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Effect of silicon content on the surface morphology of silicon-substituted hydroxyapatite bio-ceramics treated by a hydrothermal vapor method

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Abstract

Silicon-substituted nano-hydroxyapatite powders with up to 4.0 wt% silicon were prepared by a hydrothermal method. X-ray fluorescence spectroscopy, X-ray diffraction, and transmission electron microscopy analyses revealed that some SiO_4^{4-} substituted PO_4^{3-} in apatite lattice, while other SiO_4^{4-} functional groups remained in the mother liquid. The content of silicon influenced the thermal stability, density, and grain size of the hydroxyapatite bio-ceramic samples at elevated temperatures. For instance, the crystallinity declined and grain size decreased slightly with increasing silicon contents. Whisker-type particles with different diameters grew on the silicon-substituted hydroxyapatite bio-ceramic surface upon hydrothermal vapor post-synthesis treatment of the bio-ceramics.

Keywords: B. Whiskers; D. Apatite; Hydrothermal vapor

1. Introduction

Currently, there is a high demand for the preparation of highly efficient synthetic biomaterials for the replacement and repair of damaged skeleton. Numerous experts have focused on varying the bone scaffold composition by introducing growth factors, proteins, or cells for instigating and enhancing the bioactivity and biocompatibility of biomaterials [1]. Moreover, the incorporation of foreign ions, which can afford chemical compositions similar to that of natural bone has generated growing interest [2]. Recent studies show that hydroxyapatite (HA) has a non-stoichiometric composition in natural bone with insufficient amounts of Ca^{2+}, PO_4^{3-}, and OH^-. Various ions, such as Cl^-, F^-, and CO_3^{2-}, can replace OH^- (A-site substitution) and SiO_4^{4-} or CO_3^{2-} can replace OH^- (B-site substitution). Cations, such as Sr^{2+}, Zn^{2+}, Mg^{2+}, Cu^{2+}, Al^{3+}, Fe^{3+}, and Na^+, are also present in natural bone HA at trace levels (≤ 1 wt%). Though the extent of ion substitution is small, different ions play a vital role in the chemical composition, structure, surface physical and chemical properties, and thermal stability of HA [2–11].

In particular, silicon has been demonstrated to be essential to the normal growth and development of bone and cartilage, especially at the early bone growth stages [12]. Many research results reveal that silicon can enhance osteoblast proliferation and differentiation, as well as improve collagen production [13,14]. Many commercially available, synthetic bone graft materials comprising calcium phosphate and glass or glass ceramics often incorporate silicon to improve bioactive properties [1,4,6,15–19]. However, little attention has been devoted to examining the effect of silicon content on the surface morphology of HA bio-ceramics. Studies have demonstrated that the surface roughness [20], porosity [21], and crystal morphology [22] of calcium phosphate ceramics affect the adsorption, migration, and differentiation capabilities of cells.

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Recently, plasma spraying [23], electrochemical deposition [24], micro-arc oxidation, hydrothermal–electrochemical deposition [25], and biomimetic mineralization [26] have been applied to pre-process the surface of biomaterials. Furthermore, the hydrothermal vapor pretreatment has been demonstrated as an easier means to process the bio-ceramic surface when compared with other methods [22,27] though it is rarely used to pre-process bio-ceramic surfaces. To this effect, an interesting way to alter the morphology of HA bio-ceramics is by incorporating silicon ions (or silicon groups) into the apatite structure [2,28–30] and using the hydrothermal vapor method to treat the bio-ceramic surface following synthesis.

Silicon-substituted HA (Si-HA) has been prepared by various methods including aqueous precipitation [2,30], sol–gel [29,31,32], solid state reaction [33], hydrothermal synthesis [34–36], and wet mechanical process [37]. The application of the hydrothermal method usually generates HA with a high degree of crystallinity and good dispersity. Additionally, rod-like HA nanocrystals are typically produced.

In this work, we aimed to synthesize nano-sized Si-HA with varying amounts of silicon using the hydrothermal method. The effect of silicon content on the size distribution, crystallinity, morphology, and thermal stability of the Si-HA particles was investigated. Additionally, the effect of silicon content on the development of whisker-type particles on the Si-HA bio-ceramic surface processed by the hydrothermal vapor method following synthesis was examined.

