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## The Effect of phosphoric acid concentration on the Synthesis of Nano- whiskers of Calcium Metaphosphate By Chemical Precipitation Method

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**Keywords::** calcium metaphosphate; nano-whisker; chemical precipitation; phosphoric acid concentration

**Abstract.** Calcium metaphosphate (CMP) nano-whiskers were produced by a chemical precipitation method. In order to produce nano-powders, CMP was prepared by the mixing of two precursors, calcium oxide (CaO) and phosphate acid (H<sub>3</sub>PO<sub>4</sub>). Sparingly soluble chemicals, the Ca/P ratio of the mixture was set to be 0.50 to produce stoichiometric CMP, were chemical agitated in phosphate acid solution. At least 3 hours of pre-hydrolysis of phosphorus precursor were required to obtain CMP phase. The CMP powders were dried in a drying oven at 60 °C for 7 days and then followed by a heat treatment at 390 °C for 8hours. The obtained powder was analyzed using XRD, XRF, FT-IR, SEM, TG-DTA, Zeta Potential Meter, Specific Surface Area, and Particle Size Analyzer. The results showed that obtained CMP nano-whiskers have a significantly powder characteristics.

### Introduction

Calcium meta-phosphate (molecular formula, Ca(PO<sub>3</sub>)<sub>2</sub>) is an excellent new substitute material for bone tissue engineering due to its biocompatibility, biodegradability and osteoconductivity. CMP is suitable for the application of bone tissue engineering. In the last two decade, extensive attentions have been paid in CMP in the worldwide, such as the vitro, vivo and cytotoxicity experiments of CMP scaffold with three-dimensional structure<sup>[1-3]</sup>. It has been reported that nano-sized CMP particles is more effective in stimulating the proliferation and osteoblastic differentiation of human bone marrow stromal cells (hBMSCs) than micro-sized CMP particles. In addition, the stimulatory of the nano-sized CMP particle was dose-dependent<sup>[4]</sup>. If CMP was adhered to collagen, it could activate platelets and release growth factors<sup>[5]</sup>. However, hydroxyapatite (HA) particles smaller than 53 μm may cause osteolysis by inducing activation of osteoclasts and decreasing of osteoblasts<sup>[6]</sup>. Compared with HA, CMP can activate alkaline phosphatase (ALP) and promote the expressions of osteoprotegerin (OPG), osteopontin (OPN) and ALP<sup>[3]</sup>. With respect to the mechanics and histomorphometry, many literatures have been reported<sup>[7-11]</sup>. And histomorphometric and removal torque (RT) measurements are the two representative tests in studying the nature of the implant-tissue interface<sup>[7]</sup>. All the implant materials with surface modification, such as CMP-coating, anodic oxidation and blasting, show a better osseointegration and early loading. CMP can be coated on inert materials (mostly are alloy and metals) so as to bioactivate the material and shorten the healing time<sup>[12]</sup>.

Our previous work<sup>[13]</sup> propose a new method to prepare the fine powder by chemical precipitation. Based on this method, CMP powders were prepared with different concentration of phosphoric acid. The aim of this study is to investigate the effect of phosphoric acid concentrations in the powder synthesis on the properties of CMP powders.

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## Materials and Methods

Both chemicals used in this study were supplied by Nanjing Chemical Reagent Co., Ltd. and used without further purification. But the concentration of phosphoric acid used in this study was variable with the concentration of 3.0mol/L, 2.0mol/L, 1.0mol/L and 0.5mol/L, respectively. CaO was added to these different solutions with the Ca/P molar ratio of 0.5. Then the slurries were magnetic force agitated at 500 rpm for 48 hours at room temperature. Then the pH of four slurries was measured. The reacted slurries were dried at 60 °C for 7 days and the resulting powders were marked as A, B, C and D. Then the powder were heat-treated in air at 390 °C to produce CMP powder which were defined as A-1, B-1, C-1 and, D-1, correspondingly. Additionally, powder marked as E is obtained by heat-treatment of powder C at 500 °C.

The crystal phases of the synthesized powder and heat-treated powders were analyzed by X-ray Diffraction with using an X-ray diffractometer at 40KV and 20mA Co target with CuK $\alpha$  radiation (wavelength=1.54056 Angstroms). The phases were identified by comparing the diffraction patterns with ICDD (JCPDS) standards.

Fourier transform infrared (FT-IR) analysis (Thermal Nicolet AVATAR 360) was used to characterize the functional groups. TG/DSC of the synthesized powders was measured using a thermal analyzer (STA 449 C Jupiter) from room temperature to 900 °C under an air flux of 100ml/min ramping at 5 °C /min. The morphology of the powders was observed by using a JSM-5610LV SEM, and Horiba EMAX-2200 X-ray analyzer.

