

## Calcium phosphate films deposited by electrostatic spray deposition and an evaluation of their bioactivity

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A cost-effective film deposition technique called electrostatic spray deposition (ESD) was used to prepare bioactive calcium phosphate thin films. The hydroxyapatite - forming ability of calcium phosphate films after different immersion times has been investigated in Eagle's minimum essential medium solution. The microstructure of the newly-formed layer on the films was established by a combination of X-ray diffraction, field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, and Fourier transform infrared spectroscopy. The results show that the layers are carbonated hydroxyapatite after immersion for 15 days.

**Key words:** Hydroxyapatite, calcium phosphate, electrostatic spray deposition.

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### Introduction

Calcium phosphate ceramic coatings and synthetic hydroxyapatite (HAP) are being used in an attempt to obtain better stabilization of metallic implants in bone and surrounding tissue [1-3]. Several methods of HAP coating such as plasma spray, sol-gel, sputtering and electrolysis have been carried out aiming at its use for medical applications [4-6]. In the past few years, a novel spray pyrolysis technique named electrostatic spray deposition (ESD) was employed to prepare TiO<sub>2</sub>, ZrO<sub>2</sub>, SnO<sub>2</sub>, MgO and LiCoO<sub>2</sub> thin films [7-10]. In this technique, liquid precursor sols are atomized into charged droplets over several micrometers in the strong electrostatic field established between the spraying nozzle and the grounded substrate. These charged droplets are attracted to the grounded thermal substrate by an electrostatic force, and then deposit on the heated substrate to form thin films. The ESD method offers many advantages over conventional deposition techniques, such as simple and low cost set-up, high deposition efficiency, low temperature synthesis, and easy control of the composition and surface morphology of the deposited films.

However, there have been few reports of the fabrication of calcium phosphate (CaP) thin films by the ESD

method. In the present study, we prepared CaP thin films by the ESD method. Their HAP - forming abilities were investigated by *in vitro* tests.

### Experimental Procedure

A stoichiometric amount of calcium nitrate [Ca(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, Merck, Germany] and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, Merck, Germany) with the molar ratio of Ca : P = 1.67 : 1 was dissolved in absolute methanol and stirred to obtain a precursor solution.

The working principles of the ESD method have been described in the literature [7-10]. The ESD set - up consists of three parts: an electrostatic spray unit, a liquid - precursor feed unit, and a temperature control unit. The electrostatic spray unit comprises a high DC voltage power supply (SHV120-30K-RD, Converttech Co. Ltd., South Korea), a stainless steel needle (0.1 mm inner diameter), and a grounded and heated substrate holder. The liquid precursor feed unit consists of a flexible silicon tube and a syringe pump (KD100, KD Scientific Inc., PA, U.S.A.). The temperature unit for the coating temperature includes a heating element and a temperature controller.

To obtain a stable cone-jet mode of electrostatic atomization, a high voltage, 25 kV, was applied between the needle tip and the ground electrode. Si(100) was selected as substrate to facilitate the use of the analytical techniques chosen for this study. Substrates on the ground electrode were heated at 80 °C to vaporize organic compounds. A precursor solution was pumped for 5

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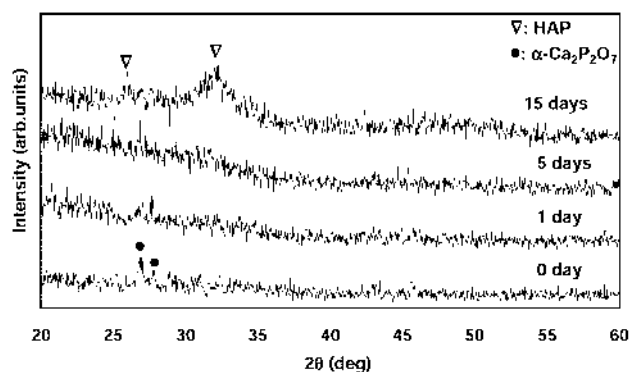
minutes (flow rate: 10 ml/60 minutes) through a nozzle which was placed 15 cm above the substrates. The as-deposited films were placed in an alumina boat and heated to 500 °C for 30 minutes in a tube furnace in the presence of air.

The *in-vitro* HAP-forming ability was tested in Eagle's minimum essential medium solution (MEM, Gibco BRL, Life Technologies, U.S.A.). The annealed films were placed in sealed polystyrene vials and immersed for up to 15 days in 20 ml MEM solution at 36.5 °C, provided by a constant temperature-circulating bath. The MEM solution was refreshed daily. After immersion, the samples were thoroughly rinsed with distilled water and dried in an oven at 30 °C.

