

Synthesis and Characterization of Hydroxyapatite Nanocrystals by Sol-gel Method using Nonionic Surfactant as a Template

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Mesostructured calcium phosphates were synthesized by a sol-gel method using a micelle template; calcium nitrate tetrahydrate and diphosphorus pentoxide were mixed in ethanol including the nonionic surfactant of Pluronic P123, which was then dried and heated in air. The inorganic/organic composite with the ordered 2D hexagonal structure was formed after drying. The heat treatment at 300°C caused the formation of mesopores with the mean size of 3.9 nm; however, the ordered mesostructure disappeared due to the combustion and collapse of P123 in heating. The crystalline hydroxyapatite was obtained by heating at 500 °C.

Key words: Hydroxyapatite, Nanostructure, Micelle Template, Nonionic Surfactant

1. INTRODUCTION

Syntheses of nanostructured inorganic crystals through micelle template techniques, such as self-assembled surfactants and block copolymers, have been paid much attention [1]. The template techniques can control crystal shapes, external structures, and higher ordered hierarchical structure, which was so called "crystal tectonics"[2]. The nano-scaled materials will be applicable for electronics [3], photonics [4], mechanical industries [5] and biomaterials [6]. The mesoporous materials, having pore diameters of 2-50 nm, such as silica based compounds [7], metal oxides [8] and metal phosphate salts [9] have been synthesized by a template method and subsequent removal of organic component, which produce the ordered mesoporous structures with higher specific surface area and controlled pore sizes.

Hydroxyapatite (HAp) has been used as bone substitutes and coatings on metal implants due to its excellent biocompatibility, and is also applied to adsorbents for liquid chromatography and catalysis supports due to its excellent affinity to organic and biological compounds. Therefore, the synthesis of mesoporous HAp is of great interest for its applications. The micelle template techniques were employed for the syntheses of calcium phosphates including HAp. Wu and Bose described the HAp nanopowders using dodecyl phosphate micelle system [10]; the surfactant concentration had an influence on the surface area and morphology of the particles. Sadasivan et al. reported the preparation of calcium phosphate nanofilaments using calcium

bis(2-ethylhexyl)- phosphate in a reverse micelle system [11]. Uota et al. synthesized high surface area HAp nanoparticles by calcination of a precursor encapsulated with calcium stearate using a mixed surfactant-containing reaction mixture [12].

In this paper, sol-gel method using a nonionic surfactant of Pluronic P123 (triblock copolymer) as the micelle template was applied for the synthesis of nanostructured calcium phosphate. The nanostructures were analyzed by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Brunauer-Emmett-Teller (BET) method and transmission electron microscopy (TEM). Formation and deformation mechanisms of nanostructured calcium phosphates were discussed.

2. MATERIALS AND METHODS

2.1 Materials

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), diphosphorus pentoxide (P_2O_5) and 99.5% ethanol were purchased from Wako Pure Chem. Ind. in Japan. Pluronic P123 ($\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CHO})_{20}\text{OH}$) as a micelle template was kindly supplied by BASF corporation. All chemicals were used without further purification.

2.2 Preparation

The $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and P_2O_5 were individually dissolved in 60 ml of ethanol, of which solutions were mixed and continuously stirred for 1 hour at ambient temperature. The Ca/P molar ratio was adjusted at 1.67 which is the

theoretical ratio of HAp composition. Twelve grams of P123 was then added in the mixed solution and stirred for 1 hour at ambient temperature to obtain a clear solution. The clear solution was kept at ambient temperature to evaporate excess ethanol for 1 day. The samples evaporated were heated at 300, 400 and 500 °C.

2.3 Characterization

XRD measurements were performed with a Rigaku RINT-Ultima III at CuK α radiation ($\lambda = 1.54184 \text{ \AA}$) at 40kV and 40mA. Thermogravimetry (TG-DTA) was conducted with a Rigaku Thermo Plus TG8120 with heating rate of 20 °C/min; the samples were weighted at 10mg and the reference was used as Al₂O₃. Diffuse reflectance FT-IR spectra were recorded with a Parkin Elmer Spectrum2000 at resolution of 4cm⁻¹ in the range of 7800-370 cm⁻¹; the samples were mixed with KBr powder. Specific surface area and pore size distribution were measured by the BET and the BJH methods with a BECKMAN COULTER SA3100 analyzer; the samples were dried at 300 °C for 3h under vacuum to remove the adsorbed water. A LEO 922 OMEGA was employed for the TEM operations; the samples were dispersed in ethanol and then mounted on a microgrid.

