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High Temperature Synthesis and Characterization of Hydroxyapatite Doped with Silver Nanoparticles

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Calcium hydroxyapatite, is a material which is closely resembles with bone apatite and exhibits excellent osteoconductivity. In this work, the synthesis of hydroxyapatite in a modified synthetic body fluid (SBF) solutions at 37 °C and pH of 7.4 was performed using novel chemical precipitation technique. Then after heat operation at 1200 ºC, on filtered precipitated result calcium hydroxyapatite were produced. Hydroxyapatite doped with silver nanoparticles was prepared by treatment with $AgNO_3$ solution and reduction of Ag^+ ions by sodium borohydrate solution. The formations of the silver nanoparticles on the calcium hydroxyapatite structure were confirmed by X-ray diffraction and transmission electron microscopy. Transmission electron microscopy image shows the nanostructure of silver particles, being formed on hydroxyapatite texture.

Key Words: Calcium Hydroxyapatite, Synthetic body fluid, Silver Nanoparticles.

INTRODUCTION

Calcium hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$], the main inorganic component of the hard tissues in bones, is a member of the apatite family, including compounds with similar structure but not necessarily of identical composition. Biological apatite, which comprise the mineral phases of calcified tissues (enamel, dentin, and bone) differ from pure calcium hydroxyapatite in stoichiometry, composition, crystallinity and in other physical and mechanical properties[1].

Synthetic calcium hydroxyapatite has excellent biocompatibility and bioactivity, and widely used in many biomedical application s such as non-load bearing implants and coating onto prostheses[2,3].

Owing to a chemical composition and structure similar to bone, synthesized calcium phosphates are bioactive and biocompatible when used as bone substitutes, but their inherent brittleness and low tensile strength confine their medical applications. In order to overcome these limitations and utilize the bioactivity of calcium phosphates as a bone substitute, a variety of approaches have been adopted. Among these approaches, coating calcium phosphates, especial hydroxyapatite (HA)

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and silicate glass on tough biocompatible metallic substrates has received considerable attention[4,5]. In fact, the deposition of calcium phosphate coatings on metallic substrates limits the release of metallic ions when used as prostheses. Furthermore, by means of calcium phosphate coating it is possible to modify the surface features of metal and accelerate bone healing and bonding of the coatings with bone[6-9].

Biocompatible nanomaterials should be capable of being in contact with bodily fluids and tissues for prolonged periods of time, while eliciting few, if any, adverse reactions. Such materials could have calcium phosphate surfaces which provide enhanced integration of the material with body tissues[10].

Silver nanoparticles (Ag NPs) are of great interest for their superior electrical conductivities, optical properties, oxidative catalysis, antibacterial effects, *etc*. The antibacterial activities of silver salts have been noticed since ancient times. Silver ions and silver based compounds are highly toxic to microorganisms, showing strong biocidal effects on as many as 12 species of bacteria including *Escherichia coli*. Silver is currently used to control bacterial growth in a variety of applications, including prostheses, catheters, burn wounds, *etc*. The antibacterial activities of colloidal Ag NPs are influenced by their dimensions, where the smaller particles give greater antibacterial effects. Therefore, in developing synthetic routes, an emphasis is made on controlling the size of Ag NPs. The most common method for synthesis of Ag NPs is the chemical reduction of silver salt solutions by reducing agents in different stabilizers such as polymers and surfactants[11]. In present work reducing agent was sodium borohydrate.

EXPERIMENTAL

The required amounts of $Ca_3(PO_4)_2$ (28.11 g) were first dissolved in synthetic body fluid (SBF)[1] solution (100 mL) contained in separate beaker. Then Na_2SiO_3 (18.39 mL) was added drop wise to the above calcium phosphate suspension and stirred at 37 ºC for 1 h. The solutions left for 1 day at room temperature without stirring. Thus formed and aged 'seeds' were removed from mother liquors by filtration and washed with 100 mL of deionized water.

The filtered product of before synthesis was dried at 80 ºC for 16 h in an electrical air oven. The dried result were individually heated at a rate of 5 ºC/min up to 1200 ºC in a muffle furnace and were stored for 2 h at this temperature and then placed in air for cooling to ambient temperature.

