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Effects of solvent on the properties of nano-sized hydroxyapatite powders directly prepared by high temperature flame spray pyrolysis

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Nano-sized, spherically shape and monodispersed hydroxyapatite (HA) powders were prepared by a high temperature flame spray pyrolysis process. The powders prepared from the aqueous spray solution without ethyl alcohol had a bimodal size distribution with nanometre and submicrometre sizes. Nano-sized and monodisperse HA powders were prepared when the volume ratio (ethyl alcohol/distilled water, V/V) in the mixed solvent was 1 : 2. Nano-sized HA powders were formed from the evaporated vapors by a chemical vapor deposition (CVD) process. The mean size of the HA powders measured from TEM images was 37 nm. The composition ratio of calcium and phosphorous components of the nano-sized HA powders was 1.63. The nano-sized powders obtained from the spray solution with a volume ratio of ethyl alcohol to distilled water at 1 : 2 had a phase pure hexagonal-dipyramidal structure of HA.

Key Words: Hydroxyapatite, Flame spray pyrolysis, Nano powder, Chemical vapor deposition.

Introduction

Hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2, HA)$ powders are widely applied in the biomedical fields because of their biocompatibility, bioactivity, and affinity to biopolymers. HA powders are mainly used as the source material to form sintered body and polymer composites. Therefore, the control of morphology and mean size of powders is important in the application of HA. The stoichiometry and purity of the powders also affect the properties of HA in many application fields such as in the orthopedic and dental fields as a paste, granules, or porous blocks for implants [1, 2].

Nano-sized HA powders with the appropriate stoichiometry, high purity and crystallinity are under development because of their enhanced densification, oseointegrative, and bioactive properties. Nano-sized HA powders are mainly prepared by liquid-solution methods, such as by sol-gel, hydrothermal, microemulsion, and precipitation [3-13]. Hosseini *et al.* established that hydroxyapatite powders can be produced using an alkoxide-based sol-gel technique. Nanocrystalline powders of hydroxyapatite were prepared using a sol-gel route [11]. Lin et al. synthesized stoichiometric single crystal hydroxyapatite nanorods with a diameter 25-40 nm and length 55-350 nm successfully via a hydrothermal microemulsion method [12]. Cao *et al.* prepared needle-like HA crystallites by a precipitation method with the

aid of ultrasonic irradiation. The mechanism and kinetics of the formation of nano-hydroxyapatite were considered in particular, and the influence of the temperature and time on the HA formation rate was also investigated [13]. Liquidsolution methods have advantages in controlling the morphology and mean size of the HA powders. However, a low preparation temperature causes contamination of the preparation additives and a low crystallinity of the HA powders.

Nano-sized HA powders have also been prepared by gas phase reaction methods [14-16]. Khor et al. synthesized ultra-fine (20 nm-2 μ m) nano-composite hydroxyapatite powders via radio frequency suspension plasma spraying (RFSPS) [14]. The influence of various plasma processing parameters and HA suspension concentrations on the characteristics of the as-sprayed powders were studied. An *et al.* prepared nano-sized HA powders by saltassisted ultrasonic spray pyrolysis [15]. The nano-szied powders prepared by salt-assisted spray pyrolysis were rod-type and single phase HA with high crystallinity and good stoichiometry.

Flame spray pyrolysis is different from spray pyrolysis in the energy source [17-19]. The high temperature diffusion flame causes melting and evaporation of powders to form the nano-sized ceramic powders. In flame spray pyrolysis, the type of solvent affects the mean size, morphology, and composition of the nano-sized powders by changing the temperature of the diffusion flame [20, 21]. In this study, HA powders were prepared by a high temperature flame spray pyrolysis process from various types of spray solution. It is found that the volume ratio of ethyl alcohol in the mixed solvent plays a key role in obtaining nanosized HA powders with a spherical shape.

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Experimental Procedure

Fig. 1 shows a schematic diagram of the flame spray pyrolysis apparatus. The system of flame spray pyrolysis has an ultrasonic droplet generator, flame nozzle, quartz reactor, powder collector and blower. Propane and oxygen were used as the fuel and oxidizer gases to create the diffusion flame. A schematic diagram of the flame nozzle is shown in Fig. 2. The flame nozzle consists of five concentric pipes. Droplets generated from the precursor solution are supplied to the diffusion flame through the central pipe by oxygen which is used as the carrier gas. The starting materials used in the synthesis of HA powders were Ca(NO₃)₂·4H₂O and (NH₄)₂HPO₄. The concentration of Ca(NO₃)₂·4H₂O and (NH₄)₂HPO₄ was fixed at 0.4 M. A mixture of ethyl alcohol and distilled water were used as the solvent.

The crystal structures of the as-prepared and post-treated HA powders were investigated using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu K α radiation ($\lambda = 1.5418$ Å). The thermal properties of the HA powders were measured using a thermo-analyzer (TG-DSC, Netzsch, STA409C) in the temperature range from 40 to 1200 °C. The morphological characteristics of the HA powders were investigated using scanning electron microscopy (SEM, JEOL, JSM-6060) and high resolution transmission electron microscope (TEM, FEI, TECHNAI 300 K).



