

A comparative study of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) using sol-gel and co-precipitation methods for biomedical applications

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In this present paper, nano HAp is synthesized by sol-gel and co-precipitation method for the application of medical field. During synthesis, the different chemical precursors like calcium nitrate tetrahydrate and diammonium hydrogen phosphate are mixed in the ratio of 1:67 ratio and ammonia solution is added to maintain the pH of 10. The synthesis of HAp powders is confirmed by Powder XRD, FT-IR, SEM and TEM. The average crystallite size for the maximum intensity peaks was found to be approximately 20 to 35 nm. The FT-IR spectrum shows that there is a presence of phosphate group at $605\text{--}634\text{ cm}^{-1}$. Particle size and morphological studies were established using SEM like sphere shaped, rod-shaped, agglomerated rod-shaped morphology was observed. The chemical compositions are also identified using EDAX analysis. Rod-shaped morphology was observed using TEM.

Keywords: Hydroxyapatite, PXRD, FT-IR, SEM, TEM.

Introduction

Hydroxyapatite (Bone mineral) is an inorganic component, and also the primary mineral component of bone matrix and hard tissues has the molecular structure of $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. HAp has an advantage of having high biocompatibility and bioactivity¹. It will support bone ingrowths and Osseointegration when used in orthopaedic. The application of HAp has useful biocompatible material mainly depends on the purity and morphology of the powder¹. This can be widely applied to repair, reconstruction and replacement of damaged musculoskeletal parts due to their compositional similarity to that of bone and teeth. Its properties influence the biological response to HAp implants. The ability to integrate into bone structures and support bone ingrowths, without breaking down or dissolving (i.e. it is bioactive). Hydroxyapatite is a thermally unstable compound, decomposing at a temperature of $800\text{--}1000^\circ\text{C}$ depending on its stoichiometric ratio. HAp is combined with various types of polymers to generate biocomposite materials that can be used for Osteoconduction in the field of orthopaedic surgery. The composition of human bone in an inorganic/organic hybrid consisting of 70% (wt) apatite calcium phosphates and 30% of (wt) organic (primarily collagen). The apatite calcium phos-

phate of bone mineral consists of carbonate, a small amount of sodium, magnesium and other trace elements. The sub microscopic crystals of calcium phosphates in bone resemble crystal structure of synthetic HAp. HAp can be prepared in different ways like sol-gel, chemical precipitation, hydrothermal synthesis, combustion synthesis etc. The molar ratio of Ca/P is 1.67 is often called as hydroxyapatite can be well synthesised by sol-gel and co-precipitation method.

Experimental

The hydroxyapatite (HAp) powders were prepared by sol-gel and co-precipitated method^{2,3}. The starting material calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and di-ammonium hydrogen orthophosphate ($(\text{NH}_4)_2\text{HPO}_4$) are used, and 1.67 molar concentrations were taken for the precursor. Many researchers already reported the synthesis process but still, there are many challenges occurs while synthesising pure HAp in nanosize particle range. As per literature, the co-precipitation process was carried out by the dropwise addition of di-ammonium hydrogen orthophosphate solution in dropwise for 3 h into calcium nitrate tetrahydrate solution⁴. Formation of white precipitate will occur and maintain the pH value of about 10, if it varies then add little amount of ammo-

nia solution to adjust the pH of the reaction mixture. All these processes were done in the continuous stirring at above room temperature around 65 to 70°C for 3 h. The formation of a white precipitate at the bottom of the reaction vessel can take place is washed 7–8 times with double distilled deionised water and dried in hot air oven at 80 to 100°C.

Table 1. Average crystallite size: co-precipitation

Center	FWHM	THETA	cos (theta)	Xs (nm)
25.93954	0.20695	12.96977	0.97448862	29.39762
31.85873	0.5731	15.92937	0.96160077	21.94865
32.34581	1.36559	16.17291	0.96042551	12.94169
32.94019	0.28221	16.4701	0.95896784	21.35578
34.09923	0.37914	17.04962	0.95605122	20.44816
39.73334	0.65365	19.86667	0.94048597	39.20158
46.70481	0.40578	23.35241	0.91808422	23.89765
49.51728	0.42846	24.75864	0.90808003	52.34682
53.25828	0.22703	26.62914	0.8939264	91.61043
64.04847	0.39267	32.02424	0.84782387	13.251608

Table 2. Average crystallite size: sol-gel

2 theta	FWHM	theta	cos (theta)	Xs (nm)
31.94014	0.768289	15.97007	0.96140555	10.77103
32.93504	0.472704	16.46752	0.95898059	17.5505
34.06557	0.500265	17.03279	0.9561373	16.63292
39.73136	0.670453	19.86568	0.94049183	12.61726
46.7049	0.412081	23.35245	0.91808391	21.02922
49.51756	0.436319	24.75878	0.90807899	20.07985
53.25828	0.231323	26.62914	0.89392638	38.47398
64.0493	0.407474	32.02465	0.84782003	23.02954
28.76631	1.406052	14.38315	0.96865624	5.841408

