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Effect of metal-ion-to-fuel ratio on the phase formation of bioceramic phosphates synthesized by self-propagating combustion

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Abstract

Synthetic calcium hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is a well-known bioceramic material used in orthopedic and dental applications because of its excellent biocompatibility and bone-bonding ability due to its structural and compositional similarity to human bone. Here we report, for the first time, the synthesis of HAP by combustion employing tartaric acid as a fuel. Calcium nitrate is used as the source of calcium and diammonium hydrogen phosphate serves as the source of phosphate ions. Reaction processing parameters such as the pH, fuel-oxidant ratio and autoignition temperature are controlled and monitored. The products were characterized by powder x-ray diffraction, which revealed the formation of a hexagonal hydroxyapatite phase. Fourier transform infrared spectroscopy (FT-IR) spectra showed that the substitution of a carbonate ion occurs at the phosphate site. The morphology of the particles was imaged by scanning electron microscopy, which also revealed that the particles are of submicron size. Thermal analysis showed that the phase formation takes place at the time of combustion. Surface area and porosity analysis showed that the surface area is high and that the pores are of nanometer size. The mean grain size of the HAP powder, determined by the Debye–Scherrer formula, is in the range 20–30 nm. Chemical analyses to determine the Ca : P atomic ratio in synthesized ceramics were performed, and it was found to be 1 : 1.66.

Keywords: hydroxyapatite, bioceramic, tricalcium phosphate, tartaric acid

1. Introduction

Hydroxyapatite is a member of the apatite family and has almost the same chemical composition as human bone. Because of its biocompatibility and osteoconductive [1] properties, it has many biological applications including as a bone graft substitute [2, 3], a sustained-release drug delivery device [4] and for protein purification. However, biological apatite differs from pure and synthetically produced calcium hydroxyapatite (HAP) in terms of stoichiometry, composition, crystallinity and other physical and mechanical properties.

Therefore, the synthesis of biomimetic hydroxyapatite is being intensely studied by various groups [5–9].

Self-propagating combustion synthesis (SPCS) is a rapid and energy-saving technique often used [5, 6, 10] for the preparation of metal oxides. During combustion metal nitrates act as conventional oxidants and organic compounds function as fuels. SPCS is an exothermic redox reaction associated with nitrate decomposition and fuel oxidation, which releases an enormous amount of heat energy. The nature of the fuel and the ratio of oxidizer to fuel control the exothermicity of the combustion.

It has been reported that carboxylic acids such as citric acid [5, 6], succinic acid [7], sucrose [8] and urea [9] can be used as fuels to synthesize hydroxyapatite by SPCS. Thongtem *et al* [11] synthesized LiNiVO_4 by this method using tartaric acid as a fuel. They reported that the particle sizes are in nanometer regime, whereas the same material prepared using citric acid [12] with starch [13] as a complexing agent does not form nanocrystalline products. Lithium, being an alkali metal, forms a complex with tartaric acid. In this work, we have synthesized hydroxyapatite in nanocrystalline form using calcium, which is an alkaline-earth metal and also can form a complex with tartaric acid. We produced submicron-size particles of hydroxyapatite with uniform morphology. The effect of the metal-ion-to-fuel ratio on phase formation has also been investigated.

