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Multiradiate Calcium Phosphate Patterns Derived from a Gradating Polysaccharide-Acidic Protein System

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1. Experimental section

Apparatus: SEM images and EDS were performed using a Philips XL 30. The XRD patterns were attained with a Rigaku D/max-γB diffractometer obtained using CuKα radiation at 40 kV and 60 mA.

Reagents: Calcium acetate was obtained from Shanghai Qianjin reagent factory. Sodium dihydrogen phosphate was purchased from Shanghai Xinhua reagent factory. All solutions were prepared with deionized water. The chitosan (deacetylation degree: 70%) was purchased from Ji'nan Haidebei Marine Bioengineering Co., Ltd (Ji'nan, China), and the average molecular weights of chitosan were about 1100 kDa.

Synthesis of poly-amino acid: PAsp's with different hydroxyl contents (named as PAsp-x%OH) were prepared by adding polysuccinimide (PSI) with different hydroxylation degrees (named as PSI-x%OH, Mw = 10000) into an excess of NaOH solution and then stirring the mixture at room temperature for 3 h to open the residual pentacyclic ring on PSI-x%OH. The final solution of PAsp-x%OH was adjusted to pH = 7.0 and was diluted to a certain concentration for the further use. The PSI-x%OH was synthesized from aspartic acid according to the procedure published in ref. (*J. Macromol. Sci: Pure. Appl. Chem.*, 2003, **40**, 511.). A typical preparation procedure of PSI-x%OH is as follows: 2.0 g PSI was dissolved in 10mL of dimethylformamide (DMF), and then a definite ethanolamine solution was added at 0 ^{o}C during a period of 10 min. The reaction flask was moved to a water bath at 25 ^{o}C and stirred for another 8 h. The solution was then precipitated in 10-fold volume of methanol. The precipitate was washed with ethanol for three times and dried at 25 ^{o}C under a vacuum. By changing the ratio of PSI to ethanolamine, the PSI-x%OH with different hydroxyl content could be prepared.

Preparation of calcium phosphate patterns: Chitosan matrices were prepared by dip

coating their acetic aqueous solution (1% acetic acid and 1% chitosan) with glass substrates, and then drying in 60 °C. After quickly mixing 0.8 g of PAsp-x%OH (10 mg/mL) and 10 mL of calcium acetate solutions (10 mg/mL), several chitosan-glass substrates were then transferred into without stirring. Then 10 mL of sodium dihydrogen phosphate solution (10 mg/mL) was added in the mixture to get a homogeneous solution. This solution was then allowed to place at 18 °C for a period from several minutes to several hours. After reacting for a period of time, the samples were taken out and dried at room temperature for further use.