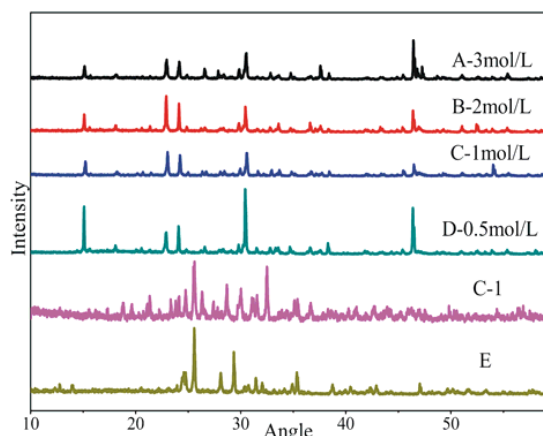
## Results and Discussion

The crystal phases of the powders either before or after sintering was identified as monocalcium phosphate monohydrate (MCPM, molecular formula,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ) and CMP the XRD pattern (Fig. 1), respectively. This could be concluded by the results of X-ray, since only a single phase without secondary phase is observed. Samples under heat-treatment at 390°C for 8 hours or no heat-treatment were both poorly crystalline, as indicated by the broad diffraction peaks, which is also characteristic of CMP prepared by an aqueous precipitation route. In contrast, the heat-treatment at 500°C CMP powder produced a diffraction pattern that corresponded to a crystalline material, with narrow diffraction peaks, which is characteristic of a powder that has been heat-treated.

TG-DSC is used to analyze the synthesized powder's physical and chemical reactions during the heating process. Fig. 2 exhibits us the TG-DSC curves of powders prepared by chemical precipitation method after drying at 60 °C for 7 days. Usually, MCPM exhibits two decomposition steps. The first step occurred at 109 °C, it releases a molecule of water with 7.14% mass losing and transformed into MCPA (monocalcium phosphate anhydrous,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ). The dehydration reaction began at 210°C with 14.28% mass losing and transformed into CMP during the second step. In this study, the powders lost weight 5.67% at about 109 °C followed by 15% quality lost at 256 °C, which was corresponded well with the nature of MCPM. With regard to the results of DSC, three peaks were observed. Both the first peak (109 °C) and the second peak (256 °C) were caused by the decomposition of MCPM, while the third peak was attributed by the melting of CMP. All the results of TG-DSC correlated well with the aforementioned XRD pattern.

The morphology of CMP powders was illustrated in the SEM micrographs, Fig.3. In Fig. 3A, the crystal is a short cylindrical whisker, some whiskers with the length of 0.5  $\mu\text{m}$  and diameter about 50 nm are observed. In Fig. 3B, the crystal is almost plate-shape, there is no whisker. The whisker crystal pile into plate is about 1~2  $\mu\text{m}$  wide. In Fig. 3C, there are only layered up to agglomerate which is about 2-3  $\mu\text{m}$  long. In Fig. 3D, the agglomerate is larger than that is shown in Fig. 3C, it is about 6  $\mu\text{m}$  long and 3  $\mu\text{m}$  wide. The morphology of D powders was showed a plate. From the above observation, it can be conclude that the

morphology of crystal is strongly depended upon the concentration of phosphoric acid. At higher concentration of phosphoric acid, the crystal is whisker-shape. As the concentration decreases, the crystal changes into the plate-shape with the increase in crystal size. And further decrease in the concentration give rise to the substantial increase in crystal size, while the crystal goes through the transition from short cylindrical whisker to layer-shaped to



agglomerate plate-shape.

Fig.1 X-ray patterns of the synthesized powders after dring at 60 °C for 7 days and heat-treated at 390 °C for 8 hours.

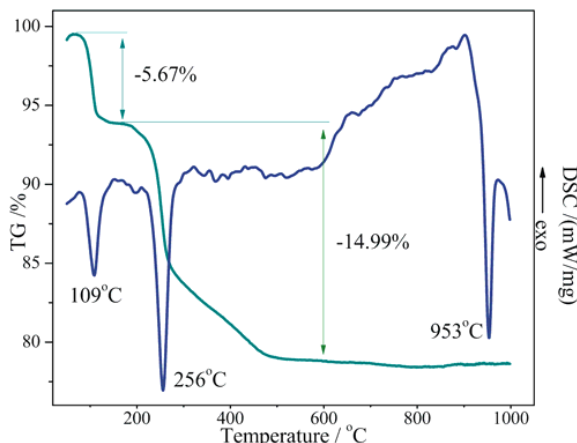


Fig. 2 TG-DTA curves of powders prepared by chemical precipitation method after drying at 60 °C for 7 days

