

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF BIPHASIC CALCIUM PHOSPHATE NANOPOWDERS

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ABSTRACT

The precipitation method has been considered as one of the versatile routes to prepare Calcium Phosphate (CaP) nanopowders due to low temperature formation, chemical homogeneity of products, narrow particle size distribution with stoichiometric structure having high surface area and small agglomerate size etc. In this investigation, biphasic nanopowders composed of hydroxyapatite and β -TCP phases had been synthesized using a facile and economical synthesis protocol. X-Ray Diffraction and Fourier Transform Infrared spectroscopy techniques were used. This manuscript has been expected to fulfill the need of opting for particular biphasic nanopowders synthesis route.

Keywords: Biphasic, nanopowders, calcium phosphate, hydroxyapatite, sol-gel

1. Introduction

Over the past decades, demands of biphasic calcium phosphate (CaP) nanoceramics have been continuously increased. Consequently, significant attention has been paid to formulate its synthesis protocols [1]. It is widely known that among the CaP salts, hydroxyapatite (HAP) is the principal inorganic constituent of human bones and teeth [2]. HAP has been extensively studied owing to its various biological characteristics viz. non-immunogenicity [2], non-inflammatory behavior [2], high osteoconductivity and/or osseointegration [2] and good biocompatibility [3,5]. Over the last many years, diverse CaP synthesis methods have been suggested claiming control over its varied properties.

After an extensive literature review to synthesize biphasic CaP based nanopowders including solid state synthesis [6-7], mechano-chemical synthesis [8,9,19], conventional chemical precipitation technique [10-11], hydrolysis [12], hydrothermal [13] and many more methods. Among these, sol-gel route offers multi-advantageous due to formation of nano-dimensional structure size, narrow particle size spread and stoichiometric Ca/P ratio (1.67) etc. Typical sol-gel process usually comprises of various steps viz. mixing of Ca^{2+} and PO_4^{3-} reagents in aqueous and/or an organic solvents followed by aging at different temperatures and periods, gelation, centrifugation/drying and finally heating at higher temperatures. A little alteration in any of these process parameters causes a dominating change in varied properties of final product. Certain investigations have been reported, revealing the effects of different Ca [14,18] and P precursors [14-18,20,21,22], water and/or ethanol as solvents [15,17], combination of stirring time [2,20-

22], aging time and temperature [2,20-22], drying temperature and time [2,3,20,21] followed by different calcination temperatures and their respective timings [2,3,20,21] on physico-chemical constitution, crystallinity, crystal size and shape, thermal behavior and finally biocompatibility aspects. Many a times, it has been a common observation that such synthesis procedures are not elaborated in a meaningful manner which further shoots up the bewilderment of naïve researchers.

Keeping it in mind, authors synthesized nano-dimensional biphasic CaP nanopowders. Resultant nanopowders were analyzed for their structural constitution in a comprehensive manner.

2. Materials and method

Calcium nitrate tetrahydrate [CNT, Merck, 98%) and phosphorous pentoxide [PP, Merck, 97%] were employed as Ca^{2+} and PO_4^{3-} ion sources. Distilled water and ethanol [Merck, 99.9%] were used as solvents. Synthesis protocol of biphasic CaP nanopowder has been shown in Figure 1.

