Original Research Paper

Synthesis of Ti(IV)-substituted calcium hydroxyapatite microparticles by hydrolysis of phenyl phosphates

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A B S T R A C T

Ti(IV)-substituted calcium hydroxyapatite (Ti-CaHap) microparticles were synthesized by hydrolyzing the phenyl phosphate ($C_6H_5PO_4H_2$) in a mixture of aqueous $Ca(OH)_2$ and $Ti(SO_4)_2$ solutions at pH = 8 and 85 °C. Then, the atomic ratio Ti/(Ca + Ti) in the starting solution was ranged from 0 to 0.20. The XRD pattern of the product formed at Ti/(Ca + Ti) = 0 was identified as CaHap. On increasing Ti/(Ca + Ti) ratio, the diffraction intensity of the CaHap peaks weakened and the unit-cell dimension c of the material was reduced. The Ti content in the particles was increased by raising Ti/(Ca + Ti) ratio and the Ti(IV) was more easily incorporated in the particles than Ca(II). All the phenyl phosphates were hydrolyzed during preparation of the particles. The CaHap formed at Ti/(Ca + Ti) = 0 was needle-like particles with the size of ca. 3.2 μm in length and ca. 0.3 μm in width. The size of Ti-CaHap particles was essentially unchanged on increasing Ti/(Ca + Ti) ratio up to 0.05. At Ti/(Ca + Ti) ⩾ 0.10, the amorphous TiO_2 particles with a size of ca. 90 nm were generated and the size of Ti-CaHap particles was decreased, leading to the steep increase of specific surface area. It can be, therefore, presumed that the Ti(IV) is substituted with Ca(II) in CaHap crystal to form Ti-CaHap microparticles at Ti/(Ca + Ti) = 0–0.05, though the incorporation of Ti(IV) in the materials impedes the crystallization and growth of Ti-CaHap particles and accelerates the formation of amorphous TiO_2 particles at Ti/(Ca + Ti) = 0.10–0.20. Diffuse reflectance UV measurements indicated that the Ti-CaHap microparticles possess a UV absorption property and the ability is enhanced on increasing Ti/(Ca + Ti) ratio. The Beer's plot revealed that the UV absorption ability of the synthetic Ti-CaHap microparticles is higher than that of amorphous TiO_2 ones.

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1. Introduction

Calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ designated as CaHap, is a principal component of hard tissues. Synthetic CaHap finds many applications such as adsorbents for chromatography to separate protein and enzyme, catalysts for dehydration and dehydrogenation of alcohols, methane oxidation and artificial teeth and bones [1–6]. Recently, CaHap is received attentions in application for photocatalyst. Nishikawa et al. have reported the generation of ·OH and O_2^- radicals on CaHap by UV irradiation and indicated the photocatalytic decomposition of methyl mercaptane and dimethyl sulfide [7–12]. While, Wakamura et al. indicated by decomposition of acetaldehyde and albumin under UV irradiation that the photocatalytic activity of CaHap is considerably enhanced by doping Ti(IV) [13]. Further, the Ti(IV)-doped CaHap (Ti-CaHap) possesses a high bactericidal effect owing to its higher affinity with proteins than titanium dioxide (TiO_2) [13,14]. Since then, various researchers investigated the structure, property and application of Ti-CaHap [15–20]. Hu et al. have indicated that the CaHap co-substituted with Ti(IV) and antibacterial ions (Ag(I), Cu(II) or Zn(II)) has a high efficiency for killing the *Escherichia coli* and *Staphylococcus aureus* [15]. Also, Anmin et al. reported that the photocatalytic activity of Ti-CaHap is related to its particle size, crystallinity, morphology, specific surface area and surface state [16]. Besides, Hung and co-workers suggested that the Ti-CaHap has a great potential for use in biomedical applications such as bioactive scaffolds and coating on Ti implants [18]. Most recently, Kandori et al. reported that the Ti-CaHap shows a high affinity to proteins such as bovine serum albumin (BSA) and lysozyme (LSZ) and the adsorbed LSZ can be completely decomposed by UV irradiation [19,20]. Thus, the Ti-CaHap has a great potential for use in industry and medical and dental fields. For these reasons, synthesis of nano-sized Ti-CaHap particles is actively investigated because of their high surface area, reactivity to molecules and catalytic activity. However, handling of the nanoparticles is generally difficult and the aggregation leads to loss of the above-mentioned properties associated with nanoscale of particles. To improve this problem, it is required to control the size of Ti-CaHap particles, however, there is no study of this subject in our best knowledge. Previously, the authors succeeded the syn-

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thesis of micro-sized CaHap particles by hydrolyzing the phenyl phosphate ($C_6H_5PO_4H_2$: PP) in aqueous Ca(II) solutions at pH = 6–8 and 85 °C [21]. It can be, therefore, anticipated that the Ti-CaHap microparticles are prepared by using PP.

