Supporting Information

Mussel-Inspired Dynamic Facet-Selective Capping Approach to Highly Uniform α-Calcium Sulfate Hemihydrate Crystals

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Comment S1: Materials and characterization for DPA-PEI and α-HH crystals

Materials: All of the chemicals and solvents used in the experiment were of analytical grade without further purification. Gypsum ($CaSO_4 \cdot 2H_2O$), calcium chloride, potassium chloride, sodium hydroxide, and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Dialysis bags (with cut off molecular weight of 3 kDa) were purchased from Shanghai Green Bird Science and Technology Development Co. (Shanghai, China). 3-(3,4-Dihydroxyphenyl) propionic acid (DPA) (98%), branch poly(ethylenimine) (PEI) (MW = 20 kDa with a ratio of 1:2:1 of primary: secondary: tertiary amines), and N-ethyl-N'-(3-dimethylaminopropyl)-carbodimide hydrochloride (EDC) (99 %) were purchased from Sigma-Aldrich.

Characterization: Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Rotaflex Dmax-2500 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) measurements were performed on a JEOL JSM-6700F microscope operated at 5 kV. Transmission electron microscopic (TEM) images were acquired on a JEOL JEM-2100F microscope with accelerating voltage of 200 kV. Thermogravimetry and differential scanning calorimetry (TG-DSC) were performed on a STA-409PC analyzer (Netzsh, Germany) with a heating rate of 5 °C min^{-1} in a nitrogen atmosphere. Fourier transform infrared (FT-IR) characterizations were done on a Bruker Tensor 27 FTIR spectrometer. ^{1}H NMR spectra were collected on a Varian Mercury Plus-400 MHz spectrometer using D_2O as the solvent and TMS as an internal standard. Compressive and flexural strengths of the crystals after hydration setting were performed on a MTS-810 analyzer (MTS, USA) following the procedure in accordance with ASTM C 472-1999, and the result was expressed as an average value of at least three independent determinations.

Comment S2: Synthesis of 3-(3,4-dihydroxyphenyl)propionic acid grafted poly(ethylenimine) (DPA-PEI)
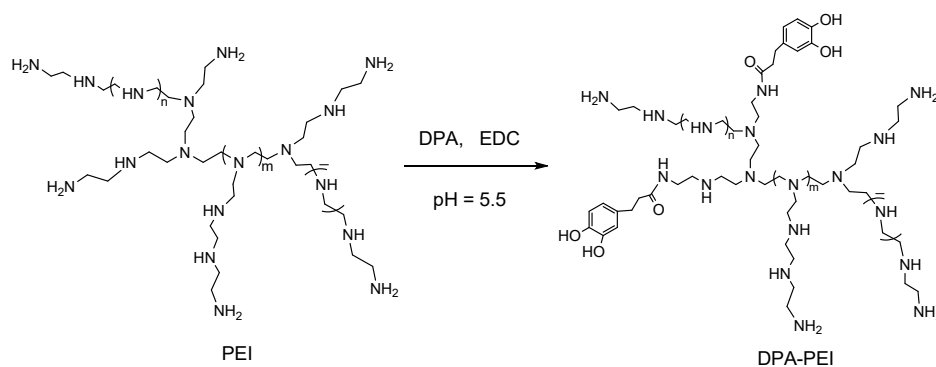
Synthetic route of DPA-PEI.

The synthesis was performed by following a reported procedure[1] with some modification, and exemplified using synthesis of the DPA-PEI with a 30% substation degree. Briefly, PEI (2.0 g, M_w = 20000 g mol^{-1}) was dissolved in 200 mL of deionized water adjusted to pH 5.5 using 1 M HCl solution. 3-(3,4-dihydroxyphenyl)propionic acid (DPA,1.06 g, 5.8 mmol) and EDC (2.24 g, 11.6 mmol) were added. The reaction was carried out at room temperature for 2.5 h during which the solution pH was kept at 5.5 by adding proper amount of 1.0 M NaOH. After reaction, the resultant mixture was dialyzed using a dialysis membrane against distilled water for 3 d to remove unreacted chemicals and byproducts. The substitution degree of DPA on the PEI chain was estimated to be 30% by the ninhydrin test.[2] The polymer has a weight-average molecular weight (M_w) of 26365 g mol^{-1} as characterized with GPC and a isoelectric point (pI) of 9.41 determined by a capillary isoelectric focusing-whole column imaging detection.[3] The molecular structure of the polymer was characterized by ^{1}H NMR and FT-IR.

