Electronic Supplementary Information

Experiments

The calcium solution [8, 10, 12 mM $CaCl_2$] and phosphate solution [300 mM NaCl, 10 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer, 12 mM K_2HPO_4, pH adjust to 7.40 ± 0.05 with 1M NaOH] were mixed by 1:1 in volume with Y-tube into the cuvette to get the calcium phosphate solutions. For the case of the mineralization in the presences of collagen-I micro-fibril, five mg/mL soluble collagen-I (rat tail collagen, GIBCO, Invitrogen, USA) were added into the phosphate solution to get the final solution with 100 μg/mL collagen-I. The final solution was then incubated for about 10 min before mixing them with the calcium solutions. All reagents used were obtained from Sigma unless otherwise indicated. Milli-Q deionized water (DI) was used for all experiments. The reactions were carried out at room temperature (25 ± 1 □). The extinctions (optical difference (OD) of 405 nm and 550 nm) of the solutions were monitored by Microplate readers with UV-Vis spectrometer (ELx 800, Bio-Tek Instruments, Vermont, USA). During the mineralization process, the particles in solution were obtained by fishing the TEM copper grid (coated with a Formvar film strengthened by carbon) in the suspension at different stages of mineralization. The progenitor solution was blotted off by using tissue paper. About 10 μl of DI water was added on the grid and blotted off twice to remove the residue sodium chloride, which may influence the TEM observation. The samples were further dried under lamp light before the TEM observation (JEM 3010F, JEOL, Japan). The same method was applied for SEM sample, which need to be coated with platinum before SEM (JEM 6700F, JEOL, Japan) observation.

Saturation indices (log (*IAP*) - log (K_{sp}), where *IAP* is the ionic activity product of precipitation, K_{sp} is the solubility product constant) of amorphous calcium phosphate (ACP, $Ca_9(PO_4)_6$, pK_{sp} = 77.1[1]) and hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$, pK_{sp} = 116.8[1]) of the initial calcium phosphate solutions were calculated using Visual MINTEQ.[2]

References:

1. S. V. Dorozhkin and M. Epple, *Angewandte Chemie International Edition*, 2002, **41**, 3130.
2. J. P. Gustafsson, Visual MINTEQ. http:// www.lwr.kth.se/English/OurSoftware/vminteq/index.htm. Stockholm, Sweden, 2006.

Table S1. Diffraction data of the synthesized hydroxyapatite (HAP), Bone, standard HAP, and octacalcium phosphate (OCP). The angular relationships distinguishing between HAP and OCP, which have very similar d-spacings.

Synthesize HAP			Bone[1]		HAP (JCPDS 9-432)[1]		OCP (JCPDS 79-0423)[1]		
plane	d (Å)	α^2	d (Å)	α^2	d (Å)	α^2	plane	d (Å)	α^2
(002)	3.46	0.0	3.44	0.0	3.44	0.0	(002)	3.43	0.0
(210)	3.11	90.0	3.10	90.0	3.08	90.0	(312)	3.05	22.1
(211)	2.83	65.5	2.81	65.5	2.80	66.5	(710)	2.83	87.9
(112)	2.79	36.7	2.77	38.0	2.78	36.9	(322)	2.77	28.7

1 M. Olszta, X. Cheng, S. Jee, R. Kumar, Y. Kim, M. Kaufman, E. Douglas and L. Gower, Materials Science & Engineering R, 2007, 58, 77.
2 Angle of plane measured with respect to (0 0 2) plane

Because the d spacing of OCP and HAP were very close, the diffraction patterns of them are similar. However, angular relationships of the diffraction dots distinguishes them from each other. The angle between (001) and (210) is 90 degree for HAP; in contrast, for the faces with similar d spacing, it is about 22 degree for OCP. In our experiments, the angle is 90 degree, which proves that the mineral is HAP. (The SAED patterns are showed in Fig. S5)

