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Process-Properties and Correlation in Hydroxyapatite Bioceramics

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Abstract
Nano-Hydroxyapatite (HAp) has been synthesized via various methods like co-precipitation, sol-gel and solid-state reaction method. Ca/P ratio has been taken for HAp is 1.67. Amalgamated powder has calcined at 750°C for the phase formation and to remove the volatile impurities.The ultimate powder has been characterized by Dynamic Light Scattering (DLS), Ultraviolet spectroscopy (UV), and X-Ray Diffraction analysis (XRD) which reveals the particle size and the phase formation of the synthesized HAp. The average particle sizes of HAp by co-precipitation, sol-gel and solid state reaction method has found 116.4nm, 171 nm, and 94.1nm respectively. More absorption has been found in UV spectra HAp synthesized via solid state reaction method.
Keywords: HAp, Co-precipitation, Sol-gel, Solid-state reaction, X-Ray Diffraction.

I. INTRODUCTION

Nano-sized particles and crystals show a significant role in the development of calcified tissues of various animals. Hydroxyapatite (HAp) $[Ca_{10}(PO_4)_6(OH)_2]$ is a naturally occurring mineral in the inorganic component of human bone and tooth enamel. The crystal size of HA in natural human bone is in nano range. The constituent elements of HAp are primarily calcium and phosphorus, with a stoichiometric Ca/P ratio of 1.67.It displays favourable properties such as bioactivity, biocompati-bility, slow-degradation, osteoconduction, osteointegration, and osteoinduction. HAp with a Ca/P ratio of 1.67 is the main mineral component of biological hard issues, such as bone and teeth and it is made up of calcium and phosphorous. It is known as a bio-ceramic because of its excellent bioactivity and biocompatibility. Nowadays, HAp-based materials have also attracted more and more attention as solid and recyclable catalysts due to its ion exchanged and absorbent properties [1]. Due to its chemical and structural similarity with the mineral phase of bone and teeth, HAp is widely used for hard tissues repair. HAp is used in the form of powders, composites or even coatings for medical application as well as tooth replacement, augmentation, pulp capping material and maxillo facial reconstruction [2, 4]. Hydroxyapatite has been acknowledged as a bone graft material in medical and dental applications due to their similar chemical composition with natural bones. Generally, bone substitution materials such as autograft, allograft and xenograft are used for bone trauma and fracture problems. Other than HAp, none of these materials provide a perfect replacement of the bone due to mechanical and biological instability and incompatibility[3].Nano-Hydroxyapatite (HAp) is used in replacing hard tissue in in the human body for the following reasons;(i)In a solid state has the melting temperature of 1250°C- won't melt in the human body, (ii) Exhibits hexagonal crystal structure- close packed, (iii) Bio-ceramic material-hard and wear resistant, suitable for human body replacements, (iv) Shows a high resistance to surface reaction with the simulated body fluid- won't react with other fluids in the body. Nano-hydroxyapatite exists as a nanopowder and forms part of the crystallographic family of apatites, isomorphic compounds with the same hexagonal structure. This is the calcium phosphate compound most commonly used for biomaterial. Hydroxyapatite can appear to have brown, yellow, or green colorations. In its powder form but is typically white [5-7].

II. MATERIALS

For preparation of hydroxyapatite calcium chloride, calcium carbonate, disodium hydrogen phosphate were used as calcium and phosphorous precursors. Reagents were purchased from Thermo Fisher Scientific India Pvt. Ltd., Mumbai; LobaChemiePvt. Ltd., Mumbai; Merck Specialities Pvt. Ltd., Mumbai. Polyethylene glycol was purchased from Sigma-Aldrich, Germany and used as surfactant and sodium hydroxide was purchased from Thermo Fisher Scientific India Pvt.Ltd., Mumbai and used as a reducing agent for precipitation.

III. METHODOLOGY

Synthesis of hydroxyapatite in three methods such as
(a) co-precipitation (b) sol-gel (c) solid-state reaction methods.

A. Co-Precipitation Method

Co-precipitation method includes calcium and phosphorous precursors such as, calcium chloride and Disodium hydrogen phosphate. In this procedure Calcium chloride and Disodium hydrogen phosphate were dissolved in water. Calcium chloride was stirred using magnetic stirrer and disodium hydrogen phosphate was added drop wise to the calcium chloride solution [8]. The mixture was stirred for a few minutes and Poly ethylene glycol was addeddrop wise to the mixture as a surfactant, which is used to reduce the surface tension. Then the reducing agent sodium hydroxide was added into the mixture drop wise which resulted in theprecipitation. Andthe above mixture was stirred for around 10 hours. Then the mixture was centrifuged(10000rpm) for 10 min, and kept in Hot oven where the temperature was maintained at 100°C. After sometime the required powder will be obtained.

B. Sol-Gel Procedure

Sol gel procedure includes calcium and phosphorous precursors such as calcium carbonate and disodium hydrogen phosphate. The calcium carbonate and disodium hydrogen phosphate was dissolved in liquor ammonium. Both the reagents was stirred for 10 hrs using magnetic stirrer. Then the mixture was kept in hot oven at temperature 100°C.

C. Solid- State Reaction Method

Egg shells were collected and washed it with running water for several time. And then washed in HCl to deprotenize. And again washed with hot water for several times. And the Washed shells are dried at 100°C for 24 hours. Then the shells are grinded into fine particles with Agate mortar and Pestle which serves as calcium carbonate. Disodium hydrogen phosphate is added to the particles and then grinded again with methanol to form nano HAp particles. Then obtained powder has calcined at 750°C for phase formation. The XRD patterns of prepared eggshell and the HAp formed from them given below.