^{1}H NMR (400 MHz, D$_2$O): δ = 2.42 (t, J = 8.0 Hz, 2H, Ar-CH$_2$), 2.40 (t, J = 8.0 Hz, 2H, O=C-CH$_2$), 2.69(m, 53H, PEI-CH$_2$), 6.55 (d, J = 8.0 Hz, 1H, Ar), 6.67(s, 1H, Ar), 6.72 (d, J = 8.0 Hz, 1H, Ar) ppm. FT-IR (KBr) v: 3445 s (NH), 2932-2850 s (CH$_2$), 1652 m (CO-NH); 1525 w (NH); 1475 w (Ar); 1043 s (C-N) cm^{-1}.

Comment S3: Controlled growth of α-HH crystals

A mixed solution (60 mL H_2O, 15.5 g $CaCl_2$, 0.5 g KCl and DPA-PEI, 0-5.0 g L^{-1}, Mw = 26365 g mol^{-1}) with different pH (4.0~8.5) was added into a 250 mL three-neck flask reactor equipped with a glass condenser. Then 47 g of gypsum ($CaSO_4 \cdot 2H_2O$) was introduced to form a slurry with stirring by a Teflon impeller at a constant rate of 180 rpm. The mixed solution was heated at a fixed temperature (97 ± 0.5 °C). During the reaction, aliquots of 5 mL slurry were withdrawn at fixed time intervals and filtrated by vacuum filtration. The solid samples were immediately washed with boiling deionized water twice and dried at 45 °C in an oven for 2 h for characterizations.

