Electronic Supplementary Information

LaMer-model-based synthesis method for fine particles of octacalcium phosphate and related functional compounds

Taishi Yokoi,[a] Tomoyo Goto,[b,c] Tohru Sekino,[b] Tomoka Hasegawa,[d] Peng Chen,[e] Hiroyasu Kanetaka,[e] Kaname Yoshida,[f] Masaya Shimabukuro[a] and Masakazu Kawashita[a]

[a] Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University (TMDU), 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan

[b] SANKEN (The Institute of Scientific and Industrial Research), Osaka University, 8-1 Mohogaoka, Ibaraki, Osaka 567-0047, Japan

[c] Institute for Advanced Co-Creation Studies, Osaka University, 1-1 Yamadaoka, Suita, Osaka 565-0871, Japan

[d] Ultrastructure of Hard Tissue, Faculty of Dental Medicine, Hokkaido University, Kita 13 Nishi 7 Kita-ku, Sapporo, Hokkaido 060-8586, Japan

[e] Division of Interdisciplinary Co-Creation (ICC-Division), Liaison Center for Innovative Dentistry, Graduate School of Dentistry, Tohoku University, 4-1 Seiryo-machi, Aoba-ku, Sendai 980-8575, Japan

[f] Nanostructures Research Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta-ku, Nagoya, Aichi 456-8587, Japan

Calculation of degree of supersaturation in the reaction environment of sample 5 with respect to OCP

The degree of supersaturation was calculated under the following conditions:
Calcium ion concentration: 0.16 mol/L
Total phosphate ion concentration: 0.12 mol/L
pH: 7.688
Dissociation constants of phosphate ions[49]

$H_3PO_4 \rightleftarrows H_2PO_4^- + H^+$ $pK_{a1}=2.196$
$H_2PO_4^- \rightleftarrows HPO_4^{2-} + H^+$ $pK_{a2}=7.185$
$HPO_4^{2-} \rightleftarrows PO_4^{3-} + H^+$ $pK_{a3}=12.19$

Solubility product of OCP[28]: $10^{-95.9}$

For simplicity, the activity coefficient was assumed to be 1 in the calculations. The degree of supersaturation was calculated by defining it as the ratio of the ion activity product to the solubility product. The degree of supersaturation for OCP (S(OCP)) was calculated using the following formula.

$$S(\mathrm{OCP})=([Ca^{2+}]^8[HPO_4^{2-}]^2[PO_4^{3-}]^4)/10^{-95.9}$$
$$=10^{81.9}$$

Here, the square brackets represent the concentration of each ionic species.

[28] S. V. Dorozhkin and M. Epple, *Angew. Chem. Int. Ed.*, 2002, **41**, 3130–3146.
[49] X. Lu and Y. Leng, *Biomaterials*, 2005, **26**, 1097–1108.

Characterisation of sample 13 (OCP with incorporated succinate ions)

Fig. S1 shows the XRD patterns of samples 8 and 13. The XRD pattern of sample 8 corresponded to plain OCP. In the XRD pattern of sample 13, the 100 reflection peak of the OCP phase was shifted to a lower angle. This shift indicated an increase of the (100) interplanar spacing, consistent with the incorporation of succinate ions into the OCP interlayers.

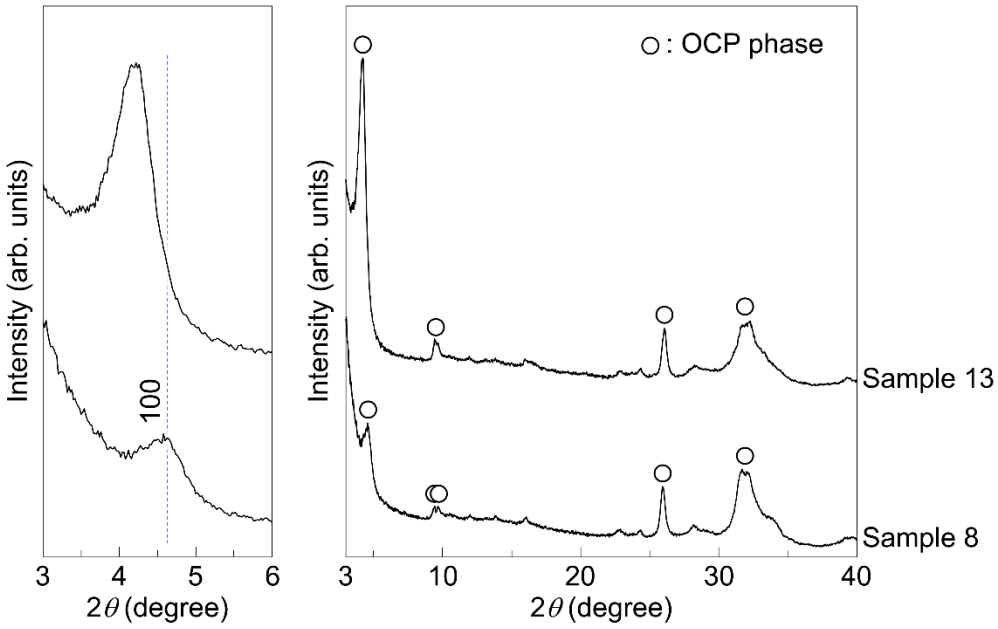

Fig. S1 XRD patterns of samples 8 and 13. Magnified XRD patterns in the range of 3°–6° are shown on the left-hand side. The blue dashed line indicates the 100 reflection peak position of plain OCP.

