

Characterization of Facile Synthesised Nano Hydroxyapatite Treated by DC Glow Discharge Plasma for Different Exposure Times

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ABSTRACT

The synthetic biomaterials such as Hydroxyapatite (HAp) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ plays an fascinating role as implants in human bone replacement. HAp is a calcium phosphate having similar morphology and composition to the human hard tissues in with stoichiometric Ca/P ratio of 1.67. It is widely used in bone tissue engineering and dental applications due to their biocompatibility, biodegradability and bioactivity. The HAp has vital role in the field of biomedical engineering and stimulates osteoblast proliferation. This present research includes synthesis of biomimetic nano hydroxyapatite from facile sol gel process and surface modified by DC Glow discharge plasma. The prepared samples are exposed to air plasma for different exposure time with electrode potential of 400V. The samples was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Energy dispersive X - ray (EDX) . Plasma treatment is an ecofriendly and economical technique for the surface modification of this synthesized biomaterial.

Keywords: HAp, DC glow discharge plasma, biomimetic, biocompatibility

I. INTRODUCTION

In the recent years, biomaterials plays an intriguing role as implants and acts as surface protecting agents in replacement of human bones. Hydroxyapatite (HAp) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is a calcium phosphate has hexagonal structure similar to the human hard tissues in morphology and composition with stoichiometric Ca/P ratio of 1.67 with identical bone apatite. HAp has challengeable features like biocompatibility, bioactivity, biodegradability and corrosion-resistance. It has an ability to integrate in bone structures but thermally unstable compound, decomposing at temperature from 800- 1200oC [1]. Plasma treatment is ecofriendly surface modification technique without altering the bulk material properties [2]. In this present work the nano hydroxyapatite obtained by

facile sol-gel method is exposed to atmospheric air plasma in DC glow discharge plasma.

II. EXPERIMENTAL PROCEDURE

The nano HAp powders were prepared by employing facile sol-gel method with 1M of calcium nitrate tetra hydrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (95% EMPLURA) and 0.6 M of di ammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ (99% SIGMA ALDRICH) respectively, used as sources for calcium and phosphorous. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ were dissolved in 500 ml of de-ionized water separately, so as to obtain the stoichiometric molar ratio of 1.67. The pH of each aqueous solution was maintained at 10 by the addition of ammonium hydroxide solution NH_4OH (99%, SIGMA ALDRICH). A gelatinous white precipitate

was produced by the dropwise addition of $(\text{NH}_4)_2\text{HPO}_4$ solution to the vigorously stirred $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ solution for an hour. Then, the precipitate was aged for 24 h at room temperature followed by washing four times with de-ionized water and dried in hot air oven at 373 K for 10 hours [3]. The dried powder was then milled using a mortar and pestle and finally calcined using silica crucible in a muffle furnace at 523 K for 2 hours. DC glow discharge plasma reactor was used for the surface modification of the synthesized HAp nanoparticles. The low temperature plasma generator have the parts namely a stainless steel chamber of 50 x 50 cm, rotary pump, a power supply, gas needle valve and two aluminum electrodes. A pressure of 0.03mbar was generated inside the chamber using rotary pump and the pressure is measured using a Pirani gauge[13]. A DC voltage of 400V was applied between the electrodes to generate plasma[4]. Before the plasma treatment the chamber was cleaned with deionized water and acetone. The synthesised HAp nanoparticles are kept inside the plasma chamber by the sample holder and is exposed to plasma for about 5 minutes, 10 minutes and 15 minutes. The surface change for untreated and plasma treated samples for the different exposure times are examined in this present work.

III. RESULTS AND DISCUSSION

3.1 XRD Analysis

The crystallographic analysis was carried out by X-ray diffraction method. The XRD pattern of Pure HAp before and after plasma treatment is shown in Figure 1(a - d). The XRD patterns shows diffraction lines of hydroxyapatite the intense peaks present at (002), (211), (310), (222) and (213) matches with data of ICDD – card No. 09-0432. In case of plasma treatment the intensity of the peak decreases with broadening. There is slight shift in the peak due to the surface etching due to the ionized air molecules of plasma.

The XRD pattern reveals the crystallinity is altered by plasma treatment.

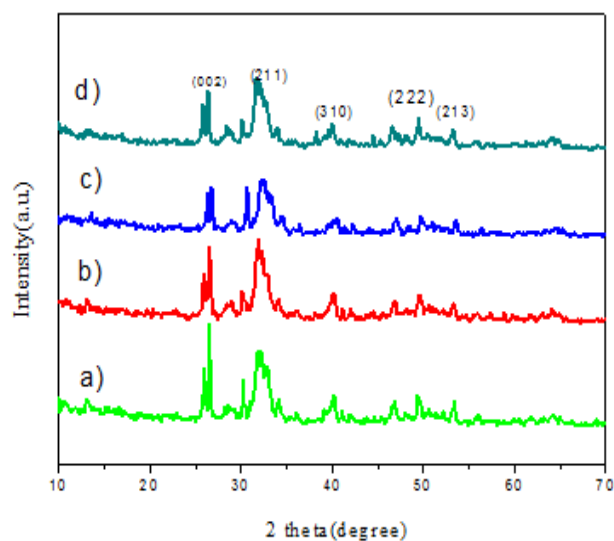


Figure 1. XRD pattern of untreated and plasma treated HAp samples (a – 0 min, b – 5 min, c – 10 min, d – 15 min)

3.2 SEM Analysis

The surface morphology of synthesized pure HAp powder was examined by using scanning electron microscope. The SEM images of HAp are shown in Figure 3. It was observed that for untreated HAp, the particles exhibit nearly platelet shape and the particle gets agglomerated due to vanderwaals force of attraction [5]. There is an improvement in the surface morphology due to exposure of atmospheric air glow discharge plasma. With the increase of plasma exposure time from 5 min to 15 min the surface roughness is produced due impingement of ions and radicals react in the surface and exhibits flakes like shape for 10 min. The SEM images confirm the surface modification produced due to variation in treatment time.

