

## Electronic Supplementary Information

### A facile method to control the structure and morphology of $\alpha$ -calcium sulfate hemihydrate

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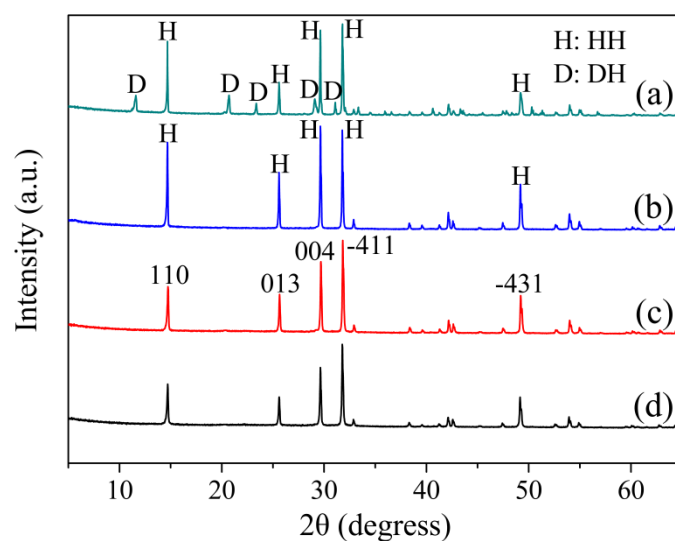
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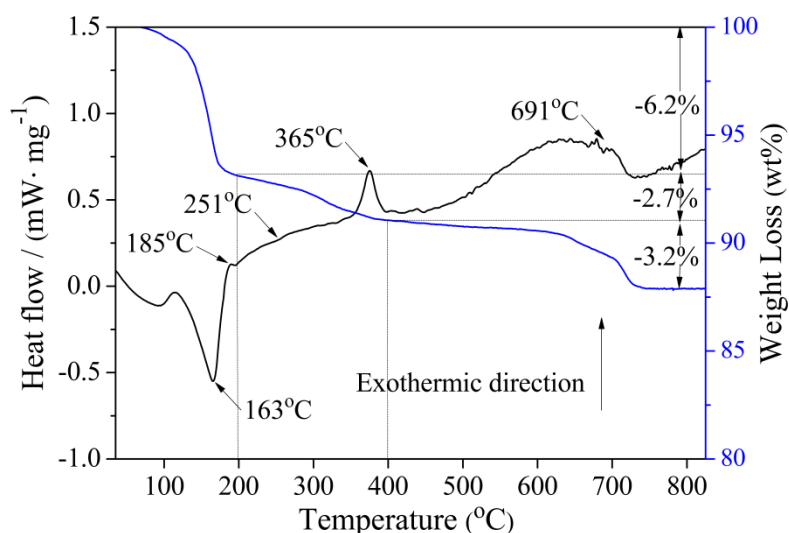
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Figure S1 shows the typical XRD patterns of the crystals synthesized at the volume ratio of ethylene glycol to water (G/W) from 0.4 to 2.5. The existence of dihydrate phase of calcium sulfate (DH, PDF-ICDD 33-0311) produced at G/W 0.4 is confirmed by the peaks at 11.57°, 20.71°, 29.08°, 31.08° and 43.60°. The typical peaks at 14.68°, 25.62°, 29.70° and 31.89° reveal the crystals synthesized at G/W 0.7 to 2.5 are composed of pure hemihydrate phase of calcium sulfate (HH, PDF-ICDD 047-0964).