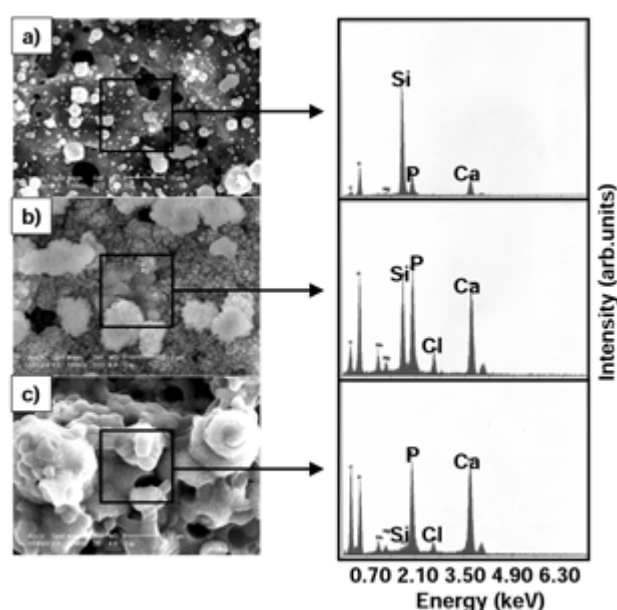
The crystal structure of the immersed films was analyzed by X-ray diffraction (XRD, D-Max-1200, Rigaku Co., Japan). Fourier transform infrared (FTIR, FTS-60, BIO-RAD Digilab Co., U.S.A.) spectroscopy was performed to analyze the chemical structure of the immersed films. The morphology and composition of the surface of the immersed films were evaluated by field emission-scanning electron microscopy (FE-SEM, S-4700, Hitachi, Japan) and energy dispersive X-ray spectrometry (EDS).

## Results and Discussion

Figure 1 shows typical XRD patterns of the surfaces of samples immersed in MEM solution for various times. It can be seen from Fig. 1 that samples immersed for 15 days are covered with newly grown-apatite layers in the MEM solution. The very large broadening peaks of (211), (112) and (300) reflections at 31 to 32.5°, and the (002) reflection (JC PDS File 24-0033) at 26° show that HAP [ $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ] crystallites are newly grown on the calcium phosphate thin film annealed at 500 °C. Two peaks at  $2\theta = 27^\circ$  and  $27.7-27.8^\circ$  of (031) and (211) reflections for  $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$  ( $\alpha\text{-CaP}$ ) (JC PDS File 09-0345) were observed on the film before immersion in the MEM solution. The newly-formed layer from the MEM solution appears to be a



**Fig. 1.** XRD patterns for the surfaces of the films after immersion in the MEM solution for various times.

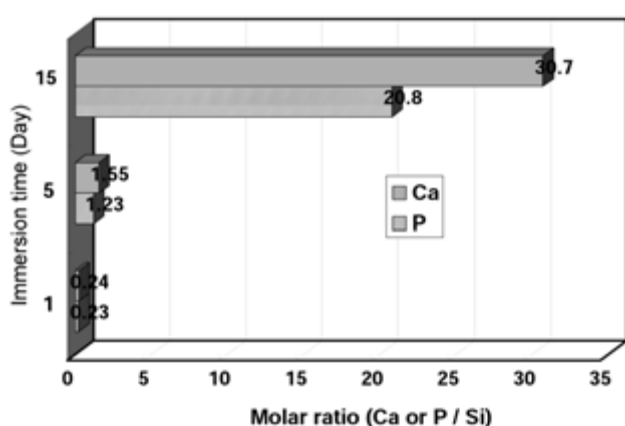


**Fig. 2.** FE-SEM images and EDS spectra for the surfaces of the films after immersion in the MEM solution for various times.

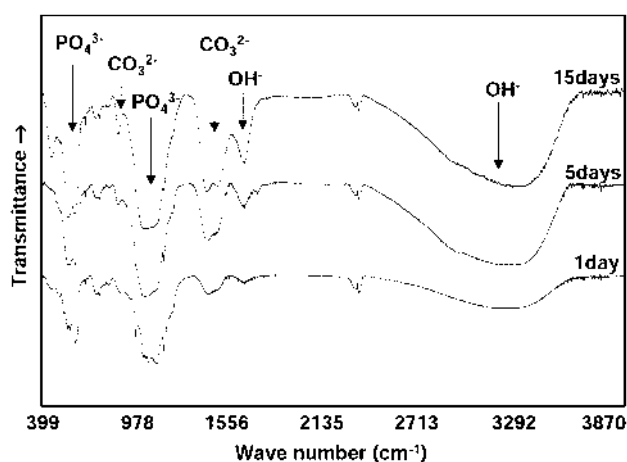
mixture of HAP and  $\alpha\text{-CaP}$ . It can be seen from Fig. 1 that the immersion time increases the HAP intensities while having an effect on the crystal phase of the annealed  $\alpha\text{-CaP}$  film.

FE-SEM and EDS analysis were performed on the samples after immersion for 1 day [Fig. 2(a)], 5 days [Fig. 2(b)] and 15 days [Fig. 2(c)] in the MEM solution. As shown in Fig. 2(a), partially adsorbed particles on the  $\alpha\text{-CaP}$  films were identified after immersion for 1 day. When the immersion time was increased to 5 and 15 days, the surface of the  $\alpha\text{-CaP}$  films was wholly covered with newly grown-crystals. From the EDS results, calcium and phosphate ions as well as Mg, Na, Cl and Si ions were detected on the surfaces of the immersed films. The peak intensities corresponding to Ca and P ions significantly increased with increasing immersion time, while the intensity from the Si substrate decreased. This is evidence of the growth of HAP crystals on the surface of the  $\alpha\text{-CaP}$  films, since the formation of HAP needs more calcium and phosphate ions.

