Preparation of calcium phosphate nano-powders prepared by sol-gel assisted-electrostatic spraying method

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Calcium phosphate based bioceramics, mainly in the form of hydroxyapatite (HAP), have been in use in medicine and dentistry for the last 20 years. Applications 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 crystals were 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 spraying (ESS) method has been commonly used to synthesize nano-sized 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]. On the other hand, sol-gel process has been widely used for materials processing, especially for nano-sized powders. In this letter, we combine these two techniques to prepare high quality nano-sized calcium phosphate (CaP) powders.

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 powders. The sol was diluted with methanol to adjust the concentration [metal $(Ca + P) : MeOH = 5 : 95$ mol%] and viscosity for preparing nano-powders by ESS. The molar ratio of metals in precursor solution was set as Ca:P = 1.67:1. A stainless steel needle (0.1 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 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 in an alumina boat and heated to 500 °C for 30 min in a tube furnace in the presence of air (flow rate approximately 150–200 mL/min). The crystal structure of the annealed powders was characterized by X-ray diffraction (XRD, D-Max-1200, Rigaku Co., Japan) θ-2θ scans. The XRD patterns were recorded using CuKα radiation ($\lambda = 1.54056$ Å) generated at 40 kV and 30 mA in the $20° < 2\theta < 60°$ range. The Fourier transform infrared (FTIR, FTS-60, BIO-RAD Digilab Co., U.S.A.) spectroscopy was performed using a KBr method with the annealed powders. The morphology of the powders was examined by means of a field emission—scanning electron microscope (FE-SEM, S-4700, Hitachi Co., Japan).

Fig. 1 shows the XRD pattern of the powders after annealing at 500 °C. Powders before annealing showed an amorphous structure, not shown here. The CaP, Ca9HPO4(PO4)OH, structure (JC-PDS File 46-0905) started to become visible with peaks corresponding to the (002), (102), (210), (211) and (300) reflections at around $2\theta = 25$–26°, 28–28.5°, 28.5–29°, 31–31.5°, and 32–33°. This implies that the final annealing process at 500 °C is effective in transforming the amorphous phase to the CaP crystalline phase.

In order to confirm the chemical structure of the annealed powder, we performed FTIR analysis, as shown in Fig. 2. FTIR measurement showed distinct v_3 (at around 1100–1150 cm^{-1}), V_2 (at around 900–950 cm^{-1}), and v_4 (at around 610–620 cm^{-1}) phosphate (PO_4^{3-}) spectral bands. Powders showed peaks at 1650 cm^{-1} and 3500–3600 cm^{-1} which is due to water absorbed from the surface. Moreover, the powder annealed at 500 °C still contained the peak at 1400–1450 cm^{-1} related to CO_3^{2-} group. This result suggests that

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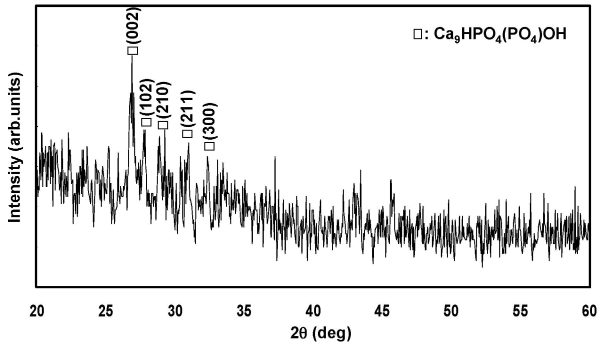

Figure 1 XRD pattern of the powder prepared at 500 °C.

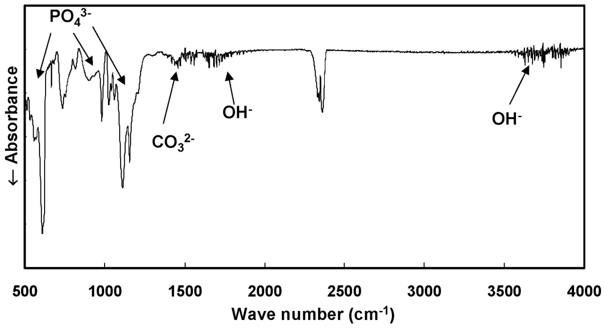

Figure 2 FTIR spectra of the powder after annealing at 500 °C.

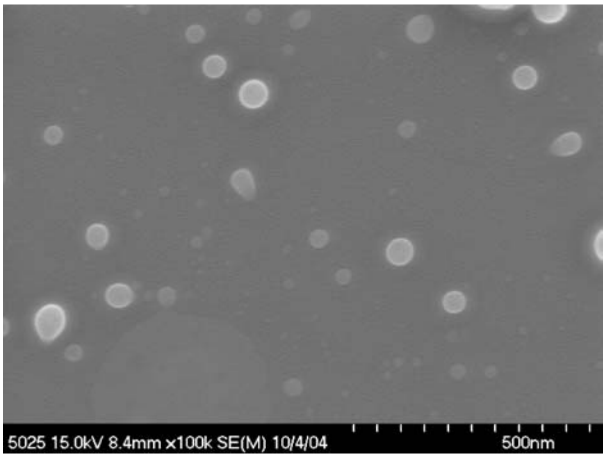

Figure 3 FE-SEM image of the annealed powder showing dispersion of nanosized CaP crystals

carbon from the organics does not pyrolyze completely and may instead dissolve into the CaP crystal for the annealed powder at 500 °C.

FE-SEM image from the annealed powders (Fig. 3) were used to confirm the presence of CaP powders. Many round-shaped particles are seen. Most well-dispersed particles have a diameter of 50 nm are observed. A simple estimate of the average particle size gives 40 nm.

In summary, the formation of nanometer-scale (average 40 nm) round-shaped CaP powders *via* sol-gel assisted ESS process has been demonstrated. In the XRD pattern, the amorphous as-dried powder transformed to CaP crystals at 500 °C. The FTIR result indicates that carbon may instead dissolve into the CaP crystal for the annealed powder.

Future *in-vitro* experiments are being designed to elucidate the formation of bone-like crystals on nanosized CaP powders.

Acknowledgements

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