Ultrasonic nebulizer

Fig. 1. A schematic diagram of the flame spray pyrolysis process.



Fig. 2. A schematic diagram of the flame nozzle.

Results and Discussion

The effects of the volume ratio (ethyl alcohol/distilled water, V/V) in the mixed solvent on the morphologies of the HA powders prepared by high temperature flame spray pyrolysis are shown in Fig. 3. In this study, the flow rates of fuel, oxidizer and carrier gas were each 5, 40 and 10 1 minute⁻¹, respectively, where the length of the diffusion flame was 20 cm.

The morphologies of the HA powders were affected by the volume ratio of ethyl alcohol and distilled water in the mixed solvent. The powders prepared from the aqueous spray solution without ethyl alcohol had a bimodal size distribution with nanometre and submicrometre sizes. One submicrometre-sized powder particle was formed from one droplet by the drying, decomposition and melting processes. However, the nano-sized powders were formed by a chemical vapor deposition (CVD) process. Evaporation of some components of the powders occurred at a high temperature diffusion flame. Nano-sized powder particles were formed from the evaporated vapors by the CVD process. The addition of ethyl alcohol to the solvent increased the number of nano-sized HA powder particles. The number of nano-sized HA powder particles increased with an increase in the volume ratio of ethyl alcohol to distilled water in the mixed solvent. Finally, nano-sized and monodisperse HA powders were prepared when the volume ratio (ethyl alcohol/distilled water, V/V) in the mixed solvent was 1:2. The addition of ethyl alcohol into the spray solution increased the temperature of the



Fig. 3. SEM images of the hydroxyapatite powders.

diffusion flame. Therefore, complete evaporation of components consisting of HA powders occurred.

Fig. 4 shows TEM images of the HA powders obtained from the aqueous and mixed spray solutions. The HA powders obtained from the aqueous spray solution had a bimodal size distribution with nanometre and submicrometre sizes as also shown in the SEM image. However, the HA powders obtained from the mixed spray solution were nanometre size with a monodispersed size distribution. The mean size of the HA powders measured from the TEM image (Fig. 4(b)) was 37 nm.

The formation mechanism of the nano-sized HA powders in the flame spray pyrolysis is described in Fig. 5. When



a) alcohol free



b) EtOH/H₂O = 5/10

Fig. 4. TEM images of the hydroxyapatite powders.



Fig. 5. A schematic diagram of the formation mechanism of the hydroxyapatite powder in flame spray pyrolysis.

the volume ratio (ethyl alcohol/distilled water, V/V) in the mixed solvent was 1:2, i.e., 50 ml absolute ethyl alcohol together with 100 ml distilled water, the temperature of the diffusion flame applied in this study was sufficiently high for vaporization of HA powders. Therefore, evaporation of the components composing the HA powders occurred inside the high temperature diffusion flame. Nano-sized HA powders were formed from the evaporated vapors by nucleation and growth processes. On the other hand, the complete evaporation of the components composing the HA powders did not occur when the aqueous spray solution was applied.

The compositions of the HA powders obtained from the aqueous and mixed spray solutions were analyzed from the TEM-EDX spectra. Fig. 6 shows the TEM-EDX spectra of the HA powders obtained from the aqueous spray solution. The compositions of nano and submicrometresized powders as shown in Fig. 4(a) were investigated. The weak peaks of Cu in the EDX spectra originated from the carbon-coated copper TEM sample grid. The compositions of HA powders are described in Table 1. The composition ratio of calcium and phosphorous components of the submicrometre-sized powders was 1.76. The composition ratio of calcium and phosphorous components in the stoichiometric HA powders was 1.67. Therefore, the submicrometre-sized powder was rich in the calcium component. On the other hand, the composition ratio of calcium and phosphorous components of the nano-sized powders was 0.98. The nano-sized powder prepared by the CVD process was rich in the phosphorous component. Fig. 7 shows the TEM-EDX spectrum of the nano-sized HA powders (Fig. 4(b)) obtained from the mixed spray solution. The composition ratio of calcium and phosphorous components of the nanosized powders was 1.63. Therefore, the nano-sized HA powders obtained from the mixed spray solution had the appropriate stoichiometry.

Fig. 8 shows the XRD patterns of the powders obtained from the aqueous and mixed spray solutions. The powders directly prepared by flame spray pyrolysis had the hexagonaldipyramidal structures of HA even after a short residence time of the powders inside the high temperature diffusion flame. Small peaks of α -tricalcium phosphate (α -TCP) phase were observed in the powders with a bimodal



Fig. 6. EDX spectra of the hydroxyapatite powder from the aqueous spray solution.



Fig. 7. EDX spectrum of the hydroxyapatite powder from the mixed spray solution.

 Table 1. The atomic ratio of Ca/P of the HA powders prepared by flame spray pyrolysis

Powder		Element		
		Ca	Р	Ca / P
alcohol free	Large size powder	44.4	25.2	1.8
	Small size powder	11.3	11.5	0.98
$EtOH/H_2O = 1/2$		6.2	3.8	1.6

size distribution with nanometre and submicrometre sizes. The decomposition of HA partly into a-TCP occurred



Fig. 8. XRD patterns of the post-treated hydroxyapatite powders.



