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Microwave hydrothermal synthesis of calcium phosphates using inorganic condensed phosphate salts as precursors

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ABSTRACT

As a potential phosphate source, inorganic soluble condensed phosphate salts represent a viable alternative to both orthophosphate and organic condensed phosphate salts. The present work demonstrates a simple but versatile microwave hydrothermal method to prepare calcium phosphates using pyrophosphate and tripolyphosphate salts. After 5-min microwave heating, white fine powders are precipitated from calcium and condensed phosphate containing solution. The as-synthesized precipitates are crystallized calcium pyrophosphate hydrate whiskers and calcium tripolyphosphate hydrate porous microspheres. After calcination, both ceramics are converted into calcium pyrophosphate. *In vitro* study reveals both precipitates and calcined powders are cytocompatible compared to microwave hydrothermally synthesized hydroxyapatite. With all of these attributes, it is expected different inorganic soluble condensed phosphate salts together with microwave can be used to generate a series of calcium phosphates with unique features.

1. Introduction

Microwave-assisted synthesis of calcium phosphates (CaPs) in liquid phase has attracted many research interests [1]. A variety of CaPs with different morphologies, including rods, whiskers, spheres and mesoporous particles, have been prepared [2,3]. It is noticed in the synthesis process, the crystal phase and morphology of as-prepared ceramics are strongly influenced by the reactants. For example, Wang et al. prepared hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) powders of rod-like or prism-like nature using microwave-assisted hydrothermal system with orthophosphate salt as precursor [4]. Meanwhile, Zhu et al. reported the microwave-assisted hydrothermal production of mesoporous amorphous calcium phosphate (ACP) microspheres with adenosine 5′-triphosphate (ATP) or adenosine 5′-diphosphate (ADP) as the phosphorus source [5,6]. Therefore it is reasonable to speculate that the replacement of regular orthophosphate salts using soluble condensed phosphate salts can induce significant changes to the as-synthesized CaPs.

In nature, condensed phosphate salts can be divided into two groups, organic and inorganic. To the best of our knowledge, only organic condensed phosphate salts have been used together with microwave energy to synthesize CaPs. Reports on the application of soluble inorganic condensed phosphate salts in microwave-assisted hydrothermally synthesizing CaPs are limited. However, it is noted that inorganic condensed phosphate salts have been applied to generate CaPs in other systems. For example, free calcium ions can react with inorganic condensed phosphate salts to form amorphous porous complex once contacted [7,8]. After that, with thermal or chemical treatment, the complex can be converted into a series of CaPs, such as calcium pyrophosphate, HA, monetite etc. [7,9]. Hence, the purpose of present work is to evaluate whether the usage of inorganic condensed phosphate salts as phosphate source can result in CaPs with unique crystal phase or morphology to regular orthophosphate one.

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2. Material and methods

Two inorganic condensed phosphate salts, $Na_4P_2O_7$ and $Na_5P_3O_{10}$, were used. Typically, $CaCl_20 \cdot 2H_2O$ was first dissolved in H_2O, followed by adding $Na_4P_2O_7$ or $Na_5P_3O_{10}$ separately to make a Ca/P molar ratio of 1.5. In order to have settled solution, the pH was adjusted to 4.5 by 1 M hydrochloric acid. Solution of $CaCl_2 \cdot 2H_2O$ and NaH_2PO_4 with Ca/P at 1.5 was used as control. Beaker with solution was placed into a 720 W household microwave oven for 5 min heating at maximum power. After that, the solution was successively filtered. The collected precipitates were washed with deionized water and dried at 80 °C overnight.

Precipitates were firstly characterized by X-ray diffraction (XRD, Rigaku) to determine the material phases. The chemical bands were analyzed using Fourier-transformed infrared spectroscopy (FTIR, Digilab). The thermal transition of precipitates was measured using a thermogravimetry differential scanning calorimetry analyzer (TGA, TAcompany). The powders, calcined at 1000 °C, were also characterized using XRD and SEM. The surface morphologies were studied using a scanning electron microscope (SEM, Zeiss). Osteoblast cells (MC3T3-E1) were used to study the cytocompatibility of precipitates before and after calcination. Wells containing 1000 mg/mL powders in 500 μl culture medium were incubated 48 h prior to the cell seeding. After that, MC3T3-E1 cells were seeded on to wells at a density of 10,000 cells/well. Immediately after seeding, powder extracts were added to the wells. The medium was changed every other day. Cell density was measured using MTT after 1 and 7 days.