Sol-gel method synthesis:

Same precursors with same ratio 1:67 were taken, and the process was carried out by the dropwise addition of diammoniumhydrogen orthophosphate solution for 3 h into calcium nitrate tetrahydrate solution. Formation of white precipitate will occur and maintained the pH value of about 10 to maintain the constant pH; ammonia solution was added to adjust the pH of the reaction mixture. All these processes were done in the continuous stirring at above the room temperature around 70 to 80°C for 6–7 h to form gel-like precipitation. The formation of a white precipitate at the bottom of the reaction vessel can take place is washed 7–8 times with double distilled deionised water and dried in hot air oven at 80 to 100°C. Finally, the crushed powders were sintered at 800°C^{5,6}.

PXRD is carried out for structural identification of the pure HAp using a Bruker D8-Advance X-ray diffractometer, with 2.2 kW Cu anode, Ceramic X-ray tube, Ni filter and a high-efficiency linear detector of Lynx eye type operated in integration mode. The patterns are scanned in the 2 θ range from 20 to 80° with a step size of 0.019724 and 46.55 measuring time per step. Fig shows the variation of intensity of diffracted X-rays as a function of 2 θ . The PXRD phase identification is performed by using JCPDS standard [09-0432]. The presence of characteristics HAp peaks at [25.87, 31.773, 32.19, 32.90, 34.04, and 39.81] represented in the fig confirms the hexagonal structure of HAp. PXRD spectra of these two methods of HAp have shown peaks characteristic for HAp. The synthesised crystals were identified with hexagonal phase by Powder X and compared with JCPDS standards.

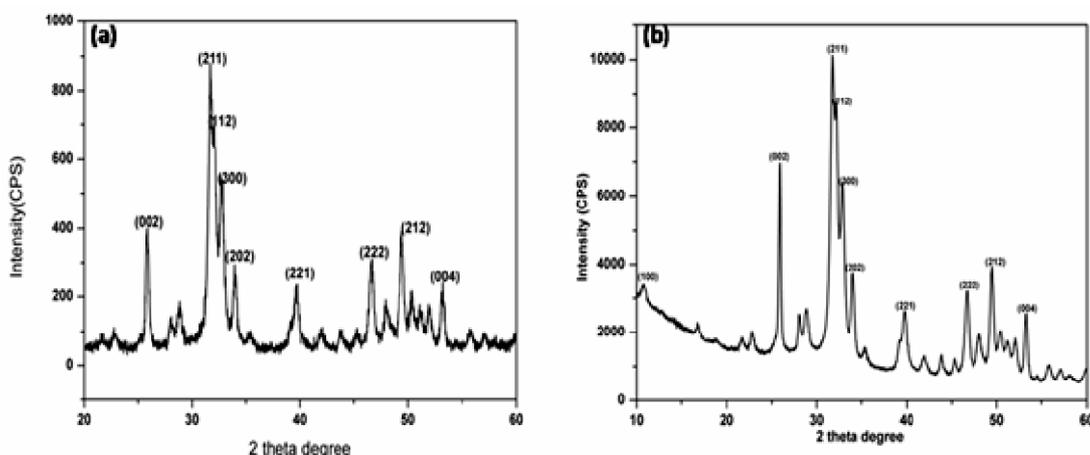


Fig. 1. PXRD: (a) co-precipitation method and (b) sol-gel method.

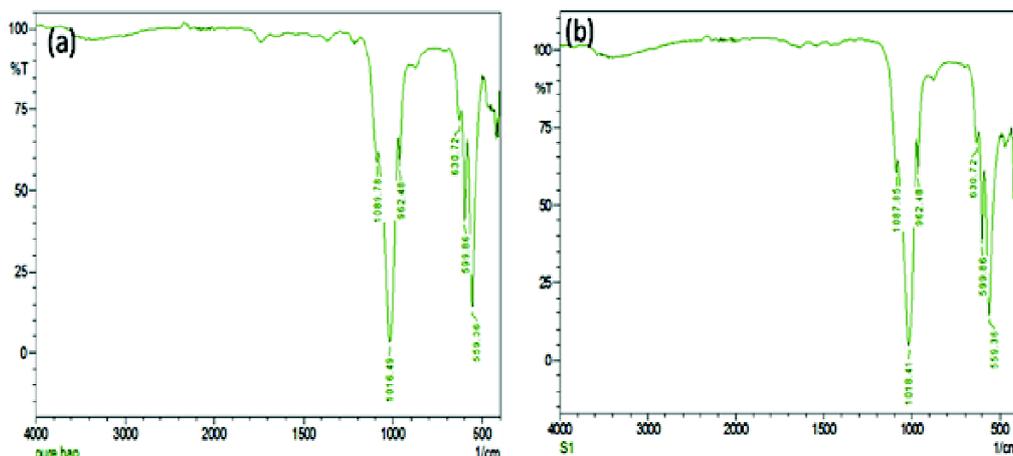


Fig. 2. FTIR: (a) co-precipitation method and (b) sol-gel method.