2. Experimental work

2.1. Synthesis

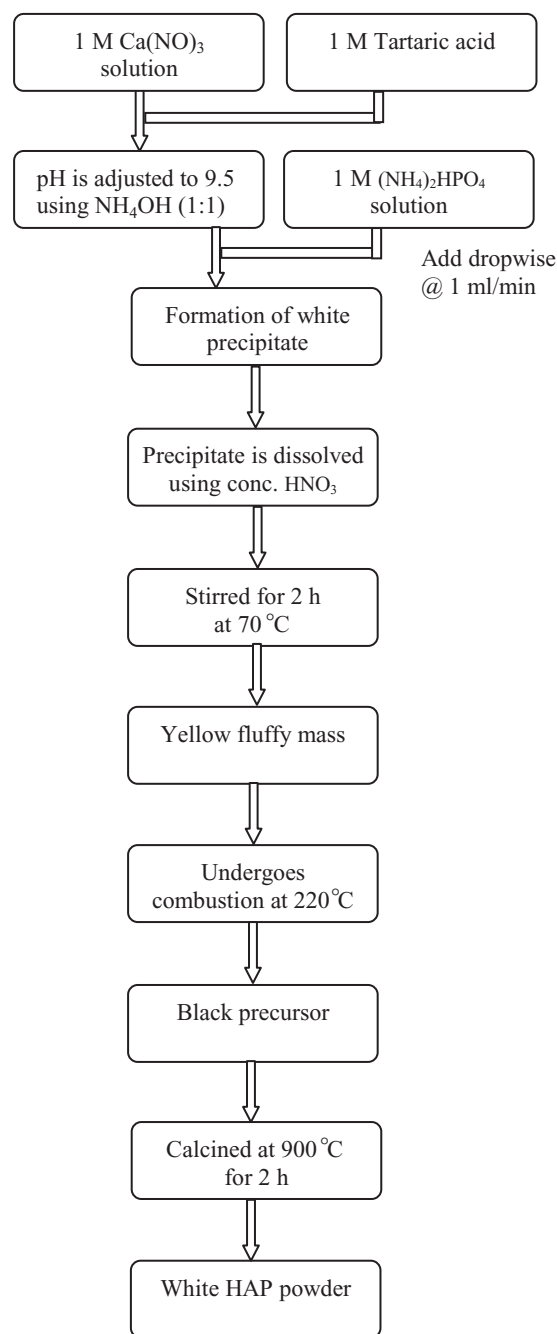
An equal volume of 1 M calcium nitrate solution was added to 1 M tartaric acid followed by thorough mixing using a magnetic stirrer. The pH of the solution was then adjusted to 9.5 by adding NH_4OH and water in a 1:1 ratio. A stoichiometric amount of 1 M $(\text{NH}_4)_2\text{HPO}_4$ solution was added to the above mixture and the precipitated mixture of phosphates was dissolved by adding concentrated HNO_3 until the pH became 1. The resultant solution was heated to 70°C and stirred until a transparent gel was formed. The gel was placed on a hot plate and the temperature was increased gradually until the gel ignited. The precursor that formed was calcined at 900°C for 2 h, which resulted in a pure white microcrystalline hydroxyapatite sample referred to as TT1. The procedure was repeated with a metal-ion-to-fuel ratio of 1:2 and the sample was named TT2 (refer flow chart).

2.2. Characterization

The phase purity of the synthesized hydroxyapatite samples was analyzed using a Philips D-500 x-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation. The chemical nature and molecular bond structure of the synthesized samples were determined by FT-IR studies (Thermo Nicolet, Avatar 330 FT-IR spectrometer, USA). The particle size and surface morphology was imaged using a scanning electron microscope (Jeol, JSM – 5600 LV). The Brunauer–Emmett–Teller (BET) technique was used to analyze the specific average surface area of the hydroxyapatite powders calcined at 700 and 900°C using a fully automated BET surface area analyzer (Micromeritics ASAP2020). The thermal analysis of the charred gel was carried out at a heating rate of $20^\circ\text{C min}^{-1}$ in air from room temperature to 1000°C using a thermal analyzer (V8.2 SDT Q600, TA Instruments, USA).

3. Results and discussion

The rate of the combustion reaction depends on the ligand groups of the molecule and the compositional ratio of fuel to



Flowchart for the Synthesis of Microcrystalline Hydroxyapatite.

metal nitrate. Therefore, the reactivity and the product phases formed by calcium nitrate with tartaric acid were investigated.

Tartaric acid plays a dual role in the synthesis; it functions as a chelating agent and prevents the precipitation of ions. A large amount of heat is released during the combustion of tartarate gel, which produces intense local heating that assists the formation of hydroxyapatite. The addition of ammonium hydroxide and nitric acid promotes the formation of ammonium nitrate, which increases the heat of combustion.

