

Electronic Supplementary Information

Formation of mesoporous calcium sulfate microspheres through phase conversion in controlled calcination

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Experimental

Reagents and materials

Analytic reagent grade ethylene glycol (solvent), anhydrous $(\text{NH}_4)_2\text{SO}_4$, and Na_2EDTA were purchased from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. Analytic reagent grade anhydrous CaCl_2 (Sigma-Aldrich Co., Llc. USA) and Ibuprofen (IBU, Tokyo Chemical Industry Co., Ltd. Tokyo, Japan) were used as received.

Synthesis and calcination of α -HH microspheres

Monodisperse α -HH microspheres with a diameter of $\sim 2 \mu\text{m}$ were synthesized by mixing 40 mM CaCl_2 and $(\text{NH}_4)_2\text{SO}_4$ solution in the presence of 10 mM Na_2EDTA at 95°C and the volume ratio of ethylene glycol to water (G/W) of 5.0.¹ Calcination of α -HH microspheres were conducted to obtain mesoporous calcium sulfate microspheres at various temperatures from 400°C to 800°C (with a deviation of $\pm 2^\circ\text{C}$) and times in programmable integrated electric furnace (SSXF-4-13Q, Lantian Co., Ltd. Hangzhou, China) in air as reaching the desired temperature. Samples were taken out immediately after given time and cooled at room temperature.

Adsorption of IBU

The nonsteroidal analgesic and anti-inflammatory drug IBU² was chosen as model drug to test the drug loading capacity of mesoporous calcium sulfate microspheres. Typically, 0.2 g of mesoporous calcium sulfate microspheres was added into 20 mL of hexane solution at different IBU concentrations of 0.25, 0.50, 0.75, 1.00, 1.25 and 1.50 mg/mL at 25°C . The mixtures were ultrasonically treated for 2 min and soaked for 24 h with constant stirring in a conical flask which was sealed to prevent the

evaporation of hexane. The IBU-loaded mesoporous calcium sulfate microspheres were separated by centrifugation, washed with hexane for several times and then dried at 60°C for 12 h. The IBU loading amount was examined after the dissolution of calcium sulfate microspheres in phosphate buffered saline (PBS) by UV-vis spectroscopy at a wavelength of 264 nm.

Characterization

The mesoporous calcium sulfate microspheres were examined by a powder X-ray diffractometer (XRD, D/Max-2550 pc, Rigaku Inc., Tokyo, Japan) with Cu K α radiation at a scanning rate of 2°/min in the 2θ range from 5° to 80°, thermogravimetry/differential scanning calorimetry analysis (TG/DSC, NETZSCH STA 409 Luxx, Selb/Bavaria, Germany) and Fourier transform infrared analysis (FTIR, IRAffinity-1, Shimadzu, Japan) over the frequency range of 400-4000 cm⁻¹ for phase and composition identification. The morphology evolution was observed by field emission scanning electron microscopy (FESEM, SU8010, Hitachi, Tokyo, Japan). The porous properties of the products were measured by N₂ adsorption at -195.8°C on a specific surface area and porosity analyzer (Micromeritics, ASAP2020M, USA). UV-visible spectra were conducted to analyze the IBU concentration on a UV-visible spectrophotometer (UV-vis, DRS: TU-1901, Shanghai, China).