The average crystallite size were also determined using Debye's Scherer formula,

$$D = \frac{0.9\lambda}{\beta \cos \theta} \text{ (nm)},$$

where D is the average crystallite size of the material, λ is the wavelength of X-ray used (1.54×10^{-10} m), β is the broadening of diffraction line (FWHM) and θ is the angle of diffraction.

FTIR spectrophotometer is used to determine the functional groups by scanning the HAp sample in the range of $400\text{--}4000 \text{ cm}^{-1}$. The powder was dispersed into pellets of KBr, and the spectrum was recorded. The spectrum can be divided into four regions with the peaks having the wave numbers around 3607.82, 1641.51, 1022.69, 604.21, 563.98 cm^{-1} . The peak observed around 3607.82 is due to -OH bond. This peak is mainly due to OH stretching vibration in HAp. The peak at 1022.69 is associated with the stretching modes of the P-O bonds of HAp. The double peak at 604.21 and 563.98 cm^{-1} is due to bending modes of P-O bonds in phosphate groups^{6,7}. Thus the presence of PO_4^{3-} -group in HAp is almost confirmed from IR studies. In spite of all efforts to remove ammonia from solution, there is a possibility of a small amount of it in HAp powder. The IR analysis shows a small broad peak at 1631.78 cm^{-1} which is characteristics peak of NH_4^+ -group.

Scanning electron microscope: The structure and morphology of the sample were studied using a HITACHI S2600N type scanning electron microscope (SEM) operated at 10.00

kV in a vacuum. The SEM studies were performed on powder samples prepared by the sol-gel and co-precipitation method. SEM morphology of synthesised hydroxyapatite powders are shown in the figure. For the elemental analysis, the electron microscope was equipped with energy dispersive X-ray attachment. Fig. 3a shows SEM morphology of HAp powder, from the morphology of particles, there is a distribution of small rod-shaped nanoparticles with some agglomerations. These agglomerates consist of fine particles that are closer together. The surface morphology of HAp using co-precipitation and sol-gel methods are found to be maximum rod-shaped morphology and the particle size was found to be 18 to 44 nm in length were analysed using image software. Fig. 3(c) shows the compositional elements present in HAp with these two methods.

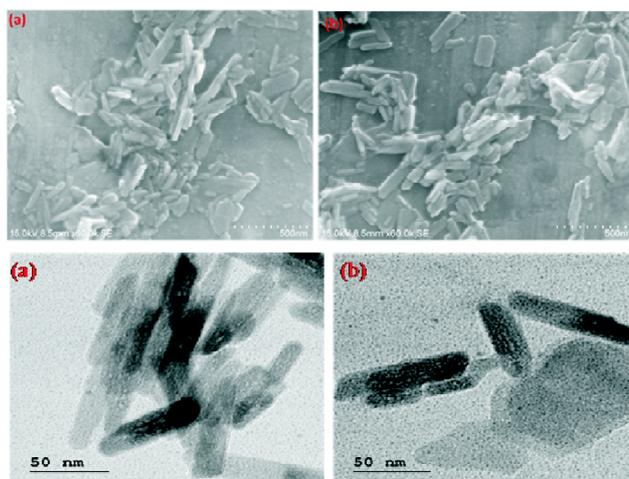


Fig. 3. SEM and TEM: (a) co-precipitation method and (b) sol-gel method.

Transmission electron microscope: TEM morphology was recorded on a JEOL-2010 electron microscope with acceleration voltage of 120 kV. Fig shows that the tiny crystals are almost rod-shaped morphology are well defined with 50 to 100 nm long and 10–15 nm wide are uniformly distributed.

Conclusions

Hydroxyapatite was synthesized by sol-gel and co-precipitation method. The synthesized HAp was characterized by PXRD, FTIR, SEM, and TEM. The formations of HAp hexagonal phase were identified using powder X. PXRD spectra of all samples have shown peaks characteristic for HAp. The development of functional groups are identified by FTIR. FTIR investigations also showed the typical absorption characteristics of hydroxyapatite and the presence of phosphate was identified around 634 cm^{-1} . SEM provides the detailed information at the nano level surface morphology and par-

ticle size was identified. The TEM image shows that the morphology is almost rod-like structure in both the methods.

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