Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Formation of Spherical Calcium Sulfate Mesocrystals: Orientation Controlled by Subunit Growth

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The microspheres synthesized in ethylene glycol-water solution at 95 °C are demonstrated to be pure HH by the diagnostic peaks at 14.72°, 25.65°, 29.71°, 31.87° and 49.34° in XRD pattern, corresponding to planes of (200), (020), (400), (204) and (424), respectively (Fig. S1).

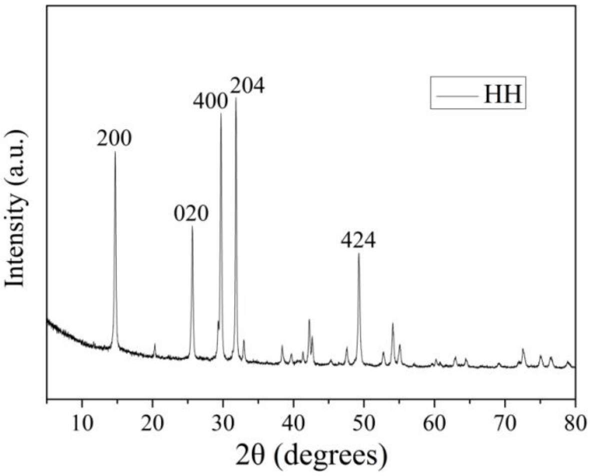

Fig. S1 XRD pattern of the microspheres synthesized in ethylene glycol-water solution with Na_2EDTA at 95 °C for 3 h to confirm the pure HH phase of the microspheres.

As the growth of external subunits into rod-like shape, a core-shell structure appears in the intermediate stage of the orientation evolution process (Fig. S2). At reaction time of 30 min, the shell thickness is about 500 ± 36 nm. The shell thickness increases gradually with the extension of reaction time until the core-shell structure disappears at the point the mesocrystal structure forms.

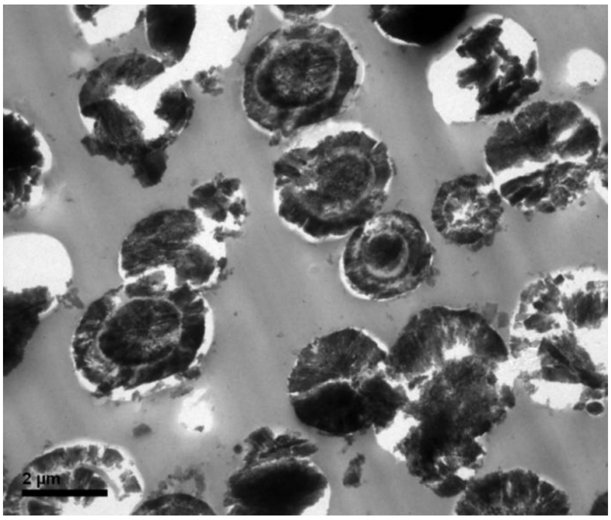

Fig. S2 TEM image of α-HH microsphere cross-sections obtained by ultramicrotomy after 30 min reaction at 95 ^{o}C to exhibit the appearance of core-shell structure during the formation of mesocrystals.

Fig. S3 presents the TG curves of α-HH microspheres obtained at different reaction times. The weight losses at temperature lower than 200 °C are attributed to the elimination of crystal water in α-HH, while the weight reductions in range of 200 to 800 °C represent the decomposition of EDTA. The microsphere contains 13.06 wt% EDTA at the early stage of 5 min. The weight loss decreases to 11.93 wt% at 1 h, indicating the EDTA is gradually excluded as the growth of subunits. When the mesocrystal forms at 3 h, the EDTA content in microspheres is 9.46 wt%. In the subsequent stage, the excretion of EDTA continues, gradually dropping to 6.25 wt% at 6 h and finally to only 2.07 wt% at 12 h.

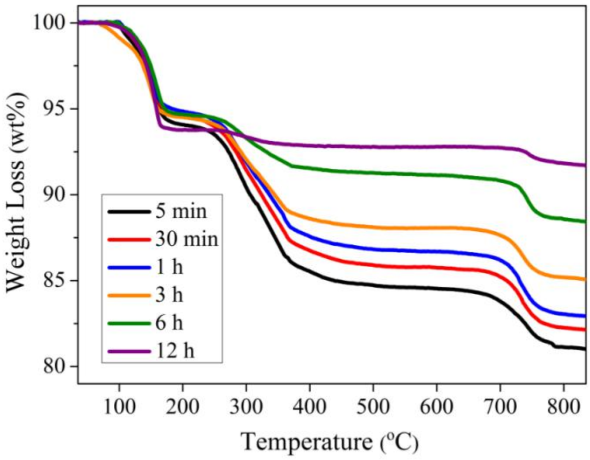

Fig. S3 TG curves of α-HH microspheres synthesized in ethylene glycol-water solution with reaction time of 5 min, 30 min, 1 h, 3 h, 6 h and 12 h at 95 °C to demonstrate the exaction of EDTA from the microspheres.

