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Preparation of Submicron Biphasic α-TCP/HA Powders

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Abstract. An amorphous calcium phosphate precursor way was utilized to prepare submicron biphasic α-tricalcium phosphate (TCP)/hydroxyapatite (HA) powders. The results showed that the addition of carbonate during the precipitation reaction could eventually lead to the formation of HA phase in the resulting powders, and even determine the relative content of HA to the range from 0 percent (pure α-TCP) to 100 percent (pure HA). Similarly, the particle size of the resulting biphasic powders depended on the carbonate content, ranging from 100nm to 500nm. The biphasic Ca phosphate with tailored α-TCP/HA ratio could be a new combination of calcium phosphate for promoting early bone formation.

Introduction

Calcium phosphates are widely used as biomaterials for hard tissue substitute. Among the calcium phosphates, but hydroxyapatite (HA) shows the ability to form a chemical bonding with the living bone tissue, it takes a little bit long time to establish such bonding because HA is almost nonbiodegradable [1,2]. Since other calcium phosphate, such as α- and β-tricalcium phosphates (α- and β-TCP) show good biodegradability, the combination of β-TCP with HA to a biphasic β-TCP/HA material has been reported to have ability to create an early bone formation due to Ca and P release from β-TCP. α-TCP has an even higher dissolubility and better biodegradability than β-TCP, hence, it is interesting to study the performance of biphasic α-TCP/HA materials.

Biphasic α-TCP/HA can be formed by further calcination of biphasic β-TCP/HA materials at higher temperature [3,4], which result in biphasic powders with a large particle size. The larger biphasic powder size is, the poorer contributions to bone growth they can make.

In this work, an amorphous calcium phosphate precursor way was utilized to prepare submicron biphasic α-TCP/HA powders with different relative phase ratios. The formation process of the biphasic α-TCP/HA powders was characterized and discussed.

Materials and methods

Poly(ethylene glycol) (PEG) was dissolved in the $Ca(NO_3)_2$ aqueous solution, then a mixed aqueous solution of NH_4HCO_3 and $(NH_4)_2HPO_4$ was added dropwise [5]. The reacting system was kept pH 10 by adding NH_4OH aqueous solution until the dropping was finished. After the reaction further proceeded for 30 minutes at 5°C, the resulting precipitate was filtrated, washed, frozen and then freeze-dried for 48 hours before calcination. The calcinations occurred in a furnace at 800°C for 3 hours, with a heating rate of 10°C per minute. In order to acquire biphasic α-TCP/HA with different phase ratio, the molar percentage of NH_4HCO_3 in mixed solution of NH_4HCO_3 and $(NH_4)_2HPO_4$ varied from 0~70%.

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Results

The XRD patterns (Fig.1) show that the freeze-dried precipitates are amorphous calcium phosphate (ACP) no matter the P precursor solution contains carbonate or not. It means adding carbonate in the reaction system does not affect the formation of ACP.

FTIR spectra of the ACP powders (Fig.2) show there are CO_3^{2-} group related bands at 1490 cm $^{-1}$, 1425 cm^{-1} and 869 cm $^{-1}$ respectively [6]. As the carbonate percent in P precursor solution increases, the intensity of the bands becomes stronger. It means the content of CO_3^{2-} in the ACP precipitate increases steadily [7].

After calcinations at 800°C, single α-TCP appears for the P precursor solutions with carbonate percentage of less than 15mol%, and only HA appears for those with carbonate percentage of more than 60 mol%. Between the two points, biphasic α-TCP/HA powders are formed, and the HA content increases with an increasing of carbonate percentage (Fig.3).

FTIR spectra of the calcined powders (Fig.4) show that the intensities of the bands at 3572 cm^{-1} and 638 cm^{-1} assigned to OH groups become stronger with increasing carbonate content. .

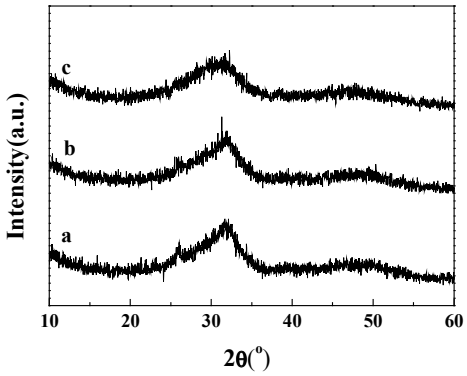

Fig.1 XRD patterns of calcium phosphates precipitates prepared with different content of CO_3^{2-} added: (a) 0mol%, (b) 10mol% and (c) 70 mol%