IV. RESULTS AND DISCUSSIONS

A. Particle Size Analysis

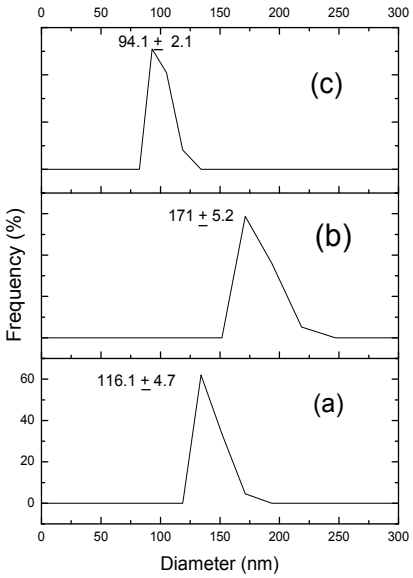

Fig 1: Average particle calculated for HAp synthesized by various methods (a) co-precipitation (b) solgel (c) solid state reaction methods

Figure 1 (a), (b) and (c) shows the average particle sizes of HAp synthesized via co-precipitation, solgel and solid state reaction method respectively. The particle size found for solid state reaction method is 94.1 nm which very low comparing to the other two chemical methods. This could be the reaction at high temperature were leads to agglomerations for the chemical methods, because of the chemical precursors reduced HAp powder tends to agglomeration. But comparing to these the solid state derived HAp is far better that has not got agglomerated.

B. Uv Analysis

The spectra of ultraviolet light for the three synthesized of HAp solutions are measured by UV spectrometer and the results are shown in Fig.2.

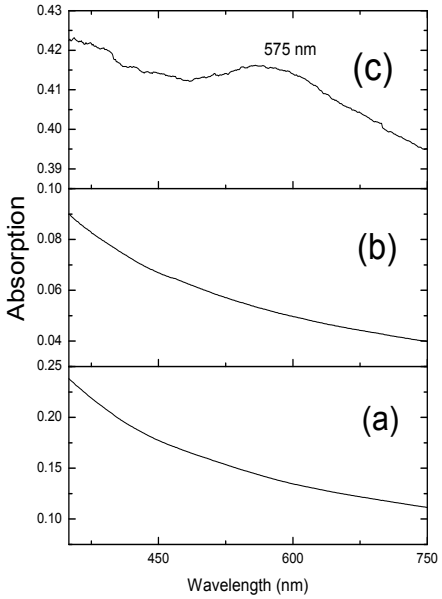

Fig 2: UV Spectrum for HAp synthesized by various methods (a) co-precipitation (b) solgel (c) solid state reaction methods.

The UV spectra result indicates that there is no absorption has found for HAp synthesized via co-precipitation and solgel derived. But the solid state reaction derived HAp ceramic absorption was found at near 575 nm. The result which indicates that the HAp synthesized via solid state reaction method could have better properties than the chemical derived nano HAp particles

C. XRD ANALYSIS

Figure 3 (a), (b) and (c) shows the XRD pattern of HAp prepared via co-precipitation, solgel, and solid state reaction method. The peaks are indexed according to the standard pattern JCPDS card no: 89-6440. As prepared and calcined via solgel HAp powder has shown (202) peak as very high. From that conclude that high calcination temperature is needed to prepare HAp via sol-gel method. Powder prepared from co-precipitation and solid state reaction method has shows excellent phase formation. That could reveal the calcination temperature used (750^{o}C) is enough to form the HAp ceramics. The particle size has found from Debye Scherer formula for co-precipitation, solgel and solid state reaction method HAp is 118 nm, 175 nm and 87 nm. Which nearly match with the average particle size calculated from DLS method.

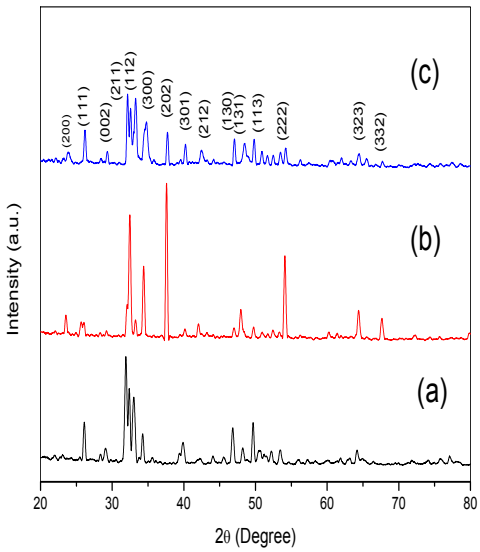

Fig.3 : X-Ray Diffraction pattern for Hap prepared by various methods a) Co-precipitation b) Sol-gel c) Solid state reaction method.

V. CONCLUSION

The nano Hydroxyapatite has been successfully synthesized via co-precipitation, solgel and solid state reaction method, and calcined at 750^{o}C to obtain pure HAp phase. The synthesized samples have been characterized with Particle size analyser, UV and XRD. The average particle size of HAp derived from solid state reaction method has smaller than other two methods. The solid state derived HAp particles has show good absorption at the range of 575 nm. And the XRD patterns reveal the clear phase formation for HAp synthesized via co-precipitation and solid state reaction method. Solgel shows some more intensity peaks from that we conclude that more calcinations temperature is needed to attain pure phase for HAp synthesized by solgel method.

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