

Electronic Supplementary Information

Coordination Effect of Citric Acid to Ca-deficient Hydroxyapatite on the Phase Transition

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Experimental Procedure S1

The hybridized amount of Cit with HA was obtained by dissolving Cit in 10 mL of an HCl aqueous solution (pH 2) to prepare the calibration curve for the quantitative analysis. In details, CP/Cit (20 mg) was added to 10 mL of an HCl aqueous solution (pH 2) and completely dissolved.^{S1} The HCl aqueous solution was placed in the reference cell for the UV–visible spectral spectrophotometer (V-750, Jasco Co., Ltd.), and the absorbance at a 211 nm (due to the absorption of the carboxy group in Cit) was observed. The correlation coefficient of the calibration curve was 0.9994. The surface coverage of Cit (%) was calculated by the following equation (S1).^{S1}

$$\frac{N_A \cdot M_{Cit} \cdot A_{Cit}}{S_{BET} \cdot 10^{19}} \quad (S1)$$

where M_{Cit} and S_{BET} were the coordination amount of Cit and the BET surface area of CP/Cit0 (i.e., 98.4 m²/g), respectively. A_{Cit} was the molecular occupied area of Cit (i.e., 0.166 nm²).

The crystalline phases were characterized with XRD (Smart Lab, Rigaku Co., Ltd.). The diffraction patterns were recorded by a powder X-ray diffractometer using an X-ray source of the CuK α radiation.

The elemental compositions were characterized with XRF (ZSX Primus II, Rigaku Co., Ltd.). The XRF analysis was performed as a pellet, which was made by pelletizing the powder without any dilution. The fundamental parameter method was carried out using software (Rigaku Co., Ltd., EZ Scan Program) for the semiquantitative analysis. The molar ratios of Ca to P, K to Ca and Cl to Ca were calculated.

The infrared spectra were recorded with a Fourier transform infrared spectrometer (FT-IR; Jasco Co., Ltd., FT/IR-4600) as the background of KBr in the range of 2000–800 cm⁻¹ with an accumulation time of 128 and a spectral resolution of 2 cm⁻¹. The FT-IR spectra were recorded using KBr powder, and the weight ratio between the sample powder and KBr was 1:10. All of the spectra were recorded after subtracting the background spectrum of the pristine KBr.

Reference

- S1 T. Kataoka, T. Hashimoto, S. Samitsu, Z. Liu and M. Tagaya, *ACS Appl. Nano Mater.*, 2022, **5**, 2305–2315.

Figure S1

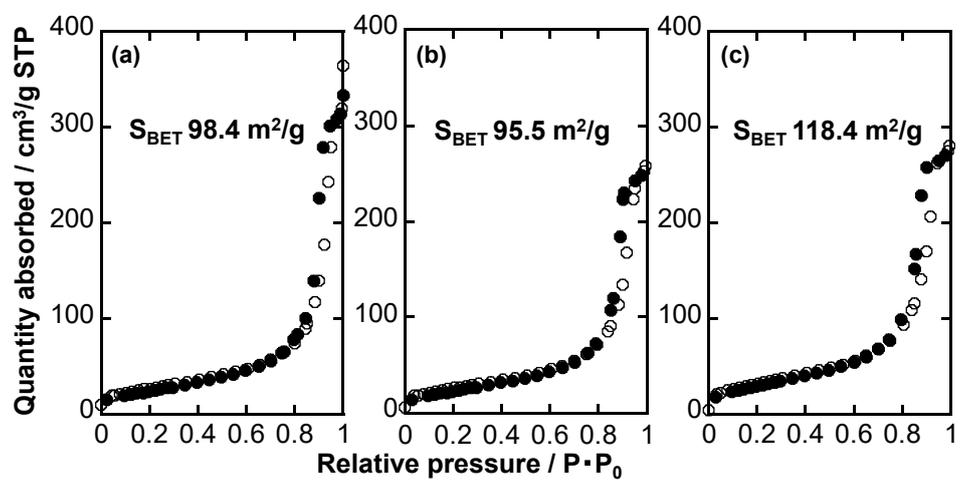


Figure S1. Nitrogen adsorption (●) and desorption (○) isotherms of (a) CP/Cit0, (b) CP/Cit1 and (c) CP/Cit2.