The FTIR spectra of samples 8 and 13 shown in Fig. S2 are similar, except in the blue-highlighted region. Unlike sample 8, sample 13 exhibited an absorption band at 1565 cm^{-1}, which was attributed to COO^-. As the XRD results (Fig. S1) indicated that sample 13 is OCP with incorporated succinate ions, the COO^- band in the FTIR spectrum (Fig. S2) can reasonably originate from succinate ions incorporated into the OCP interlayers.

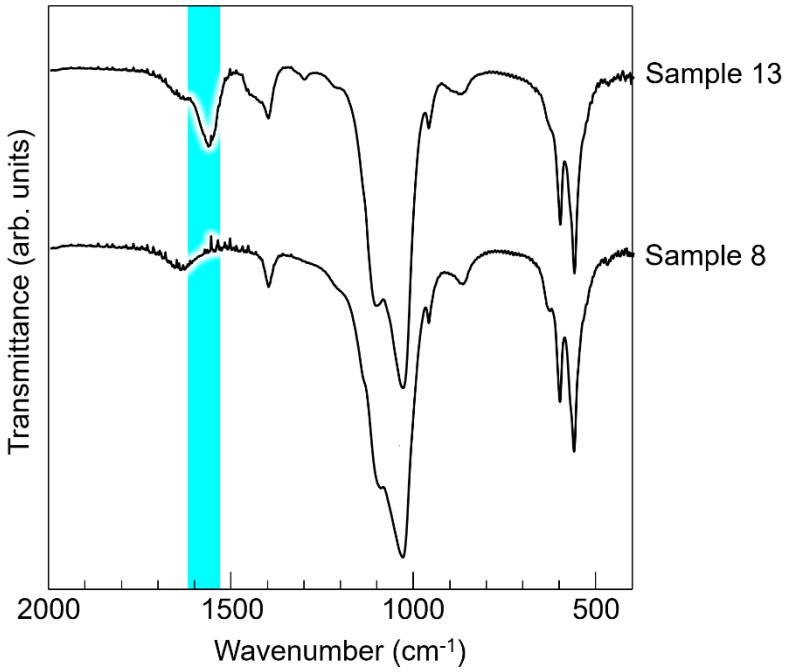

Fig. S2 FTIR spectra of sample 8 (plain OCP) and sample 10 (OCP with incorporated succinate ions). The blue-highlighted region indicates absorption bands derived from COO^- of succinate ions incorporated into the OCP interlayers.

The incorporation of succinate ions into the OCP interlayer was further confirmed by evaluating the compositions of the samples. The Ca/P molar ratios and C contents of samples 8 and 13 are summarised in Table S1. The Ca/P molar ratio of sample 13 was higher than that of sample 8 because the hydrogen phosphate ions were replaced with succinate ions. Sample 13 had a higher C content than sample 8 owing to the incorporation of succinate ions into OCP. Hence, the XRD, FTIR, and compositional analyses support the incorporation of succinate ions into the OCP interlayers.

Table S1 Ca/P molar ratios and C contents of sample 8 (plain OCP) and sample 13 (OCP with incorporated succinate ions).

Sample No.	Ca/P molar ratio	C content (mass%)
8	1.40	0.2
13	1.52	3.0

The morphologies of samples 8 and 13 are shown in Fig. S3. The particles in sample 8 had sizes of 100 nm, whereas those in sample 13 had sizes of 100–300 nm. The particle sizes of sample 13 (OCP with incorporated succinate ions) and sample 10 (OCP with incorporated isophthalate ions) were similar. Therefore, the synthesis conditions based on the LaMer model can likely be widely applied to the fabrication of OCP with incorporated dicarboxylate ions.

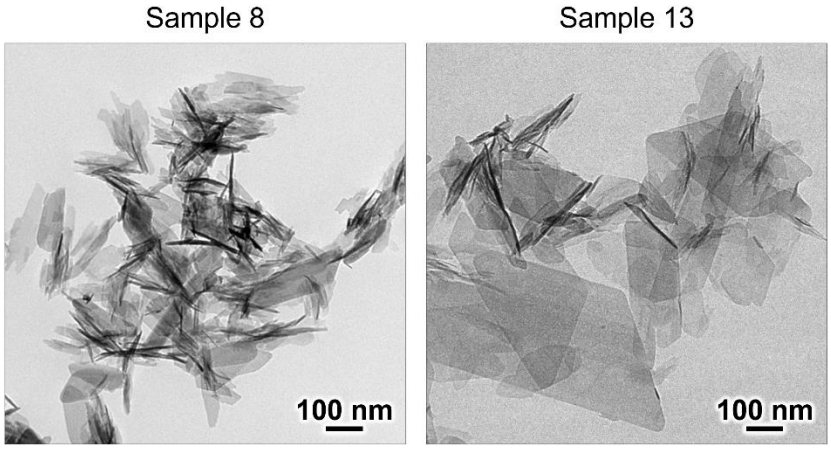

Fig. S3 TEM images of sample 8 (plain OCP) and sample 13 (OCP with incorporated succinate ions).