

Monetite (CaHPO₄) Synthesis in Ethanol at Room Temperature

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A straightforward process was developed to synthesize monetite (CaHPO₄, dicalcium phosphate anhydrous) powders at room temperature (21° ± 1°C) in ethanol solutions. The process reported here constitutes an alternative to well-publicized monetite synthesis procedures based on the dehydration of brushite (CaHPO₄ · 2H₂O, dicalcium phosphate dihydrate) powders either in acidic, hot (70°–95°C) aqueous solutions or in drying ovens (200°–225°C). Submicrometer monetite powders were synthesized in ethanol (ethyl alcohol) solutions containing small aliquots of concentrated H₃PO₄ (orthophosphoric acid, 85%). Precipitated CaCO₃ (calcium carbonate, calcite form) powders with submicrometer particles were simply stirred in the above solutions in glass bottles for 3 h. The starting Ca/P molar ratio in the synthesis bottles was 0.50. Monetite powders obtained with a stacked-nanosheets particle texture did not contain any unreacted CaCO₃. Monetite powders were also found to have the ability to completely transform into apatitic (apatite-like) calcium phosphate powders when soaked in calcium-containing saline solutions (i.e., 142 mM Na⁺, 5 mM K⁺, and 50 mM Ca²⁺ in water) for 6 days at 37°C.

I. Introduction

MONETITE (CaHPO₄, DCPA, dicalcium phosphate anhydrous) is one of the mildly acidic and soluble (at the physiological pH) calcium phosphate (CaP) phases^{1,2} and currently finding a significant place to itself in the powder components of self-hardening CaP pastes used for skeletal repair.^{3–6} Moreover, it must hereby be noted that even the world's very first patented CaP putty-like paste development study, by Driskell *et al.*⁷ back in 1974, involved CaHPO₄ mixed with those of self-hardening α -Ca₃(PO₄)₂ powders.

CaHPO₄ is also used in powder form in some toothpastes, chewing gums and in food processing industry to act as acidity regulator, anti-caking agent, dough modifier, and emulsifier (food additive number: E341).⁸

CaHPO₄ has a triclinic unit cell with the following lattice parameters; $a = 6.910$, $b = 6.627$, $c = 6.998$ Å, $\alpha = 96.34^\circ$, $\beta = 103.82^\circ$, and $\gamma = 88.33^\circ$,^{9,10} with a calculated density of 2.92 g/cm³. Its triclinic–pinacoidal structure consists of CaHPO₄ chains held together by Ca–O bonds and three types of hydrogen bonds.¹¹

The dissolution kinetics of CaHPO₄ in water at 37°C was investigated by Lebugle *et al.*¹² This study showed that Ca²⁺ and HPO₄^{2–} ions were initially released from CaHPO₄ and completely stopped after 4 days in contact with water at 37°C.¹² The Ca/P atomic ratio in water, in which these dissolution experiments were performed, also decreased with time and was 0.75 after 15 min of dissolution; it finally (after 4 days) reached a value of 0.62. The dissolution of DCPA was found to be incongruent.¹² This incongruency was explained by the formation of a thin apatitic (apatite-like) calcium phosphate (*Ap-CaP*) layer on

the surfaces of CaHPO₄ particles through a topotactic reaction, which hindered further dissolution.^{12–16} The logarithm of the thermodynamic solubility (i.e., log K_{sp}) of CaHPO₄ was reported by McDowell *et al.*¹⁶ to be –6.90 and –7.04 at 25° and 37°C, respectively. For comparison purposes, log K_{sp} values at 25°C for CaHPO₄ · 2H₂O (*brushite*), CaCO₃, Ca₁₀(PO₄)₆(OH)₂ (*hydroxyapatite, HA*), β -Ca₃(PO₄)₂ (*whitlockite*), and Ca₉(HPO₄)₅(OH) (*Ca-deficient HA*) are –6.60, –8.55, –117.1, –81.7, and –85.1, respectively.¹⁷ These numbers simply relate to the solubility of a given substance; for instance, Ca-deficient HA (–85.1) is much less soluble than CaHPO₄ (–6.90). This is basically why some self-hardening CaP pastes contain, for instance, about 25 wt% CaHPO₄^{3,4} in their powder components.

