

Characteristics and properties of hydroxyapatite derived by sol–gel and wet chemical precipitation methods

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Abstract

The synthesis of crystalline hydroxyapatite (HA) nanoparticles with expected microstructure is of primary importance because the process directly relates to the phase purity, morphology, and particle size of the final HA particles. In this work, different morphologies of HA powders were prepared via wet precipitation (HA–Wp) and sol–gel synthesis (HA–Sg) methods. The results showed that pure HA powders were successfully obtained via the two different methods, in which HA–Wp presented smaller crystallite size in accordance with the larger specific area compared with HA–Sg powders. A high surface area of $97.4 \text{ m}^2 \text{ g}^{-1}$ was obtained in HA–Wp powder, whereas that of HA–Sg powder was $9.0 \text{ m}^2 \text{ g}^{-1}$. Upon calcinations at 800–1000 °C, the calcined powders were found to be Ca-deficient apatites as HA–Wp and HA–Sg powders decomposed to the secondary phase of β -TCP at 900 °C and 1000 °C, respectively. Microstructural analysis showed significant difference in terms of HA morphologies produced via the two methods. The HA–Wp powder consisted of nanoscale needle-like structures with soft agglomerated particles, whereas HA–Sg powder exhibited nanoglobular-like structures with hard agglomerated particles. The characteristics of nanocrystalline HA powder obtained from wet chemical precipitation is known to exhibit high surface activity as a bone substitute material.

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1. Introduction

During the last several decades, HA [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] has attracted considerable attention for use in orthopedics and dentistry because of its structural and compositional similarity with natural bone. HA has been primarily used to form sintered body and polymer composites [1] as replacements for bone and periodontal defects [2,3], dental materials [3,4], and maxillo-facial implants [2]. In fact, its biocompatibility and ability to bond with surrounding tissues of HA have been experimentally

proven to be superior to any other biomaterial [5]. However, most synthetic apatites are formed via high temperature processes, resulting in a well-crystallized structure, which presents little or no activity toward bioresorption [6]. HA solubility increases from crystalline to amorphous and reduces crystal size, which are more advantageous in clinical applications [7]. Hence, in recent years, interest in the synthesis of nanosized HA with grain size less than 100 nm has increased because of its high surface activity and enhanced bioresorption [5]. Moreover, this ultrafine structure is similar to the mineral found in hard tissues and can readily promote osteointegration and subsequent bone tissue formation [5]. In addition, given its greater surface area, nanocrystalline HA exhibits improved

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sinterability at lower temperatures resulting in a high density body couple with enhanced mechanical properties [6–12] suitable for biomedical applications.

In HA synthesis, precise control of crystal growth presents the utmost challenge because it directly relates to the size and geometric shape of the final particles [5]. These primary characteristics are widely documented to majorly affect mechanical properties, biocompatibility, and bioactivity. For example, HA bioceramics with conventional microstructure cannot be used for load-bearing orthopedic and dental application because of their poor mechanical reliability [5]. Paz et al. [13] reported the formation of HA via biomimetic and wet chemical precipitation with spherical (~ 23 nm) and needle-like (~ 23 nm in width and ~ 62 nm in length) morphologies, respectively. They concluded that the morphology, crystallinity, and size distribution of the resulting nanoparticles were strongly dependent on the synthesis method. Evis and Webster [9] also found that crystalline HA with uniform morphology was obtained by increasing the ageing times to 100 h because the particles with non-uniform morphologies redissolve and recrystallize into a more ordered form during the ageing process. The authors also found that the morphology of the particles has an effect on the HA phase stability [9].

