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Rapid synthesis of citrate-zinc substituted hydroxyapatite using the ultrasonication-microwave method

Zhenyu Zhong^a, Jinli Qin^a, Jun Ma^{a,b,*}^a Advanced Biomaterials and Tissue Engineering Center, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China^b Department of Biomedical Engineering, College of Life Science & Technology, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

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ABSTRACT

Bio-inspired citrate-hydroxyapatite (HAP) nanoparticles doped with zinc ions were prepared from mussel shells via a rapid method of ultrasonication and microwave irradiation. It was found that zinc ions can interact with citrate ions in the crystallization process of HAP. The growth of nanocrystals in citrate solution was slower than that in HCl solution. The addition of zinc ions reduced the residue of citrate in the products and increased the crystallinity of HAP. Furthermore, mineral platelets with the length of 29 ± 7 nm and the thickness of 3–5 nm were obtained for Zn/(Zn+Ca) = 5 mol%, which displayed similar morphology with HAP platelets in bone. Moreover, the obtained HAP nanoparticles are promising for use as bone graft materials in biomedical applications.

1. Introduction

Hydroxyapatite (HAP) is the main mineral component of bone and teeth, and it is widely used as biomaterials in orthopedics and dentistry due to its high biocompatibility [1–4]. The biomimetic synthesis of HAP by mimicking the mineralization process has been extensively studied [3,5]. It is known that besides protein templates such as collagen, some small acidic molecules play important roles in the nucleation and crystal growth of HAP because they could interact with calcium ions and form calcium phosphate clusters in the early stage of mineralization [6,7]. As an acidic molecule represents about 2% weight of bone, citrate remains a debated role in the formation of bone [8]. Citrate ions could increase the maturation time, induce the platy morphology of amorphous precursor and control the thickness of nanocrystals during the formation of nanocrystal HAP [9]. The studies through nuclear magnetic resonance (NMR) proved that strong interactions exist between HAP and citrate molecules [10]. It was reported that the citrate anions could bridge the HAP platelets and regulate the assembling process of minerals in bone [8].

HAP nanocrystals doped with cationic ions have been extensively studied because the ionic doping can endow HAP special properties [3,11]. Zinc is one of the essential trace elements in human body, which plays a vital role in bone formation [12]. In the mineralization process, zinc ions could be doped in HAP by substitution of calcium ions [13,14]. Zinc substituted HAP (ZnHAP) possesses anti-microbial

property [15,16], immunomodulatory [17] and improved bioactivity [18]. Zinc ions could also interact with the template molecules in biomimetic mineralization process. It was reported that zinc ions could regulate the formation of HAP crystals when silk fibroin was used as template, which changed from rod-like nanoparticles into large sheets with a width of several hundred nanometers with the doped zinc ions [19]. It was suggested that the interaction between zinc ions and carboxyl groups on the template molecules influenced the growth and assembling process of HAP nanocrystals. Accordingly, the divalent cations interact with the acidic molecules in the biomimetic environments, which influence the formation of HAP platelets and their assembling process into microscale structures in the process of biomineralization [3,20]. In addition, the three carboxyl groups of citrate could strongly bind to the surface of HAP crystals in bone and regulate the formation of thin nanocrystal HAP [10].

Some natural materials, such as egg shells [21] and mussel shells [22], contain high amount of calcium carbonate, which are good candidates to be utilized as calcium sources for producing HAP based nanomaterials. It was reported that HAP generated from biogenic sources could be better accepted by living organs [23]. According to the principle of green chemistry, the calcium-containing mussel shells, as abundant bio-wastes in fish industry, can be very useful as calcium source for the synthesis of HAP. Mussel shells consist of 95–99% aragonite [24]. After the calcination treatment, aragonite is converted to calcium oxide. The calcium-containing solution can be facilely

* Correspondence to: Life Science Building, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, People's Republic of China.
E-mail address: caltary@gmail.com (J. Ma).

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prepared by dissolving the calcined shells in acids [25]. In this study, citric acid (CA) was used to dissolve the calcined shells and HCl was used for comparison. For accelerating the formation of HAP nanoparticles, a combination of ultrasonication and microwave irradiation was adopted in the mineralization process. During the formation of HAP nanocrystals, ultrasonication can control the homogeneity of crystal nucleation and growth, and the microwave irradiation can shorten the processing time [22,25].

The aim of this study is to investigate the effects of zinc ions on the formation of citrate-HAP (CA-HAP). We hypothesize that the citrate ions interact with both Ca^{2+} and Zn^{2+} ions during the mineralization process and such interaction interferes with the formation of nanocrystal HAP. ZnHAP was prepared by replacing 2% and 5% calcium ions with zinc ions in the synthesis. The phase, morphology and structure of the produced powders were characterized using X-ray fluorescence (XRF) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transforms infrared (FT-IR) spectroscopy and thermal gravity analysis (TGA).

2. Materials and methods

2.1. Materials

The mussel shells were collected from Poyang Lake, China. The shells were cleaned and dried in an oven at 80 °C for 3 h. The crushed dried shells were weighed and then heated in a furnace at 900 °C for 2 h. Calcium carbonate (aragonite) in the shells was converted to calcium oxide after the calcination and the weight loss was measured to be about 44% [22]. The obtained calcium oxide was used for the following experiments. The other chemical reagents of chemical purity grade were purchased from the local vendors. De-ionized water was used in the preparation.

