



Synthesis and characterisation of nanohydroxyapatite using an ultrasound assisted method

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ABSTRACT

Nanostructured hydroxyapatite (HAP) was prepared by a wet precipitation method using $\text{Ca}(\text{NO}_3)_2$ and KH_2PO_4 as the main material and NH_3 as the precipitator under ultrasonic irradiation. The Ca/P ratio was set at 1.67 and the pH maintained at a minimum of 9. The temperature conditions and ultrasound influences were investigated using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FT-IR). The results showed that Nano-HAP can be obtained by this method and the particles were achieved to around 30 nm.

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1. Introduction

Bone is a natural organic-inorganic ceramic composite consisting of collagen fibrils with embedded well-arrayed nano crystalline rod-like shaped inorganic material of 25–50 nm in length [1,2]. Hydroxyapatite (HAP) is the main inorganic calcium phosphate mineral component of bone and teeth, with a general formula of $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. The close chemical similarity of HAP to natural bone has led to extensive research efforts to use synthetic HAP as a bone substitute and/or replacement in therapeutic cases [3,4].

The main advantages of synthetic HAP are its biocompatibility, its slow biodegradability *in situ*, good osteoconductive and osteoinductive capabilities it offers [5–7]. Investigation by Taniguchi et al. [8] showed that sintered HAP exhibited excellent biocompatibility with soft tissue such as skin, muscle and gums. Such capabilities have made HAP an ideal candidate for orthopaedic and dental implants or part thereof. Synthetic HAP has been used widely for the repair of hard tissues and its common uses are bone repair, bone augmentation as well as coating of implants or acting as fillers in bone or teeth [9–11]. However, the low mechanical strength of normal HAP ceramics restricts its use mainly to conditions of low load bearing applications. In some cases, these deficiencies can be alleviated by combining HAP with other materials such as polymers and/or glass. Materials such as high density polyethylene (PE)

and polypropylene can be used to improve loading capabilities of HAP [12,13].

The complex structure of HAP has the added advantage of providing a very good absorption matrix for other molecules. The absorbing properties of HAP have been exploited in the formation of HAP-antibiotic and HAP-drug composites for slow release *in situ* [14–16]. This has proved effective in the treatment of diseases such as osteomyelitis as it allows better recovery from the disease [17].

Recent discoveries and further research in nanoscience and nanotechnology have reignited the need to investigate the formation of HAP in the nanosized range and define clearly the properties of HAP at that scale. This is essential in nanotechnology as the different forms of a material at the nanoscale can have marked differences in physicochemical properties [18–21]. On many other occasions, great improvements have been observed with the use of nanostructures made of HAP [22–25]. In a study of HAP particle size influence, *in vivo* on osteoblasts, it was found by Jui-Sheng Sun et al. [22] that there was an inflammatory inhibitory effect on the osteoblast cell cultures by smaller particles (0.5–3.0 μm). For any meaningful developments for the therapeutic use of nanohydroxyapatite (nano-HAP) in the medical field, macroscopic amounts of regular nano-HAP structures are needed with well-defined chemical and physical properties.

In the past several methods have been developed to synthesize HAP and calcium phosphate ceramics. These techniques include homogeneous precipitation [26,27], sol-gel [28], plasma spray [29], hydrothermal [30] and ultrasonic spray freeze drying [31] methods. Of all the methods mentioned, the wet chemical method

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is the easiest process to prepare HAP as it is economical and easy to operate without the need for expensive specialised equipment. Moreover, chemical method can be scaled up quite easily to meet high demands. However, the main difficulty of this method is the fine morphology and size control within a small parameter range.

A Wet chemical method has been used to produce crystalline materials from solutions in the desired crystalline phases at elevated temperatures. Particle size and morphology of HAP generated by this process can be controlled by varying experimental conditions that regulate nucleation, aging process and growth kinetics of the particles. The main parameters to obtain mono phase HAP are the raw starting material, preparation temperature and pH value. Using the wet chemical method, A.J. Kkhopade et al. [32] and G. Han et al. [33] observed HAP particles with plate like structure or morphology in contrast to the spherical-shaped HAP produced when using ultrasonic irradiation.

The precipitation method is the most common wet chemical method of preparing calcium phosphate ceramic and this can be either by a homogeneous or inhomogeneous process [34]. Electronic properties of HAP are sensitive to several variables such as Ca/P ratios, defects, size of crystals, temperature and preparation procedures [35]. Several chemical routes have been applied to the manufacture of HAP with varied results. Although, the benefits of low cost and simplicity of precipitation techniques have long provided a direct avenue for HAP synthesis, the deviation from *normal* HAP phase can be significant with these techniques [36]. In addition, different HAP phases can result from the influence of other molecules utilised in the HAP synthesis. This molecule template approach was used effectively by Wang et al. [37] to make nanorods of HAP.

Guo and Xiao [38] studied properties of nanocrystalline hydroxyapatite produced from the hydrothermal process and observed that the particle size decreases with increasing temperature. Meissner et al. [39], in their studies observed that the size and morphology of HAP can be controlled and are dependent on precipitation temperature and ultrasonic power. Cao-Li-Yun et al. [40] prepared monophase nano-HAP material with the use of ultrasonic power in the range of 300 W. The research on hydroxyapatite particle characteristics by Laquerriere et al. has also shown that the HAP particle size decreases with increasing temperature [41].

