

Supplementary Information

Formation of calcium-phosphate-based supra-ceramics in solutions containing glutaric acid derivatives

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Synthesis of samples

Glutaric acid (25 mmol) ($\text{HOOC}(\text{CH}_2)_3\text{COOH}$: 99.0%, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), iminodiacetic acid (1–25 mmol) (IDAA, $\text{HOOCCH}_2\text{NHCH}_2\text{COOH}$: 98.0%, Tokyo Chemical Industry Co., Ltd.), diglycolic acid (1–10 mmol) (DGA, $\text{HOOCCH}_2\text{OCH}_2\text{COOH}$: 98.0%, Tokyo Chemical Industry Co., Ltd.), or 2,2'-thiodiglycolic acid (1–20 mmol) (TDGA, $\text{HOOCCH}_2\text{SCH}_2\text{COOH}$: 98.0%, Tokyo Chemical Industry Co., Ltd.) was dissolved in ultrapure water (100 mL) at 60 °C, and the pH of the solution was adjusted to 5.5 by adding an NH_3 solution (28 mass% aqueous solution, Wako Pure Chemical Industries, Osaka, Japan). Subsequently, an H_3PO_4 solution (5.0 mmol) (85% aqueous solution, Wako Pure Chemical Industries) was added to the carboxylic acid solution, followed by the addition of CaCO_3 (8.0 mmol) (calcite phase: 99.5%, Nacalai Tesque, Kyoto, Japan). The slurry was stirred at 500 rpm at 60 °C. After 3 h, the pH of the slurry was reduced to 5.0 with HCl, and the precipitate was isolated by suction filtration, rinsed, and dried after 30 min of stirring.

H_3PO_4 (6.0 mmol) was added to ultrapure water (100 mL) at 60 °C under stirring (500 rpm) to synthesise the OCP sample that does not contain carboxylate ions, followed by the addition of CaCO_3 (8.0 mmol). After 3 h, the pH of the slurry was decreased to 5.0 by adding an appropriate amount of an HCl solution. Subsequently, after 30 min of stirring at 60 °C, the precipitate was isolated by suction filtration using a conventional filter paper, rinsed with ultrapure water and ethanol, and dried overnight at 40 °C. This sample was denoted as CONTROL.

XRD patterns of OCP with incorporated glutarate ions

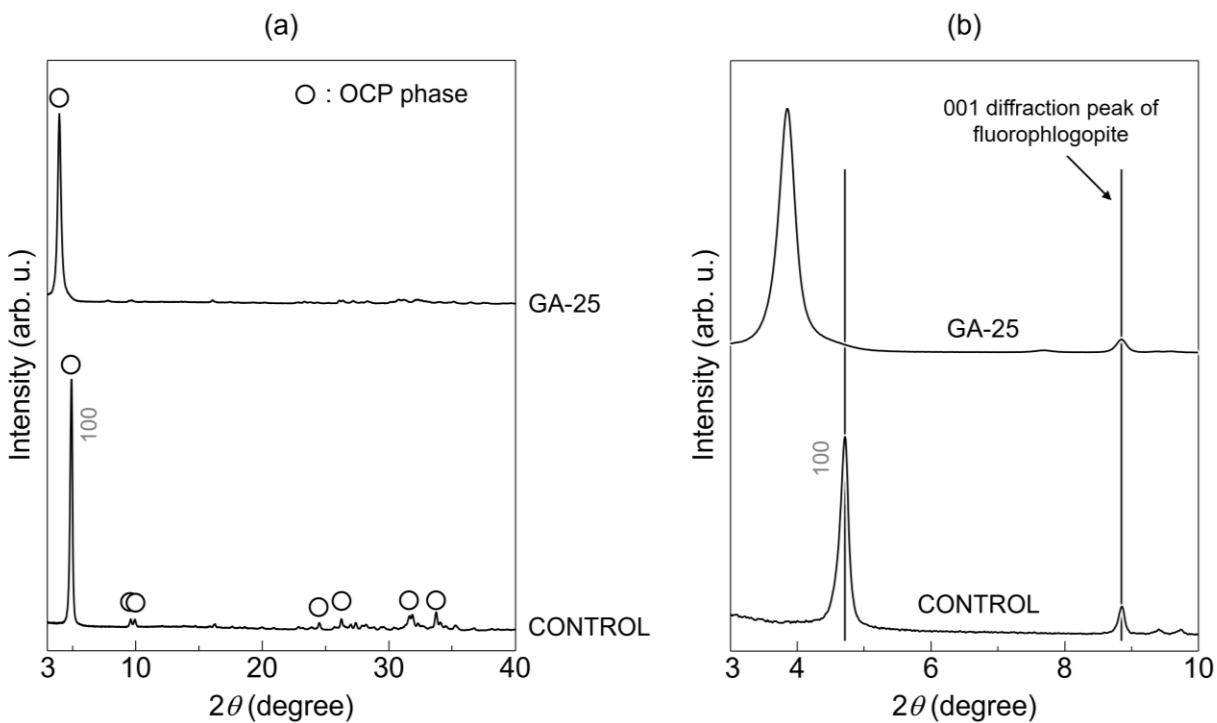


Figure S1. (a) XRD pattern of OCP synthesised in GA solution (GA-25). (b) Comparison of XRD patterns of CONTROL and GA-25 mixed with fluorophlogopite as an angular standard material.

pK_{a1} and pK_{a2} values of GA, IDAA, DGA, and TDGA

Table S1. pK_{a1} and pK_{a2} values of carboxylic acids

Carboxylic acid	pK_{a1}	pK_{a2}
GA	4.34*	5.41*
	4.46	5.26
IDAA	2.12	2.90
DGA	2.96	3.75
TDGA	3.38	4.18

*The pK_{a1} and pK_{a2} values of GA are taken from reference 59.