The aim of this study was to synthesize the micro-sized Ti-Ca-Hap particles. So that, the Ti-CaHap particles were prepared by hydrolyzing the PP in aqueous media containing Ca(II) and Ti(IV) at pH = 8.0 and 85 °C. The structure and composition of the materials thus obtained were examined by a variety of conventional techniques such as XRD, FTIR, TEM, AAS and adsorption of N_2. Further, the UV absorption property was investigated by diffuse reflectance UV measurements and the relation between UV absorption property and Ti content in the particles was discussed on the basis of results obtained.

2. Experimental

2.1. Synthesis of Ti-CaHap microparticles

The Ti-CaHap particles were prepared by the following wet method. $Ca(OH)_2$ and $Ti(SO_4)_2$ were dissolved into 850 ml of deionized-distilled water free from CO_2 in a sealed polypropylene vessel. Then, the total amount of Ca and Ti was 17.7 mmol and the atomic ratio Ti/(Ca + Ti) was ranged from 0 to 0.20. Hereafter, Ti/(Ca + Ti) ratio in the starting solution is abbreviated as X_{Ti}. To the solution were added 50.0 ml of 0.212 mmol/dm^3 aqueous PP solutions under stirring condition at room temperature. After this, the solution pH was adjusted to 8.0 by adding a 0.10 mol/dm^3 HNO_3 solution. The suspension formed was aged at 85 °C for 48 h without stirring. The resulting precipitates were filtered off, thoroughly washed with deionized-distilled water, and finally dried at 50 °C in an air oven for 1 day.

All the chemicals supplied from Wako Chemical Co. were reagent grade and were used without further purification.

2.2. Characterization

The samples thus obtained were characterized by various means. Powder X-ray diffraction (XRD) patterns were taken by a Rigaku diffractometer with a Ni-filtered Cu Kα radiation (30 kV and 15 mA). Transmission IR spectra were recorded by a JASCO Fourier transform infrared (FTIR) spectrometer with a resolution of 4 cm^{-1} using a KBr method. Ca and Ti contents were assayed by a Shimadzu atomic absorption spectroscopy (AAS) after leaching the samples in a hot concentrated H_2SO_4 solution and diluting the solution to a desired concentration with deionized-distilled water. Particle morphology was observed by a TOPCON transmission electron microscope (TEM). Specific surface area was obtained by fitting the BET equation to the N_2 adsorption isotherms measured at the boiling temperature of liquid nitrogen with a Quantachrome volumetric apparatus. Diffuse reflectance UV spectra were recorded by a Shimadzu UV–vis spectrometer with an integrating sphere. For the measurements, 175 mg of the samples were fully mixed with 3.325 g of $BaSO_4$ used as diluent.

