J MATER SCI **41** (2006) 4159–4162

Hydroxyapatite forming ability of electrostatic spray pyrolysis derived calcium phosphate nano powder

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A novel fabrication technique, *i.e.*, electrostatic spray pyrolysis (ESP), has been used in this study to prepare calcium phosphate nano powders. Final annealing was done at 400°C for 30 min in air. The hydroxyapatite-forming ability of the annealed powder has been investigated in Eagle's minimum essential medium solution. X-ray diffracton, field emission scanning electron microscope, energy dispersive X-ray spectroscope, and Fourier transform infrared spectroscope were employed to characterize the annealed powders after immersion. The powder with an amorphous structure induced hydroxyapatite formation on their surfaces after immersion for 15 days. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Calcium phosphate based bioceramics, mainly the form of hydroxyapatite (HAP) have been used in medicine and dentistry for the last 20 years. Application include coating for orthopedic and dental implants, alveolar ridge augmentation, maxillofacial surgery, otolaryngology, and scaffolds for bone growth and as powders in total hip and knee surgery [1]. Nanosized HAP was successfully applied to fabricate HAP/collagen biodegradable composites [2]. When implanted in rabbits, these materials underwent resorption and promoted new bone formation. HAP powders with nanometer particle size are suitable for the processing of bone-resembling materials [3]. Multiple techniques have been used to prepare HAP powder with wet chemical methods [4, 5] and solid-state reaction [6], as the most popular.

Recently, the electrostatic spray pyrolysis (ESP) method has been commonly used to synthesize nanosized particles of oxidic materials [7]. A liquid flowing through a capillary nozzle can be subjected to a high voltage to produce a spray. This process can be carried out in several modes, and the cone-jet mode, in which the spray emanates from the tip of a liquid cone, can produce near-monodispersed droplets [8].

In the present study, we prepared CaP nano powders by the ESP method. Their HAP-forming abilities were investigated by *in vitro* test.

2. Experimental procedure

Calcium nitrate [$Ca(NO_3)_2{\cdot}2H_2O$, Merck, Germany], and phosphoric acid (H_3PO_4, Merck, Germany) were used as reactants for synthesis of CaP nano powders. The sol was diluted with methanol to adjust the concentration [metal (Ca + P): MeOH = 56 cmol%: 956cmol%] and viscosity for preparing nano-powders by ESP. The molar ratio of metals in precursor solution was set as Ca: $P = 1.67$: 1.

The working principles of the ESP method have been described in the literature [7, 8]. A stainless steel needle (0.1 mm and 0.23 mm inner and outer diameter, respectively) was connected to a syringe pump (KD100, KD Scientific Inc., PA, U. S. A.) using a silicon rubber tube. The flow rate of the precursor solution was kept at 10 mL/60 min. In order to obtain stable cone-jet mode of electrostatic atomization, the high voltage, 25 kV, was applied between the needle tip and ground electrode by using DC power supply (SHV120-30K-RD, Convertech Co. Ltd., South Korea). A container was introduced on the

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DOI: 10.1007/s10853-006-6654-0

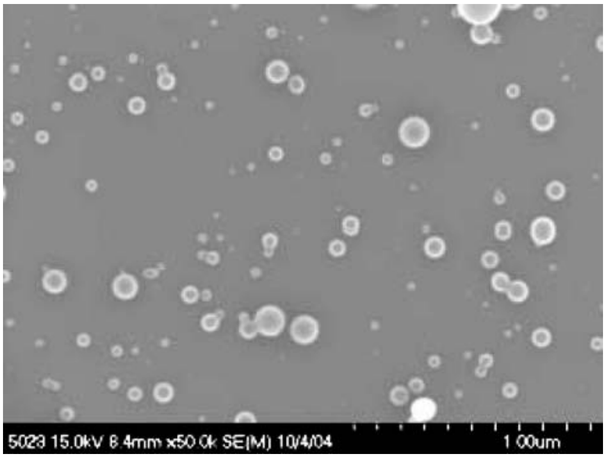

Figure 1 FE-SEM image of the powders on Si substrate after annealing at 400°C showing dispersion of nanosized particles.

