Hierarchical porous hydroxyapatite microsphere as drug delivery carrier

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Part I: Experimental

All of the reagents used in the experiments were analytical grade and purchased from Guangzhou Chemical corporation and used without further purification. In a typical synthesis, $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ with a mole ratio of 1.67 was dissolved in 60 mL deionized water, the pH was adjusted to 5 with HNO_3. Then, certain amount of $CtNa_3 \cdot 2H_2O$ was added into the solution with vigorous stirring for several minutes to ensure the complete dissolution of the solutes. The mixture was transferred into a 100 ml Teflon bottle held in a stainless steel autoclave, sealed and heated at 180 ℃in an oven for 2 h. As (After) the autoclave cooled naturally to room temperature, the resulting precipitates were washed with deionized water for three times, centrifuged, dried at 80 ℃for 1 day.

The as-prepared samples were analyzed with X-ray diffraction (XRD), carried out with a PANalytical X'Pert PRO X-ray diffractometer with Cu Kα (λ = 0.15418

nm)incident radiation, and the XRD data were collected between 10° and 60° in intervals of 0.02° and a scan rate of 1°/min. The morphology of the products was inspected using a Field Emission Scanning Electron Microscope (FESEM, Nova NanoSEM 430). Fourier Transform Infra-Red Spectra (FT-IR) was obtained in the range of 4000 – 400 cm^{-1} using Bruker Vector 33 with a resolution of 0.3 cm^{-1}. Transmission Electron Microscope (TEM) was performed using a JEOL JEM-2100 with a field emission gun operating at 200 KV. Images were acquired digitally on a Gatan 832 CCD camera.

Part II: Supplementary Figures

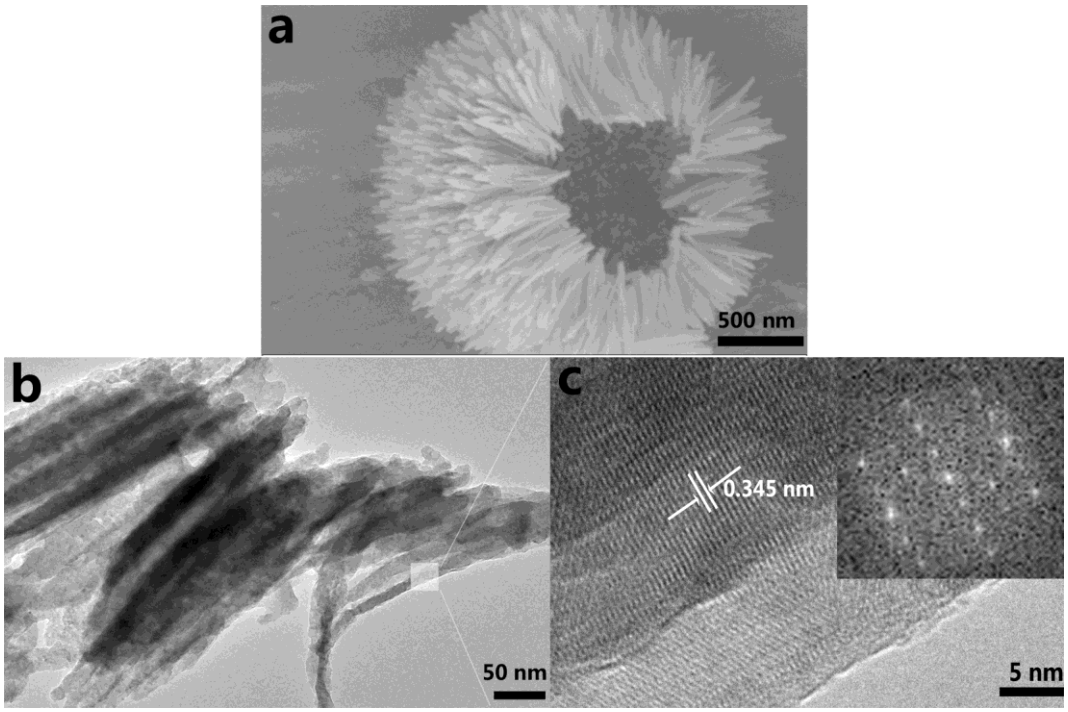

Figure S1 The SEM image of (a) MHAp and TEM image of (b) its building blocks, (c) the HRTEM images of the nano rod. The inset in (c) shows the corresponding FFT diffraction pattern.

