. The peaks at 1464, 1395, and 865 cm^{-1} could be attributed to CO_3^{2-} vibration, which was probably caused by absorption of CO_2 from atmosphere during preparation under alkaline conditions [30]. In addition, a weak peak which located

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