2. Materials and methods

2.1. Synthesis of hydroxyapatite (HA) and silicon-substituted hydroxyapatite (Si-HA)

Stoichiometric HA powder and Si-HA powders with varying silicon contents (0.8–4.0 wt%) were synthesized by a hydrothermal method using $Ca(NO_3)_2 \cdot 4H_2O$ (AR), $(NH_4)_3PO_4$ (AR), and $Si(OCH_2CH_3)$ (TEOS; AR) as sources of Ca, P, and Si. Appropriate quantities of the reactants were used to prepare Si-HA and stoichiometric HA with a Ca/(P + Si) molar ratio of ~1.67, assuming that silicate ions would substitute for the phosphate group. The molar amounts of $Ca(NO_3)_2 \cdot 4H_2O$, $(NH_4)_3PO_4$, and TEOS used to prepare stoichiometric HA and Si-HA are listed in Table 1.

$Ca(NO)_2$ (0.5 M) and $(NH_4)_3PO_4$ (0.25 M) solutions were prepared by maintaining the pH above 11 and 10, respectively, by adding concentrated ammonia solution. Then, a mixed solution of $(NH_4)_3PO_4$ and TEOS was added dropwise to a mixed solution of $Ca(NO_3)_2$ and polyethylene glycol (0.2 g; PEG, M_w 6000) using a peristaltic pump (BT100L, Leadfluid, China) at a speed of 3 mL min^{-1}. The slurries were stirred for 30 min following dropwise solution addition. The resulting milky suspension was then transferred to a Teflon vessel, sealed tightly, and heated in an oven at 200 °C for 8 h. The resulting precipitate was centrifuged three times with distilled water once and successively with alcohol twice then dried at 50 °C for 24 h.

Then, an appropriate amount of the synthesized powders were shaped using a mold with a diameter of 5 mm to prepare 5 × 1 mm bio-ceramic specimens using uniaxial compression. The compact powders were subsequently heated in a muffle furnace to 1200 °C, with a ramp of 10 °C min^{-1}, after which the temperature was maintained for 10 h. The samples were subsequently cooled to room temperature at a ramp of 4 °C min^{-1} to produce the final HA and Si-HA ceramics.

2.2. Treatment of HA and Si-HA bio-ceramics

The HA and Si-HA bio-ceramics with varying silicon contents were placed in an autoclave and heated at 121 °C for 1 h followed by rinsing with deionized water and drying at 50 °C.

2.3. Characterization

The calcium, phosphorus, and silicon contents of the samples were evaluated by X-ray fluorescence (XRF) spectroscopy using a PW4400 spectrometer (PANalytical). The results are stated as weight percentages. The phase composition of the prepared powders was determined by X-ray diffraction (XRD; D8-Advance, Bruker, Germany). Data were collected over a 2θ range of 10–60° with a step size of 0.0025°. Identification of phases was achieved by comparing the diffraction patterns with ICDD file cards 9–432, 9–348, 9–169, 40–393 for HA, α-tricalcium phosphate (α-TCP), β-TCP, and $Ca_5(PO_4)_2SiO_4$, respectively. The thermal stability of the samples was assessed by differential thermal analysis–thermogravimetry (DTA/TG; STA449C, Germany). The surface morphology of the treated bio-ceramics was investigated using a scanning electron microscope (SEM; Navo NanoSEM 430, FEI) and a transmission electron microscope (TEM; JEM-2010HR, Japan), operating at 200 kV.

Table 1
Quantity of reactants used in the synthesis of hydroxyapatite (HA) and silicon-substituted hydroxyapatite (Si-HA).

Sample	$Ca(NO_3)_2$ (mol)	$(NH_4)_3PO_4$ (mol)	TEOS (mol)	Si (wt%)	Calculated chemical formula
HA	0.0250	0.01500	0	0	$Ca_{10}(PO_4)_6(OH)_2$
0.8Si-HA	0.0250	0.01429	7.125×10^{-4}	0.8	$Ca_{10}(PO_4)_{5.715}(SiO_4)_{0.285}(OH)_{1.715}$
1.5Si-HA	0.0250	0.01367	1.330×10^{-3}	1.5	$Ca_{10}(PO_4)_{5.468}(SiO_4)_{0.532}(OH)_{1.468}$
2.0Si-HA	0.0250	0.01323	1.768×10^{-3}	2.0	$Ca_{10}(PO_4)_{5.293}(SiO_4)_{0.707}(OH)_{1.293}$
4.0Si-HA	0.0250	0.0115	3.485×10^{-3}	4.0	$Ca_{10}(PO_4)_{4.606}(SiO_4)_{1.394}(OH)_{0.606}$