How CaHPO₄ powders are produced? First of all, it is not difficult at all to convert CaHPO₄ · 2H₂O (*brushite*, dicalcium phosphate dihydrate, DCPD) powders into single-phase CaHPO₄ by dehydration. Two methods of dehydration can be envisaged and the previous literature provides ample examples to those. The first method of CaHPO₄ synthesis, which used brushite powders as the starting material, consisted of, for instance, dehydrating 400 g of brushite (CaHPO₄ · 2H₂O) in 4 L of 0.07M H₃PO₄ solution by boiling for 72 h, followed by filtering the resultant CaHPO₄ powders.^{16,18} The second method of dehydrating brushite powders to obtain CaHPO₄ simply consisted of heating brushite in a static air atmosphere over the temperature range of 200°–250°C.^{19–23} However, both of these dehydration techniques would have the following disadvantage in terms of ceramic powder science: it would be quite difficult to significantly alter the particle size and shape distribution present in the initial brushite powders. Synthetic brushite powders mostly exhibit large (i.e., 10–130 μ m) tabular, needle-like, lath-like, or rectangular prismatic crystals, and at high salt concentrations large acicular crystals are also formed.^{24–27} This large particle size (15–40 μ m) is the main handicap of currently available commercial CaHPO₄ powders. Because such an idiomorphic tabular or acicular crystal habit in brushite is very difficult to circumvent (if not impossible), monetite synthesis procedures based on the dehydration of brushite will not be able to produce submicrometer particles.²⁸

Chenot²⁹ provided solution preparation recipes for the dehydration of the crystals of brushite to monetite in aqueous slurries heated from 85° to 98°C, and observed the formation of large monetite crystals with rhombohedral diamond, plate-like, rectangular or needle-like habits. Takagi *et al.*³⁰ simultaneously and slowly (in 5 h) added, dropwise, equimolar solutions of Ca-chloride and Na₂HPO₄ (1 L each) into 1 L of water heated to 95°C, and thus obtained hexagonal prismatic crystals of CaHPO₄. Griffith and McDaniel³¹ first formed CaHPO₄ · 2H₂O crystals by reacting an aqueous Ca(OH)₂ slurry with H₃PO₄ solutions and then mostly converted those into CaHPO₄ in 2 h by increasing the temperature of the resultant suspension to about 95°C. In a very similar study, Martin and Brown³² later reported the precipitation of CaHPO₄ at 85°C from an acid–base reaction of H₃PO₄ and Ca(OH)₂, however, the aqueous slurry containing the precipitates was continuously stirred for 16 h at 85°C to ensure complete reaction between Ca(OH)₂ and H₃PO₄. The high temperatures (85°–98°C) used in the above-mentioned studies made possible the dehydration of any brushite, which might initially form, to monetite. Louati *et al.*,³³ on the other hand,

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reported the synthesis of large crystals of CaHPO_4 by slowly evaporating an aqueous solution of the stoichiometric mixture of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ at around 80°C .

There were a number of attempts to develop new powder synthesis methods, which would facilitate a reduction in the mean particle size of CaHPO_4 . Chen *et al.*³⁴ synthesized CaHPO_4 particles in oil-in-water (o/w) system and water-in-oil (w/o) system with a novel membrane microdispersion mixing technique. In this study, sodium dodecyl sulphate (SDS)-containing Ca-acetate aqueous solutions were used as the water phase, whereas butanol-phosphoric acid mixture was the oil phase. Chen *et al.*³⁴ reported the synthesis of submicrometer particles of CaHPO_4 . Tokuoka *et al.*³⁵ were reacting two solutions at room temperature for 24 h; triethyl phosphate solution in water and a solution of Ca-nitrate in water containing cetyltrimethylammonium bromide (CTAB). However, their CaHPO_4 precipitates were not submicrometer and were heavily agglomerated.

Kong *et al.*³⁶ prepared reverse microemulsions by adding calcium chloride and sodium hydrogen phosphate aqueous solutions into a mixture of Span 80[®], Tween 80[®], and *n*-heptane to get two kinds of emulsions. *n*-butanol was used to adjust the emulsions to transparent state. Calcium phosphate was prepared by adding phosphate microemulsion to the calcium microemulsion. Kong *et al.*³⁶ reported to synthesize micronsize needles of CaHPO_4 . Wei *et al.*³⁷ used reverse micelles solution of water and cyclohexane containing either CTAB or polyoxyethylene-8-dodecyl ether (C12E8) surfactants and *n*-pentanol as co-surfactant as organized reaction microenvironments for monetite precipitation. Well-crystallized CaHPO_4 nanoparticles with various morphologies such as spheres, monodisperse nanofibers, and bundles of nanowires were obtained in this study. Xu *et al.*³⁸ obtained CaHPO_4 nanoparticles by spray-drying. Jinawath *et al.*³⁹ used monocalcium phosphate monohydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) and $\text{Ca}(\text{OH})_2$ as the starting materials in an autoclave operated between $160^\circ\text{--}200^\circ\text{C}$ to obtain plate-like and large crystals of monetite. The high temperatures used in such autoclave-based techniques cannot be economically compatible with synthesis procedures performed at room temperature (RT). Thomas and Dehbi⁴⁰ formed CaHPO_4 in the solid state by ball milling $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Ca}_3(\text{PO}_4)_2$ powders together at room temperature. Ball milling of powder reactants to push solid-state reactions to completion could typically be more labor intensive and energy consuming than stirring a single powder in a simple solution at RT.