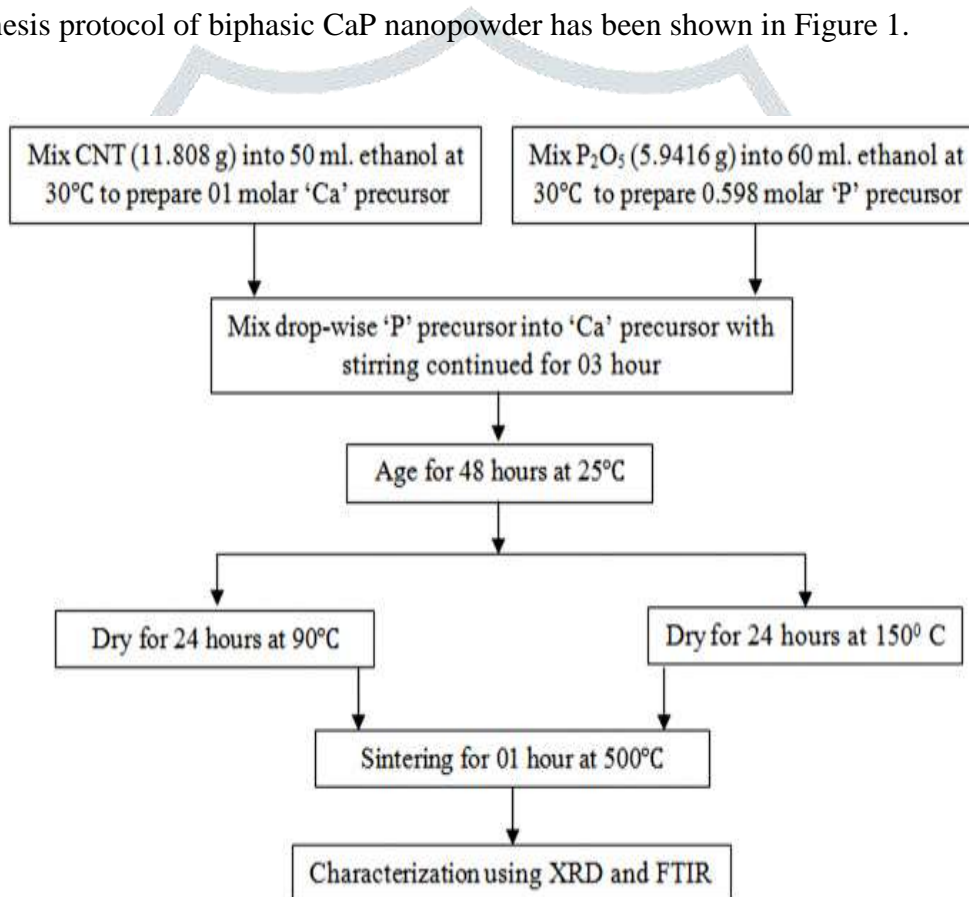


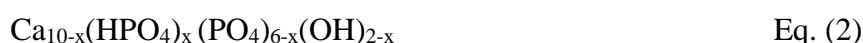
Figure 1. Synthesis methodology of biphasic nanopowders

2.1. Characterization

XRD (Philips X'Pert 1710) was employed using $\text{CuK}\alpha$ radiations. Different structural parameters were determined using fundamental crystallographic formulae. Calcium to phosphorous (Ca/P) molar ratio was calculated using Eq. (1):

$$\frac{\text{Ca}}{\text{P}} = \frac{10-x}{6} \quad \text{Eq. (1)}$$

Chemical stability of HAP powder was represented in terms of chemical equation on the basis of calcium deficiency, (x) by using Eq. (2):



FTIR (Perkin Elmer) spectra were recorded from $500\text{-}4000\text{ cm}^{-1}$ for each sample.

3. Results and discussion

3.1. Phase analysis, lattice parameters, crystallite size, weight fractions and Ca/P molar ratio of biphasic nanopowders

XRD patterns of biphasic nanopowders have been shown in Figure 2 and Table 1.