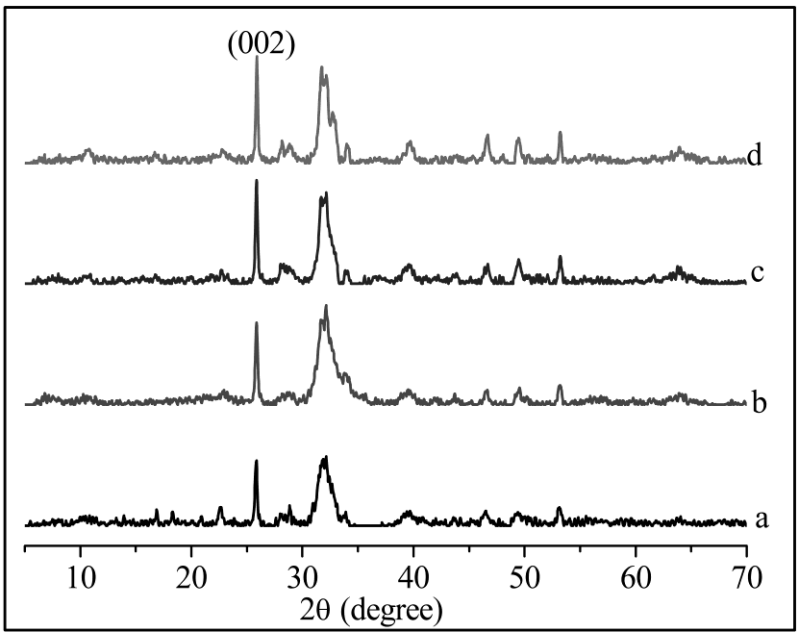

Figure S2 XRD patterns of products obtained after different reaction durations, a 25 min, b 30 min, c 40 min, d 60 min.

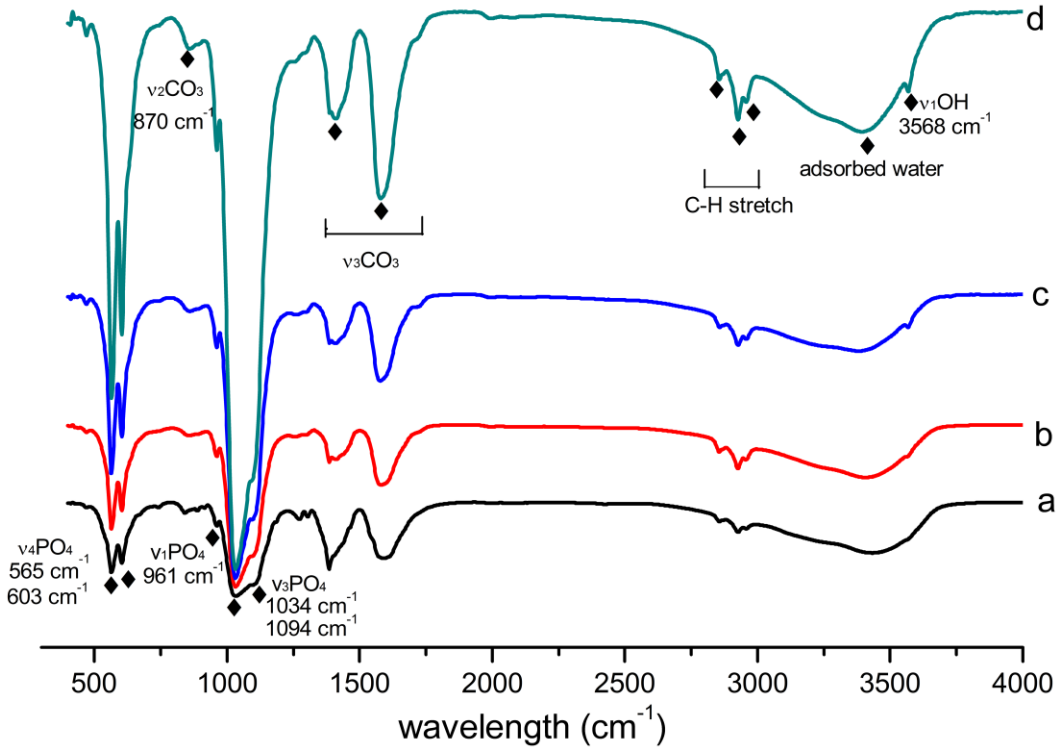

Figure S3 FT-IR patterns of products obtained after different reaction durations, a 25 min, b 30 min, c 40 min, d 60 min.