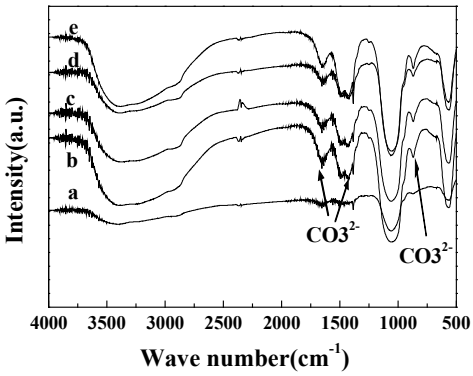

Fig.2 FTIR spectra of calcium phosphates precipitates prepared with different content of CO_3^{2-} added: (a)15mol%, (b) 20mol%, (c) 30 mol%, (d) 40 mol%,(e) 50 mol%

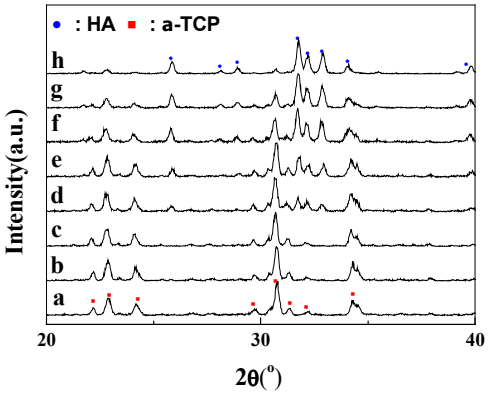

Fig.3 XRD patterns of the 800℃ calcined ACP powders with different carbonate percentage: (a)7.5mol%,(b)10mol%, (c)15mol%, (d)20mol%, (e)30mol%, (f) 40mol%, (g)50mol%, (h)60mol%.

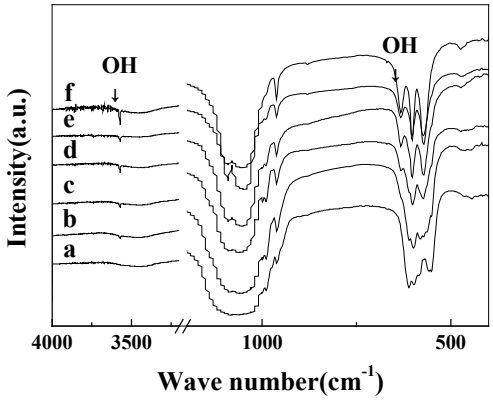

Fig.4 FTIR spectra of the 800℃ calcined ACP powders with different carbonate percentage: (a)10mol%, (b)15mol%, (c)20mol%, (d)30mol%, (e)40mol%, (f) 50mol%.

