

Fabrication of dense biocompatible hydroxyapatite ceramics with high hardness using a peroxide-based route: a potential process for scaling up

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Abstract

In this research, nanosized hydroxyapatite (HA) ceramics with high hardness at moderate temperature were prepared using a novel peroxide-based route (PBR) using calcium nitrate, phosphoric acid and hydrogen peroxide as starting materials. Single-phase HA with an average particle size of approximately 10–30 nm and a BET surface area of 23.54 m²/g were obtained after calcination at 800 °C for 2 h. Dense HA ceramics with a density of 98%, a grain size of 0.91 μm and a Vickers hardness of 5.67 GPa were achieved after sintering the HA pellet at 1,200 °C. Their biocompatibility might be anticipated by SEM images of apatite layer formation after immersion in simulated body fluid (SBF) for 14 days. © 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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1. Introduction

Hydroxyapatite (HA) is an intriguing material because it can be used in interdisciplinary fields such as chemistry, biology and medicine. Although hydroxyapatite is a major component of bone and is usually used as artificial bone [1–3], this material also acts as an effective photocatalyst [4]. However, there have been some restrictions to its practical utilization, for example, the still low biocompatibility for artificial bone and low efficiency of photoactivity. Therefore, the fabrication of HA for practical use using novel methods has gained much attention. Recently, several novel preparation processes for HA have been reported but with some drawbacks, e.g., low strength and toughness of the HA, [5] a high sintering temperature being required and the reduction of the biocompatibility due to a CaO impurity phase. Therefore, developing a state-of-the-art synthetic process of nanosized HA using a simple method might be a breakthrough in HA development as

the high surface energy of the nanostructured material would affect the sinterability, mechanical properties and biocompatibility [5].

There are several methods for the preparation of hydroxyapatite; however, each method has some disadvantages as an industrial process; for example, although simple and clean precursors of solid-state reaction are normally utilized, a large particle size and high temperature is needed [6]. In the sol–gel synthesis of HA, numerous carbon compound chemicals, e.g., alkoxides, need to be used, and a long aging time would be necessary to obtain a pure phase [7]. The precipitation process is simple and more practical; however, in general, the particle size of HA is large compared with sol-gel or nanoscale particles [4,8]. The hydrothermal method is dominant in obtaining characteristic morphology and texture; however, specific equipment is needed [9]. In addition, other chemicals, such as a reaction flux e.g., a reverse micelle surfactant [5] or polymer [10], are needed for some processes to improve the physical properties of HA.

Hydrogen peroxide is usually involved in biochemical processes, and some articles have reported the advantage of mixing H₂O₂ with HA; for example, a contribution of incorporated hydrogen peroxide into calcium phosphate was observed to reduce

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the kinetic complexity of the organic phase [11]. However, studies of the effect of H_2O_2 as mentioned above normally focus on the post-treatment of HA with H_2O_2 .

Therefore, a peroxide-based route was utilized in this work to validate the effect of H_2O_2 on the characteristics of HA.

The peroxide-based route has been attributed to the reduction of the calcination temperature in the preparation of complicated titanate compounds. $BaTi_2O_5$ can be obtained after firing the precipitated powder from the reaction of peroxotitanate with citric acid at 800 °C. Similarly, $PbTiO_3$ has been successfully synthesized at reduced temperatures (500 °C) using an organic and chloride-free peroxy precursor [12]. The chemical composition is easily controlled in the peroxide-based route, as reported in the strontium titanate family, $SrTiO_3$, Sr_2TiO_4 , $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ [13]. In addition to titanate compounds, the peroxide-based route has also been successful in the synthesis of high-surface-area (up to 275 m^2/g) nanoparticle Nb_2O_5 by peptized peroxy niobic acid [14].

The reduced calcination temperature and kinetic complexity and simple and green method of the peroxide-based route would be suitable for a scale-up process for nanosized HA production.

2. Methods

Nanohydroxyapatites were prepared using a simple, clean, fast and easy-to-scale method. Calcium nitrate tetrahydrate (Sigma Aldrich) 0.25 mol was dissolved in diluted hydrogen peroxide (Merck). A stoichiometric amount of orthophosphoric acid (RCL labscan) was then slowly added dropwise with continuous stirring into the calcium nitrate solution. White precipitates were obtained after adjusting the pH of the solution to pH 10 using ammonium hydroxide (J.T. Baker). The suspension was then continuously stirring for additional 30 min at ambient temperature. The white calcium phosphate compound powders were separated from the solution by filtering and washing with distilled water several times. Nanohydroxyapatites were obtained after drying and calcination at high temperature. Hydroxyapatite nanosized ceramics were obtained by sintering the calcined nanohydroxyapatites at 1,000–1,200 °C.

