Hydroxyapatite Thin Films with Well-ordered Crystal Orientation Fabricated by the Combination of Biomineralization-inspired Approach and Subsequent Thermal Process

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Abstract

In the present study, we investigated the effects of compositions of the crystallization solution for the biomineralization-inspired process and the subsequent thermal treatment on their structures to fabricate hydroxyapatite (HAp) thin films with controlled structures and crystal orientation. The octacalcium phosphate (OCP)/poly(vinyl alcohol) (PVA) hybrid thin films were fabricated by immersing the PVA thin-film template into the crystallization solutions with various compositions, and then the OCP/PVA hybrid thin films were converted to the hydroxyapatite (HAp)/PVA hybrid thin films by hydrothermal treatment. It was revealed that the orientation of the crystal structure in the resultant hybrid thin films could be controlled by tuning the compositions of the crystallization solution. In addition, the HAp thin film can be formed maintaining the original crystalline structures of HAp/PVA hybrids when thermally-treated at 700°C.

1. Introduction

Well-controlled nanostructures can be found in biominerals such as sea shells, bone, and teeth, which possess macroscopically oriented structures composed of organic/inorganic hybrids.[1] Inorganic crystals such as hydroxyapatite (HAp) exhibit anisotropic properties due to their crystalline structures. Thus, control of the crystal orientation in the organic/inorganic hybrid materials fabricated via biomineralization-inspired method and exposing of the mineral crystal surface by removing the organic polymers from the hybrid materials are important to fully utilize the high functionality derived from the crystal surface.

In the present study, to fabricate HAp thin films with controlled structures and crystal orientation, we investigated the effects of compositions of the crystallization solution for the biomineralization-inspired process and subsequent thermal process on their structures.

2. Experiment

The sample preparation method was referred to our previous study.[2] First, PVA thin-film templates were prepared by spin-coating and subsequent annealing process at 200°C. Plasma-pretreated silicon plates were used as substrates. As precursors of HAp/PVA hybrids, OCP/PVA hybrids were prepared by immersing the PVA templates in crystallization solutions composed of PAA and amorphous calcium phosphate at 25°C for 7 days. The OCP/PVA hybrids were then converted to the HAp/PVA hybrids by hydrothermal treatment at 80°C. The HAp/PVA hybrids were then thermally-treated at 700°C to fabricate the HAp thin films. Two crystallization solution conditions were used for the preparation of the HAp/PVA hybrids: Condition I ($CaCl_2$ (20 mM), K_2HPO_4 (20 mM), Carboxy group of PAA (10.0 mM)), and Condition II ($CaCl_2$ (20 mM), K_2HPO_4 (16 mM), Carboxy group of PAA (2.5 mM)).

3. Results and discussion

The HAp/PVA hybrids were fabricated via crystallization using the solutions containing PAA and amorphous calcium phosphate at various concentrations, and their crystalline structures were investigated. The samples with significantly different crystal orientations were obtained under the crystallization solution condition I and II.

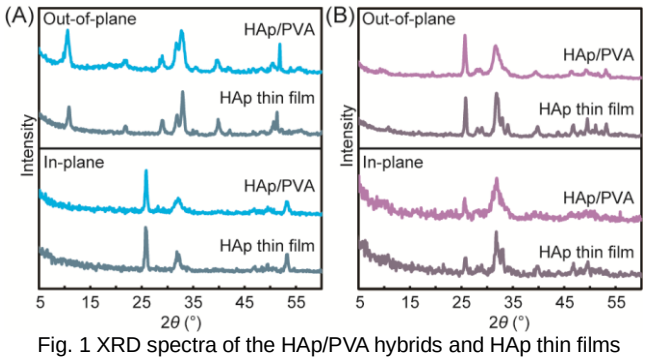

Fig. 1 XRD spectra of the HAp/PVA hybrids and HAp thin films prepared via the crystallization under the solution condition (A) I and (B) II.

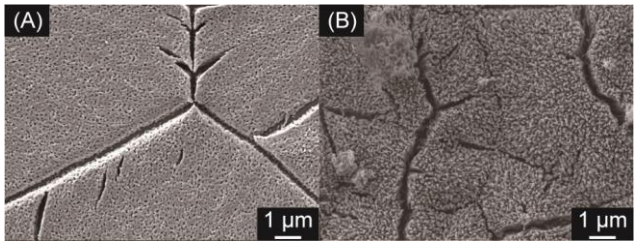

Fig. 2 SEM micrographs of the surfaces of the HAp thin films fabricated via the crystallization under the solution condition (A) I and (B) II.

Fig. 1 shows the out-of-plane and in-plane XRD spectra of the HAp/PVA hybrids and HAp thin films. As for the HAp/PVA hybrid fabricated using the solution condition I, the peaks attributed to the **00*l*** reflections (25.9° and 53.2°) were observed in the in-plane XRD spectrum, while the **00*l*** reflections mainly appeared in the out-of-plane XRD spectrum for the HAp/PVA hybrid fabricated under the solution condition II with a low PAA concentration (2.5 mM). These results indicated that the *c*-axis orientation of HAp crystals could be controlled by varying crystallization conditions. In addition, the XRD spectra of the HAp thin films were almost the same as those of the HAp/PVA hybrids, indicating that the crystalline structures were maintained even after the thermal treatment at 700 °C.

SEM micrographs of the surface of the HAp thin films are shown in Fig. 2. The HAp thin film that was fabricated via the crystallization under the solution condition I possessed relatively smooth surface. On the other hand, for the HAp thin film prepared under the solution condition II, rod or fiber-like structures were observed to exist perpendicularly. The XRD and SEM results indicated that the HAp crystals formed with perpendicularly and horizontally *c*-axis orientation to the substrate when the concentrations of the carboxy group of PAA in the crystallization solutions were 2.5 mM and 10.0 mM, respectively.

4. Conclusions

In the present study, we investigated the effects of the compositions of the crystallization solution on the resultant HAp/PVA hybrids. In addition, the HAp/PVA hybrids were thermally-treated at 700 °C to obtain the HAp thin films. The XRD and SEM results indicated that the *c*-axis orientation in the resultant hybrid thin film could be controlled by varying the compositions of the crystallization solution. The HAp thin films with the original crystalline structures of HAp/PVA could be obtained by the thermal treatment at 700 °C.

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