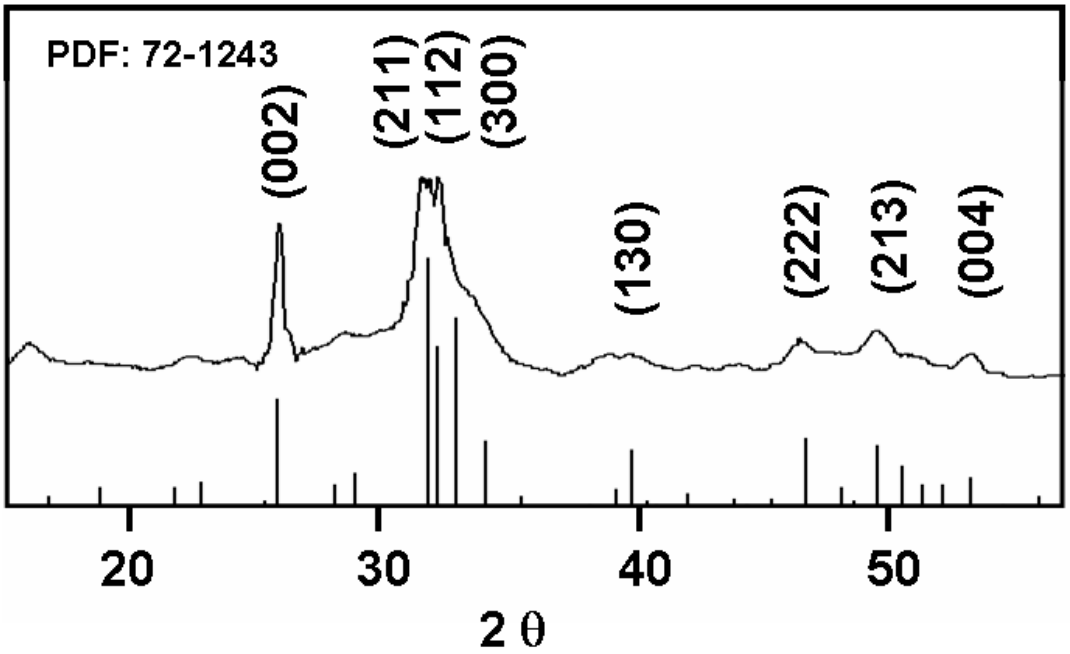

Fig. S1. The XRD of the final precipitated powder (7 hrs.).