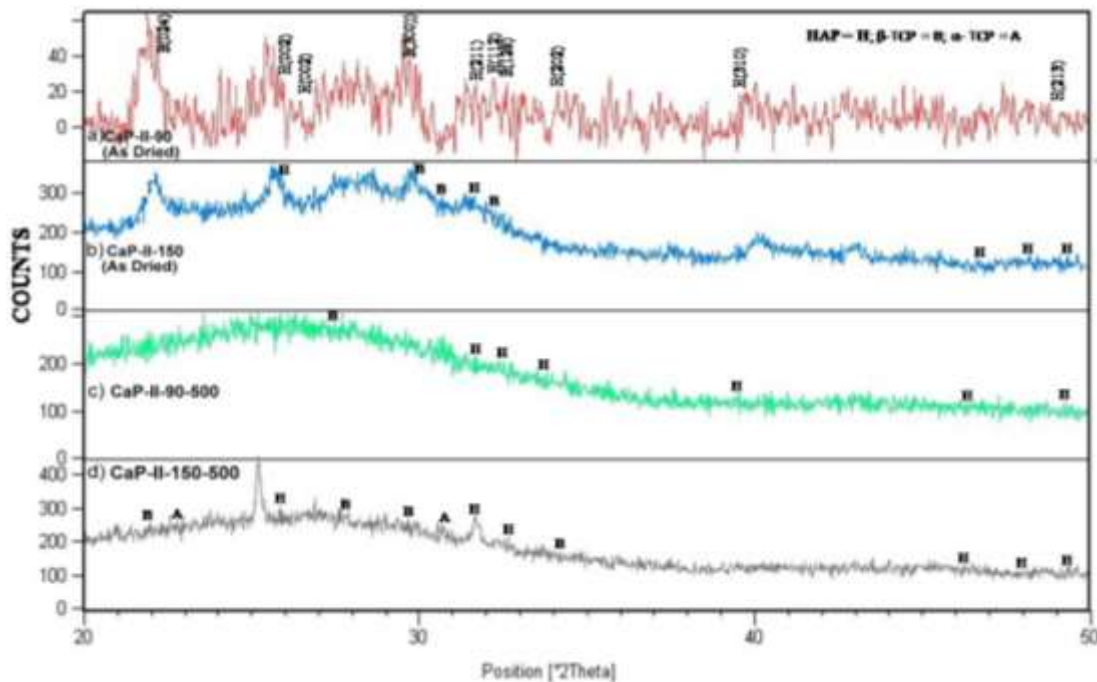


Figure 2. XRD patterns of biphasic nanopowders at (a-b) as-dried and sintered at (c-d) 500°C

Chemical reactions of Ca^{2+} and PO_4^{3-} based ethanolic solutions to form apatite ionic structures have been proposed in Eq. (3-4), respectively.

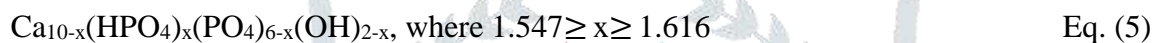


XRD diffractograms of as-dried and sintered biphasic nanopowders have been shown in Figure 2. HAP and β -TCP were observed to be the major phases present in as-dried nanopowders (Figures 2(a-b)) along with the traces of α -TCP were also originated in both the sintered nanopowders as shown in Figure 2(c-d) respectively. It revealed decomposition of HAP at higher temperatures. The crystal parameters primarily ‘c’ axis dimension and crystallite size increased with the increase of temperature [2,3,24,25]. Crystallinity of nanopowders was observed to be inferior indicating its highly amorphous nature as there is no sharp and distinct peaks can be noticed in the diffractograms shown in Figure 2. Weight percentage of HAP phase augmented with the rise in drying and sintering temperature indicating conversion of β -TCP or allied phases into apatite phases. Powder dried and sintered at 150°C and 500°C, respectively was found to have maximum weight fraction of HAP phase consequently highest Ca/P molar ratio was yielded. Nanopowders were concluded to be biphasic in nature having Ca/P ratio lie between 1.5-1.67.

Table 1. Structural properties of biphasic nanopowders

Parameters	CaP-II-90 (As Dried)	CaP-II-150 (As Dried)	CaP-II-90-500	CaP-II-150-500
Major Phases	HAP; β -TCP	HAP; β -TCP	HAP; β -TCP; α -TCP	HAP; β -TCP; α -TCP
HAP Lattice Parameters (nm)	a=9.447; c=6.872; c/a=0.727	a=9.344; c=6.874; c/a=0.735	a=9.479; c=6.900; c/a=0.727	a=9.447; c=6.900; c/a=0.730
Mean Crystallite Size (nm)	32.957	70.692	71.870	129.144
Weight Fractions	HAP=0.216 β -TCP=0.5119	HAP=0.3456 β -TCP=0.6294	HAP=0.3687 β -TCP=0.6233	HAP=0.4143 β -TCP=0.1654
Estimated Ca Deficiency, x	0.718	0.662	0.646	0.300
Ca/P Ratio	1.547	1.55	1.55	1.616

Chemical stability of biphasic nanopowders has been proposed in Eq. (5), depending upon its Ca deficiency, (x) as



The table 2 enlightened the crystalline behavior of nanopowders. Rise of drying temperature from 90°C to 150°C caused the peak widths of (310) reflection of as-dried nanopowders to decrease indicating improvement of crystallinity. On the other hand, peak width of (002) reflection of as dried nanopowders remained unchanged. Peak widths of (002) reflection of both the sintered nanopowders decreased indicating superior crystalline nature of powder dried at 150°C and can be ascribed to the loss of physically and/or chemically bound water molecules or hydroxyl groups from the respective powder [22].