In present method, Ag^+ ions are reduced by sodium borohydrate ($NaBH_4$) to aAg^0. For this purpose, 5.0 g calcium hydroxyapatite product was dissolved in 30 mL deionized water and then, added 30 mL $AgNO_3$ (4.2 g/L) to this mixture. After 1 h mixing in room temperature the color of mixture was changed from white to yellow. Then 1000 mL sodium borohydrate (0.378 g/L) was added to this mixture and rapidly filtered. The suspension was filtered and washed with deionized water and dried at room temperature. The result green dark product was designated as calcium hydroxyapatite with silver nanoparticles.

The phase composition and crystallinity of powders were recorded on a Model D8 Advanced Bruker diffractometer using Cu K_α radiation generated at 40 kV and 40 mA, in the range of $20^\circ < 2\theta < 90^\circ$ at a scan speed of 0.02 °/min.

Images of the samples were obtained on an EM208S transmission electron microscope (Philips Co., Holland) at 100 kV beam current. TEM images were utilized to study and determine the size and morphology of the nanoparticles.

RESULTS AND DISCUSSION

XRD patterns of the samples are shown in Figs. 1-3. The XRD spectra of precursors before calcinations exhibit in Fig. 3A. Fig. 3B shows that calcium hydroxyapatite content increased with increase in calcination temperature, and the apatite phase appeared at 1200 ºC. The XRD measurements of Ag NPs loaded on hydroxyapatite was carried out, to examine the structure and to estimate the mean silver particle size. According to silver nanoparticles pick at $2\theta = 38.15$ in Fig. 2 the mean size of silver nanoparticles was estimated by Scherer's equation:

$$d = 0.9\lambda/(B \cos \theta_B)$$

where, d is the mean diameter of the nanoparticle, λ is wave length of Cu K_α X-ray radiation source; B is the angular width at FWHM of the X-ray diffraction peak at the diffraction angle[12]. Mean silver particle sizes (diameters) estimated in the silica matrix varied about 12.9 nm in this sample.

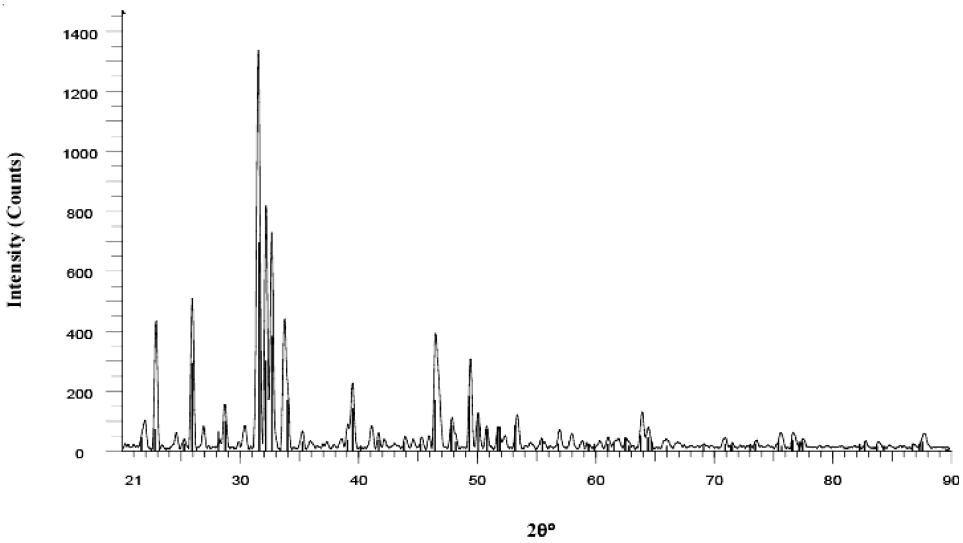

Fig. 1. XRD patterns of synthesized hydroxyapatite calcinated at 1200 ºC

TEM micrograph shows that Ag nano particles smaller than 50 nm, having a spherical shape, uniformly scattered (Fig. 4). This image indicates that the applied method for loading silver nano particles on calcium hydroxyapatite substrate were efficient procedure.