Comment S4: Mechanical strength measurement

Compressive and bending strengths of hydration molding of α-HH

The preparation of hydration molding of α-HH was done according to the procedures descried in GB/T 17669.3 (China national standard for gypsum plasters). The weight ratio of water to α-HH crystals in modeling was 0.32. The paste was cast into a stainless steel mold with the size of 20 × 20 × 80 mm and compacted by jolting. After maintained for 2 h, the molding block was demolded and stored in a curing chest maintained at 25 ± 2 °C and 65 ± 5% RH for 7-10 days. The molding block was tested for bending strength measurement with three-point loading in a span of 50 mm. The loading rate was 0.02 kN/s. The compressive strength was measured with a loading area of 0.0004 m^2 and loading rate of 0.6 kN/s. All measurements were done in triplicate.
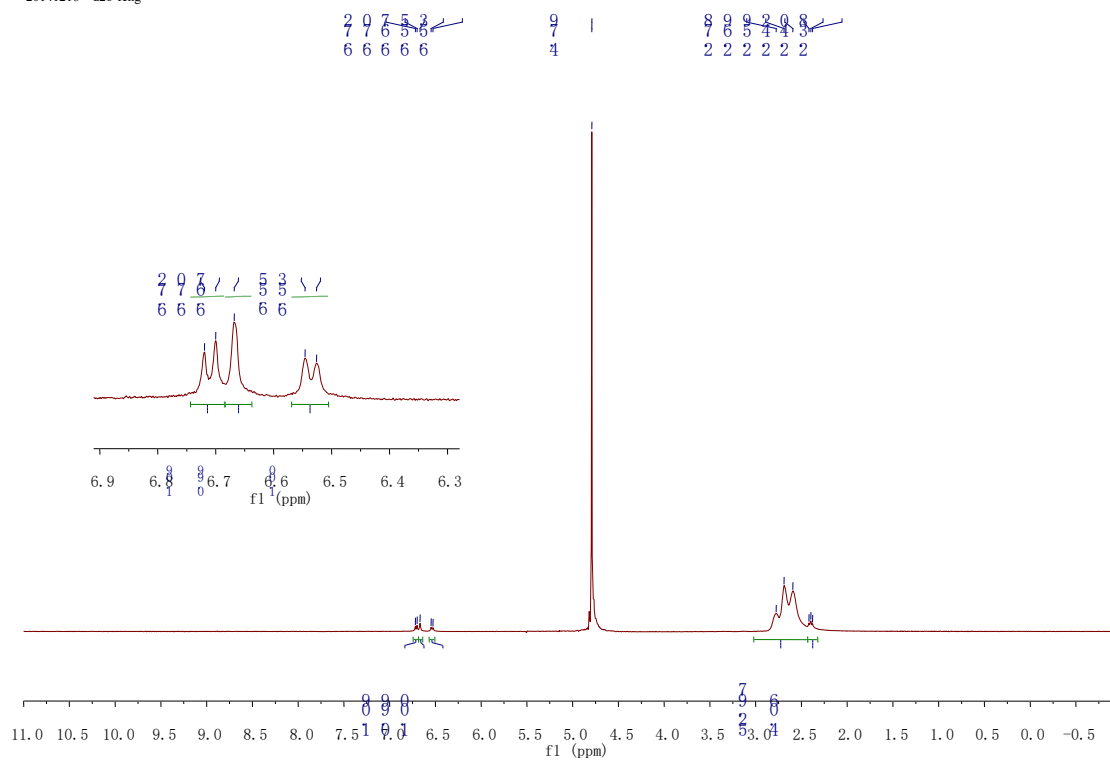
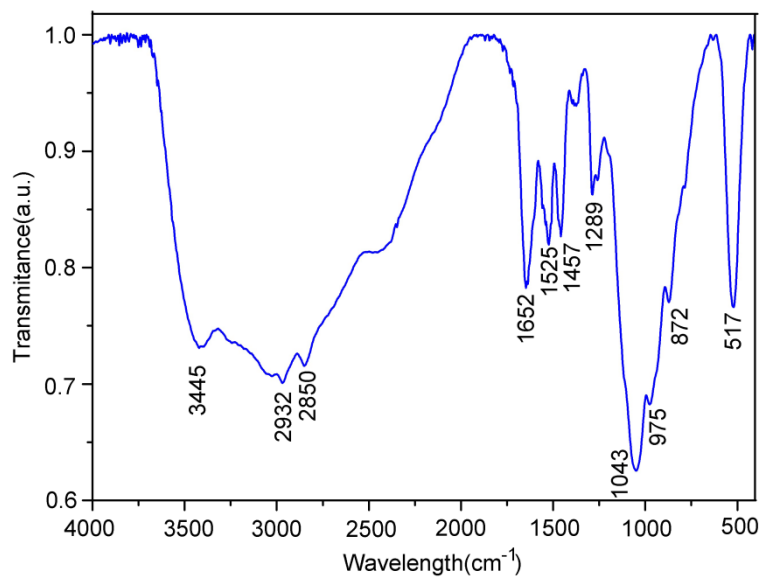**Fig. S1** ^{1}H NMR of DPA-PEI with a DPA substitution degree of 30%.

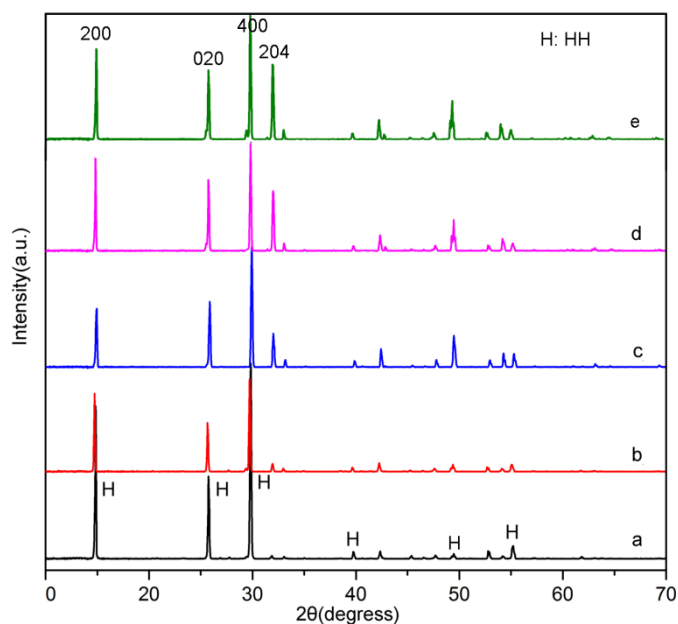**Fig. S2** FT-IR spectrum of DPA-PEI with a DPA substitution degree of 30%.

