Evaluation of calcination temperature and phase composition ratio for new hydroxyapatite

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Abstract. The demand of production of hydroxyapatite (HA) has been increasing for the purpose of medical and dental application. HA possesses the excellent properties leads to the priority choice for ceramic bone replacement. Synthesis route by wet chemical precipitation is commonly practised in industrial scale. Calcium hydroxide and Orthophosphoric acid are the precursors for production scale. The synthesis of HA is conducted by varying the synthetic condition: stirring rate, calcium-phosphate and calcination temperature. This paper is focused on the properties of HA produced by regulating the synthetic condition so that the qualities of HA can be well performed. Characterization studies were also carried out by Fourier Transform Infrared Spectroscopy (FT-IR) for functional group identification, Scanning Electron Microscope (SEM) for surface morphology analysis and X-Ray Diffraction (XRD) for phase composition and crystallinity respectively. Narrow particle size distribution contributed to better quality of hydroxyapatite for bone replacement. Both calcium-phosphate ratio and calcination temperature would affect the phase composition of calcium phosphate.

Keywords: hydroxyapatite, wet chemical precipitation, stirring rate, calcium-phosphate ratio, calcination temperature

1. Introduction
Ceramic, glass and glass ceramic materials have been introduced and use to substitute fracture bone in many clinical applications since 1970’s [1]. Calcium phosphate ceramics have gained the research attention due to their chemical compositions which similar with bone. Calcium phosphate is biocompatible and non-toxic. These excellent properties make them outstanding in medical and dental applications. The most frequently utilized in bone substitutes are hydroxyapatite (HA) and tricalcium phosphate (TCP). Currently, HA is the most commonly applied in bone grafting. HA has more stable phase to support biological apatite precipitation [2]. Hydroxyapatite is non-resorbable whereas Tricalcium phosphate is bioresorbable and can be replaced by natural bone. This is the main reason to emphasize on further researches and investigations on Tricalcium Phosphate. Therefore, beta-tricalcium phosphate (Beta-TCP) has been promoted as a biodegradable bone replacement [3].

Several methodologies have been conducted to prepare calcium phosphate ceramics including precipitation technique, sol-gel approach, hydrothermal technique, multiple emulsion technique, biomimetic deposition technique and electro-deposition technique [4]. Wet precipitation method is the
most frequently applied in industrial production because of its simplicity, low cost and easy application [5].

For wet precipitation method, processing parameters such as temperature and reaction time, might affect the results of precipitation in terms of purity, surface area and particle size distribution. For instance, the size of HA particles reduce as the reaction time at room temperature increases. In addition, the temperature can also influence the particle size of HA where increasing temperature can produce larger HA particles. On the other hand, lowering temperature causes the particles morphology become more spherical, while raising the temperature can lead to needle-shaped morphology [6].

Among the various processing parameters, this study will focus on two critical parameters which needed to take into conscious consideration during the preparation of calcium phosphates: calcination temperature and phase composition ratio. Calcination temperature could affect the strength and toughness of calcium phosphates while mechanical properties and biodegradation rate strongly depend on the phase composition (Ca/P) ratio [7]. In this research, we are reporting synthesis of HA by wet precipitation method and evaluating the effect of calcination temperature and phase composition ratio on the formation of HA.

2. Methodology

2.1. Wet Precipitation Method

Wet precipitation method was carried out to produce hydroxyapatite. Calcium hydroxide and phosphoric acid were employed as the precursors. Firstly, 100mL of 0.6M H$_3$PO$_4$ was added into 100mL 1M CaOH$_2$ solution. Different molar ratio (Ca/P =1.50,1.59,1.67) of calcium phosphate were prepared. NH$_4$OH was used to maintain the system at pH 11 with continuous stirring (150 rpm, 250 rpm, 300 rpm) for one hour at 90 °C. Later, the mixture was aged for 24 hours at room temperature. After that, precipitate was filtered and eventually the precipitate was dried at 100°C and calcinated with high temperature (600 °C, 700 °C, 800 °C). The equation of the chemical reaction was shown as in equation 1:

$$10\text{CaOH}_2 + 6\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 + 18\text{H}_2\text{O}$$ (1)

The flow chart for the synthesis of HA by wet precipitation method was shown in Figure 1. Continuous stirring was required after the reactants are combined as the calcium is slowly incorporate into the apatite structure, helping the material to achieve suitable stoichiometric Calcium/Phosphate (Ca/P) ratio.

