Supporting Information

HPAM-HABS induced synthesis of labyrinth-like surface of calcite via rhombohedral lattice growth from nanoscale

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Experimental Section

Materials

Calcium chloride ($CaCl_2$, AR grade), sodium carbonate ($NaCO_3$, AR grade) were purchased from Tianjin chemical reagent factory. Partially hydrolyzed polyacrylamide (HPAM, weight-average molecular 1.900×10^7, degree of hydrolysis=28%) and heavy alkyl-benzene sulfonate (HABS) were obtained from Daqing Donghao Investment Co.Ltd. All above reagents were obtained from commercial sources and received without further purification. Deionized water was used to prepare aqueous solutions of $CaCl_2$ and $NaCO_3$ just before crystallization experiment, which was made in our laboratory.

Preparation of scrobiculate $CaCO_3$ product

Aqueous solution of $CaCl_2$ (0.04mol/L, 250mL), aqueous solution of $NaCO_3$ (0.04mol/L, 250mL), 0.06g HABS and a certain concentration with 20 mPa·s viscosity of HPAM (1200mg/L, 250mL) were prepared beforehand. Calcium carbonate products were precipitated by the method of quickly pouring 25mL 1200mg/L HPAM solution into a 200mL beaker containing 25mL aqueous solution of $NaCO_3$, 0.06g HABS and 25mL distilled water with rapid stirring for 10 minutes (300 rpm), then pouring 25mL $CaCl_2$ solution and agitated with a magnetic stirrer (300 rpm) for 1 hour providing a constant temperature of 45℃. To study the effect of single component of HABS and HPAM, experiments were carried out by addition HPAM or HABS homogeneously instead of the HPAM-HABS hybrid components in the mother liquor, and experiments in the control system were also done. The resulting precipitates were filtered and washed thoroughly with distilled water. Finally, the product was dried in the oven at 45℃ for 24 hours and used for further measurements.

Characterization

The morphology and size information of precipitated $CaCO_3$ product were characterized on a Zeiss ΣIGMA scanning electron microscope (SEM) equipped with an accelerating voltage of 10kV. Fourier transform infrared spectrum (FT-IR) was performed on Tensor27 by using KBr pellets, with scanning times of 5 times per minute. The powder X-ray diffraction patterns (pXRD) of various precipitated $CaCO_3$ were measured on a Rigaku D/max 2000 pc diffractometer fitted with Cu-Kα radiation under the setting conditions of 40 kV, 20 mA, employing a step size of 10°/min with 2θ ranging from 10° to 80°. The elemental analysis was carried out using an energy dispersive X-ray analyzer (EDX), which was directly connected with the SEM at an accelerating voltage of 20 kV. Transmission electron microscope (TEM) observations were record (Tecnail G2S-Twin F20) at an accelerating voltage of 200 kV, and all samples were prepared by deposition of ethanol dispersions on carbon films supported by a copper grid for TEM and HRTEM measurements.

Calculation method of relative fraction of vaterite and calcite

The relative mole fraction of vaterite and calcite were calculated from their characteristic pXRD peak intensities by the following equation:

$$\frac{I_C^{104}}{I_V^{110}} = 7.691 \frac{X_C}{X_V} \tag{1}$$

$$X_V + X_C = 1 \tag{2}$$

Where X_V is the mole fraction of vaterite, and X_C is calcite. $I_C 104$ and $I_V 110$ are the pXRD intensities of the {104} planes and {110} planes represent calcite and vaterite, respectively.

Lattice calculated method of calcite

The calculated lattice parameters (d-space, Ca-O distance) and crystal structure model were acquired from the professional software (JADE.6 and Find It). And the relative errors in lattice parameters for calcite are smaller by the rigid ion model of previous research.[1]

1 A. Pavese, M. Catti, G.D. Price, *Phys. Chem. Miner*, 1992, **19**, 80-87.
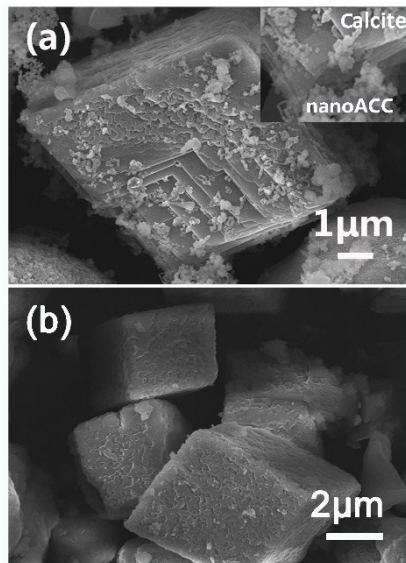
Figures