The addition of tartaric acid to aqueous calcium nitrate solution produces a colorless calcium tartarate solution, which upon the further addition of the phosphate source and nitric

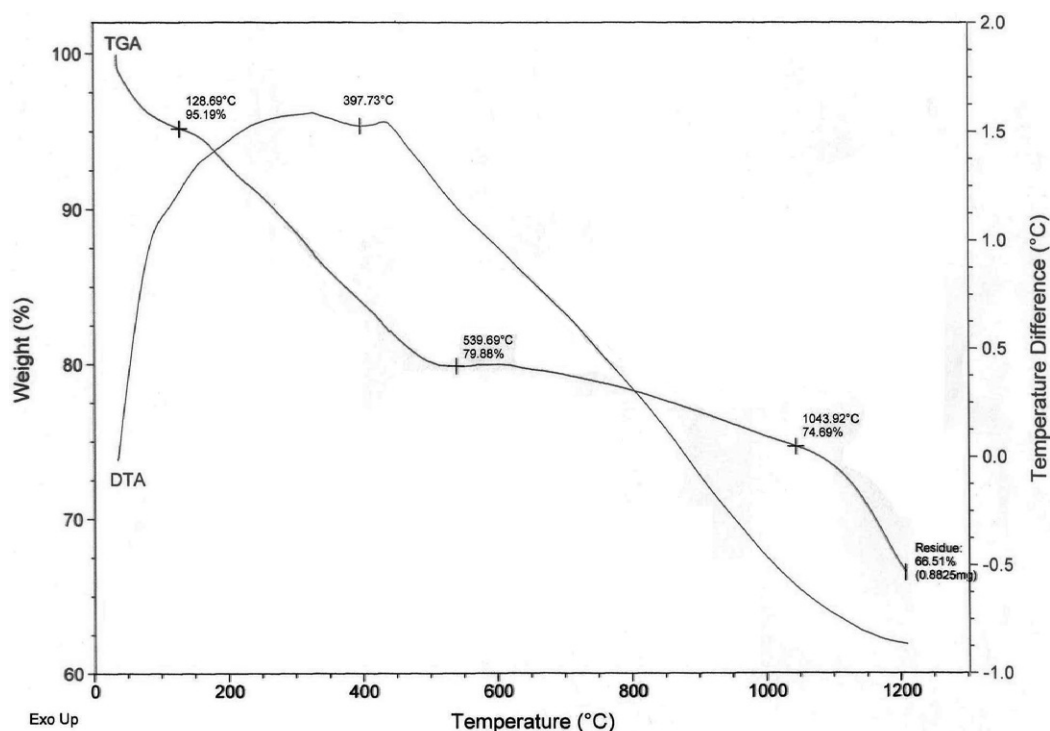


Figure 1. TGA/DTA curves of precursor synthesized using a metal-ion-to-fuel ratio of 1 : 2.

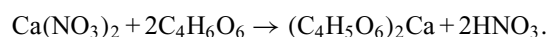
acid forms a gel network of calcium–tartarate–phosphate at a temperature of 80 °C. The transparent gel, which undergoes autoignition at 220 °C, forms a black precursor with the evolution of a large amount of gases. The evolution of dark yellow fumes before ignition indicates the formation of nitrogen dioxide due to the oxidation of the gel matrix by nitrates. The swelling of the gel before ignition is due to the evolution of carbon dioxide produced by the decomposition of tartaric acid.

The temperature was measured using a thermometer until the gelation occurred. When the gel started to decompose, a thermocouple mounted close to the surface of the gel was used to measure the temperature during combustion. For all samples, the transformation of the solution to the gel state took approximately 2 h and the time necessary for the gel to reach the autoignition temperature was about 20 min. The combustion reaction took place within 1–2 min depending on the fuel ratio. The temperature increase of 70 °C (from 220 to 290 °C) during combustion showed that intense local heating occurs during combustion, which may promote the phase formation in the precursor obtained after combustion.

Thermal analysis (figure 1) was performed for the precursor obtained after the combustion of the gel that was used to form TT2 to determine the phase transformation and the reaction enthalpies. The precursor showed a significant weight loss in the temperature range of 50 to 540 °C, which is mainly due to the decomposition of organic precursors, followed by further weight loss (5%) between 540 and 1000 °C due to the removal of residual carbon. The broad exotherm seen in the DTA plot (figure 1) between 50 and 500 °C is due to the oxidation of the

decomposed tartarate–calcium–phosphate gel (carbonaceous product) present in the precursor. As there is no organic substance remaining to undergo combustion, there is no sharp exothermic peak in the DTA plot, showing that the crystallization of the calcium phosphate phase took place during the combustion of the gel because the local temperature attained was very high.