3. RESULTS AND DISCUSSION

Fig. 1 shows the wide-angle XRD patterns of the nonionic surfactant P123 supplied and the samples dried and heated at 300, 400 and 500 °C, respectively. The P123 and as-dried sample had a broaden diffraction attributed to the P123 at around $2\theta = 20^\circ$ which completely disappeared after heating at higher than 300°C. The samples heated at 300 and 400°C showed the broaden diffraction at $2\theta = 30^\circ$ were barely detected. The heat treatment at 500 °C appeared the diffractions attributed to the low crystalline HAp phase.

Fig. 2 shows the low-angle XRD patterns of the samples. The XRD pattern of the P123 supplied indicated no existence of the ordered

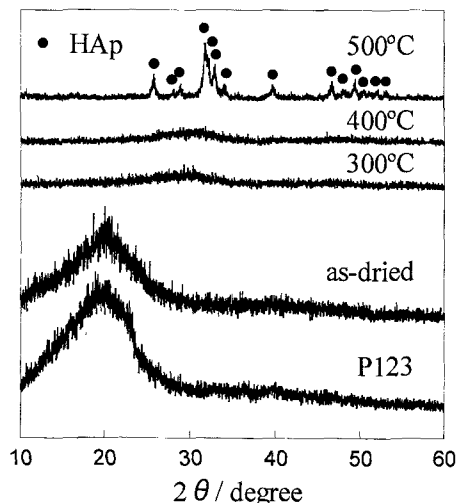


Fig. 1 Wide-angle XRD patterns of P123 surfactant and sample dried and heated at 300, 400 and 500 °C.

Table I d-spacing ratios of as-dried sample and typical mesoporous material, MCM-41, with hexagonal structure.

	as-dried sample			MCM-41* (hexagonal)		
$2\theta / ^\circ$	0.92	1.57	1.81	1.97	3.45	3.96
d / nm	9.594	5.622	4.877	4.488	2.558	2.229
d/d_{\max}	1	0.586	0.509	1	0.571	0.498

* C. Landry et al., Chem. Mater., 13, 1600 (2001)

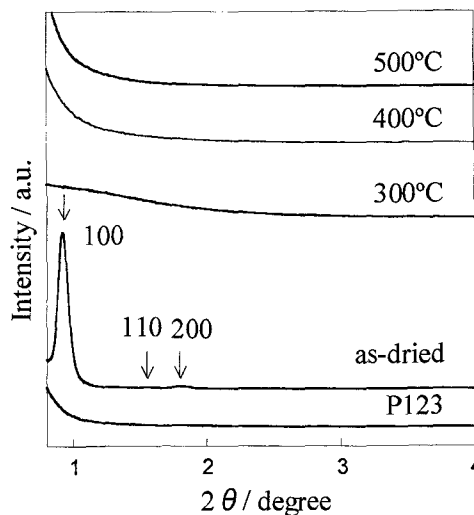


Fig. 2 Low angle XRD patterns of P123 surfactant and samples dried and heated at 300, 400 and 500 °C.

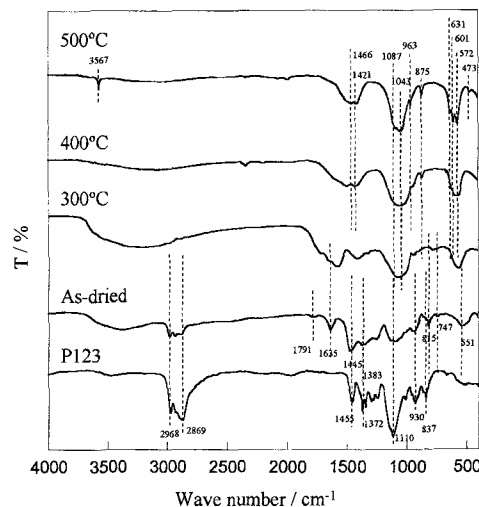


Fig. 3 FT-IR spectra of P123 surfactant and samples dried and heated at various temperatures.

structure. On the other hand, the as-dried sample had the diffractions at $2\theta = 0.92, 1.57$ and 1.81° , which indicated the ordered structure was formed; however, the samples heated at 300 °C showed the broaden diffraction, which mean the ordered structure was mostly collapsed. At above 400 °C, the low-angle diffractions were not observed, which suggested the disappearance of the structure.