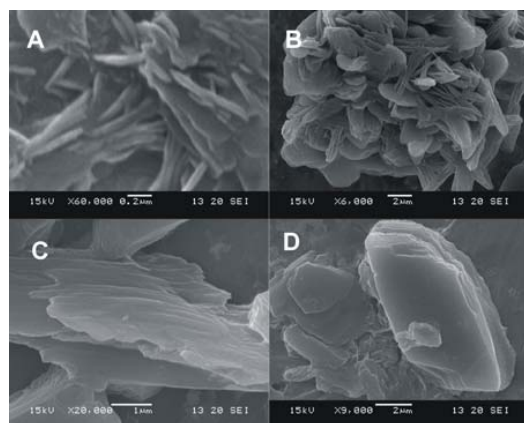


Fig.3 SEM micrographs of the synthesized powder A, B, C and D prepared with different concentration

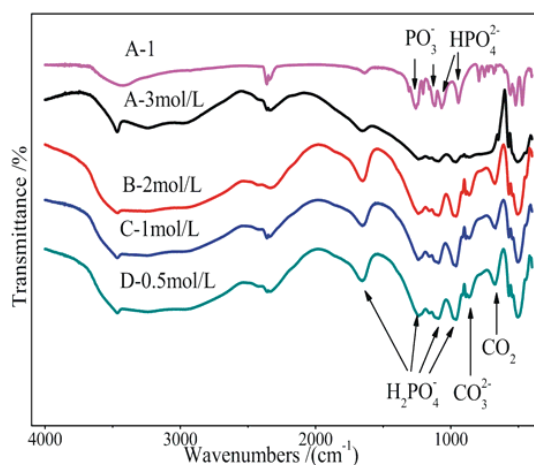


Fig.4 Infrared absorption spectra of the powder heat-treatment at 390°C for 8 hours and no heat-treatment.

The pH of four slurries prepared by 3mol/L, 2mol/L, 1mol/L and 0.5mol/L of phosphoric acid were 2.02, 2.20, 2.35 and 2.75, respectively. The influence process of initial pH values on the morphology of powders was analyzed as follows. Initial pH values influenced the balance of ions in the solution. Different pH values depended on the concentration of  $H^+$ , which could influence the concentration of  $H_3PO_4$ ,  $H_2PO_4^-$ ,  $HPO_4^{2-}$  and  $PO_4^{3-}$ . High concentration of  $H^+$  can promote the precipitation process of formation of the particles. Initial pH values directly

influenced the crystal growth habit. The schematic diagram of CMP crystal structure influenced by pH is shown in Fig.3.

Structural changes of the MCPM and CMP powders were analyzed by FT-IR, as shown in Fig.4. In the MCPM powders ( Fig. 4 A, B, C and D ), the strong characteristic absorption peak at 960, 1100, 1240 and 1655  $\text{cm}^{-1}$  were respectively corresponded with the P-OH, O-H and P-O vibration in the  $\text{H}_2\text{PO}_4^-$ . This result was consistent with the XRD. In Fig. 4, the characteristic absorption peak (865  $\text{cm}^{-1}$ ) of  $\text{CO}_3^{2-}$  was observed. This might be due to the adsorption of atmospheric carbon dioxide during the sample preparation. In addition, the characteristic absorption peak of  $\text{CO}_3^{2-}$  in A is lower than others, which was caused by the increasing concentration of  $\text{H}^+$  and indicated A contained less  $\text{CO}_3^{2-}$  than others. In this sense, the crystal grew up more uniform and less affected, from which short cylindrical whisker can be obtained. However, it is interesting noting in the heat-treatment at 390°C CMP powders (Fig. 4A-1) that no characteristic peak of  $\text{H}_2\text{PO}_4^-$  and  $\text{CO}_3^{2-}$  were found. Instead, the characteristic absorption peaks of  $\text{PO}_3^-$  (1100~1160 and 1260~1320  $\text{cm}^{-1}$ ) and characteristic absorption peaks derived from  $\text{HPO}_4^{2-}$  (1070 and 944  $\text{cm}^{-1}$ ) were observed. This could be due to the decomposition of MCPM. And the  $\text{HPO}_4^{2-}$  could be observed in the figure may be due to the incomplete dehydration.

### Summary

The effect of concentration of phosphoric acid on the morphology of the synthesized powder was studied. Then, the synthesized powder was heat-treated at 390 °C was examined. The A powder which was prepared with 3 mol/L phosphoric acid exhibit an excellent morphology. The crystal is small and uniform. With the decreasing of concentration of phosphate acid, the whisker crystal transitioned to agglomerate and grew up larger. Therefore, a reasonable choice of concentration of phosphate acid on synthesis pure and fine powder is very important.

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