The XRD patterns of both TT1 (figure 2(a)) and TT2 (figures 2(b) and (c)) show sharp and well-defined XRD peaks characteristic of hydroxyapatite. It was found that TT1 has β -TCP as a secondary phase and that TT2 is single-phase. The formation of the β -TCP phase in TT1 may be either due to the inhomogeneous distribution of calcium and phosphate ions in the gel matrix or due to the difference in energetics. However, the former reason is more likely because the ratio of metal ions to phosphate ions determines the formation of hydroxyapatite. The stoichiometry of the reaction between calcium nitrate and tartaric acid indicates that each mole of calcium ions requires two moles of tartaric acid to form calcium tartarate, as given below.



If the ratio of metal ions to tartaric acid is 1 : 1, then 50% of the calcium nitrate will not complex with the tartaric acid and will remain as calcium nitrate. This may lead to the formation of an inhomogeneous distribution of calcium and phosphate ions in the gel matrix, leading to the formation of a β -TCP phase as an impurity. The precursor calcined at the low temperature of 500 °C (figure 2(b)) formed the hydroxyapatite phase but with residual carbon, which was removed by calcining at 900 °C

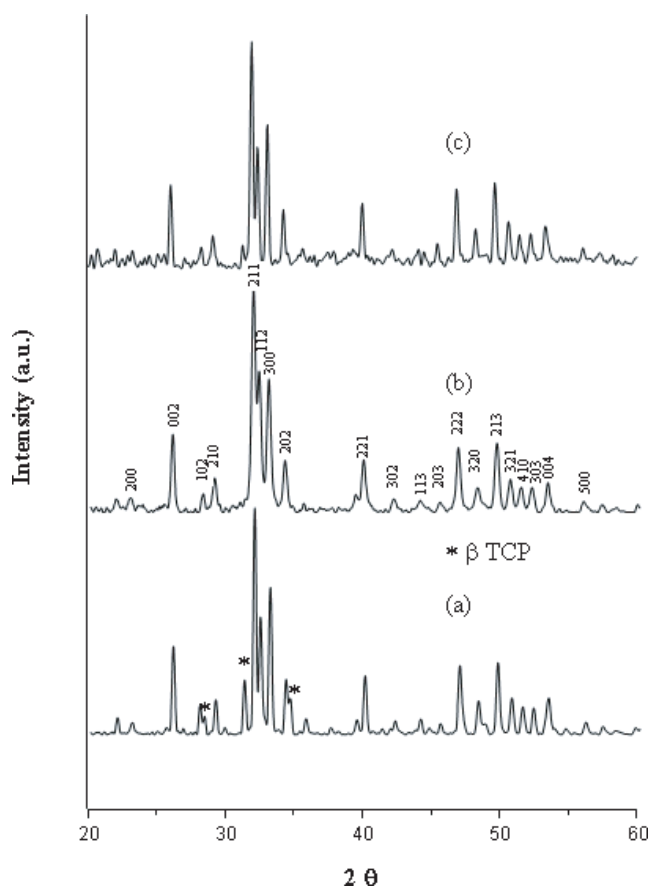


Figure 2. XRD patterns of hydroxyapatite synthesized using (a) metal-ion-to-fuel ratio of 1 : 1 followed by calcination at 900 °C, (b) metal-ion-to-fuel ratio of 1 : 2 followed by calcination at 500 °C for 5 h and (c) metal-ion-to-fuel ratio of 1 : 2 followed by calcination at 900 °C for 2 h.

for 2 h to produce pure hydroxyapatite (figure 2(c)). This can be observed from the results of thermal analysis (figure 1) as there is a 5% weight loss between 500 and 1000 °C.

The FT-IR spectra (figure 3) of the final powders (TT1 and TT2) show a broad band at 3450 cm^{-1} , which is due to moisture, and also a sharp peak at 3571 cm^{-1} due to the stretching vibration of the OH^- group present in the hydroxyapatite and a shoulder peak at 635 cm^{-1} due to the bending vibration of the OH^- group. The OH^- vibrations are not observed in the TCP samples, but TT1 has an intense OH^- peak, which is due to the presence of hydroxyapatite as a major phase. Bending vibrations of the phosphate group are observed at 473, 571 and 601 cm^{-1} , whereas stretching vibrations of the phosphate group are observed at 962, 1044 and 1089 cm^{-1} . The FT-IR spectra show that both the samples are biomimetic because a carbonate ion is substituted at the phosphate site of hydroxyapatite, as indicated by the weak bands of the carbonate group at 1465 cm^{-1} .