Fig. S3 XRD patterns of HH crystals synthesized at different concentrations.

(DPA-PEI: (a) 0.0 g L^{-1}, (b) 1.0 g L^{-1}, (c) 2.0 g L^{-1}, (d) 3.0 g L^{-1}, (e) 5.0 g L^{-1} (pH = 5.5)).

The XRD patterns show main peaks at 2θ of 14.7°, 25.6°, and 29.7°, which can be iundexed to a pure HH phase (PDF-ICDD 047-0964).
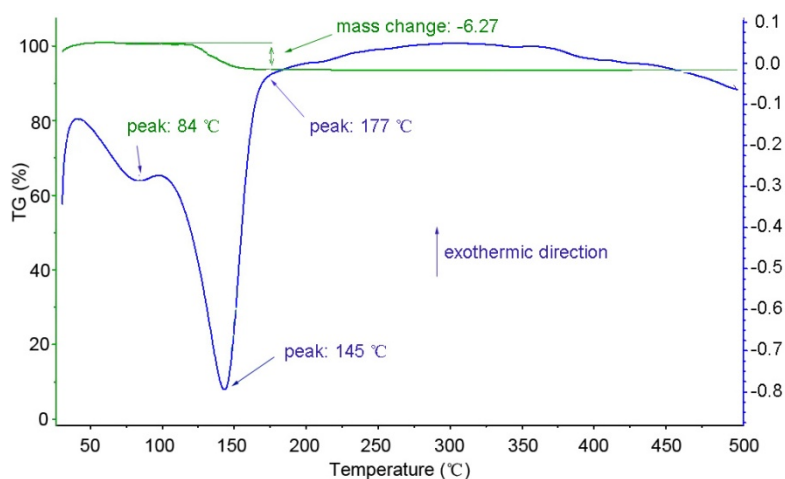

Fig. S4 TG-DSC curves of α-HH crystals synthesized at pH 5.5 and DPA-PEI 2. 0 g L^{-1}.

The TG curve reveals a water release of 6.27 wt % when the crystals are heated from 132 to 180 ℃, which is approximate to the theoretical crystal water content of 6.21 % in α-HH. The simultaneous DSC curve shows an endothermic peak at ~145 °C, followed by an exothermic peak

at ~177 ℃, which is the characteristic profile of the α-HH crystal phase.[4] Thus the obtained crystals are pure α-HH crystals, in accordance with the result from XRD.
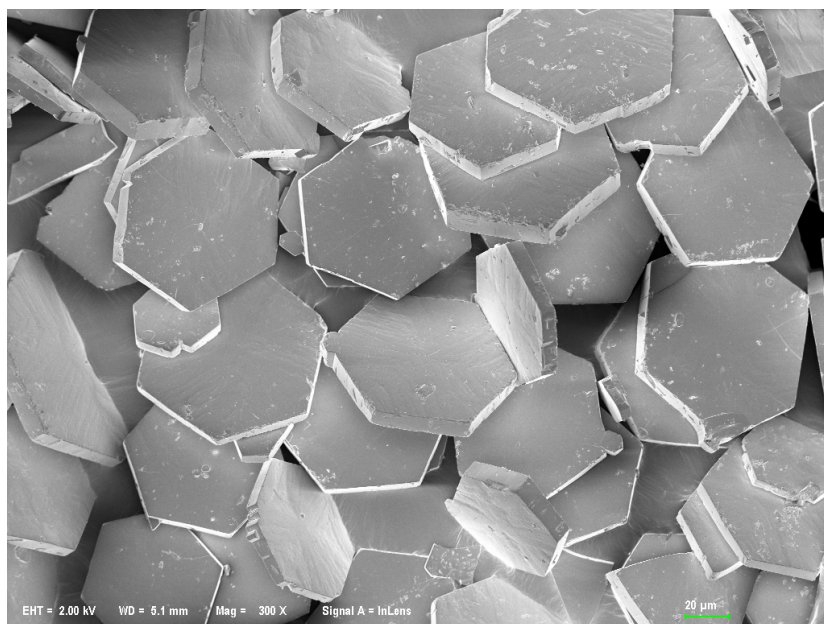