2.2. Characterization Studies

The phase composition crystallographic structural analysis was determined by X-ray Diffraction (XRD) with monochromatic Cu K$_\alpha$ = 1.5405Å radiation over the 2 range of 20–80° at a scan rate of 0.02°/min. Fourier Transform Infrared Spectroscopy (FTIR) used to identify the functional group and quality of calcium phosphate compounds. FTIR spectrum was recorded in the range of 4000–400 cm$^{-1}$ region with 2 cm$^{-1}$ resolution.The morphology of synthesized powders were studied by scanning
electron microscopy (SEM) operating with accelerating voltage of 20 kV. The magnification ranging from x800 to x2000.

**Figure 1.** The flow chart of synthesis of hydroxyapatite by using wet precipitation method.
3. Results and Discussion

3.1. Fourier Transform Infrared Spectrometry (FT-IR)

Figure 2 represented the FT-IR spectrum of Hydroxyapatite (HA) powders. FT-IR patterns were presented in Figure 2 confirmed that the formation of HA calcinated at different temperatures of 600 ºC and 800 ºC.

![FT-IR spectrum of Hydroxyapatite (HA) powders.](image)

**Figure 2:** FT-IR spectrum of Hydroxyapatite (HA) powders.

| Chemical groups | Absorption band, cm⁻¹ |
|-----------------|------------------------|
| PO₄³⁻           | 474;563;602;963; 1000-1100;2000-2100; |
| OH               | 3570;3435;             |
| CO₃²⁻           | 1414;1455;             |
| H₂O             | 1635;                  |

**Table 1.** Absorption bands of Hydroxyapatite (HA) at different synthetic conditions.
The absorption bands of chemical functional group characteristic to HA phase can be defined as follows in Table 1.

- The presence of [PO$_4$] groups that possessed tetrahedral apatite structure was proven by absorption bands at 474 cm$^{-1}$, which characteristic to [PO$_4$]v$_2$ group (v$_2$ O-P-O) bending variations; double bands at 563 cm$^{-1}$ and 602 cm$^{-1}$ with a high resolution were refer as symmetric and asymmetric deformation modes of [PO$_4$]v$_4$ group (v$_4$ O-P-O); absorption band at 963 cm$^{-1}$ corresponded to symmetric stretching mode; absorption band in the range of 1000-1100 cm$^{-1}$ demonstrated the characteristic to [PO$_4$]v$_3$ groups (v$_3$ P-O) at 1000 cm$^{-1}$ and 1100 cm$^{-1}$ asymmetrical stretching mode. The absorption in the range of 2000-2100 cm$^{-1}$ referred to the weak intensity of [PO$_4$]v$_5$, v$_1$ modes.

- The absorption bands at 3570 cm$^{-1}$ and 3435 cm$^{-1}$ referred to structural [OH] groups (O-H) in stretching and liberation modes at crystallites.

- Weak absorption bands at 1414 cm$^{-1}$ and 1455 cm$^{-1}$ referred to symmetrical and asymmetrical stretching modes of [CO$_3$]v$_3$ groups (C-O). The characteristic bands from inorganic carbonate ion recommended that carbon was dissolved in the organics from atmosphere instead dissolved into HA crystal. The presence of carbonates may enhance the bioactivity of HA since carbonates are one of the main constituents of bone structures.

- Absorption band at 1635 cm$^{-1}$ showed the deformation mode v$_2$ of H$_2$O. The existence of physically adsorbed water in the synthesized samples were verified.

The two essential functional groups such as (OH)$^{-1}$ and (PO$_4$)$^{3-}$ were presented in the region of 3570 cm$^{-1}$ and 1059 cm$^{-1}$ respectively, resulting the formation of HA. FT-IR spectra also confirmed the influence of starting reagent and synthesise condition in HA structure and their functional groups belong to.