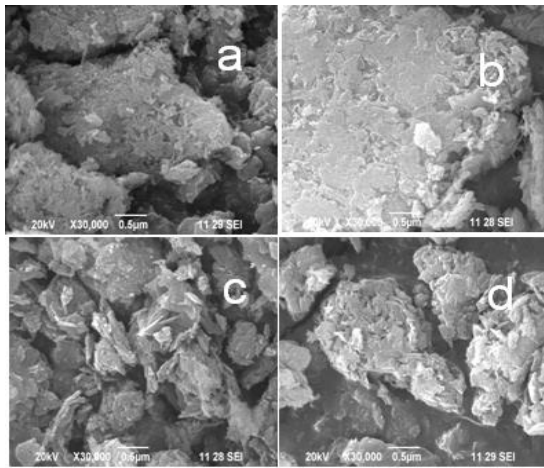


Figure 2. SEM image of untreated and plasma treated HAp samples (a – 0 min, b – 5 min, c – 10 min, d – 15 min)

3.3 FTIR Analysis

The FTIR spectrum of pure HAp nanopowders before and after plasma treatment is shown in the Figure 2(a - d). The band observed at 3429.94cm^{-1} was assigned to the presence of hydroxyl group. The peak observed at 566.59cm^{-1} indicates the presence of $\text{PO}_4^{3-}(\nu_4)$. The band observed at 1031.92cm^{-1} confirmed to phosphate stretching vibration [6]. The band observed at 1096cm^{-1} and 1031.92cm^{-1} indicates the presence of $\text{PO}_4^{3-}(\nu_3)$. The band observed at 3429.94cm^{-1} corresponds to the presence of hydroxyl group. A wide absorption bands at 3569cm^{-1} and 3429.94cm^{-1} (OH) stretching and vibration modes at the HAp crystallite surface[7]. It is evident that the band observed before and after plasma treatment functional group remains unchanged except the narrowing of the peak when plasma exposure time is increased[8- 12].

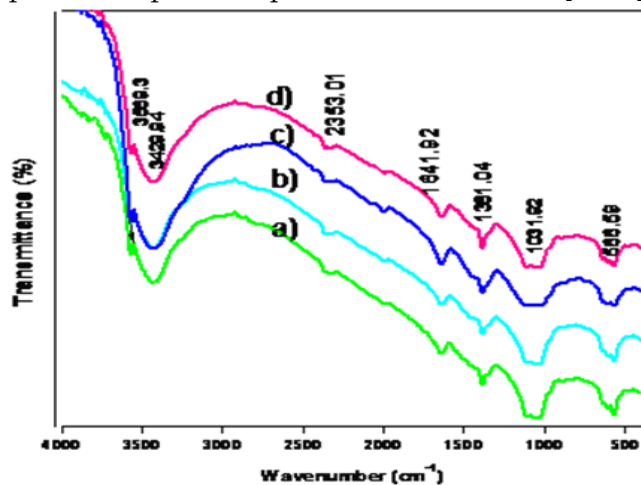


Figure 3. FTIR spectra of untreated and plasma treated HAp samples (a – 0 min, b – 5 min, c – 10 min, d – 15 min)

3.4 EDAX Analysis

Energy dispersive X-ray spectroscopy (EDAX) was used to identify the elemental particles present in the synthesised nano HAp before and after plasma treatment. The Figure 4 confirms the presence of the calcium, oxygen and phosphorus in HAp. No additional impurity peaks are identified.

It is evident that air plasma treatment does not significantly alter the elemental particles present in the synthesised samples.

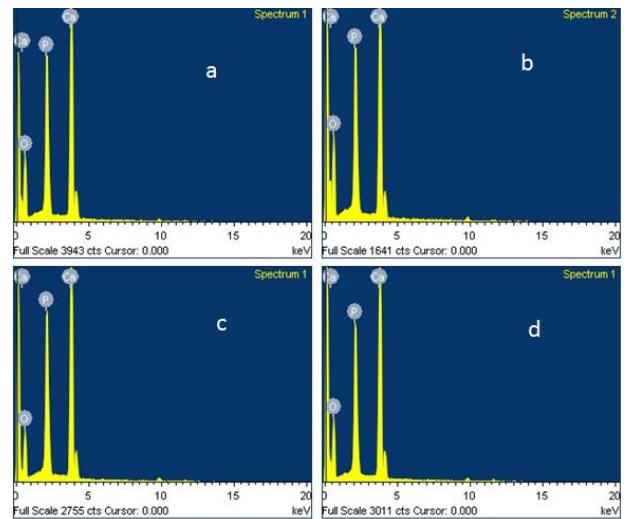


Figure 4. EDAX images of untreated and plasma treated HAp samples (a – 0 min, b – 5 min, c – 10 min, d – 15 min)

IV. CONCLUSION

The plasma modification is ecofriendly and cost effective technique to alter the surface properties of the biomaterials. It is evident from this study that the surface morphology of the synthesised HAp nano particles are modified using the air plasma exposure. Further plasma exposure does not alter the main functional group present in the sample. The percentage of elemental composition slightly gets modified by plasma treatment. However the intensity of peak in XRD decreases indicates the amorphous nature of synthesised samples gets increased which is identical for bone apatite.

V. REFERENCES

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