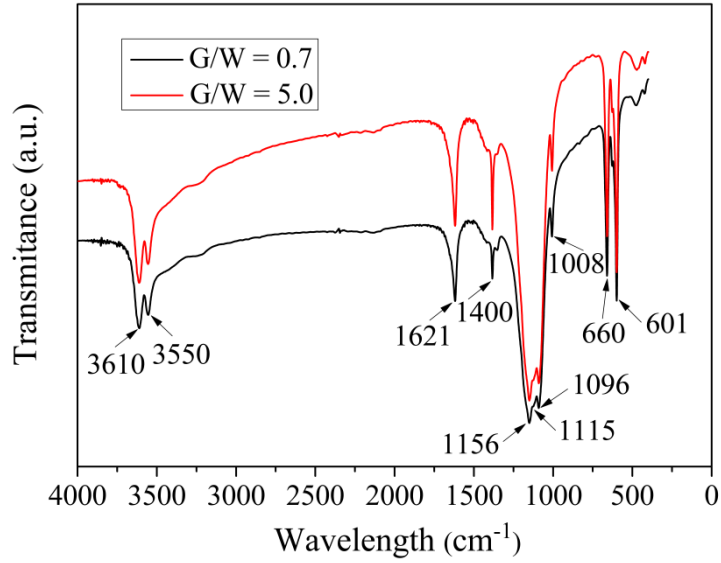
**Figure S1.** XRD patterns of crystals synthesized at 95°C with different G/Ws at: (a) 0.4, (b) 0.7, (c) 1.5 and (d) 2.5.

The TG/DSC analysis of crystals synthesized at G/W of 0.7 shows three discrete phase transformations (Figure S2). The first weight loss (- 6.18 wt%) occurring at 35 - 200°C, corresponding to the theoretical one (- 6.21 wt%) of 0.5 crystal water elimination, denotes pure  $\alpha$ -HH phase, based on the endothermic peak at 163°C and the exothermic peak at 185°C on the DSC curve. The second weight loss (- 2.71 wt%) at 200 - 400°C is ascribed to the pyrolysis of Na<sub>2</sub>EDTA according to the endothermic peak at around 251°C and the exothermic peak at 365°C. Subsequent elimination of the remained organic materials (carbon and organic compounds) occurring at 700 - 800°C results in a weight loss of - 3.23 wt%, bringing a large and broad exothermic peak at 691°C.



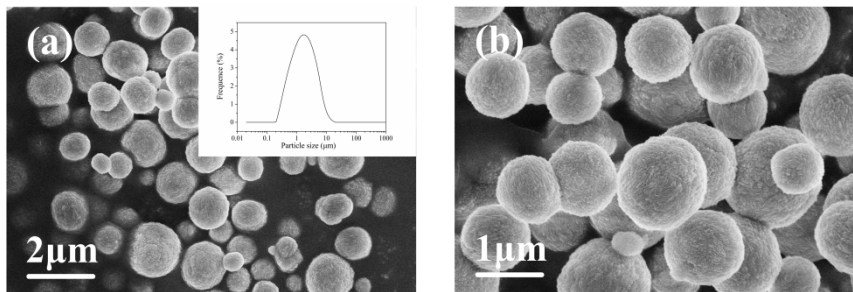
**Figure S2.** TG and DSC curves of crystals synthesized at 95°C with G/W of 0.7.

The composition of the  $\alpha$ -HH obtained at a low G/W of 0.7 and a high G/W of 5.0 were analysed respectively by FTIR (Figure S3). The characteristic peaks emerging at 3610, 3550, 1156, 1115, 1096, 1008, 601 and 660 cm<sup>-1</sup> further verify that the crystals are formed in  $\alpha$ -HH phase. The two sharp picks at 1400 and 1621 cm<sup>-1</sup> show the existence of Na<sub>2</sub>EDTA.



**Figure S3.** FTIR spectra of  $\alpha$ -HH crystals synthesized at 95°C with G/W 0.7 and 5.0.

Figure S4 shows the morphology and particle size distribution of  $\alpha$ -HH particles synthesized in 60 mM  $\text{CaCl}_2$  and 20 mM  $\text{Na}_2\text{EDTA}$  at 95°C and G/W of 5.0.  $\alpha$ -HH particles present in the shape of sphere with a diameter of  $\sim 1.4 \mu\text{m}$  and the particle size distribution can be characterized by a lognormal function.



**Figure S4.** Low resolution (a) and high resolution (b) SEM images and particle size distribution (inset) of  $\alpha$ -HH particles synthesized in 60 mM  $\text{CaCl}_2$  and 20 mM  $\text{Na}_2\text{EDTA}$  at 95°C and G/W of 5.0.