Ma *et al.*⁴¹ synthesized CaHPO_4 particles consisting of nano-sheets, by a one-step microwave-assisted heating method at 95°C using $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, NaH_2PO_4 , and SDS in water/ethylene glycol (EG) mixed solvents. The synthesis procedure of this study was quite remarkable that it resulted in spindle, flower-, or bundle-like CaHPO_4 particles (3–5 μm in diameter) consisting of stacked nanosheets. However, EG is not an environmentally friendly solvent to use. Upon human ingestion, EG is oxidized to glycolic acid, which is, in turn, oxidized to oxalic acid which is toxic. Ingestion of sufficient amounts can even be fatal.⁴²

Aoki *et al.*⁴³ studied the morphology of monetite crystals formed when $\text{Ca}(\text{OH})_2$ or CaCO_3 particles (ca. 20–100 μm in particle size) were slowly added to concentrated (10%) aqueous solutions of H_3PO_4 at 40°C . As shown by this study,⁴³ stirring CaCO_3 particles in phosphoric acid solutions does not allow one to obtain submicrometer CaHPO_4 powders. The pH of the mixtures was stabilized at around 3.5. Eshtiagh-Hosseini *et al.*⁴⁴ slowly added a solution of H_3PO_4 diluted in methanol to a solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ dissolved in methanol, followed by aging the mixed solutions from 24 h to 6 days in sealed glass containers to obtain heavily agglomerated and CaCO_3 -containing CaHPO_4 particles. Methanol is an extremely toxic solution.

The motivation of the current study was to develop a chemical synthesis method, which would

(1) allow the production of submicrometer CaHPO_4 particles, which is not present in currently available monetite powders,

(2) not involve the use (or production) of any toxic or environmentally hazardous solvents (such as methanol, butanol, cyclohexane, etc.), surfactants, or organic chemicals,

(3) be economical, time-saving, and performed at room temperature.

To satisfy these, we have developed a simple and new technique, which only required precipitated calcite powders to be stirred at room temperature ($21 \pm 1^\circ\text{C}$) for 3 h in ethanol solutions containing small aliquots of phosphoric acid.

II. Experimental Procedure

Calcium carbonate of the calcite form (CaCO_3 , Fisher Scientific, Fair Lawn, NJ, Catalog No: C63, precipitated), orthophosphoric acid solution (H_3PO_4 : Merck KGaA, Darmstadt, Germany, Catalog No: 100573, 85%), and absolute ethanol (Merck KGaA, Catalog No: 100983, >99.9%) were used to synthesize monetite (CaHPO_4) powders of this study.

In a successful synthesis run to yield only single-phase CaHPO_4 , 100 mL of ethanol was first placed into a 100 mL capacity Pyrex[®] media bottle (Fisher Scientific, Catalog No: 06-423-3B) containing a Teflon[®]-coated magnetic stir bar. 2.96 g of CaCO_3 powder (= 0.0296 mol Ca) was added into ethanol and the formed opaque suspension was magnetically stirred at RT (RT: $21 \pm 1^\circ\text{C}$) for 5 min. Finally, 4 mL of H_3PO_4 (= 0.0592 mol P) was added into this calcite suspension, the glass bottle was tightly capped and the bottle contents were stirred at RT for 3 h. At the end of 3 h, the bottle was opened; the precipitates were filtered (Whatman No. 42 paper), washed with 25 mL of ethanol, the filter paper having the precipitates was finally dried overnight at 37°C in a static air oven. During this study, the starting Ca/P molar ratios in the CaHPO_4 synthesis bottles were tested over the range of 0.5–1.0, whereas the stirring times at RT were studied from 30 min to 4 h.