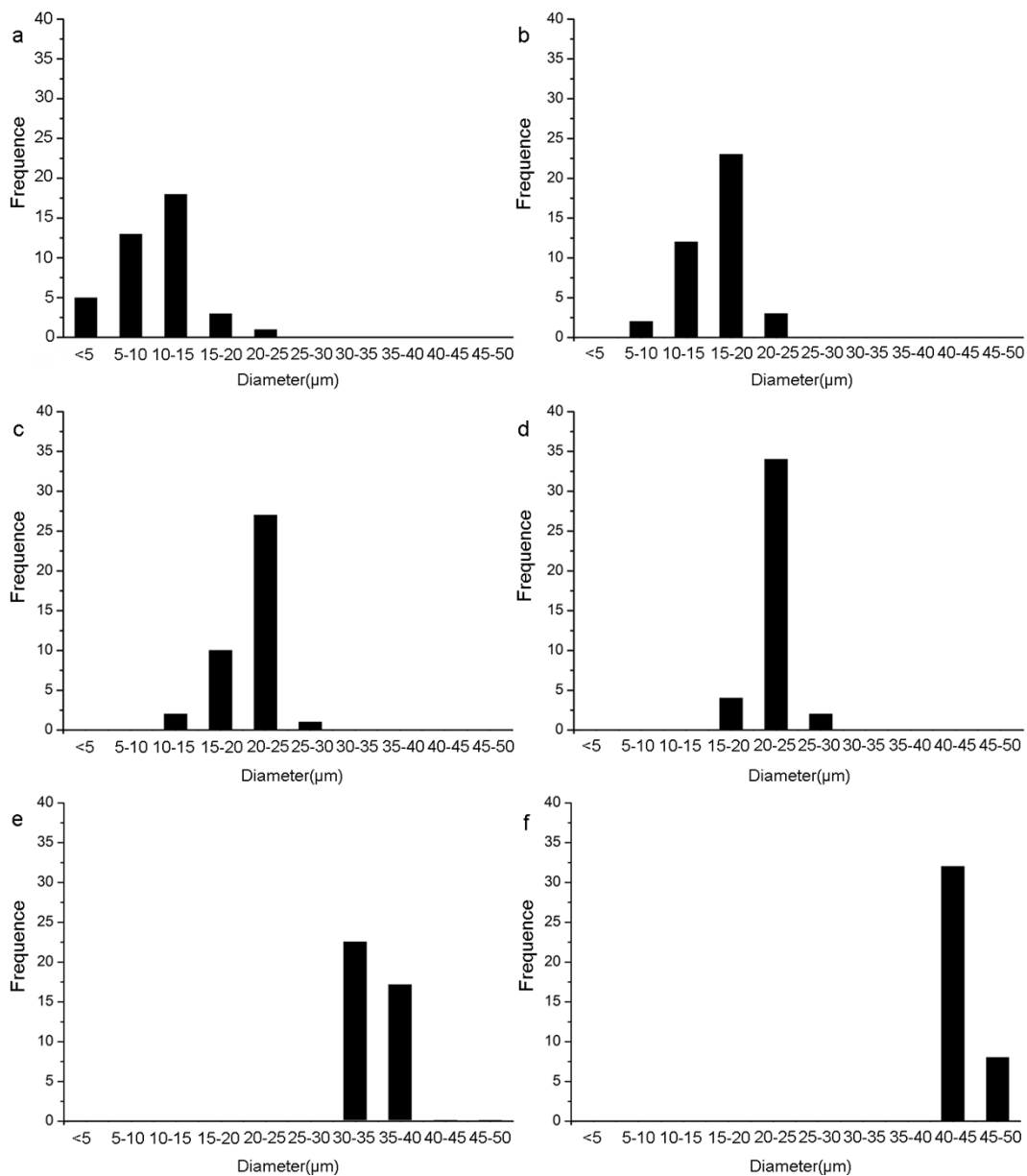**Fig. S5** SEM images of α-HH crystals with thin hexagonal plates.

