International Journal of Pharmacy and Biological Sciences
ISSN: 2321-3272 (Print), ISSN: 2230-7605 (Online)
IJPBS | Volume 8 | Special Issue 4- Chem Fest | 2018 | 161-166
2nd National Conference on Emerging Trends and Future Challenges
In Chemical Sciences-Chem Fest-18
Held at Shanmuga Industries Arts and Science College, Tiruvannamalai, 05th Oct 2018
| Seminar Proceedings | Research Article | Biological Sciences |Open Access |MCI Approved|
|UGC Approved Journal|

NOVEL SYNTHESIS OF HAP NANOPARTICLES BY SHOCK WAVE METHOD

I. Venda[a] and V. Collins Arun Prakash[a*]
[a, a*]**Department of Chemistry, Sacred Heart College (Autonomous), Tirupattur, Vellore Dist. 635 601.**

***Corresponding Author Email:** vendasugi@gmail.com, collinsnanobio@gmail.com

ABSTRACT

Hydroxyapatite HAP, ($Ca_{10}(PO_4)_6(OH)_2$ is an inorganic compound which is widely used as bioactive coating material for orthopaedic applications due to its bioactivity, high biocompatibility, and as well as its good osteoconductivity. The calcium phosphate material is widely applied as biomaterial, adsorbents, catalyst, and catalyst supports and mechanical reinforcement, etc. Especially it is the building block of human bone and dental implant material. In this research work, a novel synthesis of HAP nanoparticles using a shock wave method was attempted along with monitoring the control of surface morphology and crystal structure. This method givesnano sized hydroxyapatite powders with high degree of crystallinity. The results of characterisation have shown that synthesised HAP powder resulted in high purity powder and good crystallinity after calcination. The as synthesised powder is to be tested further for this biocompatibility.

KEY WORDS

hydroxyapatite, shock tube, nanoparticles

INTRODUCTION

Calcium phosphate is one of the most widely investigated bio ceramic material and used clinically orthopaedic and dental aspects, such as bone filling and HAP used for artificial bone (1-2). It has also been used in several field, like dental implantology and biomedical application and also used for electron spin resonance (ESR) (3). This material is the promising material for implant and bone substitutes due to their biocompatibility, low density, chemical stability, and bio ceramic (4-6). Hydroxyapatite has been one of the most important calcium phosphate biomaterials and it has been widely applied in biomedical field due to bio compatibility, bioactivity, noninflammatory nature, and excellent osteoconductivity, and nontoxicity [7-11]. HAP is a mineral form of Calcium phosphate and the formula of HAP is ($Ca_{10}(PO_4)_6(OH)_2$. The biological apatite refers to poorly crystalline nonstoichiometric carbonate contain HAP. The inorganic content varies from90% in dental and 65% in bones enamel (12). The pure HAP is a stoichiometric apatite phase, and it has a hexagonal structure. The Ca/P ratio of 1.67, which indicated to bone apatite. The most stable Ca/P salt at a normal temperature and P^H between 4 to 12 (13). It has been reported that the synthesized hydroxyapatite nanoparticles are structurally and chemically to that of natural bone tissue (14-15). The interaction of material with shock heated gas leads to formation of new stabilization of material in new crystallography phase. The phase can be induced in material under temperature and extreme pressure due to application for a very short duration (16). The phase transformation of HAP nanoparticles using different shock wave number loading technique were employed to modify its structure.

In this research the surface morphology and crystal structure of the novel synthesis of HAP nanoparticles are investigated the pre and post load shock wave. The Characterization and morphological investigation of the HAP powder was performed by using FT-IR, XRD,and SEM.

2.MATERIALS AND METHOD

2.1 CHEMICAL AND REAGENTS:

The novel synthesis of HAP nanoparticle was achieved by using shock wave method. The precursors used were Calcium nitrate tetrahydrate $Ca(NO_3)_2 .4H_2O$, Diammonium hydrogen phosphate $(NH_3)_2HPO_4$, and ammonium hydroxide NH_4OH. Deionized water was used throughout the synthetic process. All the received chemicals were of analyte grate (AR) and obtained from Merck.