To test the transforming ability of the single-phase CaHPO_4 powders of this study into apatite-like calcium phosphate (Ap-CaP), a calcium-containing saline solution with a starting pH of 10 was prepared and the CaHPO_4 powders were aged at 37°C in this solution for 6 days. This saline solution was prepared as follows. 0.1118 g of KCl (Merck, Catalog No: 104933) and 2.49 g of NaCl (Merck, Catalog No: 106404) were first dissolved, respectively, in 300 mL of distilled water. The solution thus contained 5 mM K^+ and 142 mM Na^+ , identical with the K^+ and Na^+ concentrations of human blood plasma. 2.205 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck, Catalog No: 102382), corresponding to 50 mM Ca^{2+} , was then dissolved in this solution at RT. This solution was a calcium-containing saline solution and had an initial pH of 6.1 ± 0.1 at RT. Its pH was raised to around 10 by adding a 0.01 mL aliquot of concentrated NH_4OH (Merck, Catalog No: 105423). 250 mL portions of the solution were placed into 250 mL capacity glass media bottles together with 0.5 g of the single-phase CaHPO_4 powders as synthesized above, the bottles were tightly capped, placed into a 37°C oven and kept undisturbed over the 6-day aging period. The only exception to this was the quick replenishment of the mother liquors (ca. 250 mL) at every 24 h. At the end of 6 days of aging at 37°C , the recovered powders were filtered (Whatman No. 42 paper) and washed with 750 mL of distilled water, followed by drying at 37°C in a static air oven for 24 h.

Samples were characterized by powder X-ray diffraction (XRD; D8-Advance, Bruker AXS GmbH, Karlsruhe, Germany), scanning electron microscopy (SEM; S-4700, Hitachi, Tokyo, Japan), and Fourier-transform infrared spectroscopy (FTIR; Nicolet 550, Thermo-Nicolet, Woburn, MA). Powder samples for the XRD analyses were first ground in an agate mortar by using an agate pestle and then sprinkled onto ethanol-damped single-crystal quartz sample holders to form a thin layer, followed by tapping to remove the excess of powder. The X-ray diffractometer was operated at 40 kV and 30 mA by using monochromated $\text{CuK}\alpha$ radiation. XRD data (over the typical range of $10^\circ\text{--}50^\circ 2\theta$) were collected with a step size of 0.02° and a

preset time of 1 second at each step. FTIR samples were first ground in a mortar, in a manner similar to that described for the preparation of XRD samples, then mixed with pure and moisture-free KBr powders in a ratio of 1:100, followed by forming a 1-cm-diameter thin pellet by using a uniaxial cold press. One hundred and twenty-eight scans were performed at a resolution of 3 cm^{-1} . As obtained (i.e., without any grinding in mortars) powders examined with the SEM were sputter-coated with a thin Au-Pd layer before imaging, to impart surface conductivity to the samples.

III. Results and Discussion

(1) Starting Powder

Calcite (CaCO_3) powders used in this study were selected on the basis of their mean particle size (i.e., being submicrometer) and morphology. It should be emphasized that the resultant CaHPO_4 particle size and nanotextured morphology observed in this study could not be obtained if we were using other calcite powders which have much larger rectangular prismatic or rhombohedral particles.

The precipitated calcite (CaCO_3) powders used in this study were characterized by the XRD, FTIR and SEM data given in Fig. 1. The FTIR data of calcite powders given in Fig. 1 showed a weak band at around 3643 cm^{-1} , which was indicating that these commercial powders were actually produced from the aqueous carbonation of a slurry of fine particles of $\text{Ca}(\text{OH})_2$.⁴⁵ The remaining IR bands were characteristic of the calcite phase.^{46,47} The XRD trace of the first inset of Fig. 1 also depicted that these powders were single-phase calcite. The SEM photomicrograph of the second inset depicted the particle size and shape distribution of these powders. These powders comprised spindle-like particles, 1–1.5 μm in length and 0.5 μm in width. Although these spindles were sometimes forming hard agglomerates, they had uniform dimensions throughout.

(2) CaHPO_4 Synthesis

When the Ca/P molar ratios in ethanol (EtOH) solutions were made equal to 1.0 (i.e., 100 mL EtOH+2.96 g CaCO_3 +2 mL conc. H_3PO_4), the resultant powders, even after 4 h of stirring at RT, were not single-phase CaHPO_4 . The SEM photomicrograph of the inset of Fig. 2 showed that the CaCO_3 spindles of the starting powder were mostly intact, but occasional flower-like nanosheets of CaHPO_4 were observed to form. As expected, the FTIR trace of these samples (of Fig. 2) exhibited a biphasic material, i.e., calcite and CaHPO_4 .