Fig. S6 Diameter distributions of α-HH crystals synthesized at different concentrations.

(DPA-PEI: (a) 0.0 g L^{-1}, (b) 1.0 g L^{-1}, (c) 2.0 g L^{-1}, (d) 3.0 g L^{-1}, (e) 4.0 g L^{-1}, (f) 5.0 g L^{-1}
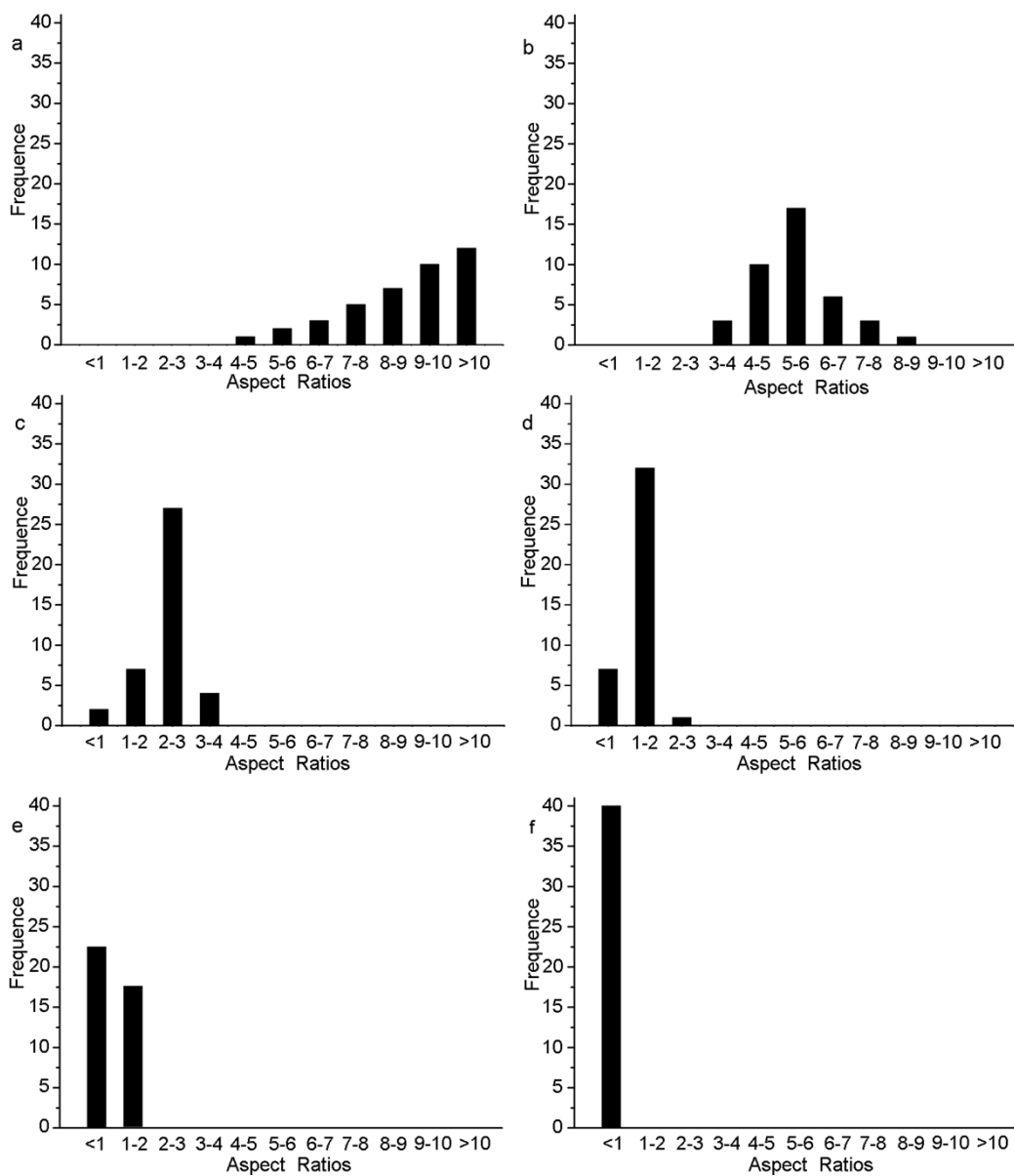
(pH = 5.5)).

