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Electronic supplementary information (ESI)

An effective route to the synthesis of carbonated apatite crystals with controllable morphologies and the growth mechanism†

Juan Shen,*[a] Jin Bo,[b] Ya-min Hu [a] and Qi-ying Jiang [a]

[a] *School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, China. E-mail: sj-shenjuan@163.com; Fax: +86 816 2419201; Tel: +86 816 2419201*

[b] *State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, China*

Solution Chemistry Calculation

The activity of the species and saturation index (SI) of the solutions as a function of the pH were calculated by using the Visual MINTEQ 3.1 speciation software. [1] SI = log (IAP) - log K_{sp}, being IAP the ionic activity product and K_{sp} the solubility product. MINTEQ database (NIST 46.4) was used for these calculations.[1] The solubility product, K_{sp}, of the solid phases (HAp: hydroxyapatite, OCP: Octacalcium phosphate, DCPD: Dicalcium phosphate, and ACP: Amorphous calcium phosphate) used in the calculation was extracted from the MINTEQ (type6) database (NIST 46.7).

Carbonate Content Calculation

The infrared spectra were recorded using KBr pellets (about 1.2 mg sample per 150 mg KBr) with a spectral resolution of 4 cm^{-1} on a Nicolet-6700 FT-IR spectrometer to evaluate the functional groups of the specimens. The ratio of the extinction of the FTIR carbonate band at about 1406 cm^{-1} (E_{1406}) to the extinction of the IR phosphate band at about 565 cm^{-1} (E_{565}) is linearly related to the carbonate content of the CHAp.[2] In experimental conditions, the equation (R^2 = 0.96, R is correlation coefficient in linear regression equation) utilized for calculating the carbonate content was

$$CO_3\ wt\% = 17.4 \times \frac{E_{1406}}{E_{565}} + 0.4$$

where CO_3 *wt%* is the carbonate content in mass. The extinction of the carbonate band at about 1420 cm^{-1} (E_{1420}) was calculated from measurement of baseline transmittance (T_2) and peak transmittance (T_1) using the relationship E = log T_2 / T_1. The extinction of the phosphate band at about 565 cm^{-1} (E_{570}) was calculated in the same way.

Supplementary Tables

Table S1. Saturation Index (SI) as a function of pH.

pH value	3.5	6.1	8.1	10.2	11.0
SI (HAp)	-4.375	4.304	7.331	8.35	9.103

SI (OCP)	-1.414	3.938	4.333	2.609	2.166
SI (ACP)	-5.11	-0.433	0.708	0.473	0.576
SI (DCPD)	-0.95	-0.279	-1.024	-2.513	-3.06

Table S2. Carbonate contents of as-prepared CHAp samples synthesized with different initial pH values.

pH value	Carbonate content (wt %)
3.5	1.88
6.1	2.11
8.1	2.77
10.2	2.91
11.0	3.28

Supplementary Figures

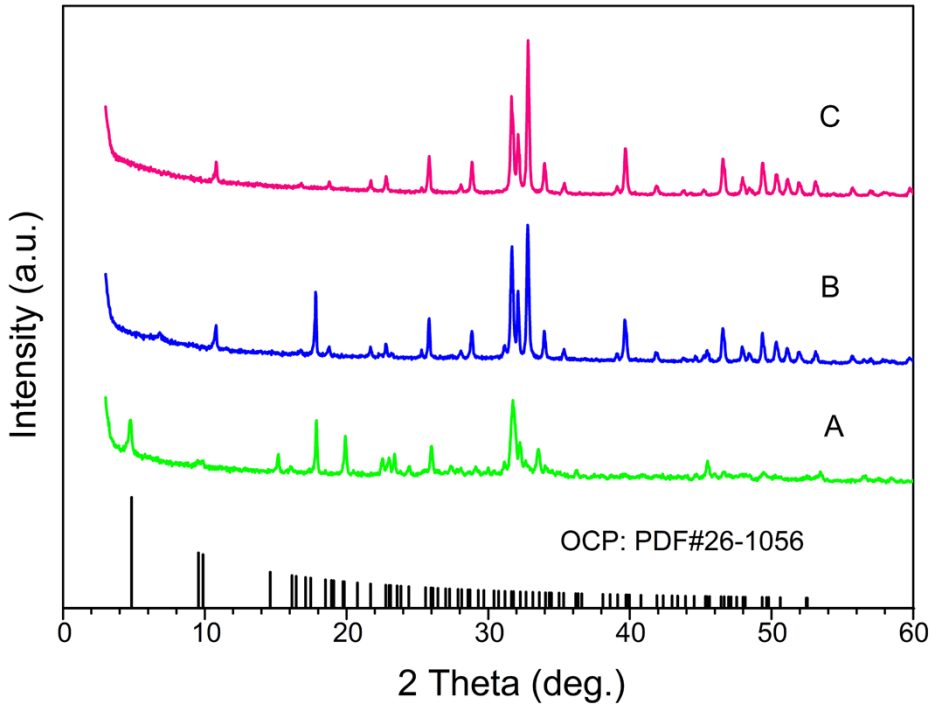

Figure S1. XRD patterns of as-prepared CHAp samples synthesized at 190 °C with initial pH 8.1 at different reaction times: (A) 30 min, (B) 1 h, (C) 4 h and the standard data of OCP (JCPDS No. 26-1056) as a reference.