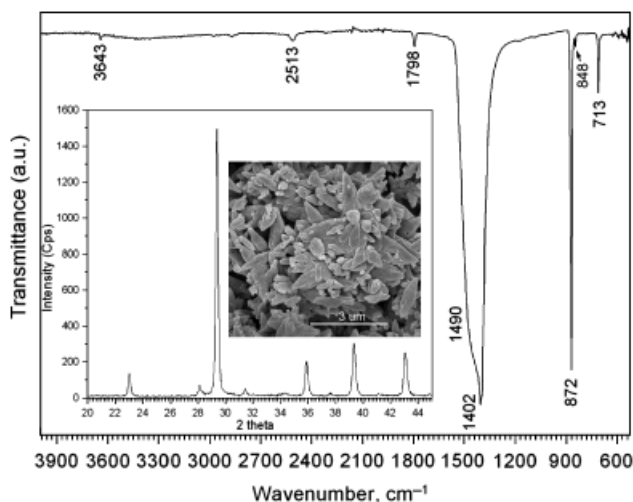


Fig. 1. Fourier-transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy data of precipitated CaCO_3 powders.

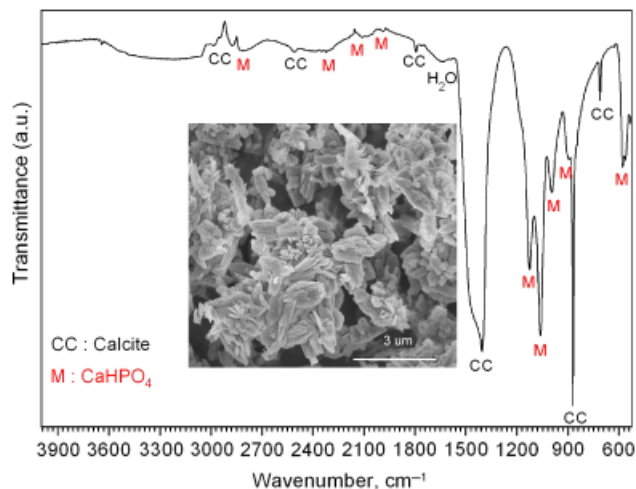


Fig. 2. Fourier-transform infrared spectroscopy and Scanning electron microscopic data of product powders obtained after reacting 2.96 g CaCO_3 and 2 mL of H_3PO_4 in 100 mL EtOH for 4 h at room temperature.

The synthesis recipe described in Section II did only differ from the above recipe in terms of doubling the H_3PO_4 concentration in the solution, bringing the Ca/P molar ratio in the synthesis vessel to 0.50. Figure 3(a) showed the FTIR and XRD traces obtained for the sample described in Section II. The FTIR

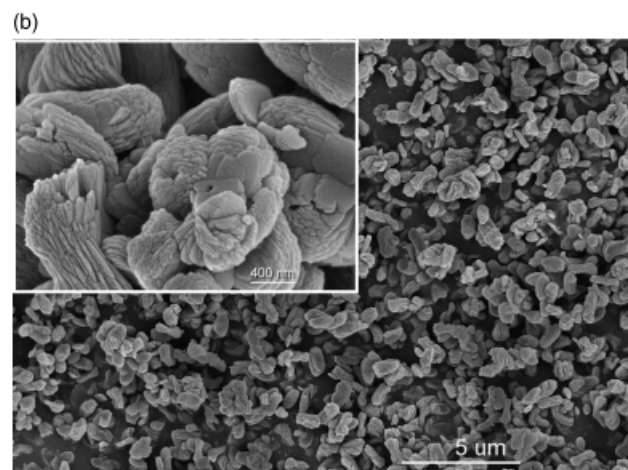
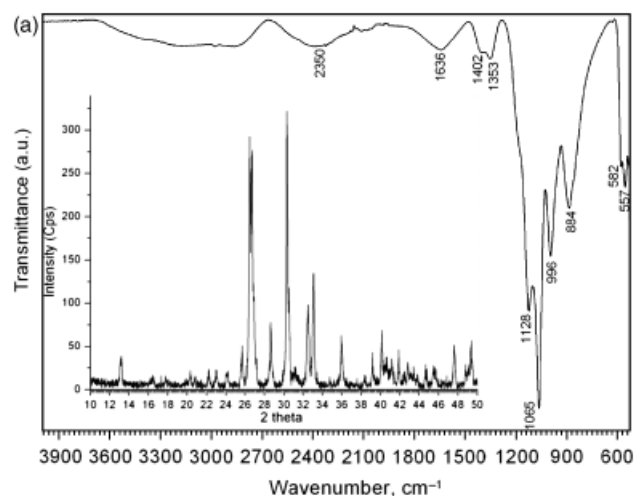


Fig. 3. (a) Fourier-transform infrared spectroscopy and X-ray diffraction spectra of single-phase CaHPO_4 powders produced by reacting 2.96 g CaCO_3 and 4 mL of H_3PO_4 in 100 mL EtOH at room temperature for 3 h. (b) SEM photomicrographs of CaHPO_4 powders of (a).

