Electronic Supplementary Information

Simultaneous synthesis of hydroxyapatite fibres and β-tricalcium phosphate particles *via* a water controlled-release solvothermal process

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Characterization

The crystallinity of products was identified by powder X-rad diffraction (XRD, D8 ADVANCE, Bruker AXS, Germany) using CuKα radiation at 40 kV and 40 mA. The fraction of each crystal phases (*F*) were calculated semi-quantitavely from XRD data using following equation:

$$F(\%) = \frac{I}{I_{HAp} + I_{\alpha-TCP} + I_{\beta-TCP} + I_{DCPA}} \times 100$$

I_{HAp} is the integrated intensity of the HAp of 211 reflection at 31.8°, $I_{\alpha-TCP}$, $I_{\beta-TCP}$, and I_{DCPA} are the integrated intensities of the α-TCP of 132 reflection at 24.18 º, the β-TCP of 214 reflection at 27.88 º, the DCPA of 002 reflection at 26.48 º, respectively.

The crystal morphology, structure and size were observed by field emission scanning electron microscopy (FE-SEM, SU9000 Hitachi High-Tech Corporation, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-ARM 200F, JEOL Ltd., Tokyo, Japan). Elemental analysis of the samples were also investigated energy-dispersive X-ray spectroscopy (EDX, JED-2200, JEOL Ltd., Tokyo, Japan) attached to TEM. The chemical composition of samples were measured using the Fourier Transform Infrared Spectroscopy (FT-IR, FT/IR 4100, JASCO Co., Tokyo, Japan) using KBr pellet method.

The specific surface area (SSA) of the samples were analyzed by multi-point BET method using the nitrogen (N_2) adsorption isotherm collected at -196 °C using NOVA 4200e (Quantachrome Instruments, FL, USA). Zeta potential of samples were measured using the electrophoretic method on an analyzer (Zetasizer Nano ZS, Malvern Instruments Ltd, Malvern, UK).

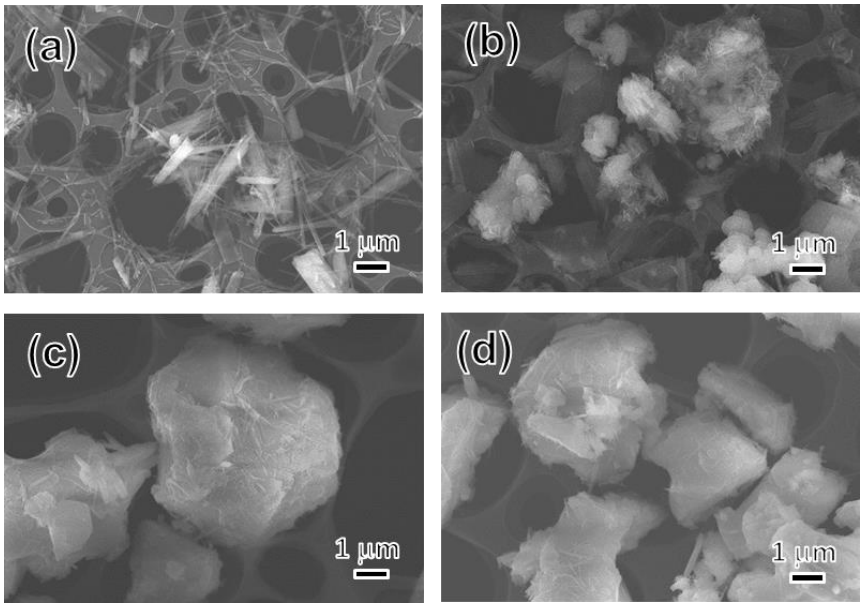

Fig. S1 Scanning Electron Microscope (SEM) images of the products after solvothermal treatment at 150 °C for 24 h, using an ethanol-acetic acid system. (a) Water, (b) E00A20, (c) E20A00, and (d) α-TCP.