2.2 SYNTHESIS OF PURE HYDROXYAPTITE BY SHOCK WAVE

Pure HAP powders were synthesized under atmospheric conditions by using shock wave method. 0.5m $Ca(NO_3)_2.4H_2O$ and 0.3m $(NH_4)_2HPO_4$ were dissolved into 100 ml of deionized water. The phosphate solution was added drop wise to the calcium solution with constant stirring in order to obtain a white precipitate. Then the P^H was maintained between 9.5 to 10 by using ammonium solution. The stochiometric ratio of Ca/P was kept constant at 1.67 throughout the experiment. Now the sample is loaded at different number of shock wave like 50,100 with Mach number 2.0 at applied pressure(2.367MPa) and temperature (896k). All the reactions were kept in an oven at 80°C for 4h. The obtained precipitate was filtered and washed three times by deionized water and ethanol for the removal of residual ammonia and unreacted reactants followed by drying in an oven at 100°C for 3h. Finally, the resulting powders were calcinated for 3 to 4hrs and to obtain pure HAP. The obtained powder was further characterized with different analytical techniques.

2.3CHARACTERZIZTION

The Fourier transform infrared (FTIR) was used to determine the functional group of the HAP sample. The spectra were recorded over the region of 400-4000 cm^{-1}. The crystal structure and phase content of the sample were analysed by X-ray diffraction. The XRD was operated at 80kv and 10MA and the 2Ө range from 10 to 80^0C with a step size was 0.040. The crystallinity size of the sample can be calculated from XRD peak by using Scherrer equation. The SEM was used to investigate the morphology and size of the powder.

3. RESULTS AND DISCUSSION

3.1 FTIR analysis of pure HAP powder

The FTIR spectra of HAP nanoparticle without the application of the shock wave is presented in **Fig.1**. The HAP structure contains OH and PO_4^{3-}group. The sharp and broad peaks at 3580cm^{-1} and 3419, 1652cm^{-1} corresponds to O-H groups and the medium band at 634 cm^{-1}corresponds to OH of HAP. The peak at 465cm^{-1} can be assigned to ν_2 mode of phosphate group and the band at 559cm^{-1} and 606cm^{-1} are due to ν_4. The peaks at 954cm^{-1} and 1029-10 cm^{-1} are due to ν_1 and ν_3 mode of phosphate groups.

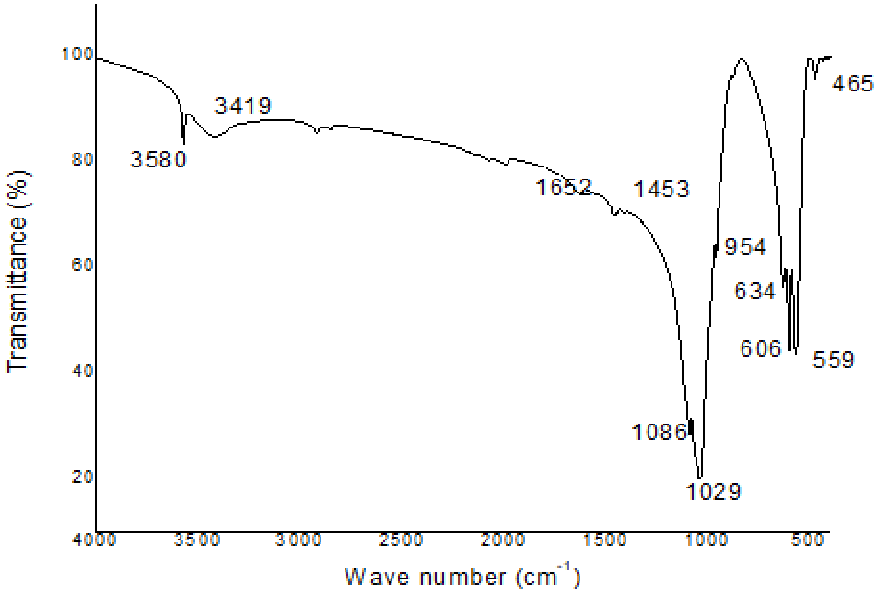

Fig.1 FTIR of HAP powder synthesized without shock wave.

The FTIR spectrum of the investigated powder obtained with the application of 50 shock wave number is shown in **Fig. 2.** The spectrum shows all characteristic peak of HAP. The broad bands at 3410cm^{-1} and 1622cm^{-1} were due to the bending modes of the absorbed water while the sharp peak at 3570 cm^{-1} is due to the stretching vibration of the lattice OH. The medium peak at 634 cm^{-1} is due to the OH bending mode of HAP. The band at 475 is assigned to the bending mode of PO_4 group (ν_2). The peak at 1039-1085 cm^{-1} and 964 cm^{-1} correspond to the stretching vibration of PO_4 group (ν_3 and ν_1). The peaks appeared at two different wave numbers like 606 and 578 cm^{-1}is due to the bending mode of PO_4 group (ν_4).

