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Biomimetic synthesis of spherical nano-hydroxyapatite in the presence of polyethylene glycol

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Abstract

Spherical nano-hydroxyapatite (nano-HA) was synthesized successfully by a biomimetic method using $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_3PO_4{\cdot}3H_2O$ as reagents in the presence of polyethylene glycol (PEG). The crystalline phase, microstructure, chemical composition, and morphology of the obtained samples were characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and transmission electron microscopy (TEM). The results show that spherical nano-HA with diameter of 30–50 nm can be synthesized in the presence of a certain concentration (2–6%) of PEG. The crystallinity of HA powder synthesized in the presence of PEG was higher than that synthesized in the absence of PEG, but the crystallinity of HA reduced with increasing the concentration of PEG. The electrical conductivity (EC) of the solution revealed that PEG reduced the transfer rate of Ca^{2+} in the process of HA crystallization, indicating the interaction between PEG and HA. The possible mechanism of formation spherical nano-HA was discussed.

Keywords: Polyethylene glycol; Hydroxyapatite; Biomimetic; Spherical

1. Introduction

Hydroxyapatite (HA, chemical formula $Ca_{10}(PO_4)_6(OH)_2$) has received much attention in recent years [1,2]. HA is used as a bioceramic due to its bioactivity and osteoconductive properties in vivo [3,4]. The advantage of using HA as a bioceramic or biomaterial compared to other bioceramics, such as bioglass or A-W glass–ceramic, is its chemical similarity to the inorganic component of bone and tooth. It exhibits no cytoxic effects and shows excellent biocompatibility with hard tissues, skin and muscle tissues [5]. Due to these, HA has been applied clinically both as a dense, sintered material and as a coating on metallic implants [6,7]. In recent years, with the rapid development of the research of the nanometer HA material, the researchers also have a further understanding of the characteristic of HA, and have developed many new ways of using the nanometer HA, such as orthopedic, drug release, biomolecules separation, etc.

The shape of HA crystal can affect many characteristics of HA, such as surface characteristics, bioactivity and so on. Therefore, if we can control the crystal shape of the nanometer HA, such as needle-like, spherical, plate-like shape and so on, then we can expand the applications of the HA.

At present many studies have reported to synthesize the nanometer HA with different shapes. For example, the needle-like HA has been synthesized by different processing methods including organic gel systems, homogeneous precipitation or hydrothermal technology [8,9]; the rod-like HA has been synthesized by precipitating calcium nitrate tetrahydrate and ammonium dibase phosphate in the presence of polyacrylic acid followed by hydrothermal treatment [10]. However, the synthesis of the spherical nanometer HA by biomimetic method was rarely reported so far.

Polyethylene glycols (PEG) are polymers from oxyethylene polymerization, which are amphipathic and biocompatible polyethers widely used for biomedical research and applications [11]. On the other hand, PEG in aqueous solution are highly mobile molecules with large exclusion volume, and mainly free of charges which can avoid the strong interaction between the constituents [12]. A significant number of studies have reported that the presence of PEG can modify or control

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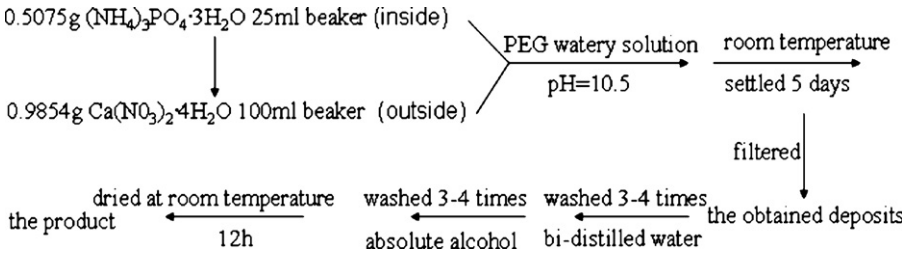

Fig. 1. Schematic illustration of the process followed for preparation of sample.

the surface of the nanometer crystal, moreover can act as the dispersing agent of the nanometer crystal in the process of synthesis [13–15].