The concentration change of SO_4^{2-} ions within the reaction time of 12 h is shown in Figure S4. The SO_4^{2-} concentration, which is 40 mM at the beginning, drops sharply to 24.01 mM in the initial 2 min and decreases rapidly to 14.09 mM at 5 min. In first stage, 64.78 wt% SO_4^{2-} ions are consumed for the nucleation and self-assembly. In the subsequent growth stage, SO_4^{2-} ions experience a gentle decline to 10.87 mM at 1 h and reaches 8.35 mM at 3 h when the α-HH mesocrystal forms. After 3 h, the crystalline growth is really slow and the SO_4^{2-} concentration gradually decreases to about 5.20 mM at 12 h.

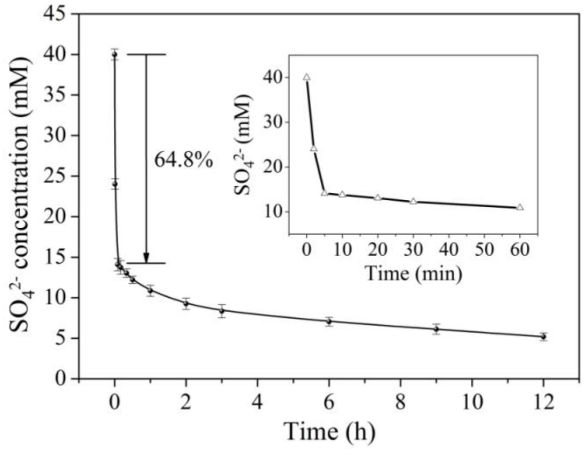

Fig. S4 Concentration change of SO_4^{2-} ions in the reaction solution at 2 min, 5 min, 10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 6 h, 9 h and 12 h to show the consumption of SO_4^{2-} ions at different stages.

The growth of the subunits in α-HH microspheres involves several paths. The partial crystalline fusion and dissolution-recrystallizaion contribute to the shape change of the subunits. In addition, the Ca^{2+} ions released from the Ca-EDTA complexes and the free SO_4^{2-} ions in the solution can also supply the growth of the subunits in form of ions or clusters (Fig. S5a). The orientation evolution of the subunits is considered to attribute to the EDTA interspaced in the microspheres. EDTA has four carboxylate groups and two are used in Ca-EDTA interaction. The other two respectively serving as the free hydrogen bonding donor (hydroxyl) and acceptor (carboxylate) group can interact with the nearby EDTA. The intermolecular hydrogen bonds align EDTA side-by-side to form a well-ordered organization, which accounts for the orientation of α-HH subunits due to the electrostatic interactions between carboxylate groups and Ca^{2+} ions (Fig. S5b).

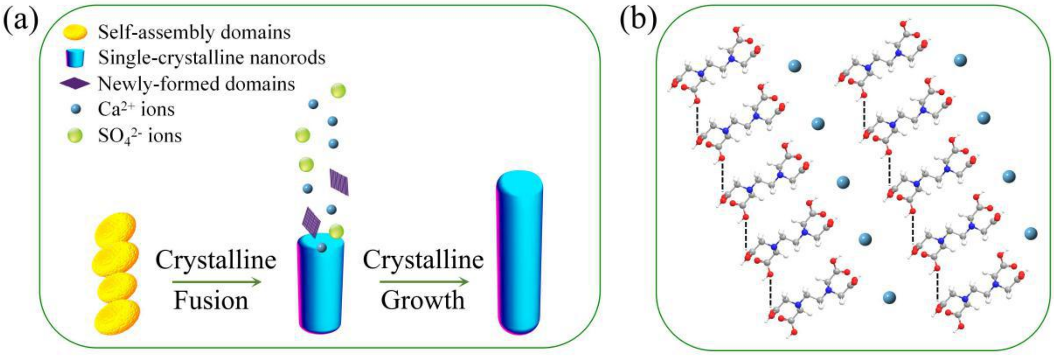

Fig. S5 Schematic illustration of the crystalline growth of the subunits into nanorods (a) and orientation mechanism of the subunits resulted from the ordered alignment of EDTA ions (b).