Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information for

Rapid and Topotactic Transformation from Octacalcium Phosphate to Hydroxyapatite (HAP): New Approach to Self-Organization of Free-Standing Thin-Film HAP-Based Nanohybrids

Satoshi Kajiyama,[a] Takeshi Sakamoto,[a] Moe Inoue,[a] Tatsuya Nishimura,[a‡] Taishi Yokoi,[b] Chikara Ohtsuki[b] and Takashi Kato[a]*

[a]*Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.*
E-mail: kato@chiral.t.u-tokyo.ac.jp
[b] *Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan.*
‡Present address: Division of Material Sciences, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan.

General Methods

Crystals formed on the substrates were observed with a polarizing optical microscope (OLYMPUS, B51). Scanning electron microscopic (SEM) (Hitachi, S-4700 operated at 3.0 kV) analyses were performed with conductive treatment using a Hitachi E-1030 ion sputterer. Orientation of thin-film hybrids was examined with XRD measurements (Rigaku, SmartLab) with Cu Kα radiation (λ = 0.154 nm) with paralleling methods. In-plane and out-of-plane measurements were conducted with 2θ and $2\theta\chi$ scanning methods, respectively. Thermogravimetric (TG) (Rigaku, TG-8120) measurement was conducted in a flow of N_2 (100 cm^3/min) up to 1000 °C at a heating rate of 5 °C/min. Fourier-transformed infrared spectra (FTIR) of the thin-film hybrids isolated from the glass substrates were obtained on KBr with a JASCO/FTIR-660 Plus spectrometer.

Birefringence Change of the Thin-film Hybrids during the Transformation from OCP into HAP

OCP/PVA hybrids and HAP/PVA hybrids were prepared by soaking in water at 80°C for 10–60 minutes and were observed with a polarizing optical microscope (Fig. S1). As the sample soaked in the hot water, the birefringence of the OCP/PVA thin-film hybrids disappeared, resulting in dark images with crossed polarizers. However, any original domain structures larger than 10 μm in the OCP/PVA hybrids were not changed significantly.

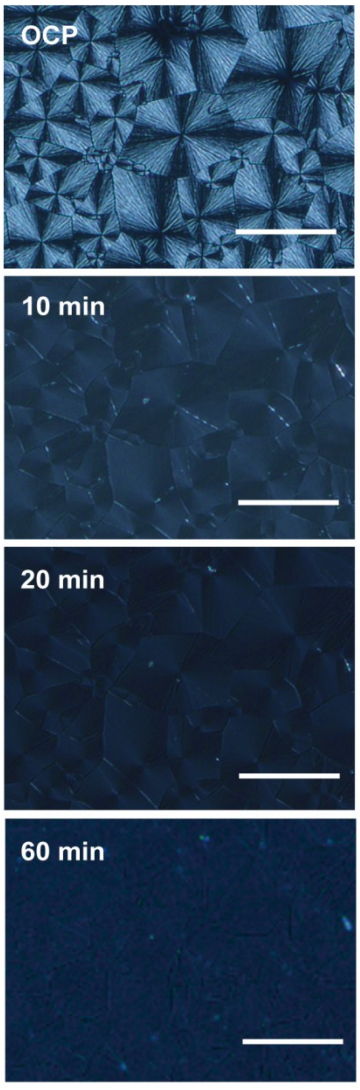

Fig. S1 Polarizing optical micrographs of the OCP/PVA hybrids and HAP/PVA hybrids prepared by soaking in a water at 80°C for 10, 20, and 60 minutes. (bar: 50 μm).

FTIR Measurements of the OCP/PVA and HAP/PVA Hybrids

Fig. S2 shows FTIR spectra of hybrid thin films of calcium phosphate and PVA. The peaks at 563 cm^{-1} and 603 cm^{-1} observed in both FTIR spectra are attributed to the bending ν_4 modes of PO_4^{3-} in crystalline calcium phosphate phases.[1] The peaks of water molecules contained in the OCP structure at 3470 cm^{-1} and 1640 cm^{-1} did not disappear completely after the transformation because the hydroxyl groups of PVA vibrate at similar frequencies and some water molecules should remain in the PVA gel. After the reaction, the peaks at 3570 cm^{-1} and 633 cm^{-1} attributed to the librational and stretching vibration of OH^- in HAP appear. In addition, the broad peak at 1580 cm^{-1} ascribed to C=O stretching in PAA were observed in both FTIR spectra. A small amount of PAA, which was dissolved in the crystallization solution for the thin-film formation, was adsorbed onto these hybrids.