3. Results and discussion

Fig. 1 shows the XRD patterns of the products formed at different X_{Ti}. Pattern a of the sample yielded at X_{Ti} = 0 exhibits the sharp diffraction peaks at 2θ = 25.8°, 31.6°, 32.1°, 32.7°, 33.9°, 39.6°, 46.5° and 49.3°. These peaks respectively correspond to the reflection from (0 0 2), (2 1 1), (1 1 2), (3 0 0), (2 0 2), (3 1 0), (2 2 2) and (2 1 3) planes of the CaHap crystal (ICDD No. 9-432). The formation of Ca-Hap particles by hydrolyzing the PP in aqueous $Ca(OH)_2$ solution was reported as the following reactions (1)–(3) [21]:
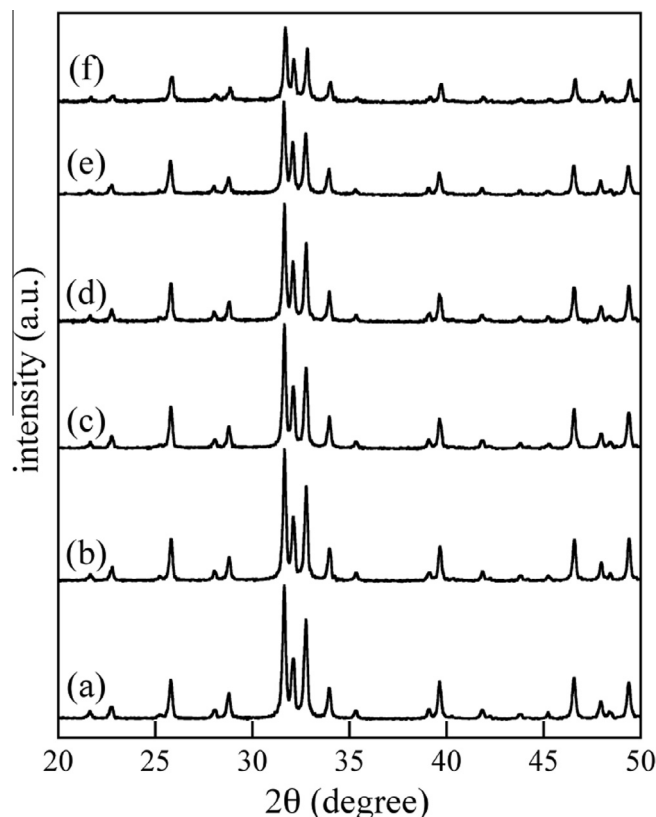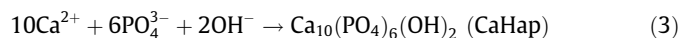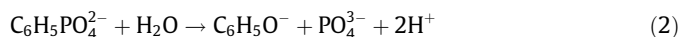

Fig. 1. XRD patterns of the products formed at different X_{Ti}. X_{Ti}: (a) 0, (b) 0.01, (c) 0.025, (d) 0.05, (e) 0.10 and (f) 0.20.

$$C_6H_5PO_4H_2 \rightarrow C_6H_5PO_4^{2-} + 2H^+ \tag{1}$$

$$C_6H_5PO_4^{2-} + H_2O \rightarrow C_6H_5O^- + PO_4^{3-} + 2H^+ \tag{2}$$

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 \ (CaHap) \tag{3}$$

The reaction (2) takes place at pH ⩽ 8.0 and 85 °C, resulting the formation of needle-like CaHap microparticles via reaction (3) [21]. With an increase of X_{Ti}, the CaHap peaks slightly weaken, while no new diffraction peaks are recognized over the whole X_{Ti} range (patterns b–f). Since the crystal structure of CaHap is hexagonal ($a = b \neq c$, $\alpha = \beta$ = 120°, γ = 90°), the diffraction intensity of (3 1 0) and (0 0 2) peaks, which correspond to the crystallinity of a- or b-direction and c-direction of the crystal, is plotted against X_{Ti} in Fig. 2. As can be seen, the intensity of (3 1 0) and (0 0 2) peaks is gradually decreased with an increase of X_{Ti}. This means the inhibition of formation and/or crystallization of CaHap by added Ti(IV). Actually, the full width at half-height of the (3 1 0) and (0 0 2) peaks of Ti-CaHap was decreased on increasing X_{Ti}, implying the reduction of crystallite size of this material. Nonetheless, exact crystallite size of Ti-CaHap yielded at X_{Ti} = 0–0.20 could not be determined because the sizes were beyond the evaluation limit of the crystallite size by the Scherrer equation (300 nm). The reduction of crystallinity of CaHap by doping Ti(IV) is also suggested by measuring the IR spectra. This will be discussed later.

Fig. 3 plots the unit-cell dimensions a and c estimated from the diffraction angle of (0 0 2), (3 1 0) and (2 1 1) peaks of Ti-CaHap as a function of X_{Ti}. The dimensions of CaHap obtained at X_{Ti} = 0 exhibit as a = 0.9457 nm and c = 0.6901 nm. McConell has reported the unit-cell dimensions of synthetic CaHap as a = 0.9416 ± 0.0002 nm and c = 0.6883 ± 0.0002 nm [22]. Comparing to the literature values reported by McConell, it can be regarded that the particles have en-