Supplementary Material (ESI) for Nanoscale

Facile Synthesis of Hydroxyapatite Nanoparticles, Nanowires and Hollow Nano-structured Microspheres using Similar Structured Hard-precursors

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Supplementary (S1):

S1.1. Experimental Section.

Analytical grade reagents (Shanghai Chemical Co.,Ltd., P.R. China) without further purification were used in this study.

Synthesis of calcium carbonate ($CaCO_3$) nanoparticles: The $CaCl_2$ and Na_2CO_3 were dissolved in distilled water, respectively to obtain 0.25 M solutions. The reactant molar ratio of Ca/CO_3^{2-} was kept at 1.0. The Na_2CO_3 solution was dropwisely added into $CaCl_2$ solution at room temperature under violent agitation to obtain a white suspension. The white precipitate was further stirred for 1 h followed by washing three times with distilled water and two times with 100% ethanol. After washing, the remaining liquid was removed by vacuum filtration, and the obtained powders ($CaCO_3$ nanoparticles) were dried at 120 °C for 24 h.

Synthesis of xonotlite [$Ca_6(Si_6O_{17})(OH)_2$] nanowires: The $Ca(NO_3)_2 \cdot 4H_2O$ and $Na_2SiO_3 \cdot 9H_2O$ were dissolved in distilled water, respectively to obtain 0.5 M solutions. The reactant molar ratio of Ca/Si was kept at 1.0. The $Ca(NO_3)_2$ solution was dropwisely added into Na_2SiO_3 solution at room temperature under stirring to obtain a white suspension. Then the suspension was transferred into the Teflon-lined stainless-steel autoclaves and heated at 200 ^{o}C for 24 h, followed by cooling down to room temperature naturally. After the hydrothermal treatment, the suspension was filtrated and washed with distilled water and anhydrous ethanol for three times, respectively. After washing, the remaining liquid was removed by vacuum filtration, and the obtained powders (xonotlite nano-wires) were dried at 120 ^{o}C for 24 h.[1]

Synthesis of hollow $CaCO_3$ microspheres: The $CaCl_2$ (0.2 M) and sodium dodecyl sulfate (SDS) (0.1 M) solutions with the same volume were mixed under vigorous stirring, then the Na_2CO_3 solution (0.2 M) was injected quickly into the above mixed solution under vigorous stirring to obtain a white suspension. The reactant molar ratio of Ca/CO_3^{2-} was kept at 1.0. The white precipitate was then stirred for 1 h followed by washing eight times with distilled water and two times with 100% ethanol. After washing, the remaining liquid was removed by vacuum filtration, and the obtained powders (hollow $CaCO_3$ microspheres) were dried at 120 ^{o}C for 24 h.[2]

For hydrothermal process, the 1 g precursors were mixed with the 85 mL Na_3PO_4 (0.2 M) aqueous solution. Then the mixtures were transferred into 100 mL stainless steel autoclaves under various reaction conditions and cooled to room temperature naturally (Table S1). The mixtures were heated at 120-180 ^{o}C for 24-72 h, followed by cooling to room temperature naturally. After the hydrothermal reaction, the obtained suspension was filtrated and washed with distilled water and anhydrous ethanol for three times, respectively. The resultant powders were dried at 180 ^{o}C for 24 h for further characterization.

Table S1 Summary of the selected reaction conditions and the resultant HAp morphologies.

Sample	Starting Conditions			HAp Product Morphology
	Precursor	Temp. (^{o}C)	Time (h)	
S1	$CaCO_3$ nanoparticles	180	72	Nanoparticles
S2	Xonotlite nanowires	120	24	Nanowires
S3	Hollow $CaCO_3$ microspheres	180	72	Hollow nano-structured microspheres

S1.2. Characterization.

The synthesized precursors and the products after hydrothermal treatment were characterized by X-ray diffraction (XRD: D/max 2550V, Rigaku, Japan) with mono-chromated CuKα radiation, Fourier transform infrared spectroscopy (FTIR: Nicolet Co., USA). The morphology and size of the as-synthesized powders were characterized by field emission scanning electron microscopy (FESEM: JSM-6700F, JEOL, Japan) and field emission transmission electron microscopy (FETEM: JEM-2100F, JEOL, Japan). The chemical composition of the obtained HAp powders was determined by X-ray fluorescence spectroscopy (XRF: PW-2404, Philips, Netherlands). The CO_3^{2-} concentration (evolved as CO_2) of the obtained HAp products was determined using thermogravimetric analyses (TGA, STA 409/PC, Netzsch, Germany). 10 mg HAp powder was heated from 25°C to 950°C at a heating rate of 20 ^{o}C min^{-1}; isothermal at 400 ^{o}C and 950 ^{o}C for 30 min, respectively. The weight loss from 400 to 950 ^{o}C represents the CO_3^{2-} content.[3,4]

Supplementary (S2):

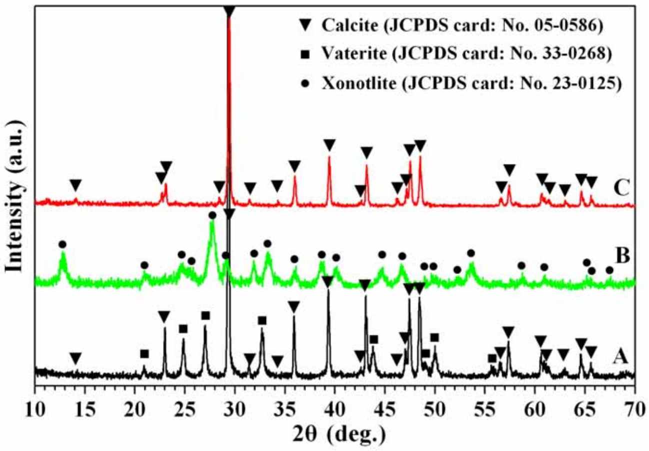

Fig. S1. XRD patterns of $CaCO_3$ nanoparticles (A), $Ca_6(Si_6O_{17})(OH)_2$ nanowires (B) and hollow $CaCO_3$ microspheres (C) precursors. The results suggested that the obtained precursors are well crystalline of the mixtures of calcite and vaterite, xonotlite and calcite, respectively.

Table S2. Chemical composition of the as-synthesized HAp powders in S1-S3.

Sample	Element Concentrations of the as-synthesized HAp powders (wt.%)				
	Na	Si	CO_3^{2-}	Ca/P molar ratio	(Ca+Na)/(P+X) molar ratio*
S1	1.56	–	2.75	1.78	1.76
S2	1.38	2.87	–	1.97	1.71
S3	1.71	–	2.51	1.82	1.80

* X denoted the anions other than PO_4^{3-}.

References:

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