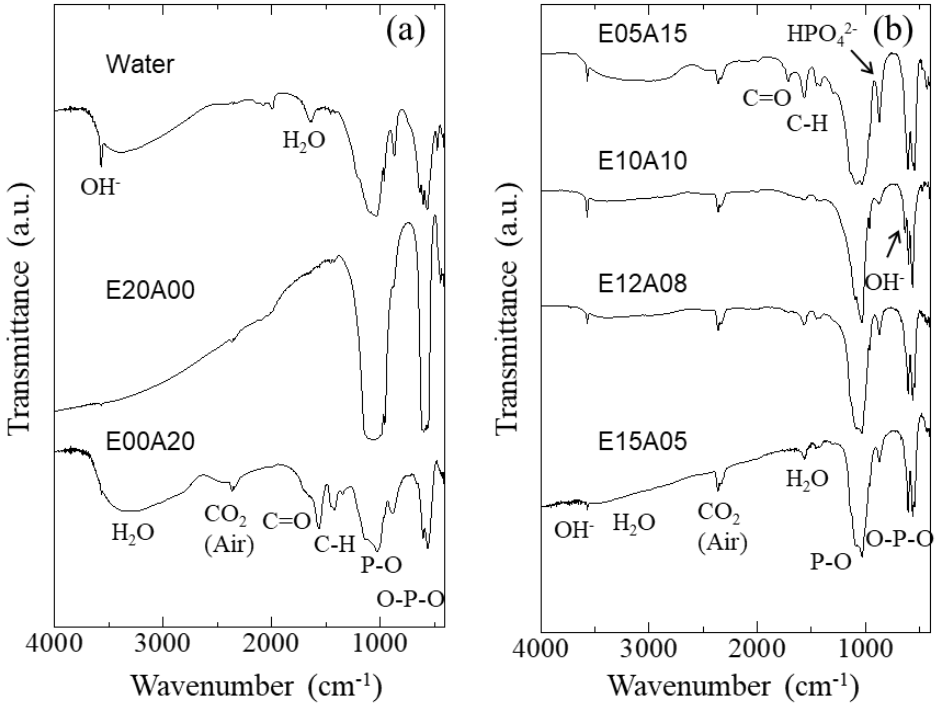

Fig. S2 FT-IR spectra of the products after solvothermal treatment using (a) water, ethanol, and acetic acid and (b) mixed solvents.