In general, the raw materials used to synthesize HA originate from commercial chemicals and natural sources. Naturally sourced HA involve extraction via heat treatment of animal cortical bones (bovine, pig, etc.) and natural waste (egg shell, clamshell) [14], as well as conversion from marine coral derivatives [15] to natural HA with acceptable porosity. HA preparation methods can technically be categorized into four groups, namely, dry methods (solid state synthesis, and mechanochemical method), wet chemistry methods (wet chemical precipitation, hydrolysis method, sol–gel, hydrothermal, emulsion method, and sonochemical method), high-temperature processes (combustion, pyrolysis), and combination procedures (hydrothermal–mechanochemical, hydrothermal–hydrolysis). Each method has been exclusively documented with their own advantages and significant results over the others. HA powders with various morphology, stoichiometry, and level of crystallinity can be obtained depending on the method of synthesis. Among these routes, wet chemistry methods, i.e., precipitation and sol–gel, present advantages of precise control over the morphology and size of the particles. Thus, these methods are the most promising for the synthesis of nanosized HA with expected morphology [5].

Wet chemical precipitation and sol–gel methods have been widely used to obtain HA with different particle morphologies. These methods have traditionally been used in the synthesis of materials for implants and are the part of the wet chemistry techniques. Sol–gel synthesis method involves the formation of a colloidal sol, which will subsequently turn into a gel [16]. This method requires no special energy conditions for the formation of the desired compound; thus, the synthesis of ceramic materials could be carried out at room temperature [16]. However, sol–gel synthesis requires a strict control of process parameters and an intimate contact mixing at molecular level (because of the slow reaction between Ca and P precursors in the sol phase) to obtain highly pure, nanosized powder with homogeneous composition. Meanwhile, wet chemical precipitation requires a special pH

value control condition for precipitation to occur because the degree of neutralization of phosphoric acid is pH dependent [5]. Moreover, the morphology (shape and size) of nanoparticles obtained via this method is highly sensitive to reactant addition rate [13], in which a lower addition rate of acid will result in a large particle size.

Therefore, although wet chemical precipitation and sol–gel methods have been classified as the simple routes employed in producing HA [17,18] and are able to produce high-purity HA [19], the production of HA nanoparticle with expected morphology via these method remain challenging mainly because of the raw materials used for synthesis.

This paper reports the comparison of the characteristics of nanocrystalline HA powders synthesized via wet chemical precipitation and novel sol–gel synthesis by using different raw materials. The different morphologies and size of powders obtained were evaluated via various physico–chemical techniques, such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM) analyses. In addition, the thermal stability of synthesized powders upon calcination was also studied via XRD analysis.

2. Experimental procedures

2.1. Powder synthesis via wet chemical precipitation

Pure HA powder was produced via a simple wet chemical precipitation method [20]. Calcium hydroxide, $\text{Ca}(\text{OH})_2$ (98% purity, R&M Chemicals), and orthophosphoric acid, H_3PO_4 (85% purity, Merck), were used as Ca and P precursors with a molar ratio of 10:6. Initially, 0.6 mol of H_3PO_4 (400 mL) was added dropwise (9 drops to 10 drops per 10 s) into 1.0 mol of $\text{Ca}(\text{OH})_2$ solution (750 mL) with vigorous stirring. During the titration process, the pH of the mixture was monitored and maintained above 10.5 by adding ammonium (NH_3) solution (85% concentration, J. T. Baker). Once titration was completed, the solution was continuously stirred for a at least another 5–6 h. The precipitate was then left for ~ 12 h at room temperature before being filtered and washed using distilled water. The filtered precipitate was dried in an oven at 60°C for 24 h. The dried cake was then crushed and sieved to obtain well-defined HA powder, hereafter referred to as HA-Wp powder.

2.2. Powder synthesis via sol–gel synthesis

Sol–gel synthesis was also employed to synthesize HA by using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and di-ammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) as starting precursors. Ethylenedinitrilotetraacetic acid (Titriplex II) was used as the chelating agent to prevent immediate precipitate formation, and urea was used as a gelling agent. A 500 mL portion of ammonium solution (25% solution, Merck) was used to alter the pH. Initially, 0.6 mol Titriplex II was dissolved in ammonia solution at 60°C with vigorous stirring. An aqueous solution of 0.5 mol $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.3 mol $(\text{NH}_4)_2\text{HPO}_4$ were then added into the Titriplex suspension, followed by adding 0.75 mol urea. The mixture was subsequently

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