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Characterisation of Suspension Precipitated Nanocrystalline Hydroxyapatite Powders

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Abstract: Hydroxyapatite (HA) is a well-known biomaterial for coating on femoral implants, filling of dental cavity and scaffold for tissue replacement. Hydroxyapatite possess limited load bearing capacity due to their brittleness. In this paper, the synthesis of nanocrystalline hydroxyapatite powders was prepared by dissolving calcium oxide in phosphoric acid, followed by addition of ammonia liquor in a beaker. The prepared solution was stirred by using magnetic stirrer operated at temperature of 80°C for an hour. This leads to the formation of hydroxyapatite precipitate. The precipitate was dried in oven for overnight at 100°C. The dried agglomerated precipitate was calcined at 800°C in conventional furnace for an hour. The influence of calcium oxide concentration and pH on the resulting precipitates was studied using BET, XRD and SEM. As result, a well-defined sub-rounded morphology of powders size of ~41 nm was obtained with a salt concentration of 0.02 M. Finally, it can be concluded that small changes in the reaction conditions led to large changes in final size, shape and degree of aggregation of the hydroxyapatite particles.

Keywords: Nanocrystalline; HA; Suspension precipitation; Morphology; Biomaterial

1. Introduction

In last two decades, hydroxyapatite has been used as synthetic biomaterials for orthopaedic research due to its special property of being highly bioactive as well as its ability to form direct interfacial bond with surrounding tissue, leading to better osseointegration [1-2]. Because of the insufficient electrical conductivity and fracture toughness, the use of HA as load bearing hard tissue replacement is rather limited. However, the use of conventional process to fabricate of HA ceramics results in poor microstructure and properties due to decomposition of HA [3]. It was also reported that oxyapatite ($Ca_{10}O(PO_4)_6$) is highly reactive at a temperature lower than 800^{o}C, even under cooling in vacuum (10^{-4} -10^{-6} torr) and forms a stable compound of oxyhydroxyapatite (Ca_{10} $(PO_4)_6O_{0.75}$ $(OH)_{0.5}V_{0.75}$, where V is a neutral vacancy in the OH site at room temperature. However, it decomposes into a mixture of tri- and tetra- calcium phosphates at temperature higher than 1050^{o}C [4]. From the above discussion, it is more important to have a Ca/P ratio of 1.67. If the stoichiometric ratio is maintained, then HA should be stable up to temperatures of 1300^{o}C without phase changes [5]. Therefore, HA-based composites have been developed by using different additives to improve the mechanical reliability [6-8]. However, these additives do not only tend to decrease the biocompatibility and bioactivity of pure HA, but also decreases the decomposition temperature of monolithic HA during conventional sintering. In this research, our main objective is to synthesis the nanocrystalline hydroxyapatite powders were made by dissolving calcium oxide in phosphoric acid and heating at 80°C for an hour to address the above issues.

2. Experimental procedure

2.1 Hydroxyapatite (HA) powder synthesis

Hydroxyapatite, Ca_{10} $(PO_4)_6(OH)_2$ is synthesized using widely used method of suspension-precipitation route [9]. The powders used were CaO (SD Fine-Chem) and H_3PO_4 (Merck). Initially, CaO was dispersed in distilled water at a concentration of 18.6 gm/l. The dispersed solution was kept on a hot plate (~80^{o}C) with electromagnetic stirrer for continuous stirring of the dispersed medium. By keeping the Ca/P ratio as desired (1.67), an equivalent amount of H_3PO_4 solution with 0.17M was added drop wise in the dispersed CaO solution. The above set up was held at 80^{o}C and stirred for 3-4

hours to result completion of reaction. Thereafter, concentrated NH_4 (Qualikems) was added drop wise to bring the pH of solution to 10. (For making 25gm of HA, about 5-10 ml of NH_4 was needed). After the completion of the reaction, the product was allowed to precipitate by keeping it at room temperature for 24 hours and was collected by filtering the solution. The collected precipitate was dried. The lump was crushed into powder in an agate mortar and subsequently calcined at 800^{o}C for 2 hours.