trace of Fig. 3(a) showed only the characteristic IR bands of CaHPO_4 .^{48–50} The IR bands observed in Fig. 3(a) were matching very well with those reported in the previous literature.^{48–50} The XRD trace shown in Fig. 3(a) conformed to all the diffraction peaks of CaHPO_4 listed in ICDD PDF 70-360 over the 2θ range of 10° – 50° .⁵¹ These samples were produced by stirring at RT for only 3 h, stirring for 4 h did not produce any noticeable changes in the data of Fig. 3(a). This meant that stirring the CaHPO_4 suspension in absolute ethanol beyond 3 h was not necessary. At the end of 3 h of stirring at RT, the pH of the mother liquors (before the filtration of the CaHPO_4 particles) were found to be constant at around 3.25 ± 0.2 .

The SEM photomicrographs of Fig. 3(b) displayed the particle morphology of CaHPO_4 powders produced in 100 mL absolute EtOH at RT by using 0.0296 mol of precipitated CaCO_3 powder and 0.0592 mol H_3PO_4 (85% solution) as the starting materials. Especially, the inset of Fig. 3(b) clearly exhibited the nanosheets of CaHPO_4 stacked together to form the ellipsoidal particles. The average particle size in these samples was measured by using the linear intercept method. The ellipsoidal CaHPO_4 particles were found to have lengths of $1.30 \pm 0.10 \mu\text{m}$ and widths of $0.7 \pm 0.15 \mu\text{m}$. The rather narrow size and shape distribution were visible from the SEM micrographs.

(3) Effect of H_3PO_4 Volume

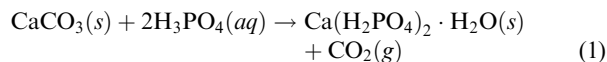
The XRD traces given in Fig. 4(a) depicted the influence of different volumes of H_3PO_4 added to the suspensions created by

mixing, in each case, 2.96 g of precipitated CaCO_3 and 100 mL EtOH, following 3 h of stirring at RT after the addition of H_3PO_4 . It was thus apparent that when the Ca/P molar ratio in the reaction vessels at the start of stirring was made equal to 0.50 (i.e., 4 mL H_3PO_4 addition), single-phase CaHPO_4 powders were obtained at the end of 3 h. Lesser volumes of H_3PO_4 additions resulted in the observation of unreacted CaCO_3 (Fig. 4(a)), identified by the most intense diffraction peak of the calcite phase (ICDD PDF 5-586) observed at $29.415^\circ 2\theta$. Orthophosphoric acid is soluble in ethanol. For example, Bradford Reagent (used in the determination of the concentration of proteins in solution) is prepared by mixing 50 mL of ethanol and 100 mL of H_3PO_4 .⁵² Therefore, dissolving small amounts (i.e., 2–4 mL) of H_3PO_4 in 100 mL of ethanol in the current study poses no solubility concerns.

(4) Effect of Stirring Time

The XRD traces shown in Fig. 4(b) showed the effect of stirring time on the phase development. All of the samples of Fig. 4(b) were produced according to the synthesis recipe of “100 mL EtOH+2.96 g CaCO_3 +4 mL H_3PO_4 .” The stirring times employed were 0.5, 1, 2, and 3 h, respectively. The experimental XRD peaks of the monocalcium phosphate monohydrate (MCPM, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) phase shown in Fig. 4(b) matched well with those of ICDD PDF 75-1521 for MCPM.

Therefore, synthesis of monetite in ethanol containing small amounts of phosphoric acid at RT, as described in this study, took place according to the below reactions in two distinct steps:



According to the XRD data of Fig. 4(b), Reaction was taking place immediately after adding small aliquots of H_3PO_4 solution into the CaCO_3 -EtOH suspension. However, at the end of 0.5 h of stirring at RT the resultant solids were biphasic (Fig. 4(b)), i.e., consisting of about 70% MCPM and 30% CaHPO_4 . This meant that Reaction was also taking place within the first 30 min. By the end of 2 h of stirring, the material formed was again biphasic, but this time comprising 70% CaHPO_4 and 30% MCPM. Three hours of stirring was obviously enough to convert all MCPM into CaHPO_4 .

