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 CaHPO$_4$·2H$_2$O/NaOH/distilled water with cetyltrimethylammonium bromide ((CH$_3$)(CH$_2$)$_{15}$N$^+$ (CH$_3$)$_3$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 (Ca$_{10}$(PO$_4$)$_6$(F, Cl, 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 pH > 4, the order of increasing solubility is as follows: tricalcium phosphate (Ca$_3$(PO$_4$)$_2$, TCP), octa-calcium phosphate (Ca$_4$(PO$_4$)$_2$·2.5H$_2$O, OCP), dicalcium phosphate dihydrate (CaHPO$_4$·2H$_2$O, DCPD) and hydroxyapatite with a hexagonal structure with space group P6$_3$/ma with lattice parameters $a = b = 9.4225$ Å and $c = 6.8850$ Å [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 PO$_4$ tetrahedral with Ca$^{2+}$ in the space between, and a chain of 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 P6$_3$, the structure was found with the space group P6$_3$/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