Fig. S1 SEM images of labyrinth-like CaCO$_3$
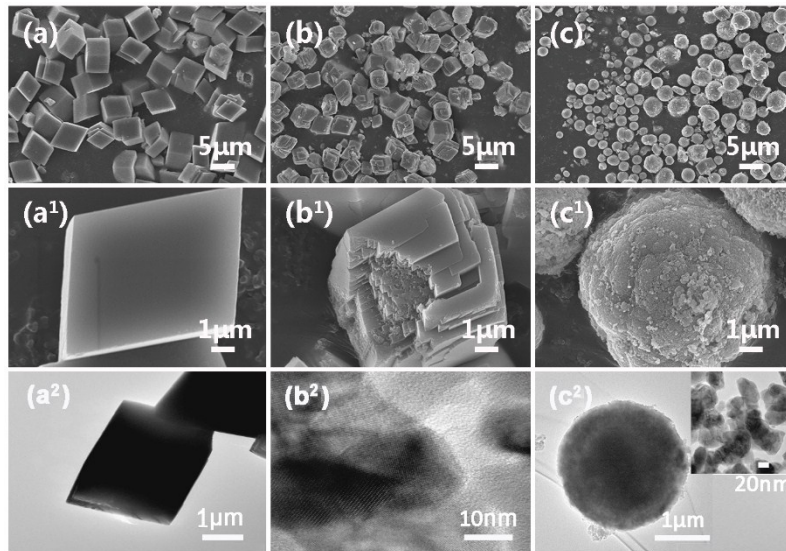
samples generated via rhombohedral lattice.

Fig. S2 SEM and TEM images of CaCO$_3$ obtained in the control system (a), in the single
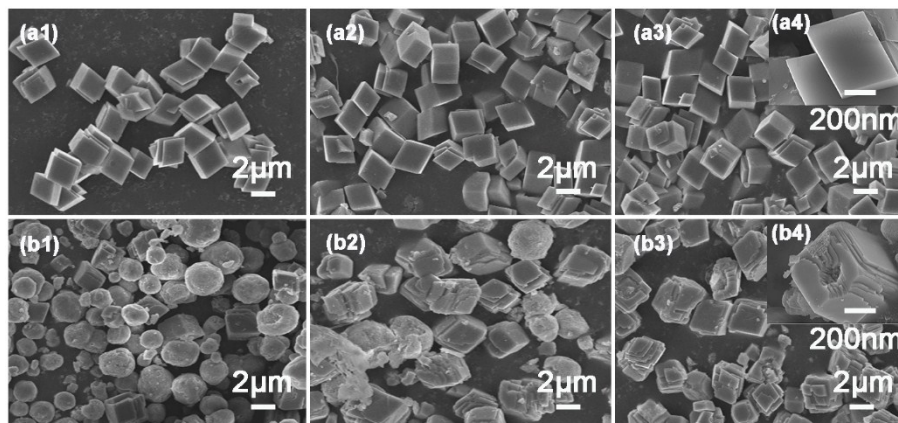
HPAM system (b) and in the single HABS system (c).

Fig. S3 SEM images of CaCO$_3$ obtained in the control system (a) and single HPAM system (b) with various

reaction time (a1, b1: 10mins; a2, b2: 30mins; a3, b3: 60mins.)
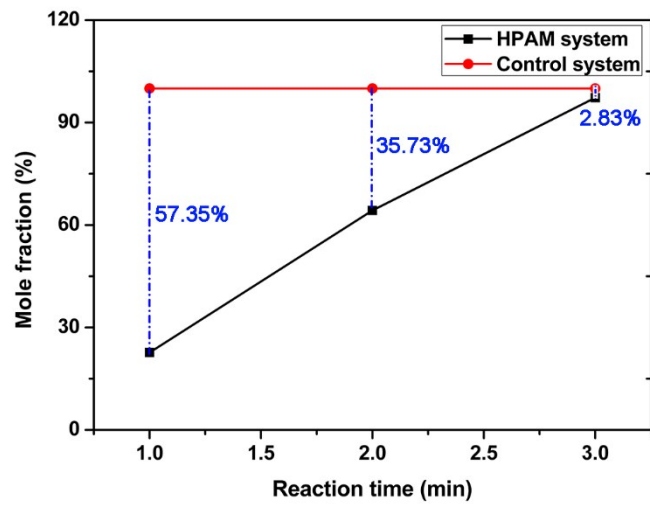
Fig. S4 Fraction of calcite obtained in the control system ( ) and HPAM system ( ).