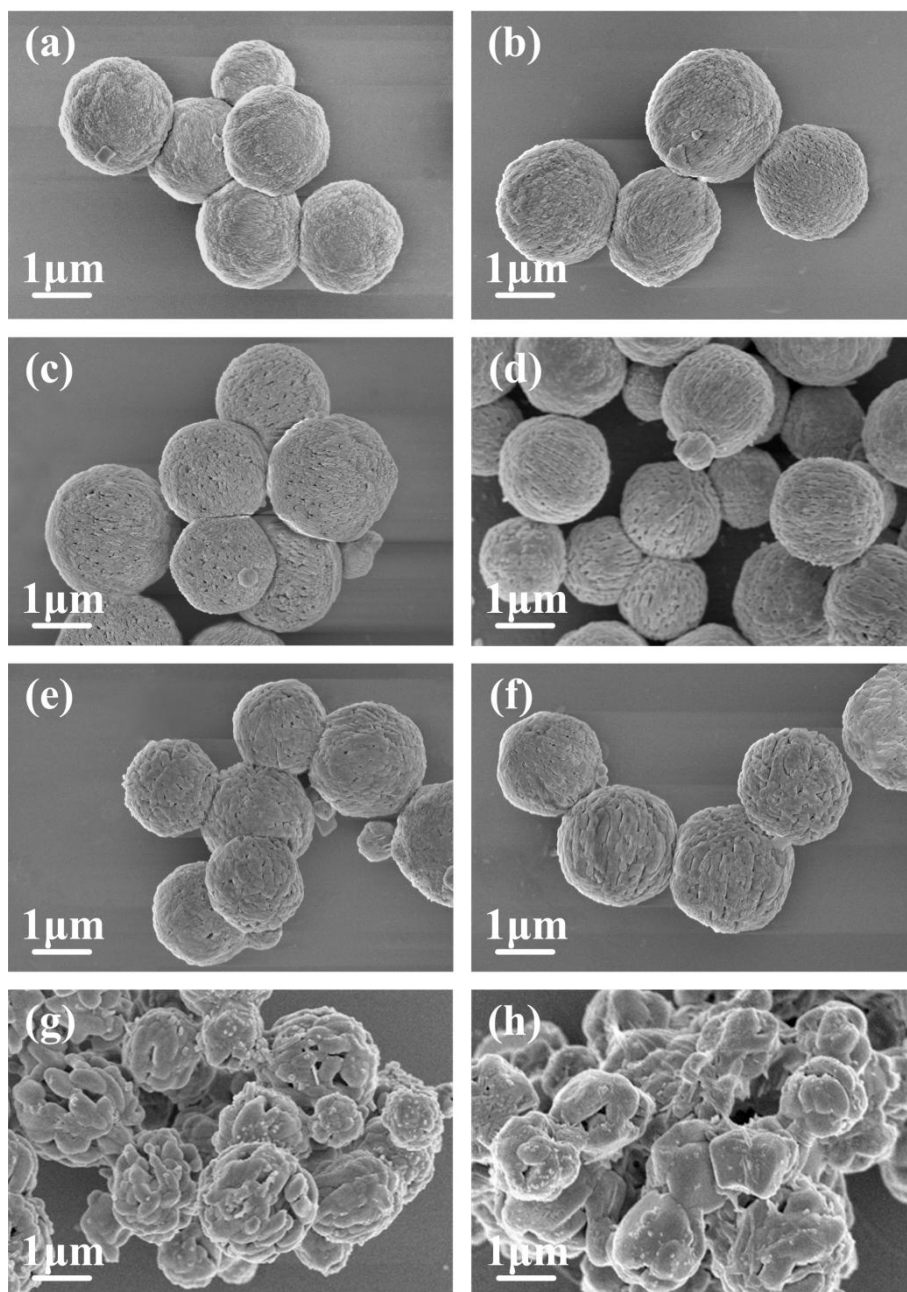


Fig. S1 Low magnification FESEM images of as-formed α -HH microspheres (a) and microspheres calcined at temperature of 200°C (b), 300°C (c), 400°C (d), 500°C (e), 600°C (f), 700°C (g) and 800°C (h) in air for 180 s.