TABLE I. Observed FTIR bands positions (cm^{-1}) and assignment for immersed samples

	Band position (cm^{-1})
Phosphate	
Asymmetric stretching ($\nu 3$)	1050
Asymmetric bending ($\nu 4$)	614
Carbonate	
Asymmetric stretching ($\nu 3$)	1410–1450
Asymmetric bending ($\nu 2$)	874
Hydroxyl	
Stretching	3300–3400
Water	
Stretching	1650

ground electrode and was heated at 80°C to vaporize organic compound in precursor solution during spraying. A precursor solution is pumped for 5 min through the nozzle which is placed 15 cm above the powder container. The sprayed powders were placed on the chemically cleaned Si in acidic solution and heated to 500°C for 30 min in a tube furnace in the presence of air (flow rate approximately 150–200 mL/min).

In-vitro HAP forming ability was tested in Eagle's minimum essential medium solution (MEM, Gibco BRL, Life Technologies, U. S. A.). The annealed nano powder on Si plate 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 powders on Si plate was analyzed by X-ray diffraction (XRD, D-Max-1200, Rigaku Co., Japan). The Fourier transform infrared (FTIR, FTS-60, BIO-RAD Digilab Co., U. S. A.) spectroscopy was performed to analyze chemical structure of the immersed powders. The morphology and composition of the surface of the immersed powders on Si were evaluated by field emission – scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan) and energy dispersive X-ray spectrometry (EDS).

3. Results and discussion

FE-SEM image from the annealed powders on Si substrate after annealing at 400°C for 30 min in air were used to confirm the presence of CaP powders. Many round-shaped nano particles are seen. Most well-dispersed particles have a diameter of about 50 nm are observed. A simple estimate of the average particle size gives 10–50 nm.

Fig. 2 shows XRD patterns of the surfaces of immersed powders on Si substrates in MEM solution for various times. It can be seen from Fig. 2 that sample immersed for 15 days are covered with newly formed-HAP layers during immersion in MEM solution. The peaks of (211) reflection at 31.5°, and the (222) reflection at 45.5° show that HAP [$Ca_5(PO_4)_3OH$] (JC PDS File 24-0033) crystallites are newly grown on the amorphous calcium phosphate nano powders annealed at 400°C. It is difficult to identify diffraction peaks correspond to crystalline for the surfaces of the samples after immersion for 1 and 5 days. The newly formed crystalline from MEM appears to be HAP after immersion for 15 days. It can be seen from Fig. 2 that ESP derived – amorphous CaP nano powder annealed at 400°C has a bioactivity to induce HAP crystalline on their surface.

FE-SEM and EDS analysis were performed on the powders on Si after immersion for 1 day [Fig. 3 (a)], and 15 days [Fig. 3 (b)] in MEM solution. As shown in Fig. 3 (a), partially adsorbed crystals on the surface of the sample were identified after immersion for 1 day. When the immersion time was increased to 15 days, the surface of the sample was wholly covered with newly formed-crystals, as shown in Fig. 3 (b). From EDS results, calcium and phosphate ions as well as Mg, Na, and Cl ions were detected on the surfaces of the immersed samples. Peak intensities correspond to Ca and P ions significantly increased with increase of the immersion time, while the intensity of the Si substrate decreased. It is evidence of the growth of HAP crystals on the surface of the samples, 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. 4. For the sample immersed for 1 day, peak intensity corresponds to Si substrate was larger than those of Ca and P ions. The sample immersed for 15 days gave the opposite result. After immersion for 15 days, increase of Ca and P ions compared to Si was noticeable. The calcium and phosphate ions required for HAP generation on the surface of the sample were derived from MEM, as indicated by an increase of the formation of CaP on the ESP derived nano powder. As clearly shown in Figs 3 and 4, the powder prepared by ESP showed a high CaP forming ability.