2.2 Microstructural Characterization

Detailed investigation of microstructure of powders was performed using Scanning Electron Microscope (SEM, FEI Quanta 200 and JEOL JSM-6330F) attached with EDS (Energy Dispersive X-ray Spectroscopy) to determine the compositional analysis. X-ray diffraction (XRD) of powders was used to characterise the phase assemblage and in particular to asses the phase purity. The powder diffraction patterns of powders was measured on a (Brucker Xpert diffractometer using a CuKα line (wavelength 1.54 Á, 40 kV, 40 mA, 0.5° divergence slit, and 0.5° antiscatter slit). The XRD data were recorded using a step size of 0.02° with a scan speed of 0.5° per minute. The recorded diffraction patterns were compared to powder diffraction files from the JCPDS database. Quantitative estimations of phase composition were made using the semi-quantitative feature in the XPert High score Plus (PANalytical, the Netherlands, v2.2b) software.

2.3 Powders size distribution using BET analysis

The distribution of powder particle sizes was measured using a Mastersizer 2000 (Malvern Instruments). To prepare samples for measurement, approximately 0.5 g of powder was ultra-sonicated in 800 mL of water for 2 min. The measurements were made over the size range of 0.02 – 2000 μm. The reported values are the means of three measurements taken for each sample.

3. Results and discussions

3.1 Microstructural analysis

X-ray diffraction (XRD) analysis is shown in the Fig.1 indicates all peaks are related to the hydroxyapatite as data obtained from JCPCDF 09-0432. There is no trace of CaO and phosphate present in the XRD pattern. It is suggested that high purity nano crystalline hydroxyapatite (HA) powders can produced by the suspension precipitation technique, which is not possible in any other methods.

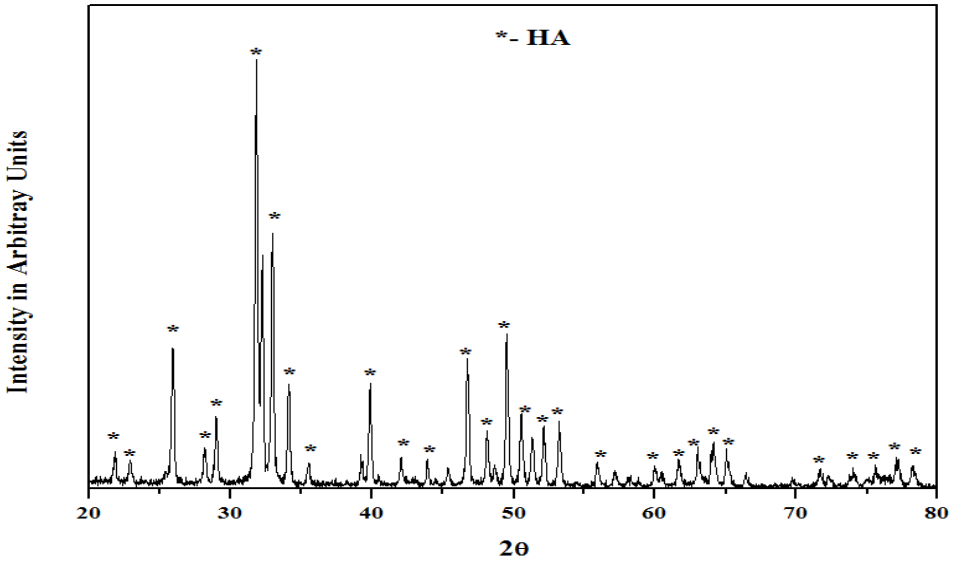

Fig.1: XRD pattern of HA powders.

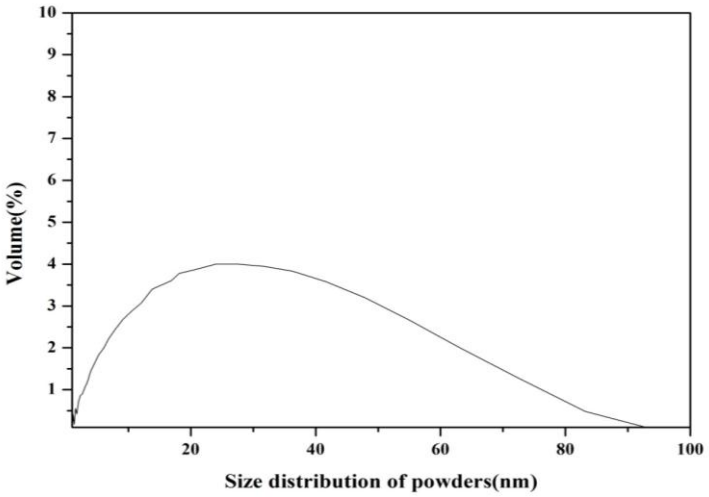

Fig. 2: Size distribution of hydroxyapatite powders.