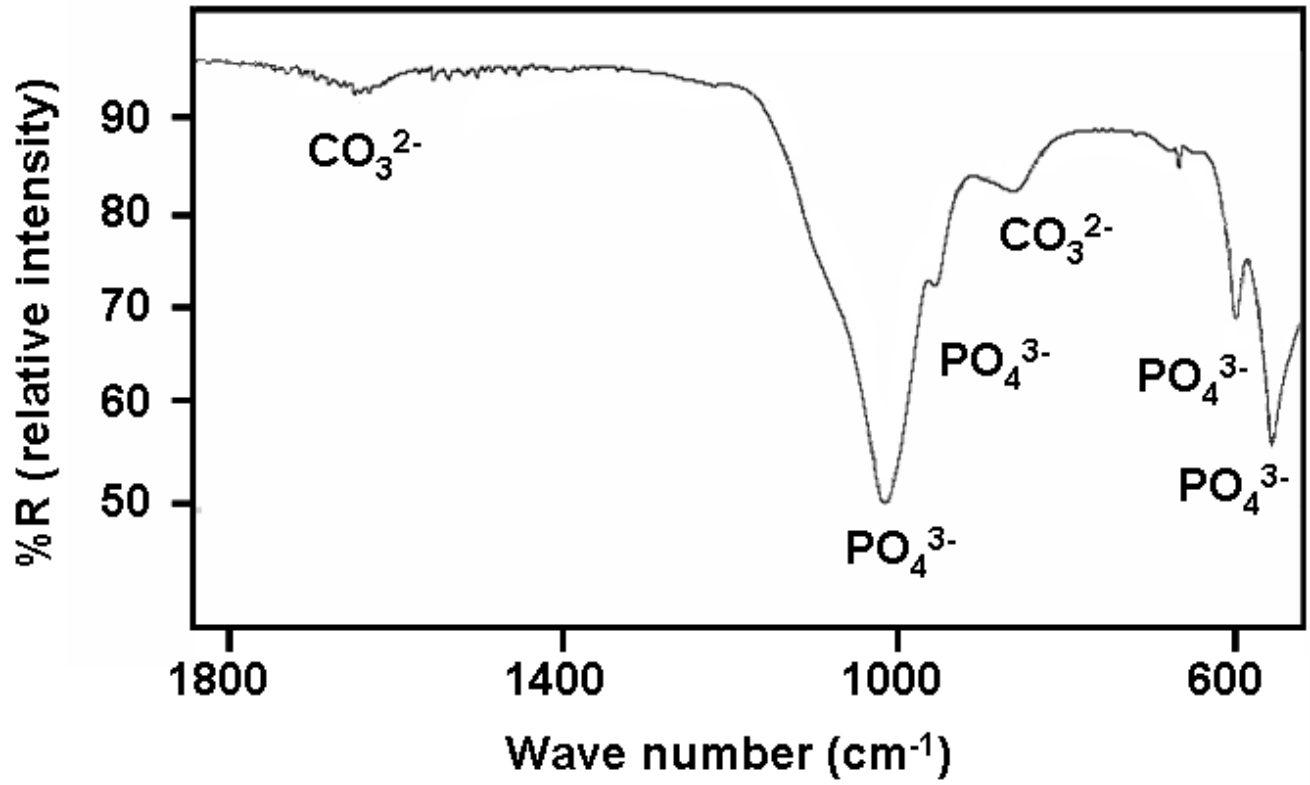

Fig. S2. The FTIR spectrums of the final precipitated powder (7 hrs.).

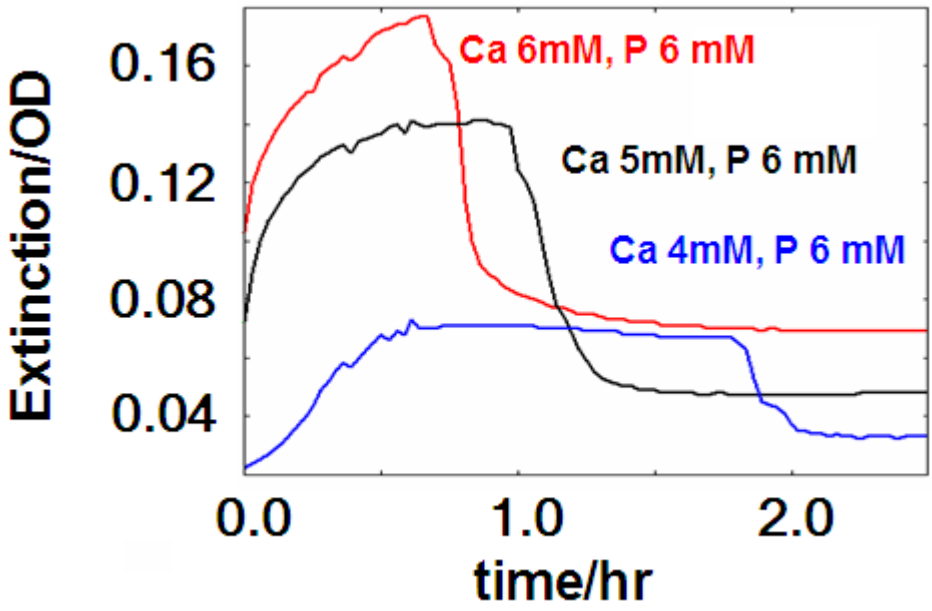

Fig. S3. Extinction curves of calcium phosphate solutions under different concentrations.