To confirm the chemical structure of the newly formed crystalline on the ESP derived nano powder, we performed

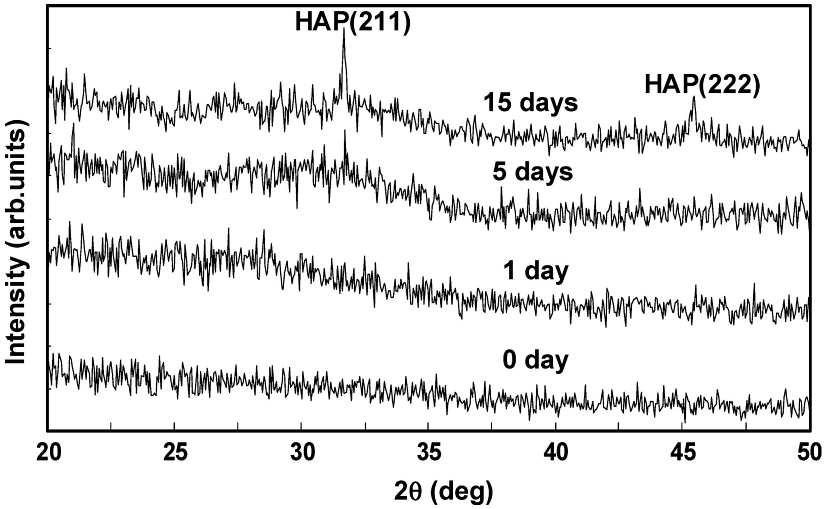

Figure 2 XRD patterns for the surfaces of the powders on Si after immersion in MEM for various times.

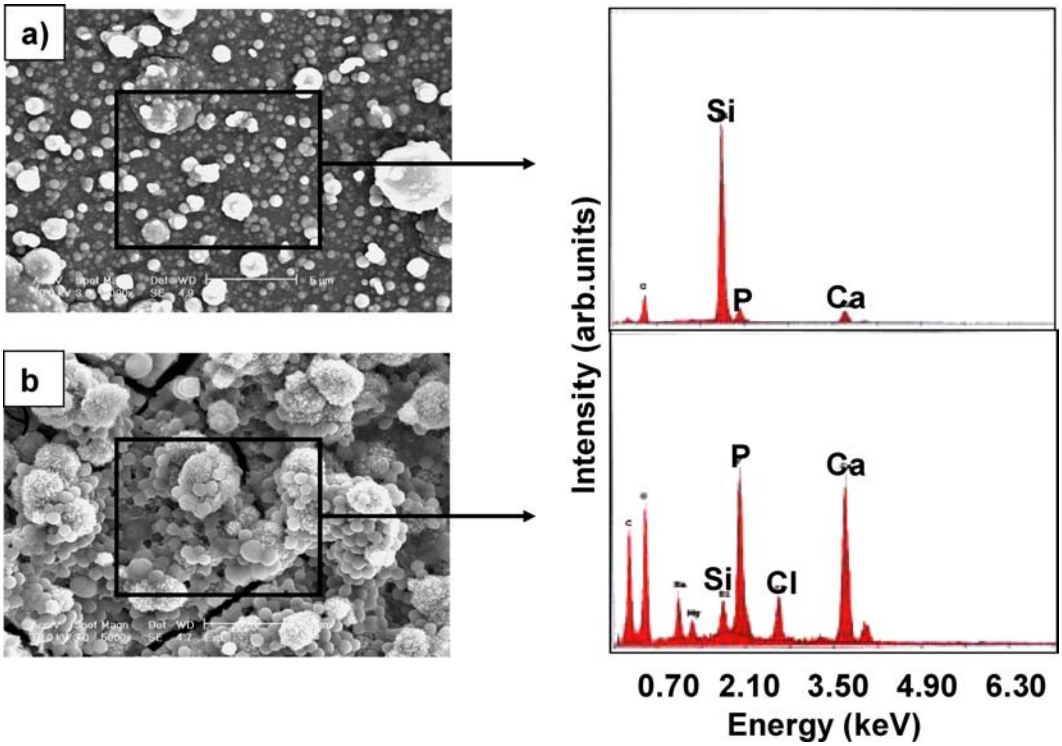

Figure 3 FE-SEM images and EDS spectra for the surfaces of the powders on Si after immersion in MEM for various times.