Figure S2

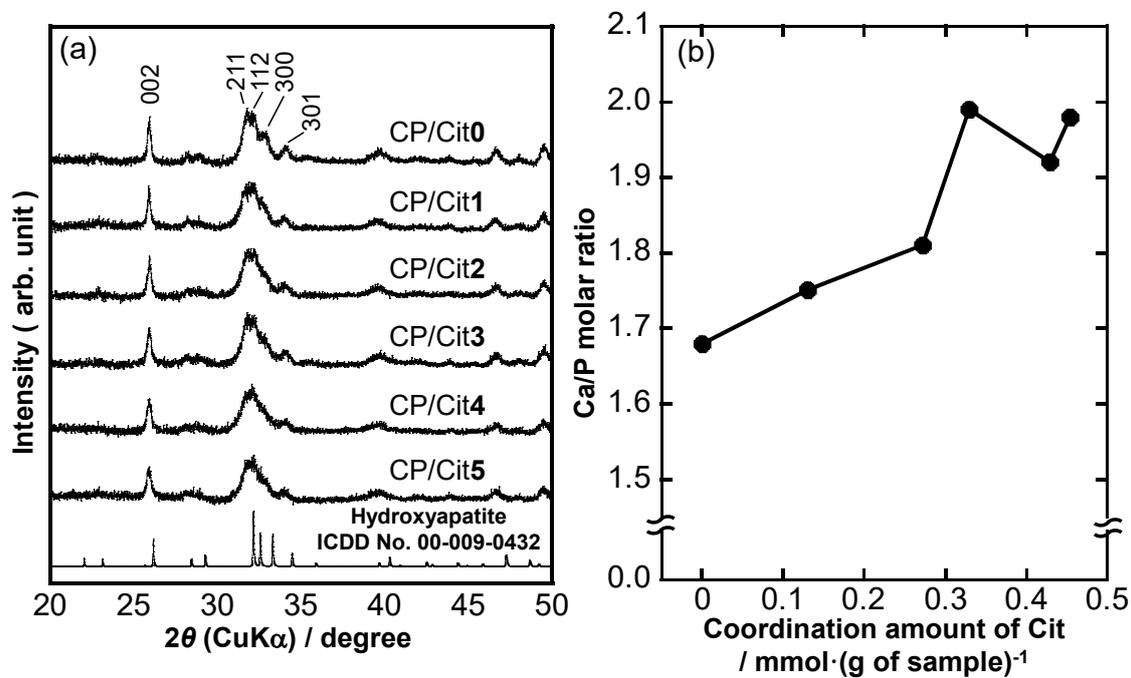
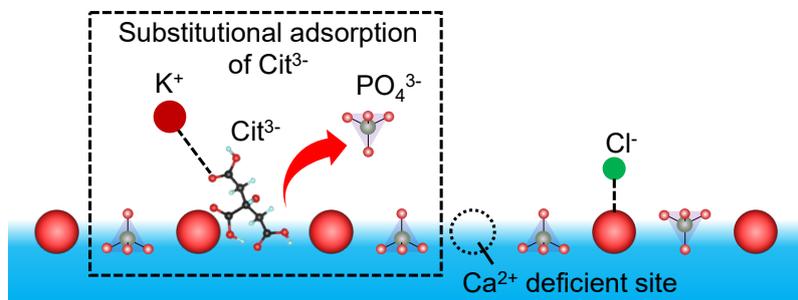


Figure S2. (a) XRD patterns and (b) Ca/P molar ratio change of the CP/Cit X particles.

Scheme S1



Scheme S1. Illustration of ion interactions on the HA surface at the initial synthetic stage.