Table I shows the d-space ratios of as-dried sample and those of typical mesoporous material, MCM-41, with the hexagonal structure [13]. The ratios of each peak were in good agreement with those of MCM-41, which demonstrates the

formation of 2D hexagonal mesostructure in the as-dried sample. The 2D hexagonal mesostructure in the inorganic/organic composite was completely destroyed after the subsequent heat treatments at higher than 300°C. TG-DTA result shows that the P123 nonionic surfactant completely burned at around 250°C with the endothermic peak.

Fig. 3 shows the FT-IR spectra of the nonionic surfactant P123 and the samples dried and heated at 300, 400 and 500 °C, respectively. The as-dried sample showed the bands at 747 and 815 cm^{-1} assigned to the NO_3 group of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ as a starting substance. The NO_3 group were not detected at temperatures above 400 °C. The bands at 2869 and 2968 cm^{-1} were attributed to CH stretching in P123 [14] and disappeared at the heat treatment of 300°C. The spectrum shapes of PO_4 bands at around 1070 and 560 cm^{-1} changed with the heating temperatures. The as-dried sample showed different positions compared with the samples heated. Furthermore, the samples heated at 300 and 400 °C had each one band at around 1060 and 580 cm^{-1} , however the sample at 500 °C showed the separation of the each bands to 1087 and 1043 cm^{-1} , and 473, 572 and 601 cm^{-1} , respectively. These positions of the PO_4 bands were matched to those of HAp [15].

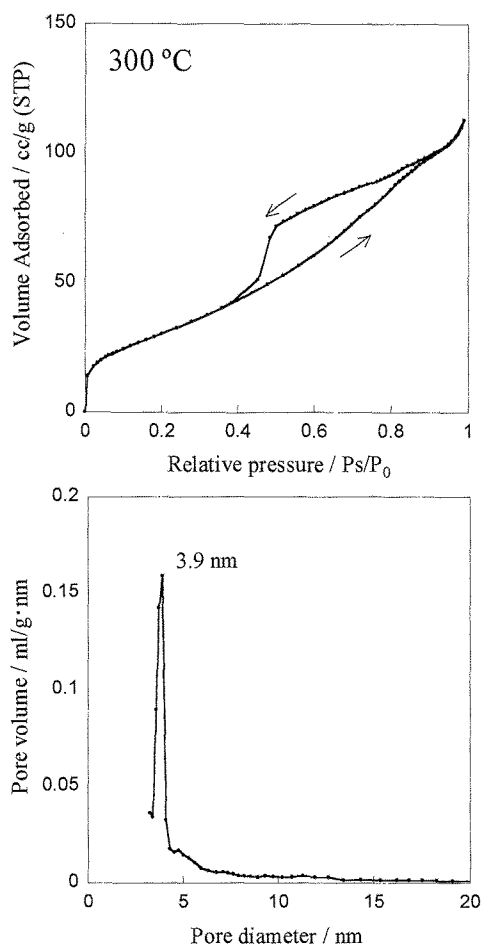


Fig. 4 Nitrogen adsorption-desorption isotherms and BJH pore-size distribution of the sample heated at 300 °C.

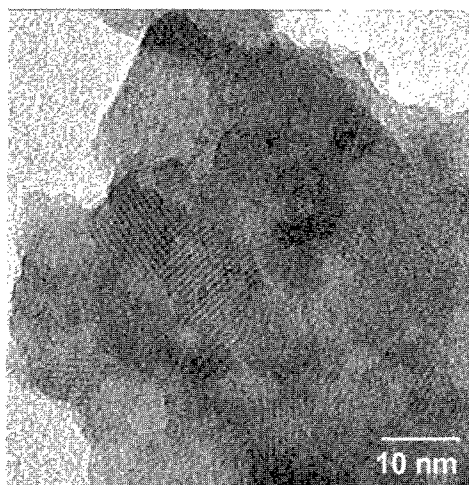


Fig. 5 TEM photograph of the sample heated at 500 °C.

The samples heated at 500°C had the OH bands at 631 and 3567 cm^{-1} . In addition, the bands at 875, 1421 and 1466 cm^{-1} were attributed to CO_3 group substituted in the PO_4 group in HAp lattice. The incorporation of CO_3 group could be occurred in the heating process. These results of FT-IR spectra were almost matched to those of XRD patterns.