FTIR analysis according to the immersion time, as shown in Fig. 5. Table I shows the FTIR bands positions (cm^{-1}) and assignment for immersed films. FTIR measurements showed distinct ν_3 (at around 10506 ccm^{-1}) and ν_4 (at around 614 cm^{-1}) phosphate (PO_4^{3-}) spectral bands for all the samples. There was also an indication that carbonate ion may be present in the newly formed layer. As summarized in a previous report [9, 10], the carbonate ions occupy two different sites: the band at 874 cm^{-1} is due to the ν_2 vibration mode, and bands at 1419 cm^{-1} and 1455 cm^{-1} are sue to the ν_3 vibration mode carbonate ion. As shown in Fig. 5, the characteristic peaks of carbonated HAP are seen in the spectra, CO_3^{2-} ν_2 at 874 cm^{-1} and CO_3^{2-} ν_3 at 1410–1450 cm^{-1}. The carbonate HAP is known to exist in three different forms: In the *A* type the carbonate is located at monovalent anionic OH$^-$ sites; in the *B* type it is at trivalent phosphate (PO_4^{-3}) sites; and in the third form the carbonate is at labile environment sites of HAP [9]. In the biological HAP, two sets of corresponding bands have been reported for the *A* type 1545, 1450, and 890 cm^{-1} and for the *B* type 1465, 1412 and 873 cm^{-1} [9]. 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

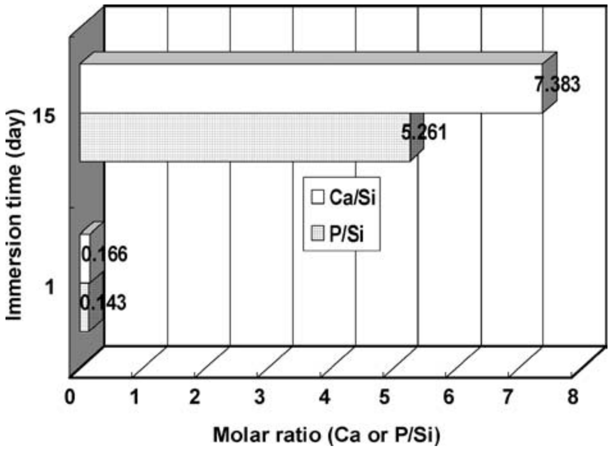

Figure 4 Molar ratio of the Ca and P ions compared to Si of the surfaces of the powders on Si after immersion in MEM for various times.

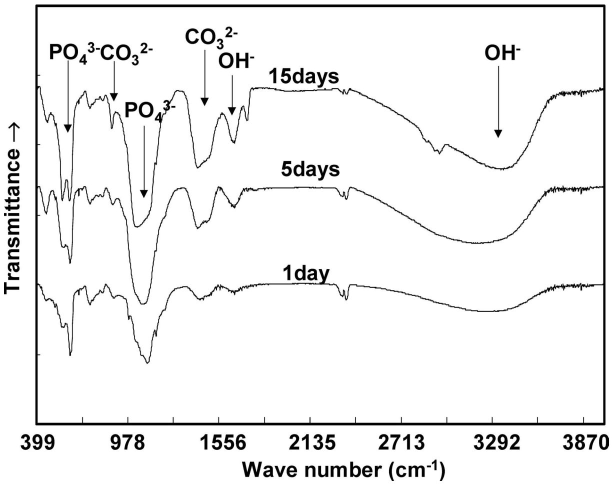

Figure 5 FTIR spectra for the surfaces of the powders on Si after immersion in MEM for various times.

contribution of B-type (CO_3^{2-} ν_2 at 874 cm^{-1}) carbonated HAP seems to be stronger than A type.

Furthermore, the broad peak at 3300–3400 cm^{-1} indicated a hydroxyl stretching band and the peak that appeared at 1650 cm^{-1} was assigned to physically adsorbed water. The absorption bands according to OH^- ion strongly suggest the formation of HAP on the ESP derived nano powder during immersion in MEM.

4. Conclusions

We prepared CaP nano powders on Si substrates by the ESP method. Their HAP-forming abilities were investigated by *in vitro* test. From XRD results, the newly formed phases from MEM appears to be HAP crystalline. For the sample immersed for 1 day, Si peak was larger than those of Ca and P ions, on the contrary, increase of the peak intensity corresponds to the Ca and P ions compare to Si was noticeable after immersion for 15 days. The absorption bands derived from FTIR strongly suggest the formation of HAP on the ESP derived nano powders during immersion in MEM.

Acknowledgements

This study was supported by a grant of the Korea Sanhak Foundation, Republic of Korea.

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Received 25 June
and accepted 29 August 2005