

ABSTRACT

Biomaterials field is an exciting, multidisciplinary and rapidly evolving area of research involving principles of science, medicine and materials engineering. Current trends in research are focusing on the development of new as well as improved products at competitive prices for biomedical applications. Among the important biomaterials, Hydroxyapatite (HAp) is a calcium phosphate ceramic material used as bone substitute, since it exhibits chemical composition similar to that of mineral component of bone and tooth. Usually in HAp $\{Ca_{10}(PO_4)_6(OH)_2\}$, Ca positions in living organisms is substituted by different cations in order to maintain a normal metabolism. Strontium is one of the major elements in living bones, showing beneficial effects by enhancing the strength and density of bone.

Strontium substituted Hydroxyapatite (Sr-HAp) has evoked keen interest among researchers with emphasis on cost effective synthesis for use in drug delivery for osteoporosis and bone replacements. In recent times, combustion synthesis has emerged as a simple and cost-effective exothermic reaction method, initiated by a fuel allowing uniform and homogeneous substitution of dopants in materials. Limited research work has been reported on the ecofriendly Solution Combustion (SC) synthesis of Sr-HAp nano powders and the influence of process parameters on powder quality. In the present work, SC synthesis of 0 to 30% Sr-HAp nano crystals in a single step is reported. Investigations on crystal structure, phases present, lattice parameters, substitutions in lattice, crystallite sizes and crystallinity were carried out using X-Ray Diffraction (XRD). Presence of functional groups such as phosphates and hydroxides were examined using Fourier Transform-Infrared (FTIR) spectroscopy.

Morphology of the particles, particle size distributions, amount of each elements present and its distribution in the synthesized powders were investigated using Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS). Investigations to determine individual particle morphology, clustering as well as aspect ratio and porosity of nanorods were carried out using High Resolution Transmission Electron Microscopy (HRTEM). Crystal structure, lattice parameters and interplanar distance were determined using Selective Area Diffraction (SAD) and Filtered Fourier representation Technique (FFT) modes in HRTEM. Selected Sr-HAp powders were consolidated to 15 mm diameter with 1.95 to 3 mm thick pellets and characterized for their physical as well as corrosion properties.

Pure HAp and 15% Sr-HAp nano powders were synthesized at 500°C using energy efficient, cost effective and eco-friendly technique. By characterizing the as-synthesized powders, a solution pH of 7.4, a temperature range of 400 to 600°C and synthesis times between 20 to 40 minutes were chosen as parameters for SC synthesis of 0, 15 and 30% Sr-HAp powders. Optimization of process parameters were done for SC synthesis of Sr-HAp powders to achieve 60 – 90% crystallinity, with > 95% purity in as-synthesized Sr-HAp nano powders for improved bioactivity. Twenty seven trial experiments were designed using Design of Experiments (DoE) based Response Surface Methodology (RSM) - Full Factorial Design (FFD) approach. As-synthesized powders were then characterized using XRD to determine the response variables. Optimum conditions were obtained by superimposing (i) % Sr substitution (Sub%) versus Time, (ii) Time versus Temp and (iii) Sub% versus Temp contour plots. A temperature of 500°C and a synthesis time of 30 minutes were chosen as the optimum parameters for obtaining the preferred response variables. 0 – 30% (at 5% increments) Sr-HAp powders were SC synthesized under optimized conditions to validate the

models predicted. With increasing amount of Sr substitution, XRD patterns showed peaks shifting, variation in peak intensities and broadening. FTIR spectra of 15% and 30% Sr-HAp samples synthesized at 500°C for 30 minutes confirmed the presence of functional groups like PO_4^{3-} , OH^- and CO_3^{2-} .

TEM micrographs revealed nano rods with smooth edges having greater than 5 nm diameter and 15 nm length in pure HAp and Sr-HAp powders. Dark field images of corresponding HAp and Sr-HAp samples also revealed the orientation contrast within the agglomerates confirming the nanorod shape and aspect ratio (ranging from 3.8 to 7) of the primary Sr-HAp nano rods. HRTEM and FFT fringes also confirmed the highly crystalline lattice arrangement in as-synthesized Sr-HAp samples.

A mechanism has been proposed for Sr-HAp nano rod formation after nucleation and growth of nucleus with the following stages: (i) sheet formation due to preferential growth in one direction, (ii) curling of sheets, (iii) rolling up into rods (similar to graphene sheets forming carbon nano tubes), (iv) formation of aggregates and (v) secondary agglomerations. These stages have been confirmed with TEM investigations of the Sr-HAp powders. SEM images of the sintered samples showed 19 to 23% ultrafine porosities with average pore sizes ranging from 500 nm to 10 μm in the surface of the Sr-HAp pellets.

Maximum deposition was observed in 15% Sr-HAp sample of about 0.16 gm / gm after 25 days of soaking. 15% Sr-HAp pellets showed higher deposition rate than 30% Sr-HAp in the dissolution studies, which was confirmed by the Icorr values obtained (521 pA and 11.9 nA for 15% and 30% Sr-HAp respectively) in potentiostatic tests. (Ca+Sr) / P ratio achieved was from 1.56 to 1.7 and found to meet the requirements as per ASTM F1185-88 standards for HAp powders suitable for implant materials.