

# Synthesis of nano-hydroxyapatite under a sonochemical/hydrothermal condition

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## Abstract

In this study, hydroxyapatite (denoted as HAp) nanostructure with uniform morphologies, controllable size, nano-dispersion and narrow size distribution in diameter has been synthesized successfully by low-temperature hydrothermal process, and the as-synthesized powders were characterized by XRD, scanning electron microscopy, high-resolution transmission microscopy, FT-IR, Zetasizer and inductively coupled plasma. In the present work, a novel sonochemical technique using  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}/\text{NaOH}/\text{distilled water}$  with cetyltrimethylammonium bromide ( $(\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-)$  designated as CTAB) under a hydrothermal condition to synthesize HAp nanostructure was described. Furthermore, the usage of a high basic condition and a water environment are the two crucial keys in ensuring the formation of HAp in the hydrothermal/sonochemical processes. However, the crystallite size and crystallinity degree of the HAp increased with increasing annealing temperature. Indeed, the present work will introduce a new method in synthesizing HAs for scientific and medical engineering.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

There is an escalating interest in calcium phosphates, particularly apatites, which seems to be driven mainly by the requirements for the development, understanding and manufacture of biomaterials [1]. Compounds with the apatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}, \text{Cl}, \text{OH})_2$ ) structure have been widely studied due to their potential applications as biomaterials [2], catalysts [3], ionic exchangers [4], oxide ion conductors and luminescent materials [5]. Many synthetic strategies have been developed to produce these nanostructures, such as the solid-state reactions [6] and sol-gel method [7]. Recently, hydrothermal reactions have been used successfully as a non-traditional way of producing nanopowder, single crystals and nanostructure [8–16]. Depending on the supersaturation level and the solution pH, a number of calcium phosphates may be formed at ambient temperatures and pressure. In an aqueous solution of  $\text{pH} > 4$ , the order of increasing solubility is as follows: tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ , TCP), octa-calcium phosphate ( $\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$ , OCP),

dicalcium phosphate dihydrate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , DCPD) and hydroxyapatite with a hexagonal structure with space group  $\text{P6}_3/\text{m}$  and lattice parameters  $a = b = 9.4225 \text{ \AA}$  and  $c = 6.8850 \text{ \AA}$  [17]. There are two formula units per unit cell and the arrangement is typical of the calcium apatites and can be viewed as consisting of unconnected, robust  $\text{PO}_4^{3-}$  tetrahedral with  $\text{Ca}^{2+}$  in the space between, and a chain of  $\text{OH}^-$  ions along the  $c$ -axis to balance the charge (figure 1). Monoclinic structures with four formula units per unit cell have also been reported [18–22], where the monoclinic unit cell is obtained from the hexagonal one by doubling the  $b$  lattice parameter and by having different arrangements of the anion chains. Difficulties in obtaining the stoichiometric compound, particularly with regard to the hexagonal phase of HAp, present a problem. Following failed attempts to fix x-ray diffraction data using the space group  $\text{P6}_3$ , the structure was found with the space group  $\text{P6}_3/\text{m}$  through the addition of two mirror planes perpendicular to  $[001]$  and passing through  $z = 1/4$  and  $z = 3/4$ . However, this structure has four possible sites for the two OH groups per unit cell, a difficulty which was