Wet milling is an important application in sample preparation. The use of ultrasonic irradiation in wet milling is an efficient means for grinding, dispersing, and deagglomerating the sample particles. The sonochemical effect in liquids is predominately that of acoustic cavitations. Some of the advantages of ultrasound in manufacturing superfine-size slurries include increased reaction speed and reaction output, and more efficient energy usage [42]. In previous chemical precipitation methods, several raw materials have been investigated with varied degrees of success for fine control of shape and size. In this paper we report a recently developed chemical route with the use of calcium nitrate and potassium hydrogen phosphate as the main raw materials. The necessary pH control was provided by the addition of NH_4OH . This hydrothermal method was also assisted by ultrasonic irradiation followed by heat treatment to manufacture the nanosized HAP.

2. Experiment

2.1. Materials

The chemicals used in this work include $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99% pure), KH_2PO_4 (99% pure) and ammonia solution which were used as Ca^{2+} , PO_4^{3-} , and OH^- sources respectively. These were supplied by CHEM-SUPPLY. The ultrasonic processor was an UP50H (50 W, 30 kHz) supplied by Hielscher ultrasound technology.

Table 1
Nano-HAP sample preparation conditions.

| Sample | Ultrasonic power (W) | Heat treatment temperature ($^{\circ}\text{C}$) | Heat treatment duration (h) | pH (minimum) |
|--------|----------------------|---|-----------------------------|--------------|
| S-1 | 50 | 100 | 12 | 9.0 |
| S-2 | 50 | 200 | 2 | 9.0 |
| S-3 | 50 | 300 | 2 | 9.0 |
| S-4 | 50 | 400 | 2 | 9.0 |
| S-5 | 25 | 100 | 12 | 9.0 |
| S-6 | 25 | 200 | 2 | 9.0 |
| S-7 | 25 | 300 | 2 | 9.0 |
| S-8 | 25 | 400 | 2 | 9.0 |
| S-I | 0 | 100 | 12 | 9.0 |
| S-II | 0 | 200 | 2 | 9.0 |
| S-III | 0 | 300 | 2 | 9.0 |
| S-IV | 0 | 400 | 2 | 9.0 |

2.2. Procedure

HAP was synthesised by adding a 2.5 ml ammonia aliquot to 40 ml of 0.32 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution under ultrasound irradiation. The pH value was checked and maintained at nine at all times. Whilst under ultrasound irradiation, 60 ml of 0.19 M KH_2PO_4 solution was slowly added dropwise. A white precipitate was formed and the mixture was continuously irradiated with ultrasound power ranging from 0 to 50 W (30 kHz) of maximum amplitude for 1 h. The Ca/P ratio was kept at 1.67. The solution was filtered by centrifugation and after filtration the white precipitate was proportioned into a number of samples. These samples were then transferred into ceramic boats and placed in an electric tube furnace for thermal treatment at temperatures varying from 100 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$ for a fixed time period. The duration of heat treatment time for the white precipitate at temperature of 100 $^{\circ}\text{C}$ was 12 h, while the duration of heat treatment time for the white precipitate at temperatures ranging from 200 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$ was 2 h. The longer heat reaction time for the 100 $^{\circ}\text{C}$ samples was necessary so as to produce crystalline and harder samples as initial work indicated mixed crystalline and amorphous soft end product. A total of 12 samples were matched to the power of ultrasound irradiation and heat reaction temperature used (see Table 1). The general procedure is graphically shown as a flow chart in Fig. 1.

2.3. Characterisation

The obtained final products were grinded into fine powder and characterised using XRD, SEM and FT-IR spectroscopy. Powder XRD spectra were recorded, at room temperature, using a Siemens D500 series diffractometer. XRD data collection details were: radiation – $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$); Generator settings – 40 kV and 30 mA; Speed – 0.04 $^{\circ}$ step size with acquisition time of 2.0 s; 2θ range – 20 $^{\circ}$ –60 $^{\circ}$; and flat plane geometry. The powder XRD spectra give identifications of the purity of the final products (HAP) and any other phases that may be present. The crystalline size of the synthesized HAP was calculated from the XRD pattern using the Debye–Scherrer equation and determined by analysing corresponding field emission scanning electron microscopy (FESEM) images.

The macrostructural and morphological features of HAP powders were investigated using FESEM. All scanning electron micrographs were taken using the high resolution field emission Zeiss 1555 VP-FESEM at 3 kV, 30 μm apertures under 1×10^{-10} torr pressure.

FT-IR spectroscopy was performed using the Bruker Optics IFS 66 series FT-IR spectrometer. FT-IR spectra were taken for HAP samples prepared from a mixture of approximately 2 g of HAP powder with 5–10 gm of spectroscopic grade KBr pressed to disk shape at 12–15 kPa. All FT-IR spectra were recorded in the 400–4000 cm^{-1} region.

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