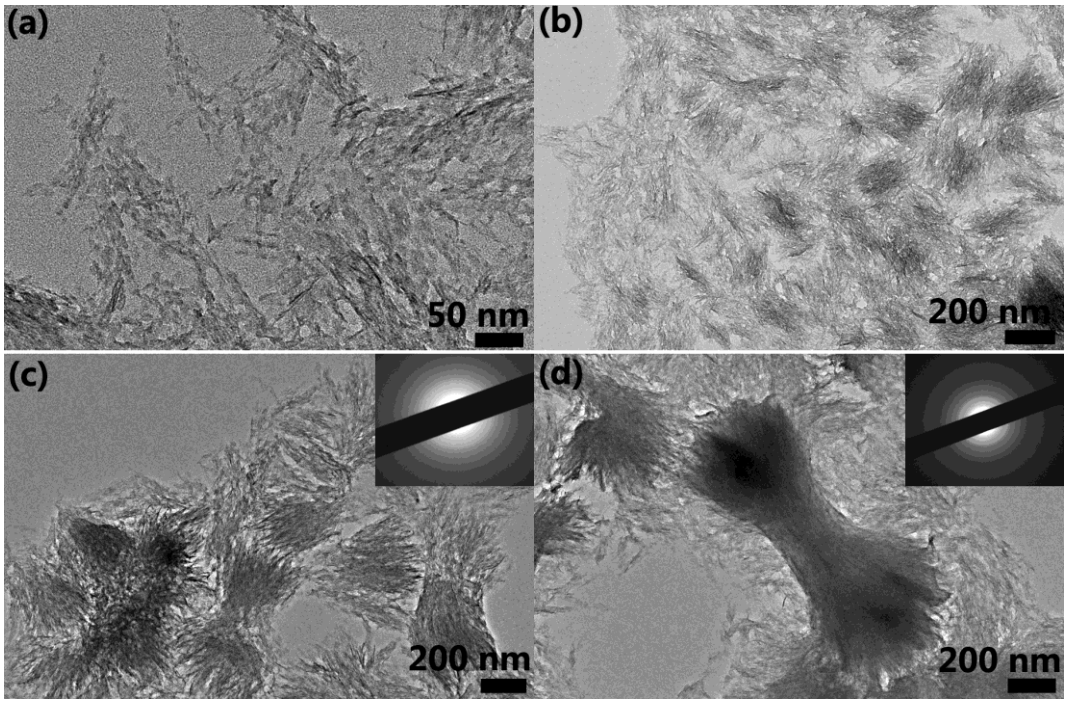

Figure S4 TEM images of progressive stages of the self-assembled growth of the precursor phase of HAp: from nanowires through paralleling mutually to dumbell shapes calcium phosphate with low crystallinity.

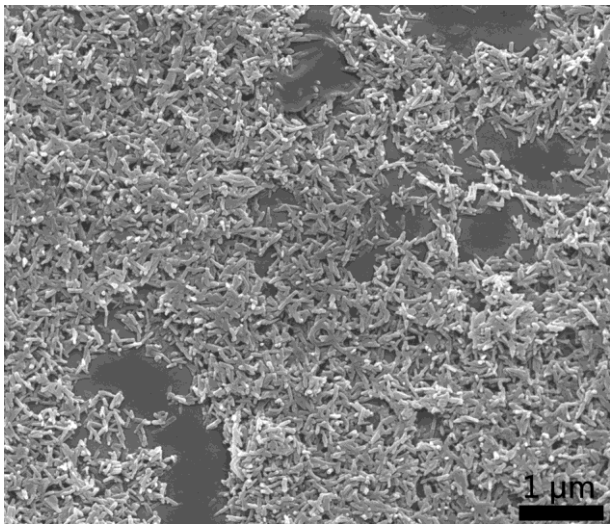

Figure S5 SEM image of HAp prepared at 180 ^{o}C for 2 h with the initial pH value at 6.4 and without adding sodium citrate. The synthesizing condition and the concentration of reagents was the same as the system of microsphere.

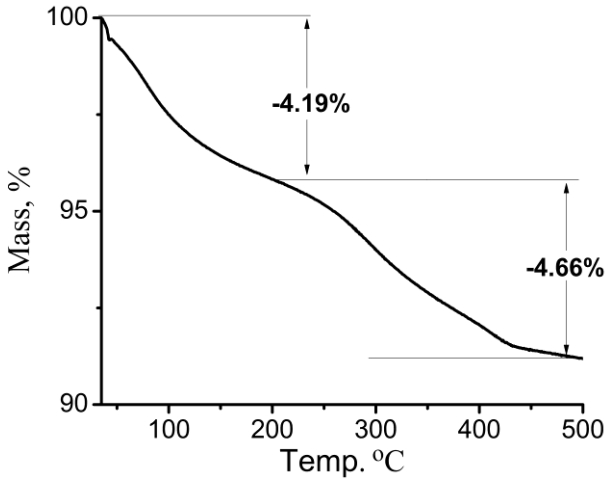

Figure S6 Weight change vs temperature for TG analysis of the microsphere performed at 10 °C/min up to 500 °C in flowing O_2.

sample	pH of PBS solution	Concentration of citrae (g/L)	Releasing amount of citrate (mass ratio)
1	**7.4**	**0.073474**	**35%**
2	**5.4**	**0.082335**	**40%**

Table S1 the concentration of citrate after soaking in PBS solution for 36h