3. Results and discussion

All precipitates are white fine powders. As shown in Fig. 1(a), the precipitates from Ca-P are HA as expected (PDF #09-0432). In previous work we have shown that a calcium orthophosphate solution under microwave irradiation can only generate HA due to the thermal driving force unless stabilizer added [10]. It is known condensed phosphates can easily react with Ca^{2+} to produce amorphous complex in aqueous solution. However, due to HCl addition and microwave-assisted HCl evaporation, these complexes follow a precipitation-dissolution-precipitation process in response to pH change, and the end product is found to be crystallized. The precipitates from Ca-P2 are mainly crystallized calcium pyrophosphate hydrate (CPPH, $Ca_2P_2O_7 \cdot 2H_2O$, PDF #41-0488). However, the material phase of precipitates from Ca-P3 is unidentified. In FTIR (Fig. 1(b)), all precipitates showed peaks at 1010 cm^{-1}, referred to phosphate. Absorption peaks from water were shown in 1656 and 3448 cm^{-1} for all precipitates. In addition, both Ca-P2 and Ca-P3 precipitates show various P–O bands at wavelengths of 766, 918, 1093, 1162, and 1238 cm^{-1}, attributed to the presence of condensed phosphate bands (Fig. 1(b)). Therefore, it is suggested Ca-P3 precipitates should be calcium condensed phosphate. After calcination, both Ca-P2 and Ca-P3 become dehydrated crystallized CPP ($Ca_2P_2O_7$, PDF #09-0346) (Fig. 1(c)). In the TGA experiment (Fig. 1(d)), Ca-P3 presents a sudden weight change between 100 and 200 °C, possibly caused by the loss of absorbed water in Ca-P3. After that, both Ca-P2 and Ca-P3 show similar weight change behavior with loss of crystal water. In our previous work we have shown amorphous complex of Ca^{2+} and

Table 1.
Compositions of aqueous mixture used in microwave hydrothermal experiment.

Sample	$CaCl_2 \cdot 2H_2O$ (g)	Phosphate source (g)		H_2O (mL)	Ca/P
Ca-P	0.294	NaH_2PO_4	0.16	200	1.5
Ca-P2	0.294	$Na_4P_2O_7$	0.177	200	1.5
Ca-P3	0.294	$Na_5P_3O_{10}$	0.1635	200	1.5

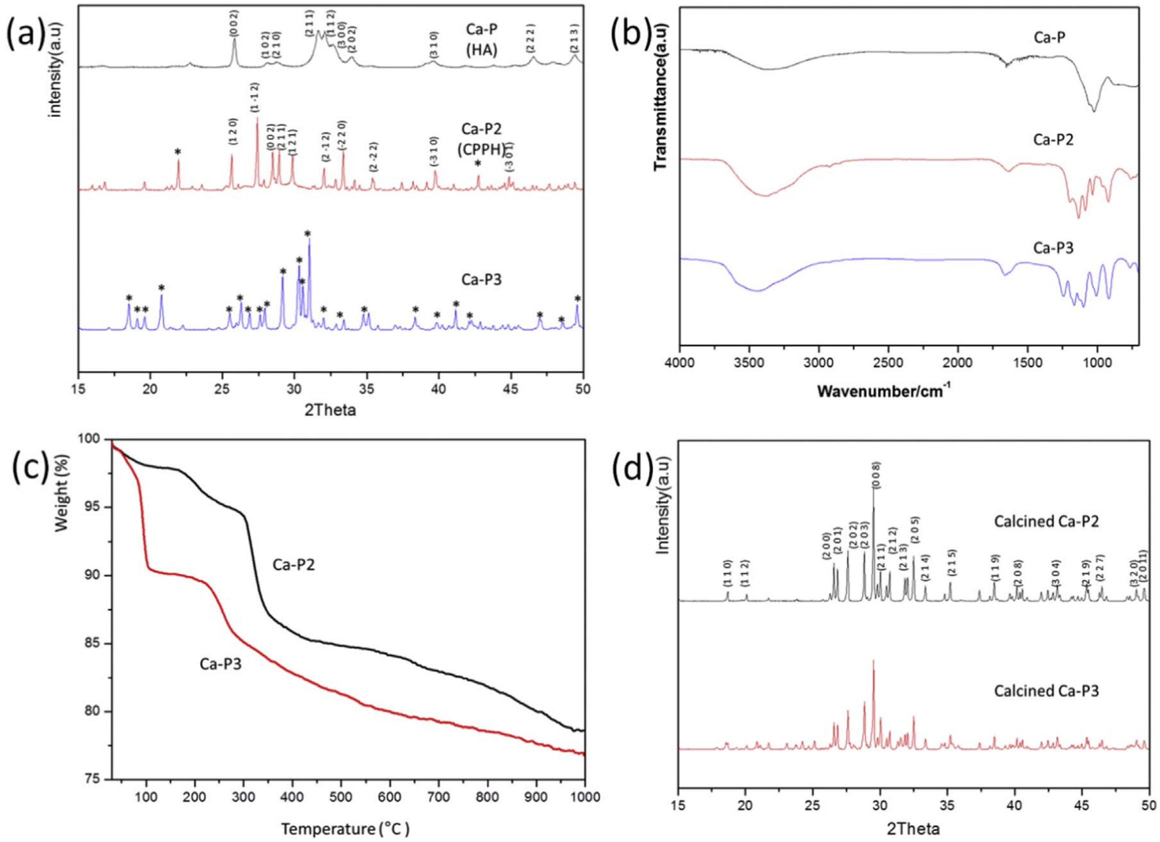

Fig. 1. (a) XRD of precipitates, "*" refers to unidentified pattern; (b) FTIR of precipitates; (c) TGA of Ca-P2 and Ca-P3; (d) XRD of calcined powders.