Electronic Supplementary Material (ESI) for CrystEngComm

Modulation of Hydroxyapatite Crystal formed from Alpha-Tricalcium Phosphate by Surfactant-free Hydrothermal Exchange

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Supporting Information

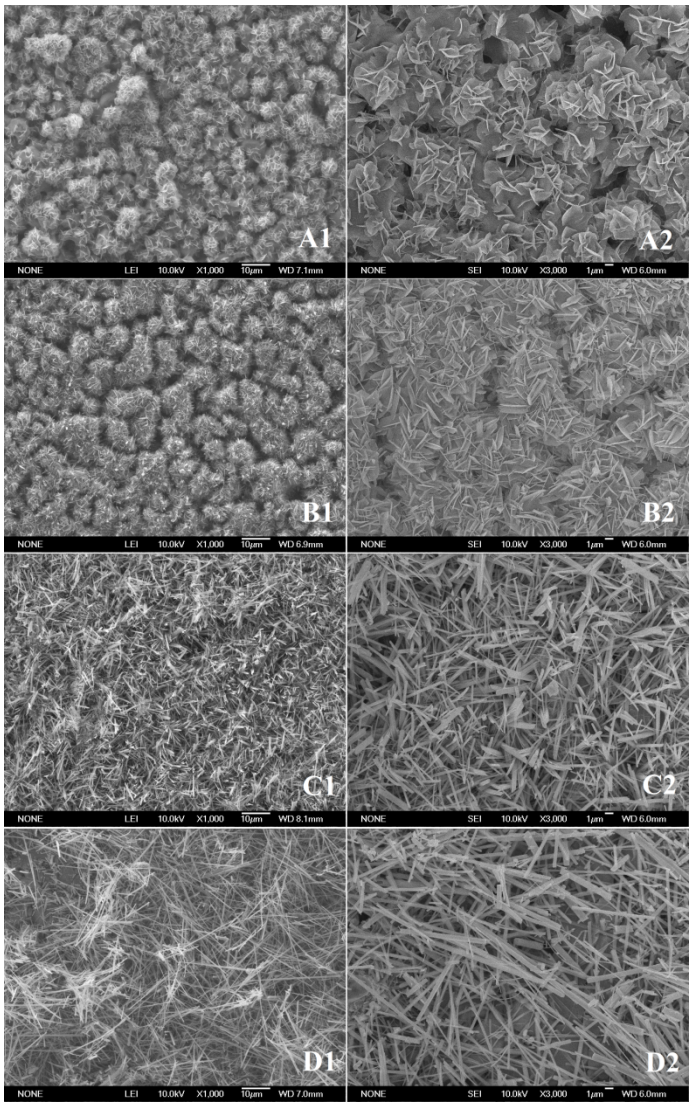

Figure S1 FESEM images of the group with initial Ca/P molar ratio set at 1.33. A1, A2 : (initial Ca/P molar ratio = 1.33, 90 ^{o}C, 72h; S1), B1, B2: (initial Ca/P molar ratio = 1.33, 100 ^{o}C, 24h; S2), C1,C2: (initial Ca/P molar ratio = 1.33, 140 ^{o}C, 24h; S3), D1,D2: (initial Ca/P molar ratio = 1.33, 180 ^{o}C, 24h; S4). Samples A and B exhibited a typical plate morphology very similar to the HA crystals obtained by hydrolysis of alpha-TCP at, or near physiological environment[22,25], while sample B had a longer shape which resulted from the faster growth rate of *"c"* direction under a higher temperature. The effect of extra P ion (enhance the formation of HA sheets and plates) on HA morphology under relatively low temperature was reported in others' work[21]. Sample C were mainly composed of HA rods, which were quite different from S3, but still, some of the HA rods were packed parallel to each other. Comparing to S4, Sample D were HA fibers with a very high

length-diameter ratio. The reason for the morphology of sample C and D could also be explained by selective adsorption of Ponser Clusters. While Ca^{2+} ion prevented the growth in *"c"* direction, PO_4^{3-} ions enhanced the growth in *"c"* direction by occupying the adsorption sites of Ponser Cluster on the positively charged *a, b* planes, resulting in the morphology observed.