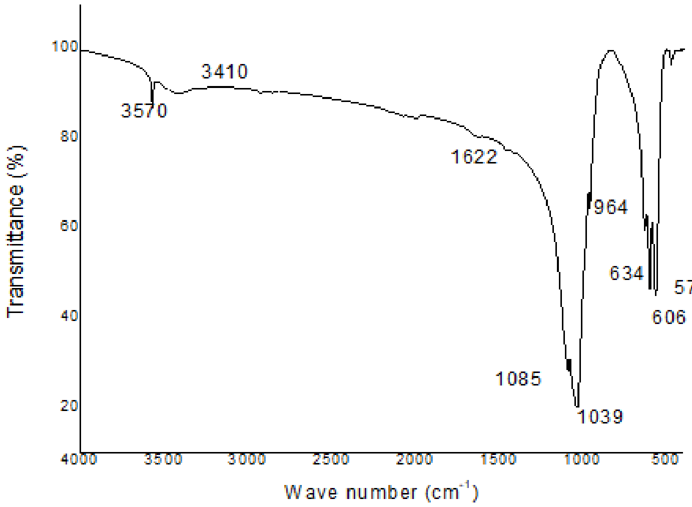

Fig. 2 FTIR of HAP powders synthesized by SW (50).

The FTIR spectrum showed in **Fig.3**representsthe HAP synthesized with 100 number. The spectrum contains the OH broad peak at 3432cm^{-1} and the peak at 1632cm^{-1}is attributed to bending mode of adsorbed water. The medium peak at 625cm^{-1}is due to the OH bending mode of HAP. The sharp peak at 3580cm^{-1} is due to the stretching vibration of the lattice OH group. The ν_1 and ν_3 band of phosphate groups occur at 948 and 1086-1048cm^{-1} respectively. The stretching frequency of the phosphate group was observed at 609cm^{-1} and 578cm^{-1} is corresponded toν_4. The peak at 484cm^{-1} in can be assigned to ν_2 mode

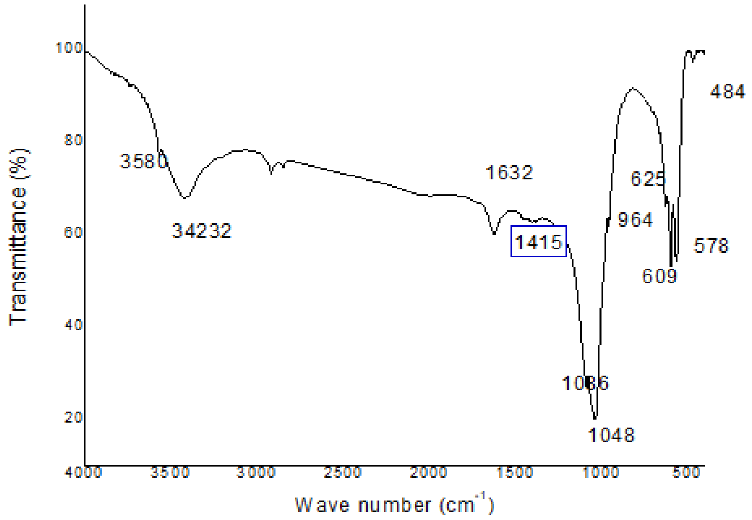

Fig.3 FTIR of HAP powder synthesized by SW (100)

3.2. XRD Characterization of pure HAP powder

The powder diffraction and phase analyses were carried out by powder X-ray diffraction technique and a good correlation of data was obtained with stoichiometric hydroxyapatite (17). **Figure 4** shows the XRD patterns of the synthesised HAP powder with and without shock wave. The XRD patterns of pre-shock wave loaded HAP sample gives sharp peaks at 25.80, 31.68, 32,79 two theta values, while peaks at 25.87, 31,73, 32.86 were obtained for HAP samples with 50 shock number. For sample loaded with 100 shock number, peaks appeared at 25.86, 31.71, 32.86 two theta values. It was found that the XRD patterns of the HAP sample are in good agreement with standard value of JCPDS data base (09-0432) for HAP which indicated that the crystal structure of HAP sample is similar to the pure hydroxyapatite. These findings confirm the successful formation of HAP. The particle size calculations of pre and post shock wave loaded HAP is given in **Table1.** The particle dimensions showed a steady decrease when compared with pre-shock and post shock wave loaded HAP. The pre-shock wave HAP showed lower crystallinity when compared to shock loaded HAP.The crystallinity size of the sample was calculated from XRD peaks by using Scherrer's equation.