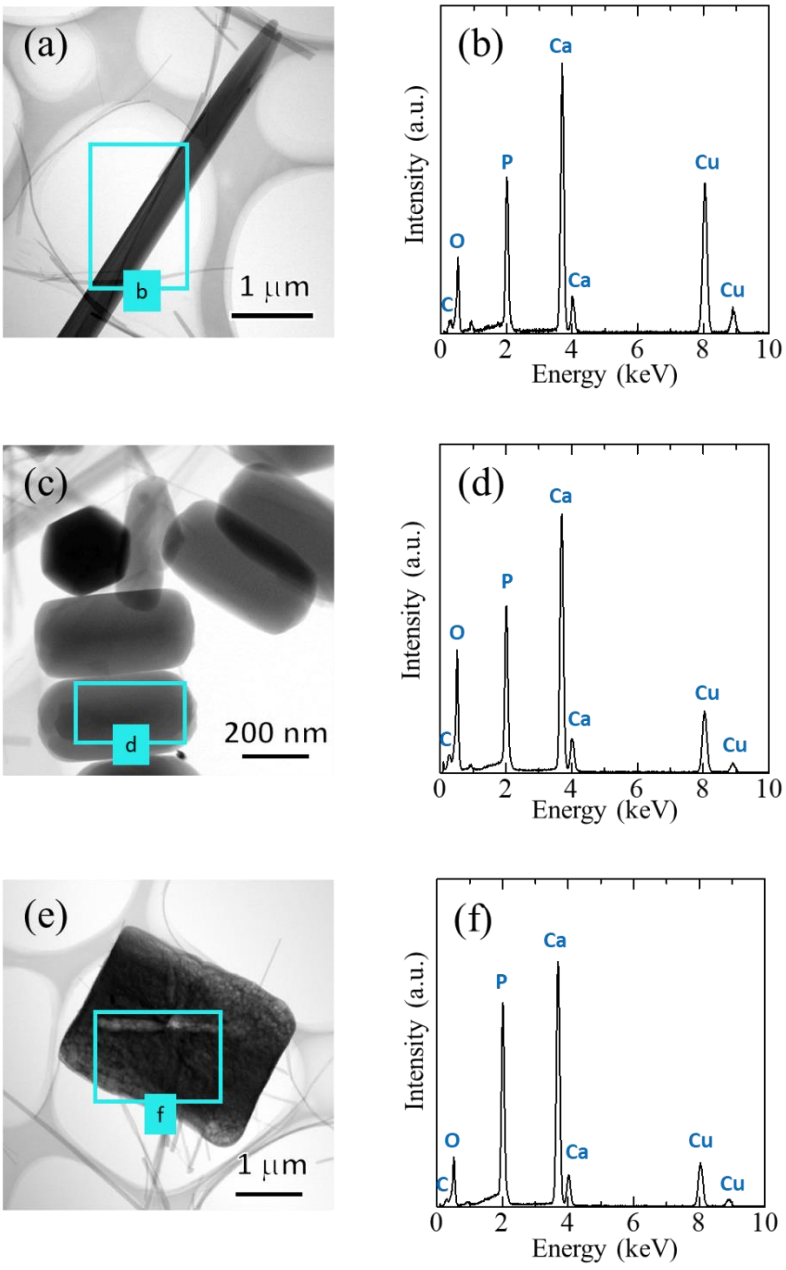

Fig. S3 TEM images and EDX spectra of different crystals via TEM-EDX analysis: (a, b) needle-shape crystal, (c, d) rice-like crystal, and (e, f) plate-shape crystal. The frame in TEM image shows the EDX analysis area.

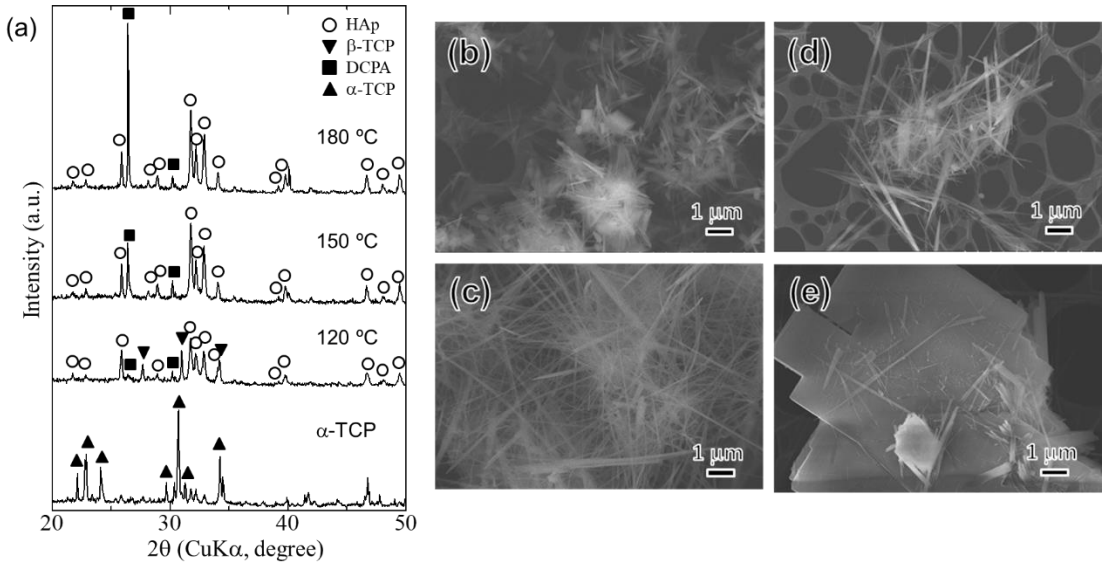

Fig. S4 (a) XRD patterns and (b–e) SEM images of the products after the solvothermal treatment at various temperatures using E10A10 with constant stirring: (b) 120, (c) 150, and (d, e) 180 ºC.