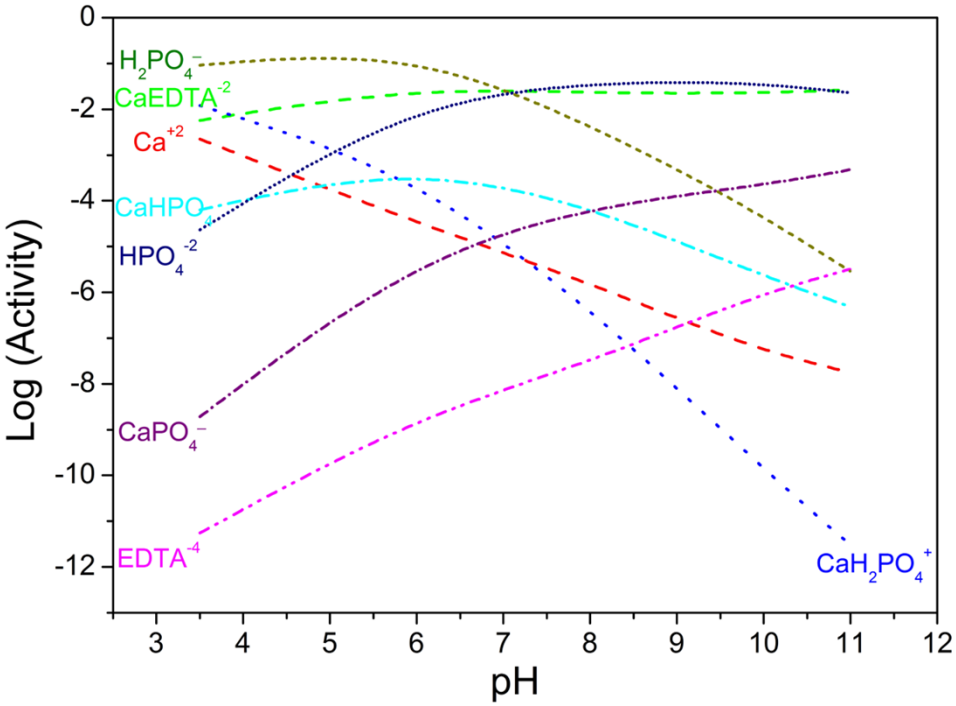

Figure S2. Activity evolution versus pH of the main calcium, EDTA, and phosphate species and ion pairs in the mother solution at 100 °C.

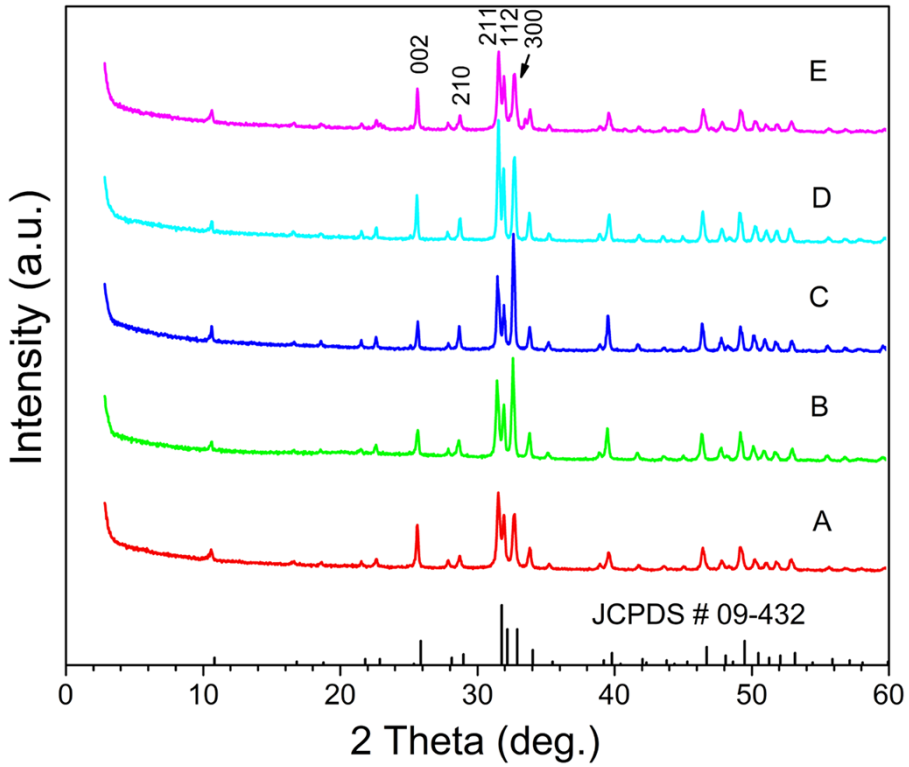

Figure S3. XRD patterns of as-prepared CHAp samples synthesized at 190 °C for 4 h with different initial pH values: (A) pH = 3.5, (B) pH = 6.1, (C) pH = 8.1, (D) pH = 10.2, and (E) pH = 11.0 and the standard data of HAp (JCPDS No. 09-0432) as a reference.