In order to compare ion contents more clearly, we determined the molar ratio (Ca/Si and P/Si) for different immersion times, as shown in Fig. 3. For the sample immersed for 1 day the Si peak intensity was larger than those of Ca and P ions. The samples immersed for 5 and 15 days gave the opposite result. After immersion for 15 days, the increase of Ca and P ions was noticeable. The calcium and phosphate ions required for HAP generation on the film surface were derived from the MEM solution, as indicated by an increase of the formation of CaP on the ESD-derived film. As clearly shown in Figs. 2 and 3, the film deposited by ESD showed a high CaP-forming ability.



**Fig. 3.** Variation in the Ca and P contents compared to Si of the surfaces of the films after immersion in the MEM solution for various times.



**Fig. 4.** FTIR spectra for the surfaces of the films after immersion in the MEM solution for various times.

To confirm the chemical structure of the newly formed layer on the  $\alpha$ -CaP films, we performed FTIR analysis according to the immersion time, as shown in Fig. 4. Table 1 shows the FTIR bands positions ( $\text{cm}^{-1}$ ) and assignment for immersed films. FTIR measurements showed distinct  $\nu_3$  (at around  $1000\text{--}1100\text{ cm}^{-1}$ ) and  $\nu_4$

**Table 1.** Observed FTIR bands positions ( $\text{cm}^{-1}$ ) and assignment for immersed HAP films

	Band position ( $\text{cm}^{-1}$ )
Phosphate	
Asymmetric stretching ( $\nu_3$ )	1000-1100
Asymmetric bending ( $\nu_4$ )	610
Carbonate	
Asymmetric stretching ( $\nu_3$ )	1430-1480
Asymmetric bending ( $\nu_2$ )	874
Hydroxyl	
Stretching	3300-3500
Water	
Stretching	1650

(at around  $610\text{ cm}^{-1}$ ) phosphate ( $\text{PO}_4^{3-}$ ) spectral bands for all the samples. The peak intensity of the absorption spectra according to the phosphate ions became deeper as the immersion time increased to 5 and 15 days. There was also an indication that carbonate ion may be present in the newly - formed layer. As summarized in previous reports [11, 12], the carbonate ions occupy two different sites: the band at  $874\text{ cm}^{-1}$  is due to the  $\nu_2$  vibration mode, and bands at  $1419\text{ cm}^{-1}$  and  $1455\text{ cm}^{-1}$  are due to the  $\nu_3$  vibration mode of the carbonate ion. As shown in Fig. 4, the characteristic peaks of carbonated HAP are seen in the spectra,  $\text{CO}_3^{2-}\nu_2$  at  $874\text{ cm}^{-1}$  and  $\text{CO}_3^{2-}\nu_3$  at  $1430\text{ cm}^{-1}$ – $1480\text{ cm}^{-1}$ . The carbonate HAP is known to exist in three different forms: In the *A* type the carbonate is located at monovalent anionic  $\text{OH}^-$  sites; in the *B* type it is at trivalent phosphate ( $\text{PO}_4^{3-}$ ) sites; and in the third form the carbonate is at the labile environmental sites of HAP [11]. In the biological HAP, two sets of corresponding bands have been reported for the *A* type 1545, 1450, and  $890\text{ cm}^{-1}$  and for the *B* type 1465, 1412 and  $873\text{ cm}^{-1}$  [11]. According to our FTIR measurements it seems that *AB* - type carbonates formed on the surfaces of coatings after the *in vitro* MEM test. However, the contribution of *B* - type ( $\text{CO}_3^{2-}\nu_2$  at  $874\text{ cm}^{-1}$ ) carbonated HAP seems to be stronger than *A* type. Furthermore, the broad peak at  $3300\text{--}3500\text{ cm}^{-1}$  indicated a hydroxyl stretching band and the peak that appeared at  $1650\text{ cm}^{-1}$  was assigned to physically adsorbed water. The absorption bands according to the  $\text{OH}^-$  ion strongly suggest the formation of HAP on the ESD - derived  $\alpha$ -CaP films during immersion in the MEM solution.

## Conclusions

We prepared  $\alpha$ -CaP thin films by the ESD method. Their HAP - forming abilities were investigated by *in vitro* tests. From the XRD results, the newly - formed layer from the MEM solution appears to be a mixture of HAP and  $\alpha$ -CaP. For the sample immersed for 1 day, the Si peak intensity was larger than those from Ca and P ions, by contrast, the increase of the peak intensity corresponding to Ca and P ions was noticeable after immersion for 5 and 15 days. The absorption bands derived from FTIR strongly suggest the formation of HAP on the ESD - derived films during immersion in MEM.

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