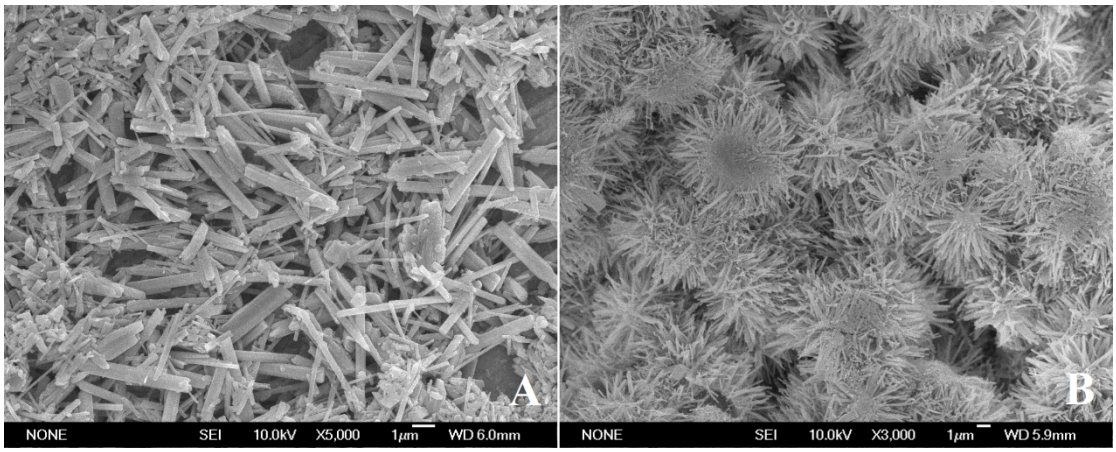

Figure S2 FESEM images of the intermediate phases for samples S1 and S4. A: rod-like structure but not well developed (initial Ca/P ratio = 1.50, 90°C, 24h), B: chrysanthemum-like structure with a solid core, which proved that HA crystals were grown in a radial way to construct the chrysanthemum-like HA flowers(initial Ca/P ratio =1.50, 180°C, 1h).

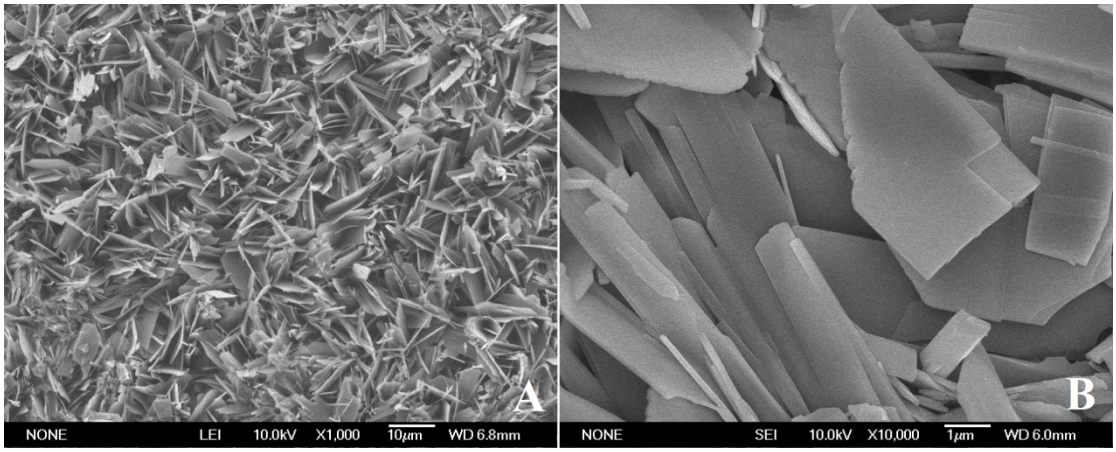

Figure S3 A, B, FESEM images of sample prepared by adding extra calcium ions (initial Ca/P ratio = 1.50, 90°C, 72h). Due to the effect of Ca^{2+} ion, the growth in "*c*" direction was prevented and the combination of *a, b* planes was enhanced. From picture B, it could be clearly observed that the HA plates was grown from the parallel packing of HA rods. Comparing to the morphology of sample S1, the experimental results further approved the function of Ca^{2+} ion.