Figure S3

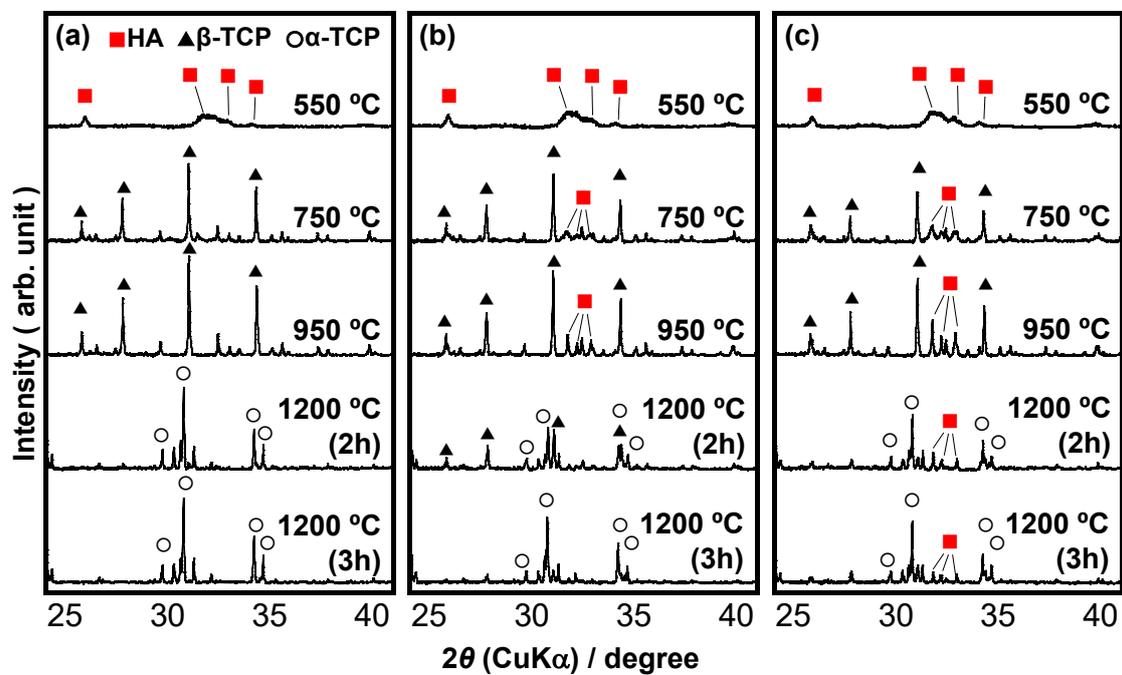


Figure S3. The magnified XRD patterns of (a) CP/Cit0, (b) CP/Cit1 and (c) CP/Cit2 particles calcined at the different temperatures.

Figure S4

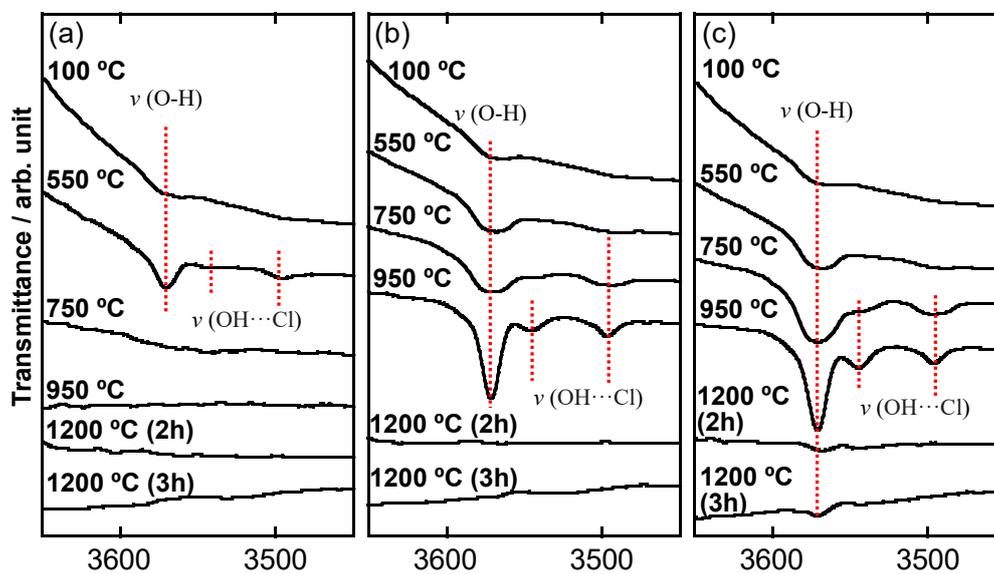


Figure S4. FT-IR spectra in the region of O-H absorption bands of (a) CP/Cit0, (b) CP/Cit1 and (c) CP/Cit2 with the different calcination temperatures.