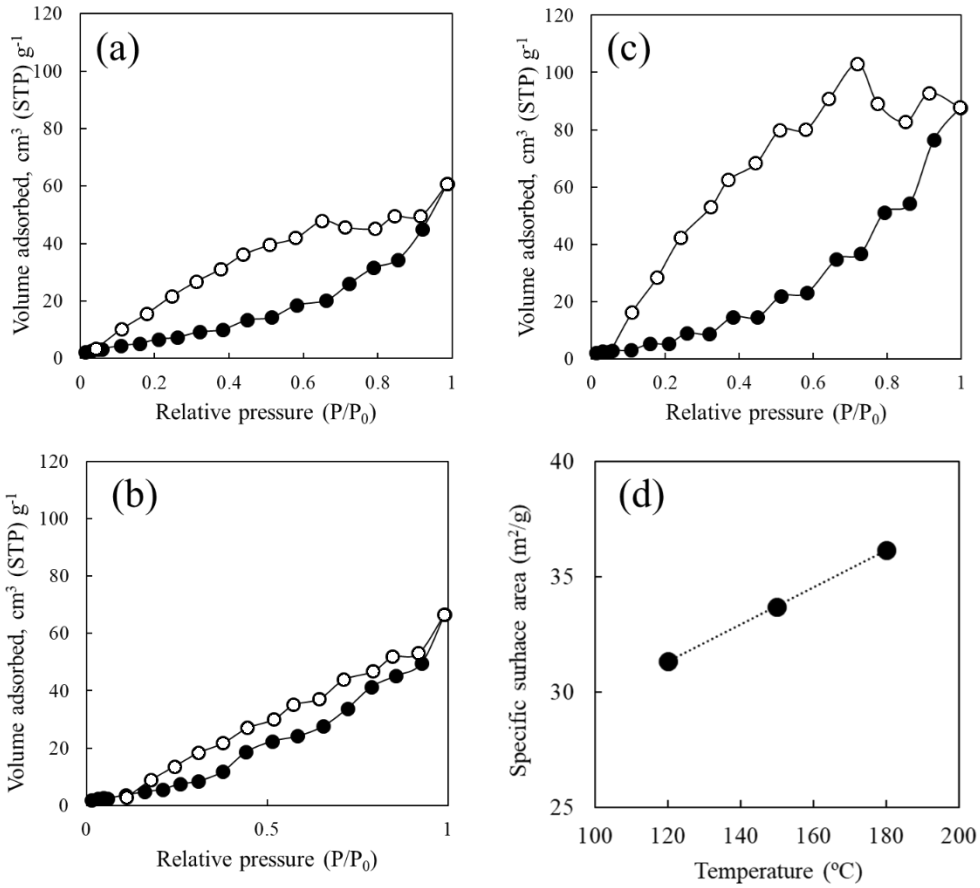

Fig. S5 N_2 adsorption-desorption isotherm of the samples solvothermally synthesised at (a) 120, (b) 150, and (c) 180 ºC, and (d) their specific surface areas.