Fig. 4 shows the nitrogen adsorption-desorption isotherm and the BJH pore size distribution of the sample heated at 300°C. The adsorption-desorption isotherm was matched to the typical type IV isotherm, which suggested the formation of an ordered mesoporous structure. The mean pore size calculated from the N_2 desorption isotherm based on the BJH method was 3.9 nm with a narrow distribution, and the pore volume was 0.17 ml/g. P. Yang et al. reported the preparation of crystalline mesoporous metal oxides such as ZrO_2 , TiO_2 and WO_3 using P123 as a template; the pore size and pore volume are 3.5-6.5 nm and 0.43-0.50 ml/g, respectively [8]. The low pore volume obtained in this study would be caused by an imperfect elimination of the surfactant after combustion and/or the collapse of the ordered structure. The specific surface area of the samples heated at 300, 400 and 500°C were 112, 65 and 51 m^2/g from the BET measurements. This indicates that the sintering of calcium phosphates was promoted at the temperatures.

Fig. 5 shows the TEM image of the sample heated at 500°C. The aggregate of plate-like crystals with the size of 10-20 nm was observed. No mesoporous structures were observed in the crystalline HAp powders. The electron diffraction pattern showed the (002) and (004) spots, which indicated the developed face of the crystal parallel to the [001] direction.

Many reports indicated that the collapse of mesoporous structure is caused by an amorphous-crystalline transition during heating [16, 17]. The sample obtained in this study also had similar behavior. We considered amorphous

inorganic species should crystallize to HAp in the presence of triblock copolymer template to obtain a crystalline mesoporous HAp. The crystalline HAp phase is thought to be kept an order mesoporous structure after combustion. Further studies are in progress.

4. CONCLUSIONS

The self-assembled P123 and amorphous calcium phosphate composite with 2D hexagonal mesostructure was formed by the sol-gel method and subsequent drying. The composite heated at 300 °C had a mesoporous structure; however, the ordered structure disappeared. The composite heated at 500 °C showed a crystalline HAp phase which had round shape with the size of 10-20 nm.

5. REFERENCES

- [1] S. Yu and H. Colfen, *J. Mater. Chem.*, 14, 2124-2147 (2004).
- [2] S. Mann, "Biomaterialization: Principles and Concepts in Bioinorganic Materials Chemistry", Oxford Press, Oxford, (2001).
- [3] S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs and C. Dekker, *Nature*, 386, 474 (1997).
- [4] A. Polman, *Nature Mater.*, 1, 10-12 (2002).
- [5] T. R. Kelly, H. D. Silva and R. A. Silva, *Nature*, 401, 150-152 (1999).
- [6] T. Takahashi, Y. Yamada, K. Kataoka, Y. Nagasaki, *J. Controlled Release*, 107, 408-416 (2005).
- [7] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 120, 6024-6036 (1998).
- [8] P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 11, 2813-2826 (1999).
- [9] B. Tian, X. Lui, B. Tu, C. Yu, J. Fan, L. Wang, S. Xie, G. D. Stucky and D. Zhao, *Nature Mater.*, 2, 159-163 (2003).
- [10] Y. Wu and S. Bose, *Langmuir*, 21, 3232-3234 (2005).
- [11] S. Sadasivan, D. Khushalani and S. Mann, *Chem. Mater.*, 17, 2765-2770 (2005).
- [12] M. Uota, H. Arakawa, N. Kitamura, T. Yoshimura, J. Tanaka and T. Kijima, *Langmuir*, 21, 4724-4728 (2005).
- [13] C. C. Landly, S. H. Tolbert, K. W. Gallis, A. Monnier, G. D. Stucky, P. Norby and J. Hanson, *Chem. Mater.*, 13, 1600-1608 (2001).
- [14] R. Gonzalez-McQuire, J-Y. Chane-Ching, E. Vignaud, A. Lebugle and S. Mann, *J. Mater. Chem.*, 14, 2277-2281 (2004).
- [15] S. Koutsopoulos, *J. Biomed. Mater. Res.*, 62, 600-612 (2002).
- [16] D. Li, H. Zhou and I Honma, *Nature Mater.*, 3, 65-72 (2004).
- [17] J. N. Kondo, T. Yamashita, K. Nakajima, D. Lu, M. Hata and K. Domen, *J. Mater. Chem.*, 15, 2035-2040 (2005).