2. Figures of supporting information

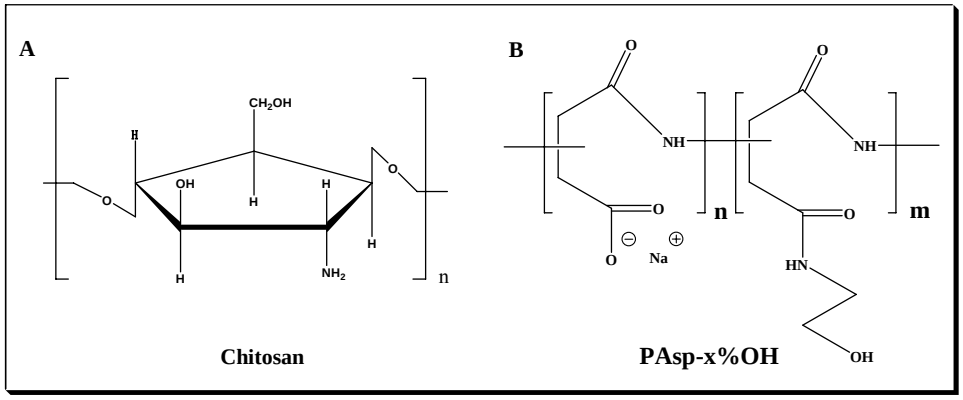
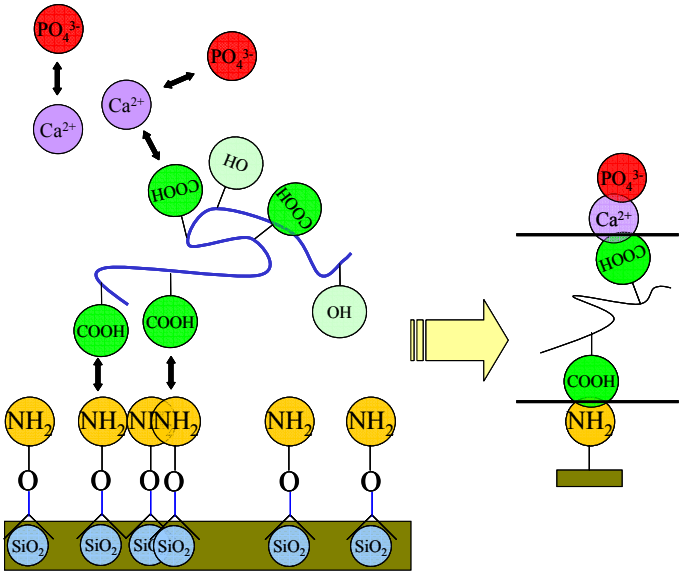


Fig. S1 Structures of (A) chitosan and (B) polyaspartic acids with different hydroxyl contents (PAsp-x%OH, x = m/(m+n)×100%).



Scheme S1 Schematic interaction among chitosan, PAsp-x%OH and calcium ions.

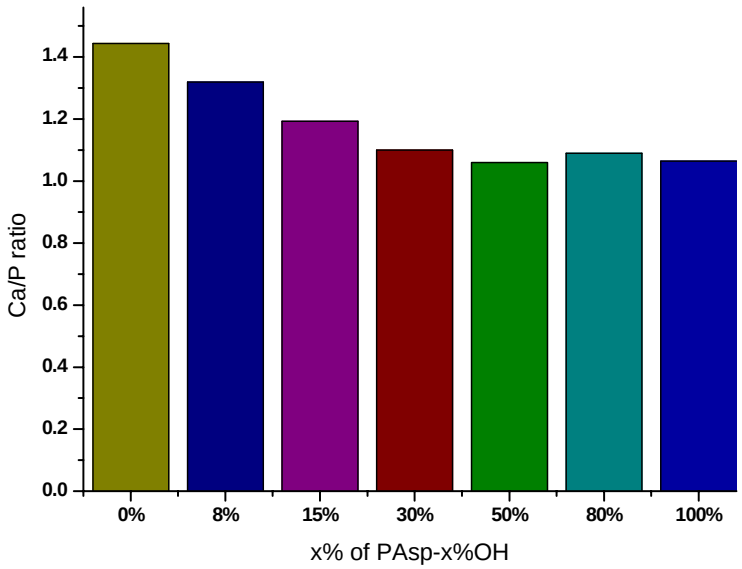


Fig. S2 Ca/P ratios of the as-synthesized calcium phosphate materials for the reaction of 4 hours in the presence of PAsp-x%OH.