The synthesis procedure described here is, therefore, not depositing CaHPO_4 crystals on top of calcite particles. A comparative examination of the SEM pictures of Figs. 1, 2, and 3(b) would reveal that within few hours of stirring at RT in H_3PO_4 -containing ethanol solutions, the initially present calcite agglomerates totally disappeared. Precipitated calcite particles were not stable in phosphate-containing ethanol solutions of pH around 3.2. $\text{H}_2\text{PO}_4^{2-}$ ions initially present in these solutions rapidly reacted with CaCO_3 to form transient MCPM (see Reaction and Fig. 4(b)) crystals. Highly acidic MCPM, on the other hand, would not in turn be stable in such ethanol solutions, and they had to transform into CaHPO_4 . The use of ethanol solutions prevented the formation of brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, in accord with the purpose of this study.

(5) Conversion of CaHPO_4 into Ap-CaP

The comparative FTIR and XRD traces of Fig. 5(a) showed the transformation of CaHPO_4 into Ap-CaP within 6 days of ageing at 37°C in the calcium-containing saline solution of this study. The symmetric and anti-symmetric stretching of the PO_4^{3-} group were observed at 1090, 1025, 958, 602, and 560 cm^{-1} . The weak shoulder at around 1297 – 1300 cm^{-1} was attributed to the smaller presence of HPO_4^{2-} ions.^{53,54} HPO_4^{2-} ions do also have

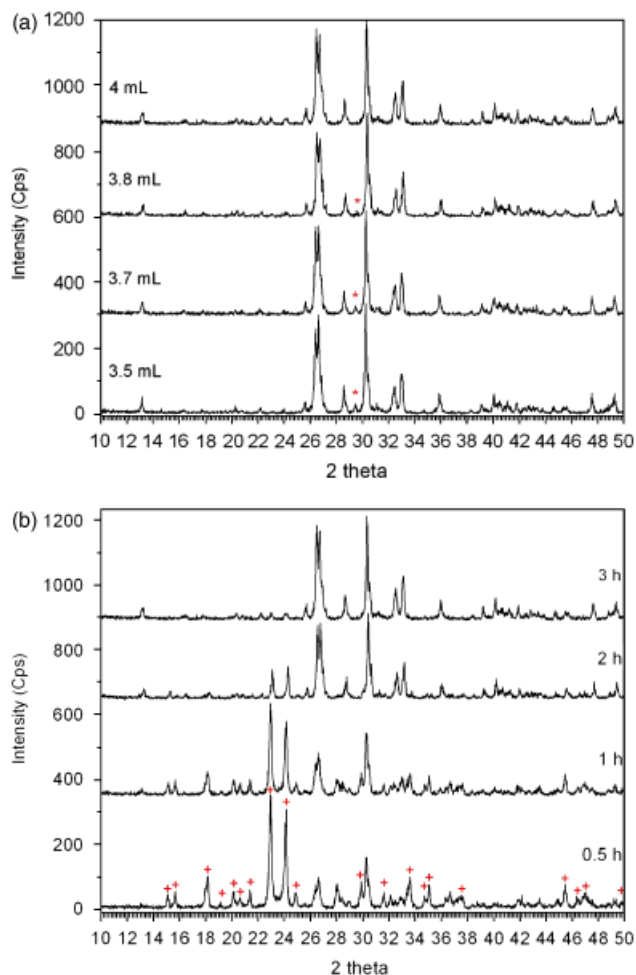


Fig. 4. (a) X-ray diffraction (XRD) traces showing phase development in 2.96 g CaCO_3 and 100 mL EtOH mixtures containing different aliquots of H_3PO_4 (room temperature (RT), 3 h stirring each; *calcite peak). (b) XRD traces showing phase development in 2.96 g CaCO_3 and 4 mL H_3PO_4 in 100 mL EtOH mixtures as a function of increasing stirring time at RT (+MCPM peaks).