The specific surface area obtained for TT2 by the BET method is between 10 to 20 $\text{m}^2 \text{g}^{-1}$ for the powders calcined at 900 and 700 °C. This agrees with the literature on the surface area [14] measurement of nanocrystalline hydroxyapatite. Before the analysis, the adsorbed moisture on the fine powder surface was eliminated by preheating the

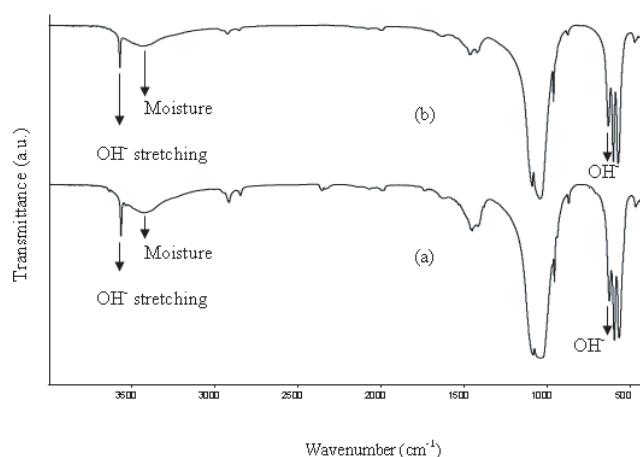


Figure 3. FT-IR spectra of hydroxyapatite synthesized using (a) metal-ion-to-fuel ratio of 1 : 1 followed by calcination at 900 °C (TT1) and (b) metal-ion-to-fuel ratio of 1 : 2 followed by calcination at 900 °C (TT2).

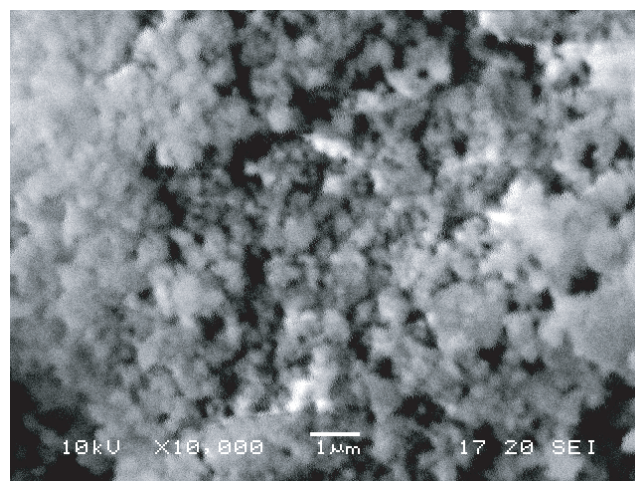


Figure 4. SEM images of single-phase microcrystalline hydroxyapatite synthesized using metal-ion-to-fuel ratio of 1 : 2 followed by calcination at 900 °C.

powders at 250 °C for 2 h. Porosity analysis indicates that the average pore diameter is approximately 22 nm. SEM images (figure 4) confirm the results of surface area analysis by the BET method as they indicate that the particles are of submicron size and highly porous. Bogdanoviciene *et al* [15] prepared hydroxyapatite by the sol-gel method using tartaric acid as a complexing agent and reported a microrod-shaped morphology, whereas the SEM images (figure 4) of our samples indicate agglomerated spherical particles. This shows that a different processing method leads to a change in morphology, as expected.

The average crystallite size of the HAP powder determined by the corrected Debye-Scherrer formula [16] relating the crystallite size, full-width at half-maximum of the peak, wavelength (0.154059 nm) and diffraction angle, is between 20 and 30 nm for TT2 irrespective of the calcination temperature. This is in accordance with the BET measurements because there is little difference in

the surface area of TT2 calcined at 700 and 900 °C. The SEM images also confirm that most of the particles are of submicron size.

4. Conclusion

Submicron hydroxyapatite powder can be synthesized by the self-propagating combustion method using tartaric acid as a fuel. It was demonstrated that the ratio of metal ions to fuel should be maintained at 1 : 2 to obtain single-phase hydroxyapatite. The process is found to save energy and time compared with other conventional methods of synthesis. The product obtained is biomimetic as it contains a substituted carbonate group. In addition, it is confirmed that, for the same complexing agent, varying the conditions of synthesis affects the morphology of the particles.

Acknowledgments

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