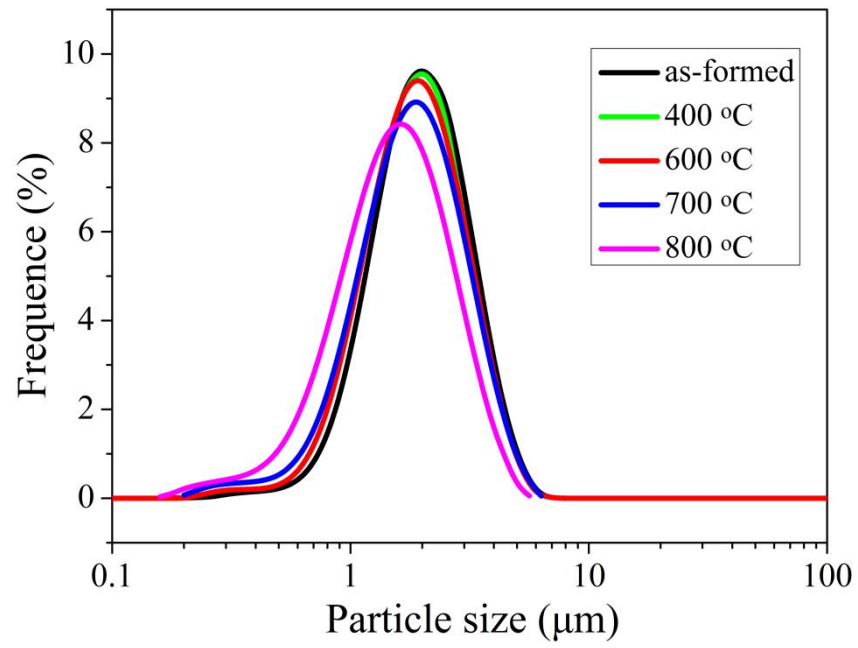


Fig. S2 The particle size distributions of as-formed α -HH microspheres and microspheres calcined at temperature of 400°C, 600°C, 700°C and 800°C in air for 180 s.

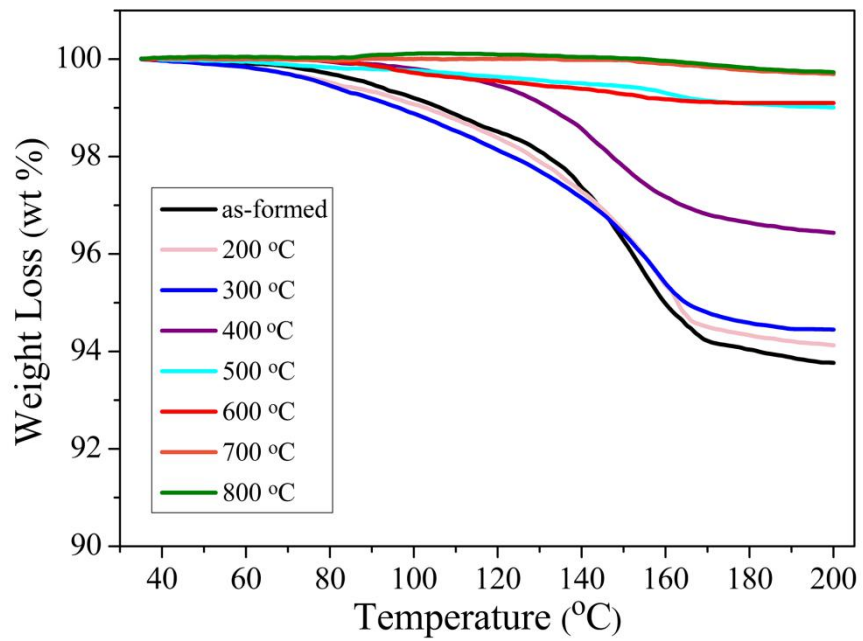


Fig. S3 TG curves of as-formed α -HH microspheres and microspheres at temperatures from 200 to 800°C in air for 180 s.

Table S1. Surface areas of calcium sulfate microspheres calcined at different temperatures from 400 to 800°C in air for different times from 10 to 300 s.

$T(^{\circ}\text{C}) \backslash t(\text{s})$	10	20	30	40	50	60	90	120	150	180	210	240	270	300
400	3.21	4.08	6.11	7.48	8.52	9.66	10.23	12.89	15.57	18.3	20.15	22.7	16.34	13.75
500	2.18	3.77	6.69	8.22	13.48	15.43	24.87	30.62	25.41	20.67	18.16	10.78	7.63	4.43
600	3.21	5.67	11.5	12.64	16.35	17.39	26.48	17.94	14.71	9.19	7.19	5.57	3.42	2.38
700	11.02	15.7	23.71	21.04	18.36	15.21	12.78	10.24	7.26	5.8	4.01	3.28	2.13	2.09
800	18.59	16.36	15.33	14.71	12.56	11.63	8.68	5.13	4.05	2.9	2.45	1.9	1.54	1.27

References

- 1 Q. Chen, G. Jiang, C. Jia, H. Wang and B. Guan, *CrystEngComm*, 2015, **17**, 8549-8554.
- 2 C. Hu, S. Liu, Y. Zhang, B. Li, H. Yang, C. Fan and W. Cui, *Acta Biomater.*, 2013, **9**, 7381-7388.