Fig. 9. FT-IR spectrum of the hydroxyapatite powders.

because of the high temperature of the diffusion flame above 2000 °C [22]. However, the nano-sized powders obtained from the spray solution with a volume ratio of ethyl alcohol to distilled water at 1 : 2 had a phase pure hexagonal-dipyramidal structure of HA.

The FT-IR spectrum of the nano-sized HA powders obtained from the mixed spray solution with a volume ratio of ethyl alcohol to distilled water at 1 : 2 is shown in Fig. 9. In the FT-IR analysis, mainly the peaks from PO_4^{3-} and OH^- groups in the hydroxyapatite can be identified. The IR band at 3571 cm¹ belongs to the vibration of hydroxyl, the bands observed at 1052 and 961 cm¹ are characteristic of the phosphate stretching vibration, and the bands observed at 603, 569, and 471 cm¹ are due to the phosphate bending vibration. The bands appearing at wavenumber values of 1469, 1422, and 879 cm¹ reveal the presence of carbonate ions in the resultant HA crystallites due to the interaction between HA and ambient CO₂ in the processing.

Conclusions

Nano-sized HA powders were directly prepared by a

high temperature flame spray pyrolysis process from various types of spray solution. When the volume ratio (ethyl alcohol/distilled water, V/V) in the mixed solvent was 1 : 2, the temperature of the diffusion flame applied in this study was sufficiently high for evaporation of HA powders. Therefore, evaporation of the components composing the HA powders occurred inside the high temperature diffusion flame. Nano-sized HA powders were formed from the evaporated vapors by nucleation and growth processes. The nano-sized HA powders obtained from the spray solution with ethyl alcohol and distilled water had a spherical shape, good stoichiometry and a monodispersed size distribution.

References

- 1. H. Oonishi, Biomater. 12 (1991) 171-178.
- D.G Lange and D.C. Putter, J. Oral Implantol. 19 (1993) 136-137.
- 3. M.H.Fathi and A. Hanifi, Mater. Lett. 61 (2007) 3978-3983.
- Z.H. Zhou, P.L. Zhou, S.P. Yang, X.B. Yu and L.Z. Yang, Mater. Res. Bull. 42 (2007) 1611-1618.
- X. Zhang and K. S. Vecchio, J. Cryst. Growth 306 (2007) 133-136.
- 6. S. Kannan, J.H.G. Rocha, S. Agathopoulos and J.M.F. Ferreira, Acta Biomater. 3 (2007) 243-249.
- A. Wang, D. Liu, H. Yin, H. Wu, Y. Wada, M. Ren, T. Jiang, X. Cheng and Y. Xu, Mater. Sci. Eng. C 27 (2007)

865-869.

- 8. A. Wang, H. Yin, D. Liu, H. Wu, M. Ren, T. Jiang, X. Cheng and Y. Xu, Mater. Lett. 61 (2007) 2084-2088.
- 9. K. Ioku, M. Yoshimura and S. Somiya, Nippon Kagaku Kaishi 9 (1988) 1565-1570.
- M. Yoshimura, H. Suda, K. Okamoto and K. Ioku, J. Mater. Sci. 29 (1994) 3399-3402.
- H.E. Hosseini, M.R. Housaindokht and M. Chahkandi, Mater. Chem. Phys. 106 (2007) 313-316.
- K. Lin, J. Chang, R. Cheng and M. Ruan, Mater Lett. 61 (2007) 1683-1687.
- 13. L. Cao, C. Zhang and J. Huang, Ceram. Inter. 31 (2005) 1041-1044.
- K.A. Khor, R. Kumar and P. Cheang, Surf. Coat. Technol. 177-178 (2004) 740-746.
- 15. G.H. An, H.J. Wang, B.H. Kim, Y.G. Jeong and Y. H. Choa, Mater. Sci. Eng. A 449-451 (2007) 821-824.
- J.S. Cho and Y.C. Kang, J. Alloy. Compd. 464 (2008) 282-287.
- Y.C. Kang, D.J. Seo, S.B. Park and H.D. Park, Mater. Res. Bull. 37 (2002) 263-269.
- D. Dosev, B. Guo and I. M. Kennedy, J. Aerosol Sci. 37 (2006) 402-412.
- A. Camenzind, R. Strobel and S.E. Pratsinis, Chem. Phys. Lett. 415 (2005) 193-197.
- X. Li, H. Liu, J.A. Wang, H.M. Cui and F. Han, Mater. Res. Bull. 39 (2004) 1923-1930.
- 21. X. Li, H. Liu, J.A. Wang, H.M. Cui, S.L. Yang and I.R. Boughton, J. Phys. Chem. Solids 66 (2005) 201-205.
- 22. S. Raynaud, E. Champion, D. Bernache-Assollant and P. Thomas, Biomater. 23 (2002) 1065-1072.