

Characterization, physicochemical properties and biocompatibility of La-incorporated apatites

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Abstract

In this study, the physicochemical properties and biocompatibilities of La-containing apatites were intensively investigated together with their characterizations in terms of composition, structure, valent state and morphology using X-ray diffraction, Fourier-transform infrared spectra, X-ray photoelectron spectroscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy, respectively. The results indicate that the La^{3+} ion can be incorporated into the crystal lattice of hydroxyapatite resulting in the production of La-incorporated apatites ($\text{La}_x\text{Ca}_{10-x}(\text{PO}_4)_6(\text{OH})_{2+x-2y}\text{O}_{y-x}$ ($x \leq 0.5$, $y < 1 + x/2$) or $\text{La}_x\text{Ca}_{10-x}(\text{PO}_4)_6\text{O}_{y-x}$ ($0.5 < x < 2$, $y = 1 + x/2$)) by high-temperature solid phase synthesis. For La content $< 20\%$, the product is composed of the major phase, La_xOAP , as well as a small amount of tricalcium phosphate, but for a La content of 20% , the product is pure La-incorporated oxyapatite with the formula $\text{La}_2\text{Ca}_8(\text{PO}_4)_6\text{O}_2$ ($\text{La}_2\text{-OAP}$, $x = 2$, $y = 2$). It is also found that the La content plays important roles in both the physicochemical properties and biocompatibilities of the La-incorporated apatites. In contrast to La-free apatite, La-incorporated apatites possess a series of attractive properties, including higher thermal stability, higher flexural strength, lower dissolution rate, larger alkaline phosphatase activity, preferable osteoblast morphology and comparable cytotoxicity. In particular, the sintered La-incorporated apatite block achieves a maximal flexure strength of 66.69 ± 0.98 MPa at 5% La content (confidence coefficient 0.95), increased 320% in comparison with the La-free apatite. The present study suggests that the La-incorporated apatite possesses application potential in developing a new type of bioactive coating material for metal implants and also as a promising La carrier for further exploring the beneficial functions of La in the human body.

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1. Introduction

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HA), owing to its similarity to the inorganic phase of human bone and thus excellent bioactivity and biocompatibility, has become one of the most extensively researched and widely applied biomedical materials. In fact, biological apatite is not pure HA, but a non-stoichiometric HA with a general formula $\text{Me}_{10-x}\square_x(\text{PO}_4)_6-y$

$(\text{HPO}_4)_y(\text{OH})_{2-2x}\square_{2x}$ [1], where the Me/P atomic ratio can vary widely over the range 1.50–1.67. Also, in this formula, Me are often associated with a wide variety of trace ions such as Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , Na^+ , K^+ , Pb^{2+} , Zn^{2+} , Cu^{2+} , Fe^{3+} , etc.; PO_4^{3-} can be substituted by CO_3^{2-} , SiO_4^{4-} , $\text{P}_2\text{O}_7^{4-}$; and OH^- can be substituted by F^- and Cl^- [2–4]. It has been demonstrated that the incorporation of some of these ions instead of equivalent Ca^{2+} or PO_4^{3-} or OH^- into the apatite crystal lattice had significantly improved the physicochemical and biological properties of HA [5–9]. For example, introducing CO_3^{2-} [5] or SiO_4^{4-} ion [6] into the crystal lattice of HA is effective in improving its degradation rate. It is worthy of attention that the incorporation of Sr^{2+} into HA instead of equivalent Ca^{2+} in the form of Sr-incorporated HA bone cement exhibits preferable biocompatibility, better bioactivity,

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higher compressive strength and a faster biodegradable rate than conventional Sr-free HA bone cement [7–9].

Rare earth elements (REE) are one type of important strategic resource widely used in various fields, including industry, agriculture, medicine and daily life, but eventually accumulated in the human body. Naturally, the effects of REE on human health are increasingly the concern of scientists. REE, including all lanthanide elements could be found in bovine whole blood reference material at a wide concentration range of 0.90–1880 pg g⁻¹ [10]. In particular, lanthanum (La) is one of the most important REE widely researched in recent years. He et al. [11] evaluated the neurotoxicity of La by exposing Wistar rats to lanthanum chloride and found that La exposure played a dose-dependent role in brain functions. Huang et al. [12] investigated the effects of La on the femur bone mineral of male Wistar rats, and the result confirmed that La was finally accumulated in bone and would be lost with bone mineral degradation. More interestingly, La³⁺ promotes the formation of osteoclast-like cells and significantly increases the number and surface area of the resorption pits at the concentration of 1.00 × 10⁻⁸ mol l⁻¹, but inhibits bone-resorption activity at higher concentrations [13]. In addition, La³⁺ has also shown other beneficial functions, such as restraining the Ca pump of the human red cell [14], treating hyperphosphataemia [15], resisting or preventing cancer cells from defusing [16], depressing the release of insulin-like growth factor binding proteins (IGFBP) from cell types (>80% for GM10 and T98G cells and <65% for MDBK cells) [17] and mediating the effect on platelet function by decreasing the lipid fluidity of the surface membrane of human platelet [18]. Based on this existing research, the introduction of REE (especially for La) at controlled doses into some biomedical material or carriers could become one effective way to improve human health.