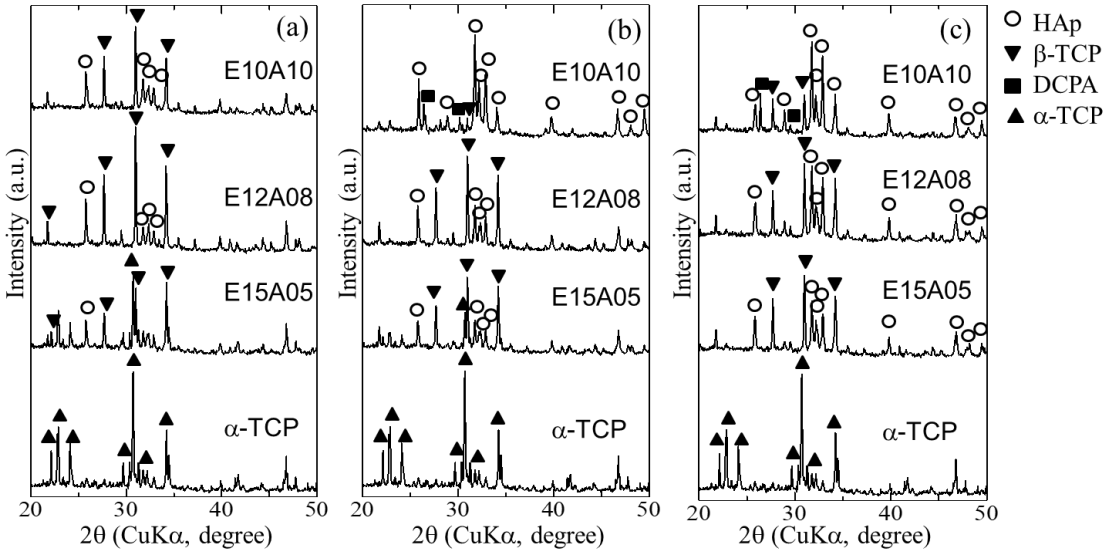

Fig. S6 XRD patterns of the products after solvothermal treatment for 24 h at (a) 120, (b) 150, and (c) 180 ºC.

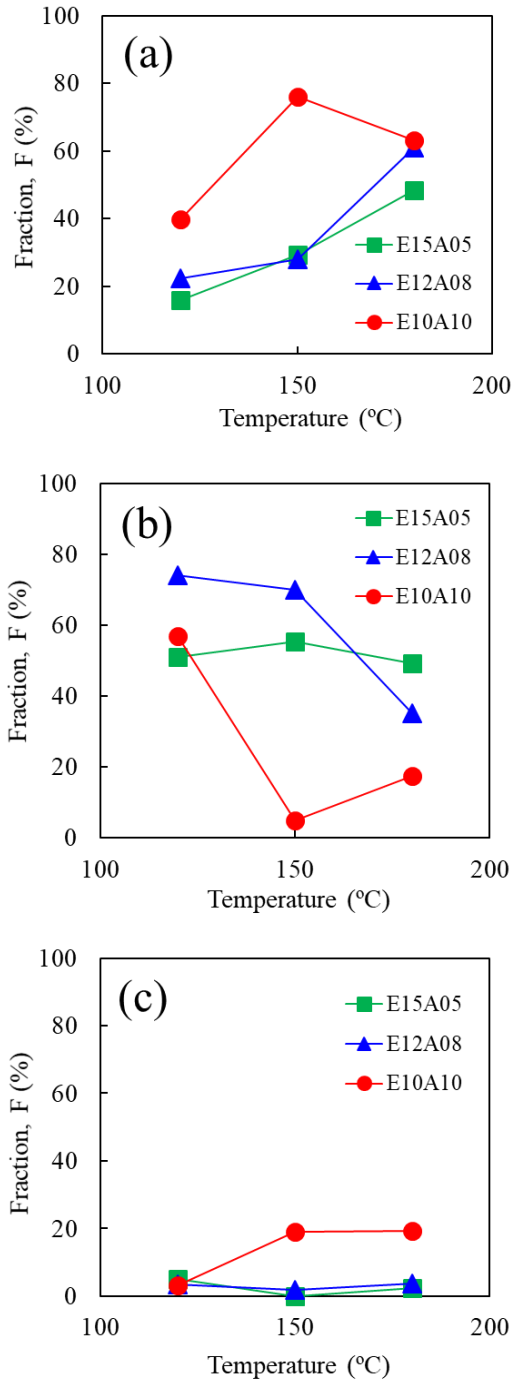

Fig. S7 Fraction of integrated intensity against the treatment temperature of WCRSP without stirring as derived from the XRD pattern: (a) HAp, (b) β-TCP, and (c) DCPA.

Table S1. Starting materials of solvothermal treatment of α-TCP using WCRSP

Notation	Water	Ethanol	Acetic acid	α-TCP
	(mL)	(mL)	(mL)	(mmol)
E05A15	0	5	15	0.81
E10A10	0	10	10	0.81
E12A08	0	12	8	0.81
E15A05	0	15	5	0.81
Water	20	0	0	0.81
E20A00	0	20	0	0.81
E00A20	0	0	20	0.81

Table S2. Elemental analysis of each area crystals via TEM-EDX

Shapes	Element composition (at. %)					
	Ca	P	O	C	Others	Ca/P
Needle	15.66	24.46	6.20	28.75	24.94	0.64
Rice-like	25.97	33.74	18.85	n.d.*	21.44	0.77
Plate	25.21	34.03	9.85	15.25	15.67	0.74

*n.d.: not detected