XRD data were collected using a Rigaku Mini Flex II X-ray diffractometer. The specific surface area of the powder samples was evaluated by nitrogen adsorption at 77 K using the Brunauer–Emmett–Teller (BET) method (Micromeritics TriStar II). Scanning electron microscopy and transmission electron microscopy were performed using a JEOL JSM-6335 F and JEOL JEM-2010 electron microscope, respectively. The density and porosity were obtained using Archimedes' principle. The Vickers hardnesses of the ceramics were determined using a STARTECH SMV-1000. Density measurements were performed using a GR-200 (Max 210 g, Min 10 mg). A mineralization study of the ceramics was performed with SBF for 14 days and the apatite layer formation was verified using SEM images.

3. Results and discussions

The DTA thermogram of as-prepared HA powders using the peroxide based route after filtering and drying contains two hardly observable peaks at approximately 100 °C and 400–700 °C, which might represent an endothermic reaction of water decomposition and an exothermic peak due to phase formation, respectively. The exothermic peak is consistent with the XRD spectra presented in Fig. 1, which shows that pure phase HA could be obtained at 500 °C.

The XRD patterns of the as-prepared white powder after drying and calcination at various temperatures reveal mainly the broad peak of the hydroxyapatite phase with tricalcium phosphate (TCP) and CaO as small additional peaks at low temperatures (Fig. 1). The intensity and crystallinity of the HA phase increase with increasing temperature, whereas the presence of TCP gradually decreases and disappears at 500 °C calcination. Notably, no CaO, which is a major impurity phase from the sol-gel method [8] can be detected at 500 °C. A probable explanation for why this stable impurity phase is not observed is that calcium peroxide (CaO_2) might be formed in the solution and would be an inhibitor of CaO formation because CaO_2 will decompose into calcium hydroxide and O_2 . The CaO_2 powders can be produced from the solution of $Ca(NO_3)_2$, H_2O_2 and NH_3 (Supplementary Fig. S1). It can be concluded that the peroxide-based route is an intriguing method for HA preparation as this approach is simple, clean, fast and easy to scale.

To clarify the advantages of the peroxide-based route, the co-precipitation method without any hydrogen peroxide addition was also examined for comparison. Using this method, TCP was observed after calcination at 800 °C, which is different from the results for the peroxide-based route. Some reports have observed that the reaction model of bone with H_2O_2 is complex, and H_2O_2 acts as a deproteinating agent, leading to the reduction of the

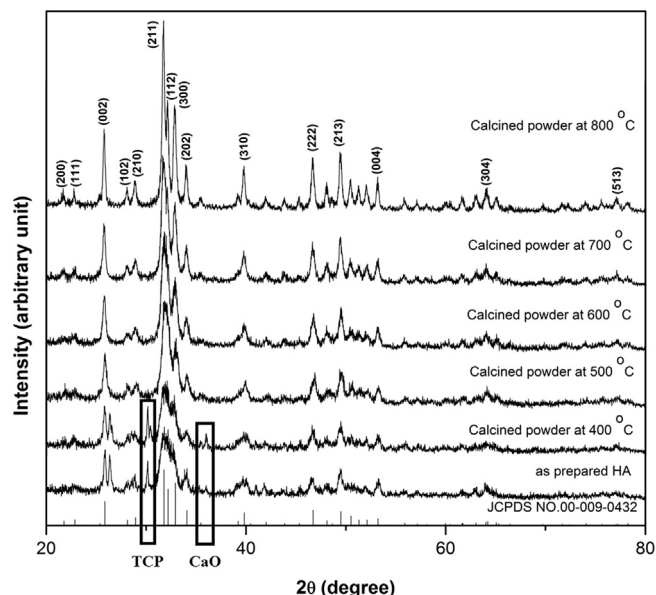


Fig. 1. XRD patterns of the as-prepared powder after calcination at various temperatures for 2 h.

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