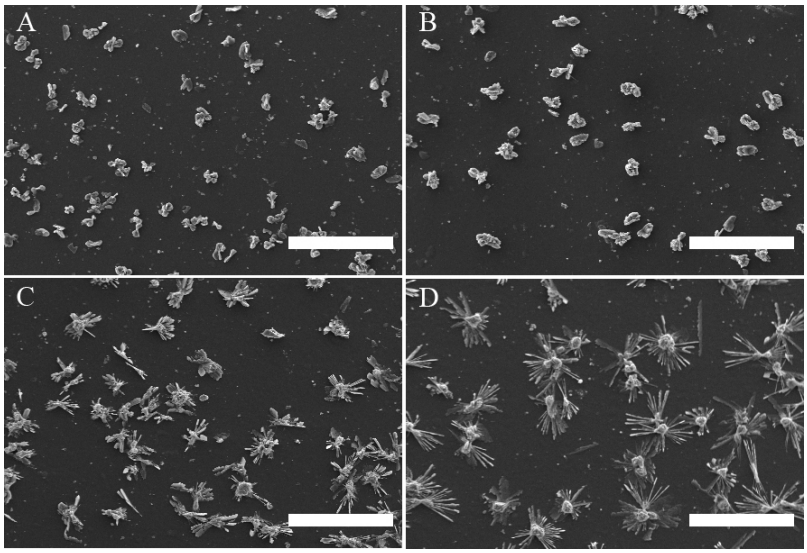


Fig. S3. Morphology transformation of samples within the initial reaction time of (A) 5 min, (B) 10 min, (C) 15 min, (D) 20 min in presence of PAsp-15%OH. The scale bar is 200 μm.

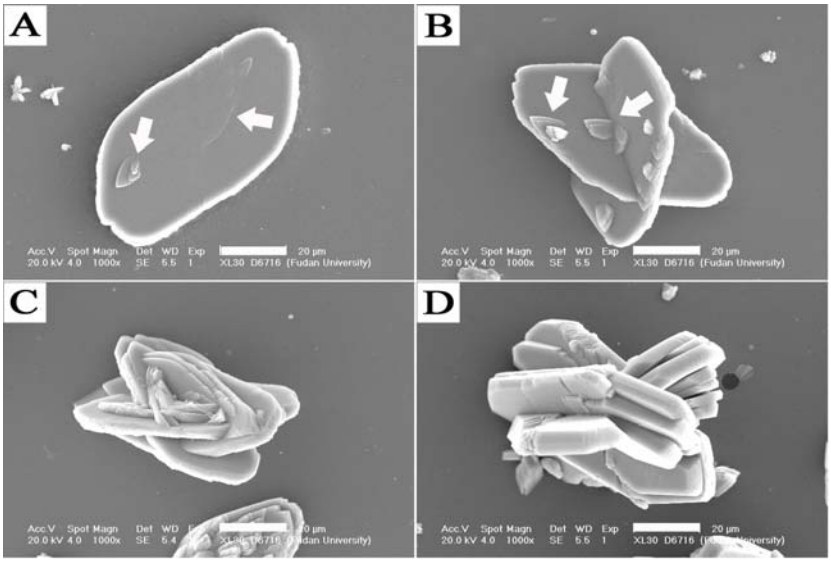


Fig. S4 Morphology transformation of samples within the initial reaction time of (A) 5 min, (B) 10 min, (C) 15 min, (D) 20 min in presence of PAsp-100%OH. The scale bar is 20 μm.

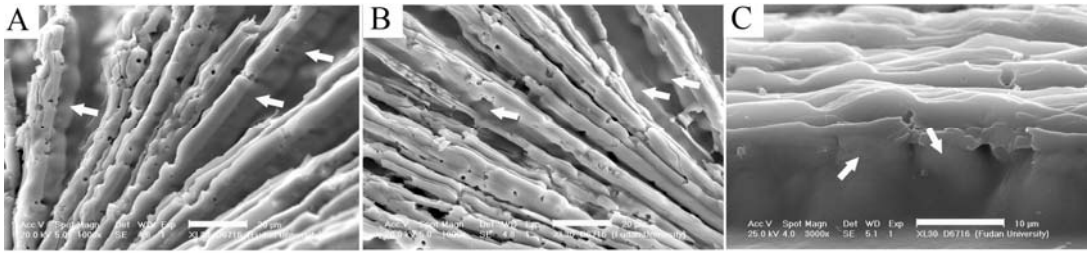


Fig. S5 SEM images of calcium phosphate prepared by using PAsp-0 (A), 8 (B), 15 (C) %OH for the reaction of 4 hours. The white arrows mean the part of raised root of chines between inorganic mineral and organic chitosan matrix.