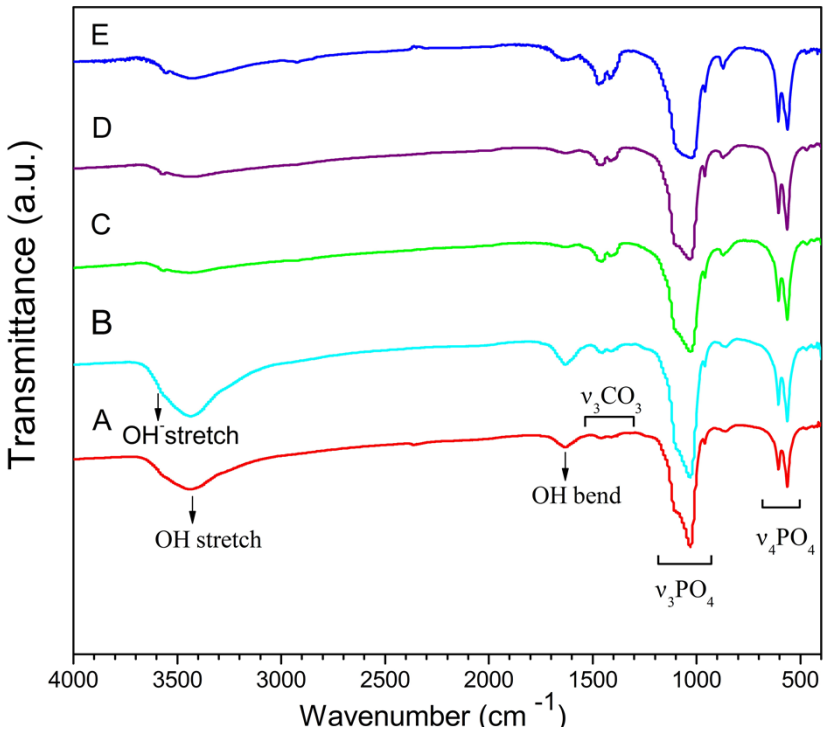

Figure S4. FT-IR spectra of as-prepared CHAp samples synthesized at 190 °C for 4 h with different initial pH values: (A) pH = 3.5, (B) pH = 6.1, (C) pH = 8.1, (D) pH = 10.2, and (E) pH = 11.0.

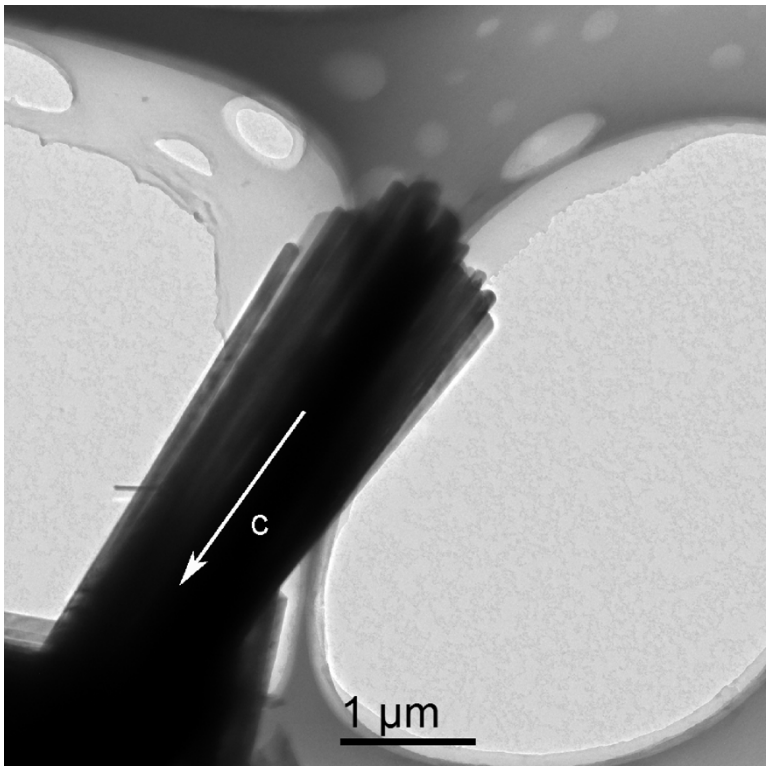

Figure S5. TEM image of CHAp powders synthesized at 190 °C with pH = 8.1 for 4 h. The formation of the nanosheet HAp nanocrystallites facilitates aggregation parallel to the *c* axis.

References

1 J. P. Gustafsson, Visual MINTEQ, Version 3.1. 2013. Stockholm. Available from: http://www.lwr.kth.se/English/OurSoftware/vminteq

2 J. D. B. Featherstone, S. Pearson, R. Z. Legeros, An infrared method for quantification of carbonate in caronated apatites. Caries Res, 1984, **18**: 63–66.