2.2. Preparation of HAP and ZnHAP

The calcined shells (CaO, 0.56 g) were dissolved in 30 mL 1 M CA solution. Subsequently, 70 mL water was added and 100 mL 0.06 M Na_2HPO_4 solution was added slowly. The reaction was conducted in a 75 °C water bath under ultrasonication and consistent stirring at a speed of 350 rpm. The pH value was adjusted to 9.5–10.5 using NaOH. After 30 min, the obtained slurry was treated in a domestic microwave oven for 10 min at 700 W. The slurry became blurry and the precipitate was separated by centrifugation at 9000 rpm for 15 min. After centrifugation, the supernatant was discarded and the precipitate was re-suspended with de-ionized water. The product was washed twice and the dispersion was freeze-dried to produce CA-HAP powders. CA-ZnHAP-2% and CA-ZnHAP-5% were prepared by replacing calcium oxide using zinc nitrate with the Zn/(Zn+Ca) molar ratio of 2% and 5%, respectively. For comparison, 1 M HCl instead of CA was used to prepare HCl-HAP and HCl-ZnHAP-5%.

2.3. Characterization

The Zn/(Zn+Ca) molar ratios in the powder samples were measured by X-ray fluorescence (XRF, EAGLE III, EDAX, USA) spectroscopy. X-ray diffraction spectra were recorded on an XRD-7000 diffractometer (Shimadzu, Kyoto, Japan) in 2 θ angle between 10° and 80° with Cu-K α radiation. The crystalline phase was determined by comparing XRD patterns with the standard data (PDF no. 09-0432). The TEM samples were prepared by dispersing the freeze-dried powders in ethanol and subsequently applying on copper grids with carbon films. The samples were examined on a TEM G2 (FEI, Holland) at a voltage of 200 kV. Selected area electron diffraction (SAED) was done on the same machine. The morphology of the samples was observed on a field emission scanning electron microscope (SEM,

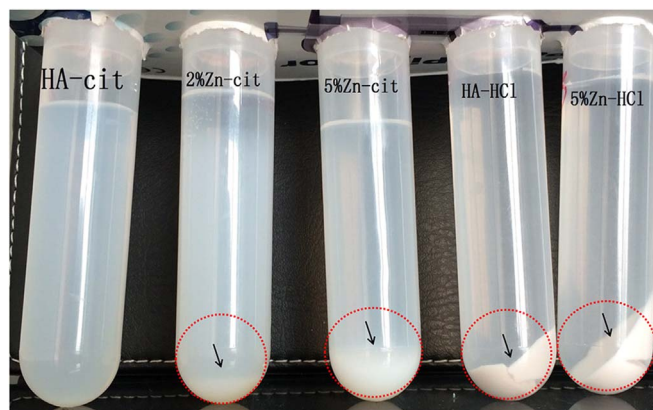


Fig. 1. The reaction slurries after centrifugation.

Nova NanoSEM 450, FEI, Holland) using an accelerating voltage of 10 kV and a working distance of about 6 mm. All of the samples were placed on a double-sided adhesive tape and gold sputter coatings were applied to avoid charging. The FT-IR spectra were obtained on VERTEX 70 (Bruker, Ettlingen, Germany) in the wavenumber range of 4000–400 cm^{-1} using the compressed pellets mixed with KBr. TGA and differential thermal analysis (DTA) were carried out on a Diamond TG/DTA system (PerkinElmer, Waltham, MA, USA) purged with nitrogen gas at 100 mL/min and the temperature increased from room temperature to 900 °C at a rate of 10 °C/min.

3. Results

3.1. Mineralization process

Citrate can strongly bind to the surface of nanocrystal HAP in solution and regulate the morphology evolution [26]. Divalent cationic doping in HAP can also be influenced by citrate [27]. As shown in Fig. 1, for CA-HAP without doping zinc ions, the obtained slurry after the microwave irradiation looked like colloid and it was difficult to separate the mineral particles through centrifugation and/or filtration. Furthermore, the amounts of precipitates were obviously different after centrifugation in the same condition. The amounts of precipitate from the three samples prepared using CA were much fewer than the other samples using HCl. The freeze-dried CA-HAP powder was quite sticky, which suggested that a high residue of citrate existed. As observed by Martins et al. [28], the absorbed citrate ions on the crystal facets of HAP would give rise to electrostatic inhibition of rectangular facet-to-facet particle aggregation. In the modified synthesis procedure, we added ethanol in the slurries to facilitate separation of nanoparticles and the amounts of freeze-dried final powders in each group were almost the same.

According to the XRF measurements, the Zn/(Zn+Ca) molar ratio in CA-ZnHAP-2% was 2.3% which indicated that zinc ions were successfully incorporated into the products. The Zn/(Zn+Ca) molar ratio was 4.4% in CA-ZnHAP-5% and 6.1% in HCl-ZnHAP-5%, respectively. It was suggested that the zinc substitution ratio was influenced by the addition of citrate.

3.2. Morphology by SEM and TEM

The synthesis process aided by ultrasonication and microwave irradiation in the precipitation of HAP has very high heating rate and fast reaction, so HAP nanoparticles with uniform crystal size could be obtained [22,25]. From the TEM images as shown in Fig. 2, the samples prepared using HCl were flake-shaped nanoparticles with good dispersity. The size of HCl-HAP particles was measured to be approximately 62 ± 15 nm in length with irregular shapes. In comparison, the HCl-ZnHAP-5% nanoparticles changed to flakes with a length of 90 ± 30 nm, which were seriously agglomerated. The agglomerates were

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