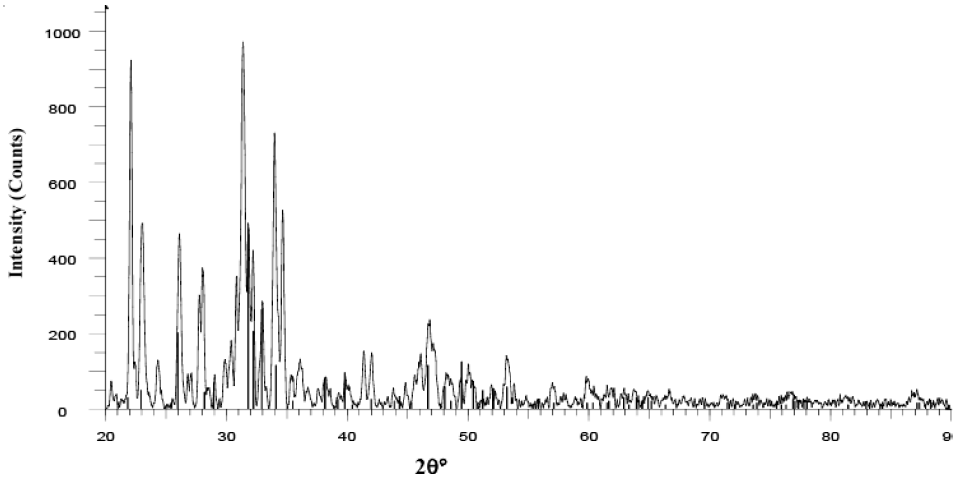

Fig. 2. XRD patterns of silver nanoparticles (Ag NPs) loded on hydroxyapatite

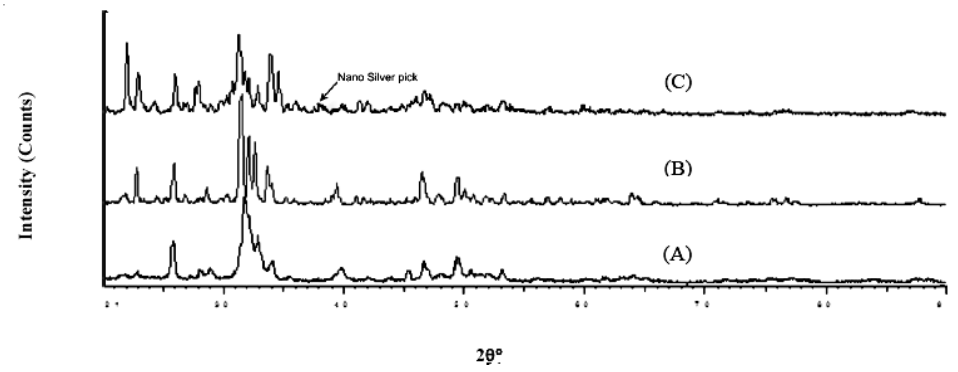

Fig . 3. XRD patterns of (A) Precursors before calcinations, (B) Hydroxyapatite and (C) silver nanoparticles (Ag NPs) loaded on hydroxyapatite

Conclusion

Chemically homogeneous calcium hydroxyapatite powders have been synthesized successfully from a modified and novel synthetic body fluid solution, at the physiological and biomimetic conditions of pH 7.4 and 37 ºC, containing dissolved calcium phosphate and sodium silicate in appropriate amounts by a chemical precipitation technique. The produced powders were heated at 1200 ºC for 2 h in an air atmosphere oven. The calcium hydroxyapatite powders also contained trace amounts of other inorganic ions, provided and incorporated into the calcium hydroxy-apatite structure by the synthetic body fluid (SBF) solution used.

Silver nanoparticles were successfully loaded to calcium hydroxyapatite substrates. XRD and TEM studies reveal that the average sizes of the silver nanoparticles were smaller than 50 nm.

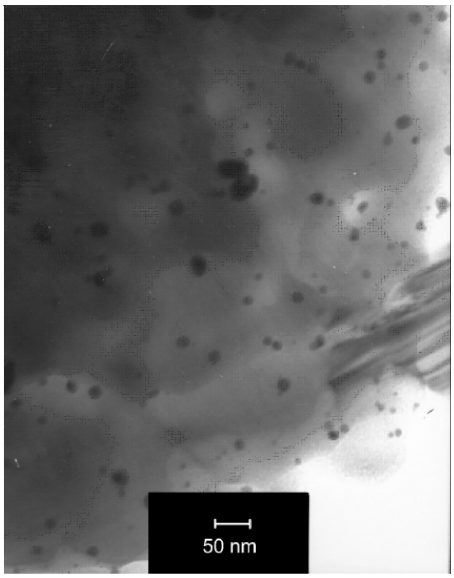

Fig. 4. TEM micrograph of silver nanoparticles (Ag NPs) loaded on hydroxyapatite

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