3.2. Scanning Electron Microscope (SEM)

Figure 3 showed the SEM images of HA powder synthesized at different synthetic conditions. HA powders were produced with various morphologies, such as sphere, rod and layer by controlling the synthetic conditions. The HA powders formed were highly agglomerated. Besides, the HA powders were appeared as aggregates, rough, granular to dense.
From the images shown, the morphology of HA powders had small particles distribution and large agglomerates. This results were similar with Santos et al. [8] and Mobasherpour et al.[9]. The shape of HA powders produced were not obviously spherical. This might cause by the crushing procedure during synthesis of HA powder. The crushing was done by mortar and pestle which the dispersion coefficient was not balance. Thus, the HA powders had large agglomerates.

3.3. X-Ray Diffraction (XRD)

Figure 4(a) and Figure 4(b) showed the XRD pattern produced at different condition. XRD patterns in Figure 4 confirmed that the hydroxyapatite was produced in this sample and no other traces of calcium phosphate impurities was discovered.
Based on the result, no foreign elements were detected. Whitlockite is the mineral name of tricalcium phosphate. The chemical formula of whitlockite is Ca$_3$(PO$_4$)$_2$. Calcium-phosphate ratio and calcination temperature would affect the phase composition of calcium phosphate. Hydroxyapatite was transformed into secondary bone mineral, whitlockite.

4. Conclusion
Chemical precipitation technique was applied in this present work due to its simplicity, great reproducibility in addition to affordable benefits it provided upon commercial size. In this investigation, calcium hydroxide and orthophosphoric acid were used as starting reagents. The functional group detected were (OH)$^-_1$ and (PO$_4$)$^{3-}$, resulting the formation of Hydroxyapatite (HA). The HA powders produced in this present approach were large agglomerates and narrow particle size distribution, resulting better quality of hydroxyapatite for bone replacement. In conclusion, both calcium-phosphate ratio and calcination temperature would greatly influence the phase composition of HA. Besides, secondary phases were only discovered when calcium deficiency HA and the calcination temperature at 800 °C.

5. References
[1] D.Bellucci, A.Sola, M. Gazzarri, F. Chiellini, and V. Cannillo, A new hydroxyapatite-based biocomposite for bone replacement. Materials Science & Engineering: C, vol 33, no 3, pp. 1091–1101, 2013.
[2] Y-K.Jun, S-H., Hong, and Y-M. Kong, Effect of Co-Precipitation on the Low-Temperature Sintering of Biphasic Calcium Phosphate. Journal of the American Ceramic Society, vol 87, no 7, pp. 2295-2297, 2006.
[3] J.S.Al-Sanabani, A.A Madfa, and F.A.Al-Sanabani,Application of calcium phosphate materials in dentistry. International Journal of Biomaterials, vol 2013(2013), pp.1-12.2013.
[4] A.K.Nayak, (2010). Hydroxyapatite Synthesis Methodologies : An Overview, International Journal of ChemTech Research, vol 2, No 2,pp. 903–907,2010.
[5] P.Gentile, C.J.Wilcock, C.A.Miller, R.Moorehead and P.V.Hatton, Process optimisation to control the physico-chemical characteristics of biomimetic nanoscale hydroxyapatites prepared using wet chemical precipitation, *Materials*, vol 8, pp. 2297-2310, 2015.

[6] Q.Tian, L.R.Castaneda, Z.S.Dunn, & H.Liu, Bioceramics for orthopaedic device applications: Hydroxyapatite. In: Thian, E.S., Huang, J., & Aizawa, M.: Nanobioceramics for Healthcare Applications. World Scientific Publishing Europe Ltd, pp.49-78, 2017.

[7] S.Ramesh, C.Y.Tan, M.Hamdi, I. Sopyana, and W.D. Teng, W. D., The influence of Ca / P ratio on the properties of hydroxyapatite bioceramics, International Conference on Smart Materials and Nanotechnology in Engineering, vol 6423, 2007.

[8] M.H.Santos, M.De Oliveira, L.Palhares., D.F.Souza, H.S.Mansur, and W.L.Vasconcelos, Synthesis Control and Characterization of Hydroxyapatite Prepared by Wet Precipitation Process, *Material Research*, vol. 7, no. 4, pp. 625–630. 2004

[9] I.Mobasherpour, M.S. Heshajin, A. Kazemzadeh, M. Zakeri, Synthesis of nanocrystalline hydroxyapatite by using precipitation method, *Journal of Alloys and Compounds*, vol. 430, Issue 1-2, pp. 330–333, 2007