Table:1. Grain size calculated using Scherrer equation

S.No	Sample	2θ value	D grain size value (nm)
1	Shock number 50	25.87	43
		31.73	28
		32.78	28
2	Shock number 100	25.86	45
		31.71	29
		32.87	37
3	Controlled	25.80	49
		31.68	33
		32.79	41

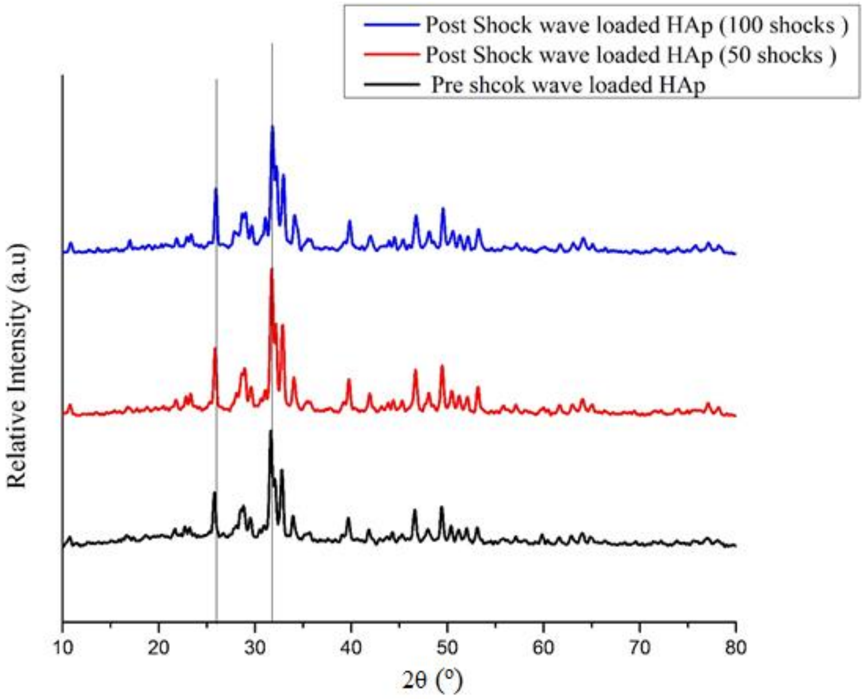

Fig.4.XRD patterns of pure HAP powder synthesized by shock wave method

3.3 SCANNING ELECTRON MICROSCOPIC STUDIES

The surface morphology, size and the crystallinity of the synthesized HAP powder were investigated by using scanning electron microscope.

SEM image of HAP powder synthesized by without shock wave is shown in **Fig. 5.** It shows that the HAP particles are almost of equal size and distribution. SEM micrographs shows agglomeration like structure with in the range of 1µm for pre-shock samples.

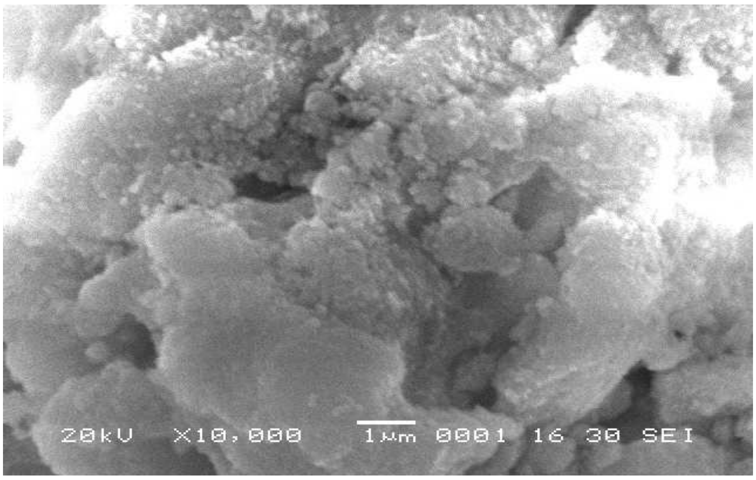

Fig.5. SEM micrograph of HAP powder synthesized without shock wave.

SEM image obtained for HAP nanoparticles loaded with shock wave is shown in **Fig 6.** From the figure, the particle size of HAP powder ranges from 20-30 nm with irregular shape. SEM micrographs shows slight agglomeration like structure in the range of 200 nm. The image shows the HAP particles are almost of almost equal size and distribution.