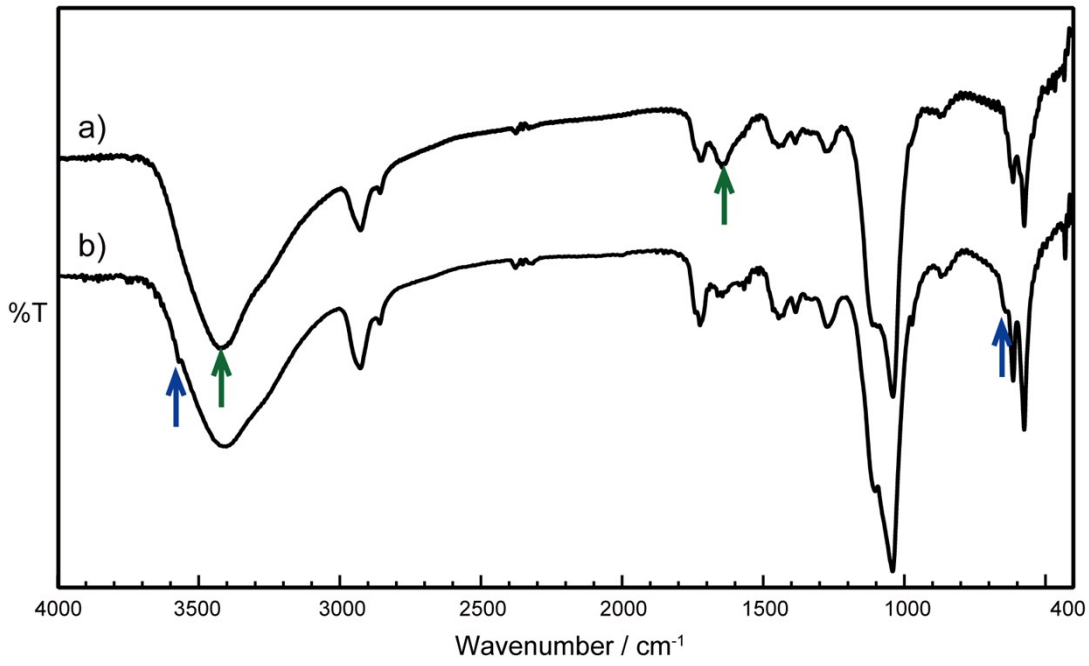

Fig. S2 FTIR spectra of the OCP/PVA hybrids (a) and HAP/PVA hybrids (b) isolated from the glass substrates. Blue arrows and light green arrows indicate characteristic peaks of hydroxyl groups in HAP and the water molecules in OCP, respectively.

Calculation of the Composition by TG Analysis

In the OCP/PVA hybrid thin film, 55.2 wt% of inorganic components remained up to 1000°C in a N_2 atmosphere. It was reported that this atmosphere, OCP lose about 10% of its weight.[2] According to that report, the hybrids include 61.4 wt% of OCP crystals. The inorganic crystals remaining at 1000°C were suspected to be β-TCP and apatite crystals, converted from OCP crystals non-stoichiometrically. OCP have been reported to lose the water molecules in its crystal structure at 75°C and 146°C according to the reactions described in (S1) and (S2), respectively.

$$Ca_8H_2(PO_4)_6{\cdot}5H_2O \rightarrow Ca_8H_2(PO_4)_6{\cdot}4H_2O + H_2O\uparrow \quad \text{(S1)}$$

$$\rightarrow Ca_8H_4(PO_4)_6(OH)_2 + 2H_2O\uparrow \quad \text{(S2)}$$

Following the above dehydration, the hybrids should have lost around 3.4 wt% attributed to the three water molecules per OCP crystal by 200°C if no adsorbed water molecules were included in the hybrids. TG curve shows the weight loss of 8.3 wt% below 200°C ascribed to adsorbed water molecules in addition to those from inside the OCP crystals. Therefore, resultant the OCP/PVA hybrids included 4.9 wt% of adsorbed water molecules. This gives a final composition of OCP/PVA hybrids as 4.9 wt% water molecules, 33.7 wt% organic polymers and 61.4 wt% OCP crystals.

The HAP crystals were stable up to 1000°C. The weight losses from HAP/PVA hybrids were ascribed to the adsorbed water molecules and organic component. Water molecules adsorbed in the PVA matrix were removed below 200°C, and the organic component decomposed from 200°C to 600°C. The composition of the HAP/PVA hybrids was calculated to be 6.2 wt% adsorbed water molecules, 42.7 wt% organic polymers and 51.1 wt% HAP crystals.

Dissolution of the Inorganic Components during the Conversion into HAP

We estimated the amount of the inorganic crystals that dissolved in the hot water during the transformation of OCP into HAP. The transformation of OCP into HAP proceeds in water following the reaction described in equation (S3).[3]

$$5Ca_8H_2(PO_4)_6{\cdot}5H_2O \rightarrow 4Ca_{10}(PO_4)_6(OH)_2 + 6H_3PO_4 + 3H_2O \qquad (S3)$$

The reaction is a hydrolysis that removes phosphoric acids from the OCP crystals. If all the OCP crystals in the hybrids are transformed into HAP crystals without dissolution in hot water, the composition of HAP/PVA hybrids would be 5.5 wt% water molecules, 37.9 wt% organic polymers and 56.5 wt% inorganic crystals. The difference between the estimated and observed values is caused by the dissolution of inorganic crystals during the transformation. We calculated the ratio of dissolved inorganic crystals under the hypothesis that the water and organic polymers of the hybrids were not changed by the reaction. This means that 19.7% of the inorganic crystals in the OCP/PVA hybrids were dissolved in the water during the reaction.

References

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