EFFECTS OF ETHYLAMINE ON THE CRYSTAL GROWTH OF HYDROXYAPATITE

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Abstract Plate-like hydroxyapatite (HAp) crystals whose preferential crystal plane is the *a*-plane were obtained by hydrothermal treatment in the presence of ethylamine. The HAp precursor slurry was treated hydrothermally with various amount of ethylamine at 200 °C for 5 hours. TEM revealed that the products synthesized with 5 wt% or more ethylamine are plate-like crystals, in contrast the products obtained without ethylamine has a granular or rod-like shape. XRD patterns of plate-like crystals orientated preferentially indicate that the grown face of the plate-like crystals is *a*-plane of HAp. It can be suggested that ethylamine captured PO_4^{3-} ions in the solution by chelation and retarded a supply of PO_4^{3-} to HAp nuclei and consequently crystal growth along a particular axis was inhibited.

INTRODUCTION

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HAp) has been attracting attention as the material for column packing of liquid chromatography to separate and/or purification of protein¹, because of the adsorptive properties of HAp. Protein tends to adsorb on a specific crystal plane of HAp². As a consequence, recent studies concerned with the morphology control of HAp crystals have become an extremely important part of HAp research due to the insight such investigation can give into the improvement of the adsorption and/or purification characteristics for protein. While, participation of biopolymer in crystal growth, orientation and nucleation of mineralization in the body such as bone formation has also been interesting. In this laboratory, the morphology control of HAp crystals was studied by hydrothermal synthesis in the presence of alcohols containing hydroxy groups, with special attention being paid to the effect of hydroxy groups on crystal growth of HAp^{3,4}.

In the present paper, this theme was extended by investigating the morphology control by hydrothermal method in the presence of ethylamine containing amino group which is another functional group consisting in biopolymer.

EXPERIMENTAL PROCEDURE

The HAp precursor slurry was prepared as follows; 0.06 mol CaCO_3 and 0.09 mol $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were agitated in a pot mill using 500 g ZrO_2 balls and 200 ml H_2O for 24 hours at 50 r.p.m. to yield the HAp precursor. Various amounts of ethylamine were added to the 200 ml HAp precursor. This mixture was treated in an autoclave with stirring under hydrothermal conditions at 180 °C for 5 hours to crystallize the HAp.

Phases of products were analyzed by powder X-ray diffraction (XRD; MAC science, MXP³) which employed a graphite monochromated $\text{CuK}\alpha$ radiation, operation at 20 kV and 40 mA. In order to determine the crystal plane grown extensively by XRD, the plate-like samples dispersed in ethanol was dropped onto a glass plate and dry to create an oriented layer. Infrared spectra (IR; JASCO, FT/IR-8000S) were measured of KBr pellets. The morphology of the particles was observed by transmission electron microscopy (TEM; JEOL, JEM-4000FX) at 300 kV. The Ca/P ratio of the products and the solution before hydrothermal treatment were determined by inductively coupled plasma emission spectroscopy (ICP, Seiko Denshi Kogyo, SPS7000A).

RESULTS and DISCUSSION

TEM photographs of the products synthesized hydrothermally with varying amount of ethylamine indicated that the shape of crystals changed by ethylamine added (Fig. 1). The products obtained without ethylamine addition were granular-like crystals, about 200 nm in size, while those prepared when 5 wt% or more ethylamine added to the HAp precursor were plate-like crystals, about 50 - 300 nm in size.

FIGURE 1. TEM micrographs of the products synthesized hydrothermally (a) without ethylamine and (b) with 10 wt% ethylamine. (scale shown represents 100 nm)

The peaks of XRD pattern of the precursor were broad, which indicated the precursor to be incompletely crystallized. The peaks of XRD patterns of the products treated hydrothermally with various amount of ethylamine were very sharp and the d values of these peaks of those products were in good agreement with the JCPDS value of HAp (Fig. 2(a)). This indicated that the products were well crystallized HAp independently of amount of ethylamine added. Fig. 2(b) illustrates the X-ray diffraction patterns of the plate-like samples layered preferentially on the substrate glass. The peaks (100), (200) and (300) planes are apparently larger than those produced by the conventional powder X-ray diffractometry, shown in Fig. 2(a). From these results, the preferential crystal plane of plate-like products can be defined as the a -plane.

FIGURE 2. Powder X-ray diffraction pattern of (a) the random orientated plate-like product and (b) the preferentially orientated plate-like product. (The plate-like product was synthesized hydrothermally with 15 wt% methanol at 200 °C for 5 hours.)

TABLE. Ca/P ratio of the products synthesized hydrothermally and the ions in the solutions before synthesis.

amount of ethylamine added (wt%)	Ca/P ratio	
	products synthesized hydrothermally	ions in the solutions before synthesis
0	1.657	7.047
5	1.673	
15	1.685	0.068
50	1.689	

ICP results showed that Ca/P ratio of the products changed as a function of the amount of ethylamine added (Table). Ca/P ratio of the products synthesized without ethylamine is 1.657, which is closed to that of stoichiometric HAp. Addition of 50 wt% ethylamine led to increase Ca/P ratios to 1.689. On the other hand, Ca/P ratios of the ions in the solutions filtrated from the slurry before hydrothermal treatment decreased and a marked increase of P concentration in the solution was observed, when ethylamine is added into the slurry. It can be explained from these results in the following way. Ethylamine captured PO_4^{3-} ions in the solution by chelation and retarded a supply of PO_4^{3-} to HAp nuclei. HAp crystals grew under the condition that PO_4^{3-} were not supplied sufficiently, therefore crystal growth of HAp was inhibited along a particular axis.

SUMMARY

The summary of the results described on this paper are as follows.

- (1) Plate-like HAp crystals whose preferential crystal plane is the α -plane with size 200 nm were have been synthesized hydrothermally with ethylamine at 200 °C for 5 hours.
- (2) The amount of ethylamine required enough to obtain only plate-like crystals was at least 5 wt% in the HAp precursor slurry.

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