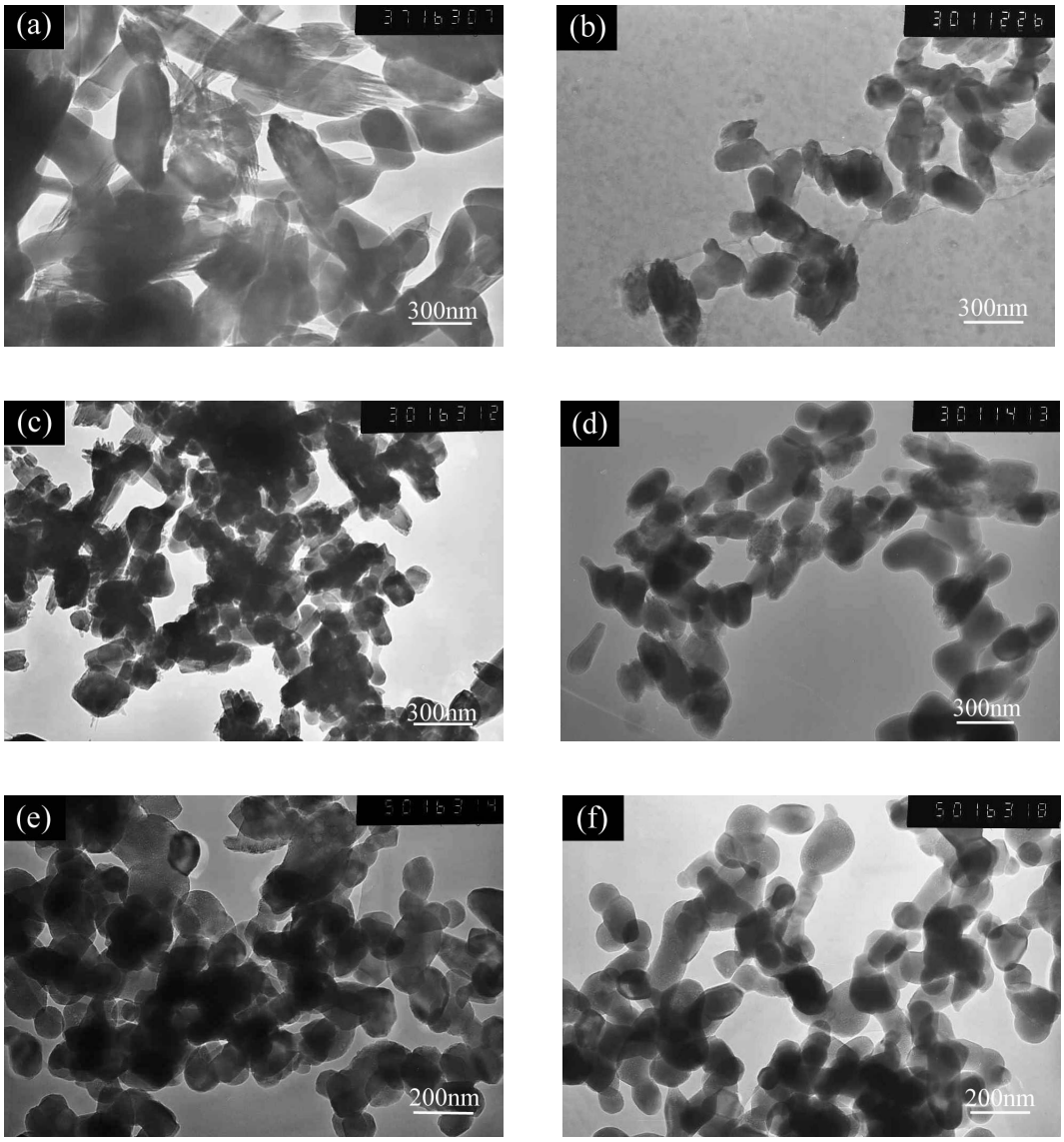

Fig.5 TEM micrographs of the 800°C calcined ACP powders with different carbonate molar percentage: (a)10mol%, (b)15mol%, (c)20mol%, (d)30mol%, (e)40mol%, (f)50mol%

The TEM micrographs (Fig.5) show that α-TCP/HA powders have a particle size ranging from 100nm to 500nm, more carbonate content, smaller particle size.

Discussion

During ACP formation, the carbonate has been incorporated into its structure (Fig.2) but does not induce crystallization (Fig.1). Since the HA phase content in the calcined ACP powders increase with the carbonate content, this indicates that the existence of carbonate in ACP increases the Ca/P ratio of ACP.

The ACP precipitation reaction with carbonate presence could be written as[8]:

$$\text{polymer-}Ca^{2+} + PO_4^{3-} + CO_3^{2-} \rightarrow Ca_{(9+x)}(PO_4)_6(CO_3)x \cdot h(\text{polymer}) \cdot kH_2O$$

$$\rightarrow [Ca_{(9+x)}(PO_4)_6(CO_3)_x]_n \cdot (\text{polymer})_{m-l}(H_2O)_l \quad (0 \le x \le 1) \quad (1)$$

CO_3^{2-} groups are considered to substitute for OH or PO_4^{3-} in ACP [9]. Since the Ca/P ratio varies from 1.5 to 1.67 with increasing carbonate content, the calcined powders should have two phases,

TCP and HA, as described below

$$[Ca_{(9+x)}(PO_4)_6(CO_3)_x]_n\cdot(m\text{-}l)\text{polymer}\cdot lH_2O\rightarrow[Ca_{(9+x)}(PO_4)_6(CO_3)_x]_n\cdot rH_2O\rightarrow$$

$$Ca_{10}(PO_4)_6(OH)_2 + Ca_3(PO_4)_2 + CO_2 \qquad (2)$$

In Equation 2, the tricalcium phosphate in biphasic powders exists as metastable α-TCP rather than stable β-TCP, which is attributed to that ACP transform to α-TCP fast then to β-TCP[10].

The calcined powders have small particle sizes (Fig.5) due to the small particle size of the as-precipitated ACP precursors (~30nm). The particle size becomes smaller with increasing carbonate content in ACP, such effect is attributed to that gaseous product (CO_2) on calcining loosens the contact among the particles, and in turn hinders particle growth and agglomeration.

Conclusion

After 800°C calcinations, a precipitated carbonate-containing amorphous calcium phosphate precursor could transform to submicron biphasic α-TCP/HA powders. In this process, carbonate plays critical role, incorporation of carbonate along with more Ca ions into ACP structure leads to the increase of Ca/P ratio during the precipitation reaction. As a result, the relative phase ratio of the biphasic α-TCP/HA powders could be tailored through adjusting carbonate content in ACP precipitation reaction system. The particle size of the biphasic powders ranges from 100nm to 500nm. More carbonate addition results in smaller particle size of the calcined powders. These biphasic Ca phosphate with tailored α-TCP/HA ratio could be a new combination of calcium phosphate for promoting early bone formation.

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