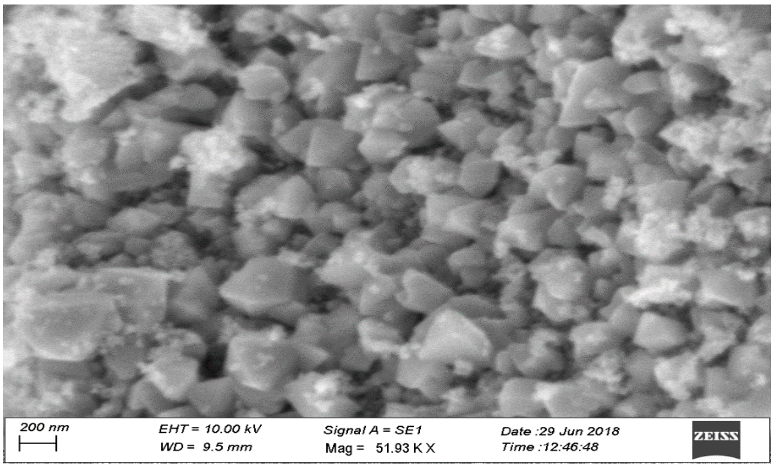

Fig. 6. SEM micrograph of HAP powder synthesized by SW (100).

CONCLUSION

In present study the Hap nanoparticles were successfully synthesised by shock wave method. The shock wave method offers several advantages over conventional methods, the most important of them being cleanliness, short reaction time, and improvement of the product formation and also nanosized particles. The FT-IR results have shown that obtained HAP powder did not contain any other calcium phosphate impurity phases. As the shock wave number is increased, the crystallinity and size of the particles decreases as a result of cavitation like process and was evident from the XRD and SEM findings. The Hap nanoparticle synthesized by this method can serve as a good biomaterial for various biomedical application.

REFERENCES

1. M. Jarcho, Calcium phosphate ceramics as hard tissue prosthetics, Clin. Orthop. Rel. Res., 157, (1981), 259.
2. P.M. Pilliar, H.U. Cameron, A.G. Binnington, J.A. Szvek, Bone ingrowth and stress shielding with a porous surface coated fracture fixation plate, J. Biomed. Mater. Res., 13, (1979) ,799.
3. Ziaie, F., Hajiloo, N., Alipour, A., Amraei, R. and Mehtieva, S.I. Retrospective dosimetry using synthesized nano-structure hydroxyapatite. Radiation Protection Dosimetry 145 No. 4,(2011), 377.
4. M.H. Fathi, A. Hanifi, Evaluation and characterization of nanostructure hydroxyapatite powder prepared by simple sole gel method, Mater Lett. 61, (2007), 3978.
5. M.H. Fathi, A. Hanifi, V. Mortazavi, Preparation and bioactivity evaluation of bone like hydroxyapatiteNano powder, J. Mater Process Technol. 202, (2008), 536.
6. K. Nayak, “Hydroxyapatite Synthesis Methodologies: An Overview,” International Journal of Chemtech Research., vol. 2, (2010).
7. H. Aoki, Science and medical applications of hydroxyapatite, Japanese Association of Apatite Science, Tokyo, Japan, 1991.
8. L.L. Hench, J. Am. Ceram. Soc., 74, (1991), 1487.
9. W. Suchanek, M. Yoshimura, Processing and properties of hydroxyapatite-based biomaterials for use as hard tissue replacement implants, Journal of Materials Research 13, (1998), 94.
10. J.C. Elliot, Structural and chemistry of the apatite’s and other calcium orthophosphates, Elsevier, Amsterdam, 1994.
11. K. M. Govindaraju, V. Collins Arun Prakash, D. Gopi and L. Kavitha Novel methods to prepare nanohydroxyapatite (ICMSRN) Mother Theresa Women’s University, Kodaikanal, February (2008) 27-29.
12. Cazalbou S., Combes C., Eichert D., Rey C., Adaptative physic-chemistry of bio- related calcium phosphates, J. Mater. Chem 14, (2004),2148.
13. S. Koutsopoulos, Synthesis and characterization of hydroxyapatite crystals: a review study on the analytical methods, J. Biomed. Mater. Res. 62, (2002) 600.
14. Ciobanu, C.S.; Popa, C.L.; Predoi, D. Sm:HApNano powders Present Antibacterial Activity against Enterococcus faecalis. J. Nanomater. (2014), 1.
15. Suchanek, W.; Yoshimura, M. Processing and properties of hydroxyapatite-based biomaterials for use as hard tissue replacement implants. J. Mater. Res. 13, (1998), 94.
16. K. Vasu, H.S.S.R. Matte, Sharmila N. Shirodkar, V. Jayaram, K.P.J. Reddy,Umesh V.Waghmare, C.N.R. Rao, Chem. Phys. Lett. 582 (2013) 105.
17. A. Costescu, I. Pasuk, F. Ungureanu, A. Dinischiotu, M. Costache, F. Huneau, S. Galaup, P. Le Coustumer, D. Predoi, Digest Journal of Nanomaterials and Biostructures, 5, (2010) 989.