This study takes $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_3PO_4{\cdot}3H_2O$ as reagents to successfully synthesize the spherical nanometer HA in the presence of a certain concentration(2–6%) of PEG by biomimetic method, and it provides one new method to change the crystal habit of HA. At the same time the correlation of the crystal shape of the nanometer HA and the concentration of the PEG is also investigated. According to this correlation, the spherical nano-hydroxyapatite, whose size is about 30–50 nm, can be synthesized in the presence of a certain concentration of the PEG by biomimetic method.

2. Materials and experimental methods

2.1. Materials

Polyethylene glycol (MW6000), $(NH_4)_3PO_4{\cdot}3H_2O$ (AR), $Ca(NO_3)_2{\cdot}4H_2O$ (AR), absolute alcohol (AR) and ammonia solution (AR), which were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanhai, China) were used as the initial chemicals.

2.2. Preparation of the samples

First, 0.9854 g $Ca(NO_3)_2{\cdot}4H_2O$ was spread at the bottom of a 100 ml beaker; at the same time, 0.5075 g $(NH_4)_3PO_4{\cdot}3H_2O$ was spread at the bottom of a 25 ml beaker. The preparation of the sample is based on the following reaction equation with Ca/P molar ratio of 1.67, which was standard stoichiometry for pure HA [16]:

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- = Ca_{10}(PO_4)_6(OH)_2$$

Then, the 25 ml beaker was put inside the 100 ml beaker just above the bottom of the 100 ml beaker. The mass percent concentration of PEG watery solution is respectively 0.00, 0.01, 0.10, 1.00, 2.00, 3.00, 4.00, 5.00 and 6.00% (the pH of the PEG solution was adjusted to 10.5 by the addition of NH_3 solution), which was slowly dripped into the 25 ml beaker using the fixed isopiestic-pressure-funnel until the 25 ml beaker was full. Then, the PEG solution was dripped into the 100 ml beaker at the same way until the outside liquid level almost reached the inside liquid level. After the whole system was kept still for 5 min to let calcium ions react with PEG, PEG solution was dripped again until the liquid level was 5 mm higher than the height of the 25 ml beaker. The big beaker was sealed with the preservative film and settled for 5 days under room temperature. The obtained deposits were washed 3–4 times by bi-distilled water and the absolute alcohol, respectively. The obtained deposits were filtered, then dried at room temperature for 24 h. The schematic illustration of the process followed for preparation of samples is shown in Fig. 1.

2.3. Characterization of the samples

The morphologies of as-prepared samples were observed by Hitachi 600 Transmission Electron Microscopy (TEM). The surface composition and structure of as-prepared samples were determined by using X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Phases identification was achieved by comparing the diffraction patterns of HA with ICDD (JCPDS) standards. Philips X'Pert MPD diffractometer with Cu Kα radiation was used, the X-ray generator was operated at 40 KV; and 40 mA. Date sets were collected within the range of 5–90° with a step size of 0.02° and a count rate of 3.0 °/min. FTIR spectra were obtained by using Nicolet Avatar 360 spectrometer. Spectra were obtained at 4 cm^{-1} resolution averaging 64 scans. The electrical conductivity was determined by the conductometer DDS-11A (Shanghai, China). The pH values of the PEG solution were measured using a digital pH meter (828, Orion).

3. Results

3.1. The crystal shape of the obtained products

Fig. 2a–h are the TEM micrographs of the samples which were synthesized using $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_3PO_4{\cdot}3H_2O$ as reagents with or without PEG. Fig. 2a is the TEM micrograph of the sample which was synthesized in the absence of PEG, the granules agglomerate seriously, and the shape of the samples is mainly the shape of floccule. Fig. 2b and c are the TEM micrographs of the samples which were synthesized in the low concentration of PEG (lower than 1%), as shown in figure, most of the particles are spherical, some are small needle-like. Fig. 2d–g are the TEM micrographs which were synthesized in the high concentration of PEG. As shown in Fig. 2d–f, with increasing the concentration of PEG (2–4%), the shapes of particles are mainly spheroid, but the edge of the granules is not very smooth. When the concentration of PEG is high than 5%,