Table 2. Peak width measurement of (002) and (310) reflections to represent crystalline behavior of biphasic nanopowders

	Planes	CaP-II-90 As Dried	CaP-II-150 As Dried	CaP-II-90-500	CaP-II-150-500
Peak Width (2 θ)	(0 0 2)	0.0502	0.0502	0.1004	0.0669
	(3 1 0)	0.5353	0.4080	0.0612	0.0612

3.2. FTIR analysis

Ionic constitution of biphasic nanopowders has been shown Figure 3.

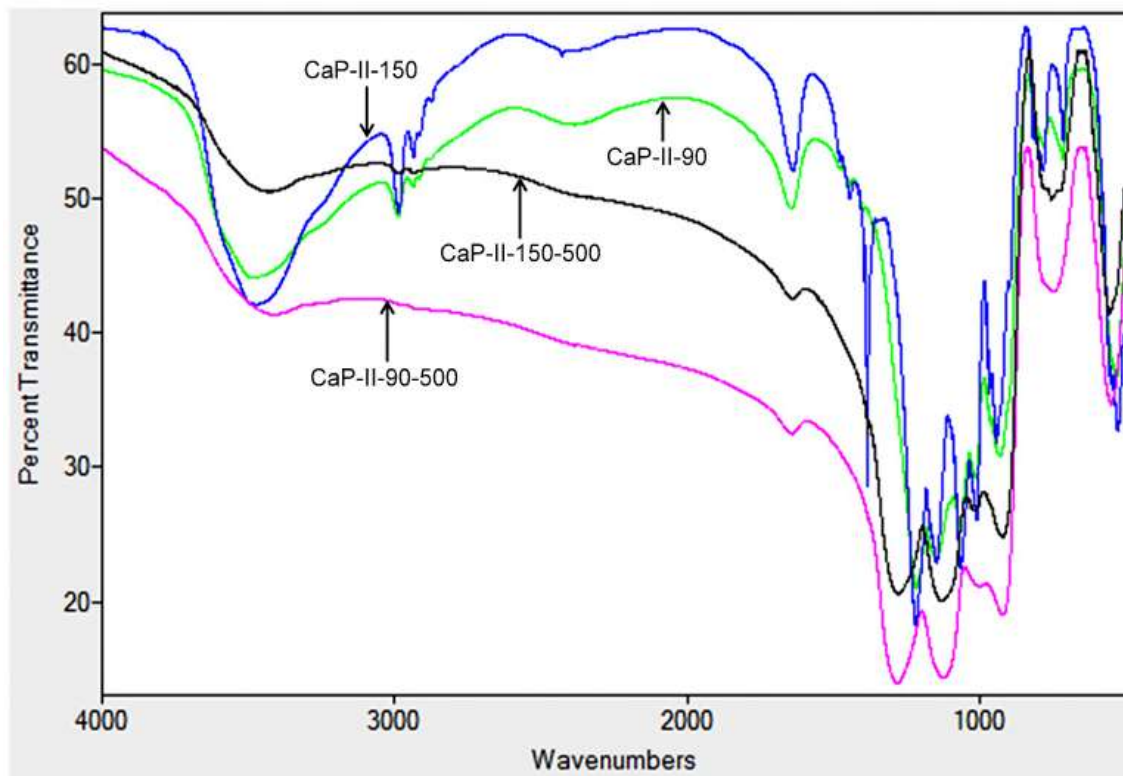


Figure 3. FTIR spectra of biphasic nanopowders

Ionic constitution of biphasic nanopowders has been shown in Figure 3 and confirmed the presence of water-adsorbed deformation ($3420, 3424 \text{ cm}^{-1}$); OH water adsorbed deformation ($1640, 1636 \text{ cm}^{-1}$); carbonate stretching band ($1443, 1384 \text{ cm}^{-1}$); $\delta\text{OH HPO}_4^{2-}$ ($1219, 1218 \text{ cm}^{-1}$); $\nu_3 \text{HPO}_4^{2-}$ ($1148, 1134, 1126 \text{ cm}^{-1}$) followed by $\nu_1 \text{PO}_4$ (968 cm^{-1}) respectively.

4. CONCLUSION

Biphasic calcium phosphate nanopowders composed of HAP and β -TCP phases were successfully synthesized. Based on the results, structural constitution of all synthesized nanopowders was noticed to resemble having little variation in one or two parameters. Reduced decomposition temperature of apatite to β -TCP was also observed. Other textural properties including high thermal stability and nano-dimensional crystal size recommended the particles suitable for biomaterial applications.

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