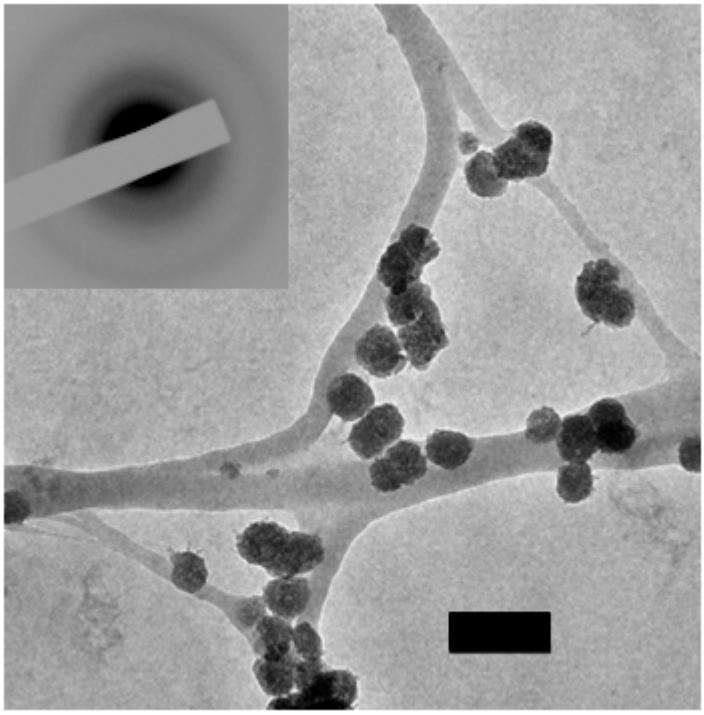

Fig. S4. The discrete ACP particles were formed with the addition of collagen-I micro-fibril (TEM image, 17 min). Bar: 200 nm.

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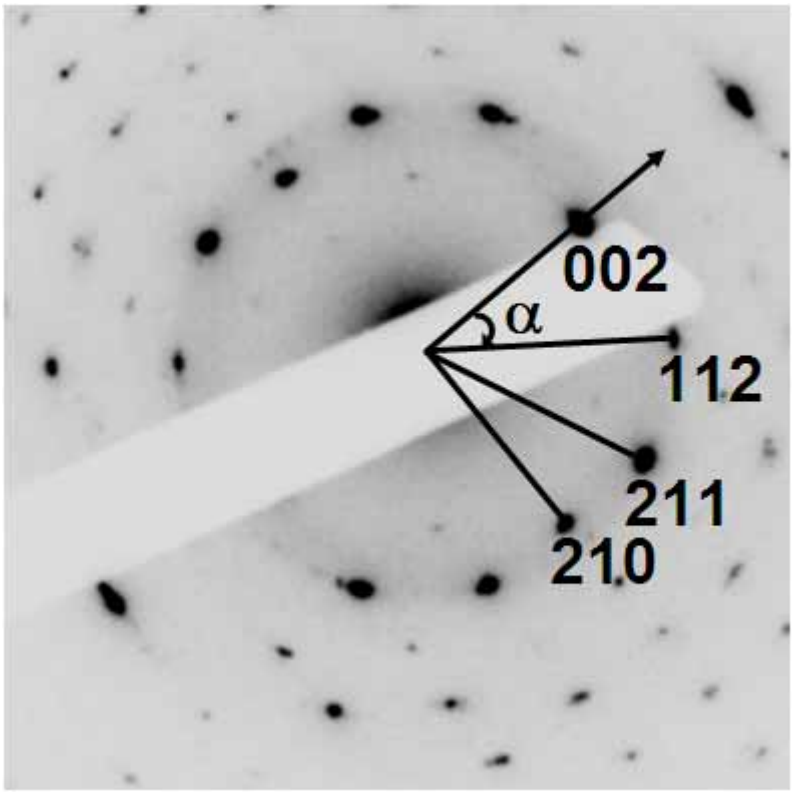

Fig. S5. SAED patterns of the platelet of the final spherulite hydroxyapatite. The angular relationships confirm the phase to be HAP rather than OCP; details in Table S1.