Naturally, one question would be raised: what will happen to the structure and properties of La-containing apatite after La is incorporated into its crystal lattice instead of equivalent Ca²⁺? It was reported elsewhere [19] that La element could be incorporated into the crystal lattice of HA, but the characterizations presented for the La-incorporated apatite are poor, and the investigations in physicochemical properties and biological properties are also few. Thus, the present study characterized La-incorporated apatites with various La content by combining multi-techniques, and initially investigated their physicochemical and biological properties, which were considered for two potential purposes (1) to test the possibility of improving clinical serving functions of HA (e.g., serving as a bioactive coating of metal implants) via La incorporation; (2) to develop a potential carrier of REE in the form of REE-incorporating apatite, through which the beneficial functions of these elements on human health would be further extended.

2. Materials and experiments

2.1. Starting materials and synthesizing methods

The La-incorporated apatites with La content (i.e., the molar ratio of La/(Ca + La)) of 5%, 10% and 20%, respec-

tively, were synthesized from a series of stoichiometric mixtures composed of calcium carbonate (CaCO₃), diammonia hydrogen phosphate ((NH₄)₂HPO₄) and lanthanum oxide (La₂O₃) through a high-temperature solid-state reaction. As a control, the La-free apatite was prepared by a similar method, but its precursor consisted of only CaCO₃ and (NH₄)₂HPO₄ in a stoichiometric mixture. The sintering steps and parameters shown in Table 1 are similar to those of Series A reported elsewhere [19]. The heating units of the high-temperature furnace were silicomolybdc rods. For the purpose of accelerating the solid-state reaction dominated by a diffusion mechanism, before sintering the stoichiometric mixtures were first refined by a ball-milling process with a liquid medium of absolute ethyl alcohol. The dosage of liquid medium used here was 30 ml in volume per 50 g raw powder. The materials of the milling ball and vial were alundum (Al₂O₃) and nylon, respectively, where the milling balls used for each milling include 100 smaller balls with a diameter of 5 mm, and 15 larger balls with a diameter of 10 mm, and the capacity of the vial was 200 ml in volume. The total mass and the mean size of the raw powders were 50 g and 30–50 μm, respectively, and the rotation rate was 400 rpm. The apparatus used was planet ball-milling machine (QM-1SP, Nanjing University Instrument Corp., China). After sintering, the products were crushed and then wetly ball-milled again for 24 h. The mean size of the final ground powder particles was in range 2.71–3.93 μm, determined by a laser particle analyzer (JL9200, Jinan Weina Device Ltd. Corp., China).

2.2. Flexural strength measurements

A standard three-point flexural test with a span of 20 mm was used to fracture the specimens at a cross-head speed of 0.5 mm min⁻¹ on a computer-controlled high-frequency all-purpose fatigue testing machine (100HFP5100, Zwick/Roel Corp., German). The samples for testing flexural strength (FS) were processed as follows: first, the as-prepared powders were pressed into the quadrate blocks of width 5 mm, height 4 mm and length 45 mm, where the pressure used for each pressing was 20 MPa, and polyvinyl alcohol with a suitable dosage was used as the additive for easy pressing; secondly, the pressed samples were sintered at 1500 °C for 2 h, followed by an in situ cooling process in a furnace. During testing, the loading–displacement curve was recorded on a computer. A mean FS value was determined from at least six samples under

Table 1
Sintering steps and parameters of La-free and La-incorporated apatite with different La content.

La content (x, %)	1st step	2nd step
0	950 °C (2 h) + 1100 °C (48 h)	–
5	950 °C (2 h) + 1100 °C (48 h)	+1200 °C (24 h)
10	950 °C (2 h) + 1100 °C (48 h)	+1200 °C (60 h)
20	950 °C (2 h) + 1100 °C (48 h)	+1450 °C (120 h)

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