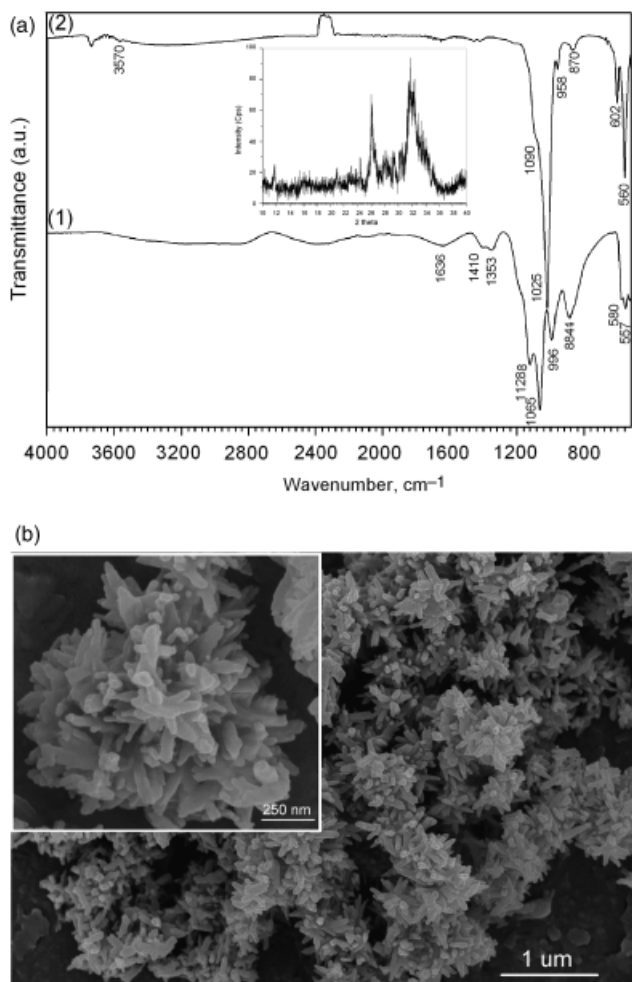


Fig. 5. (a) Comparative Fourier-transform infrared spectroscopy spectra of single-phase CaHPO_4 powders synthesized in EtOH (trace-1) and those of Ap-CaP powders synthesized in Ca-containing saline solution at 37°C for 6 days of soaking of CaHPO_4 (trace 2); X-ray diffraction spectrum of Ap-CaP powders synthesized by soaking CaHPO_4 powders in Ca-containing saline solution at 37°C for 6 days was shown in the inset. (b) Scanning electron photomicrographs of Ap-CaP powders synthesized by soaking CaHPO_4 powders in Ca-containing saline solution at 37°C for 6 days.

a band at 870 cm^{-1} . The stretching mode of the O–H group was observed in Fig. 5(a) at 3570 cm^{-1} .

The XRD data of the inset of Fig. 5(a), on the other hand, depicted a poorly crystallized (or nanocrystalline) Ap-CaP pattern, contradicting what was previously reported by Lebugle *et al.*¹² Because the XRD data shown in Fig. 5(a) were generated from ground powders, it negated the assertion (by Lebugle *et al.*¹²) that the CaHPO_4 particles will be covered by a thin external layer of apatitic CaP in water at 37°C and thus it will hinder the further transformation of monetite. This was certainly not observed in the present study.

The rather smooth conversion of CaHPO_4 into Ap-CaP was quite an expected result because CaHPO_4 is one of the very interesting compounds of the calcium phosphate family which is not thermodynamically stable in solutions with pH values > 5.5 . This was why CaHPO_4 has been one of the indispensable compounds used in self-hardening orthopedic and maxillofacial cement development.^{3–6}

The pH values of the aging solutions (at the end of every 24 h, just before full replenishment of the used solutions with fresh solutions) were recorded as 5.7 ± 0.1 at $36^\circ\text{--}37^\circ\text{C}$.

The SEM photomicrographs of Fig. 5(b) depicted the nanosize particles of the Ap-CaP obtained from the starting powders of CaHPO_4 of this study. The entire process reported in this study can also be regarded as a low-cost method of producing

Ap-CaP powders free of any ionic impurities, such as NO_3^- , NH_4^+ , etc.

It should be remembered that CaHPO_4 powders can be readily converted into those of carbonated Ap-CaP (some call the end-product as “hydroxyapatite” although it was not stoichiometric at all) if they were hydrolyzed in hot solutions, such as NaHCO_3 , Na_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$, or NaOH solutions at temperatures between 75° and 100°C .^{53–62} In the current study, we have deliberately chosen our hydrolysis temperature as 37°C , which is the physiological temperature. Again in this study, we preferred to develop a hydrolysis solution (for monetite) to be as benign as possible so that in the follow-up studies, for instance, one could easily add certain proteins or growth factors to such hydrolysis solutions of nanotextured monetite (as shown here) to form biomimetic Ap-CaP powders.

IV. Conclusions

(1) CaHPO_4 (monetite, DCPA) powders with submicrometer particles and a nanosheet microtexture were synthesized, in 3 h, at room temperature by stirring precipitated CaCO_3 powders in ethanol solutions containing small aliquots of phosphoric acid.

(2) CaHPO_4 powders of this study were fully converted at 37°C , in 6 days, into nanoapatite powders in a solution comprising 142 mM Na^+ , 5 mM K^+ and 50 mM Ca^{2+} .

Notes: Certain commercial equipment, instruments or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the author, nor does it imply that the equipment or materials identified are necessarily the best available for the purpose.

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