The presence of agglomerated powders of HA is revealed by the bimodal size distribution, as shown in Fig.2. Secondary electron SEM (SE-SEM) images of HA powders are presented in Fig.3 (a & b). The images reveal considerable agglomeration between the particles, which increases the size of the crystalline powders.

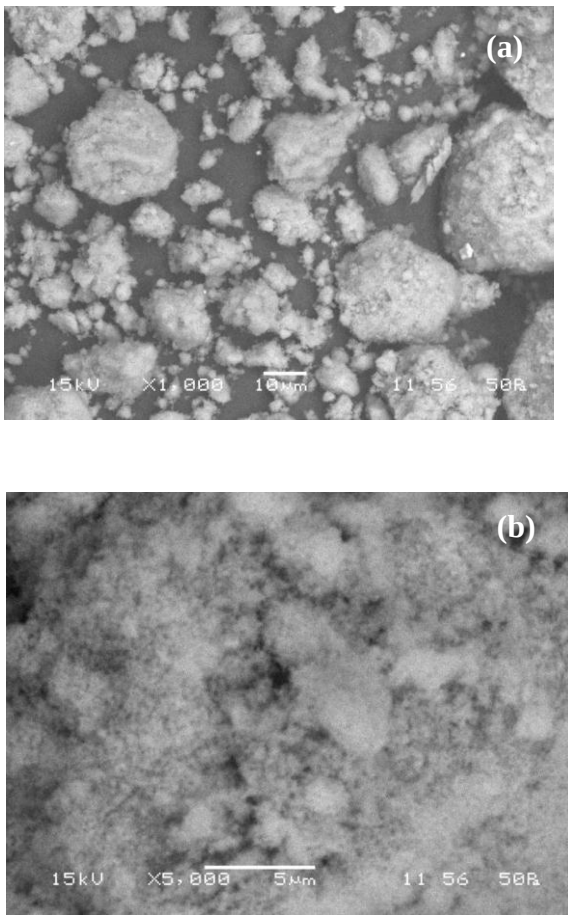

Fig. 3 (a & b): SEM images show the morphology of hydroxyapatite powders.

In the Energy-dispersive X-ray spectroscopy (Fig.4), compositional analysis of powders reveals the presence of Ca, O and P. While the larger peaks of O that of the comparatively smaller peaks reveal

peaks of Ca and P. From the table 1, it can observed that stoichiometry ratio of Ca/P is approximately 1.67, which indicates the stability of hydroxyapatite will be enhanced in further processing of the powders. It is clearly indicated that the purity of HA powders without any impurities can be synthesised using the suspension precipitation technique.

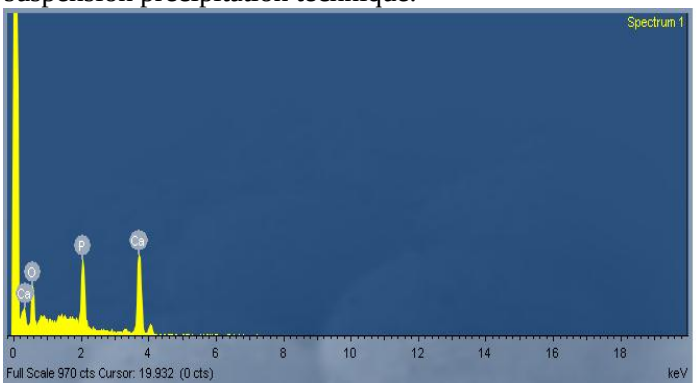

Fig. 4: EDS analysis of hydroxyapatite powders.

Table 1: Shows EDS analysis of the atomic % of Ca, P and O present in the powders.

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
O K	11.46	0.5645	44.99	2.91	65.08
P K	12.05	1.4386	18.59	1.40	13.89
Ca K	16.63	1.0136	36.41	2.14	21.02
Totals			100.00		

4. Conclusion

From the above study, the following conclusion would be derived that the XRD, SEM and BET analysis indicates the nano crystalline of hydroxyapatite (HA) powders could be produced by controlling the temperature and pH of the suspension. EDS analysis indicates composition of Hydroxyapatite (HA) is in the stoichiometry ratio of Ca/P is ~1.65.

Acknowledgement

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