Fig. S7 Aspect ratio distributions of α-HH crystals synthesized at different concentrations.

(DPA-PEI: (a) 0.0 g L^{-1}, (b) 1.0 g L^{-1}, (c) 2.0 g L^{-1}, (d) 3.0 g L^{-1}, (e) 4.0 g L^{-1}, (f) 5.0 g L^{-1}
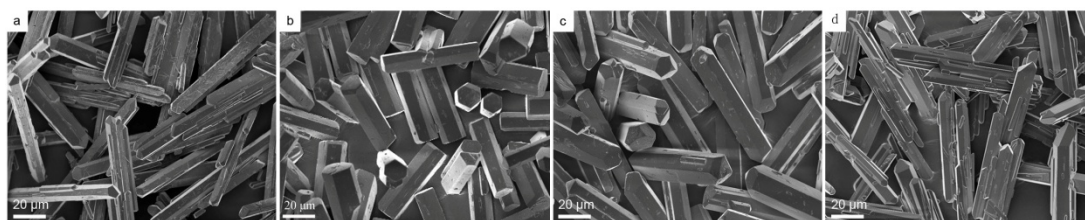
(pH = 5.5)).

Fig. S8 SEM images of α-HH crystals synthesized at different pH.

((a) pH 4.0, (b) pH 5.5 ,(c) pH 7.0, (d) pH 8.5 (DPA-PEI = 2. 0 g L^{-1})).
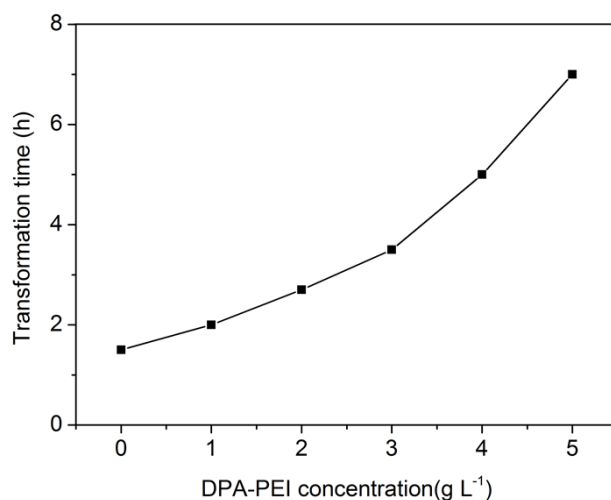
Fig. S9 Concentration effect of DPA-PEI on the time for complete transformation of α-HH from
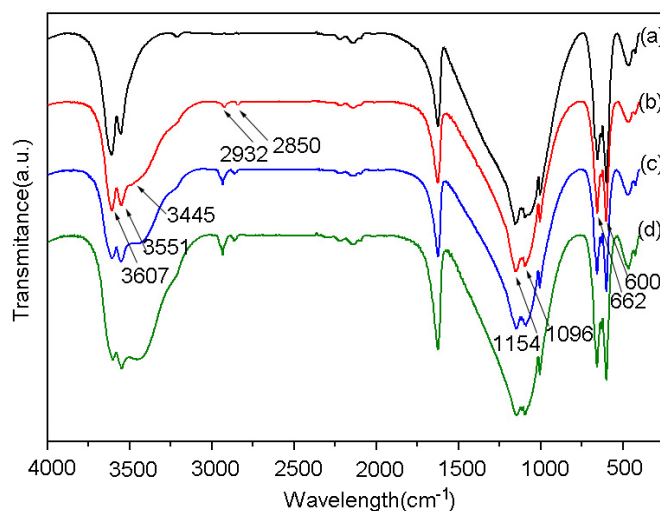
gypsum (pH = 5.5).

Fig. S10 FT-IR spectra of α-HH synthesized at different concentrations of DPA-PEI.

((a) 0.0 g L^{-1}, (b) 1.0 g L^{-1}, (c) 3.0 g L^{-1}, (d) 5.0 g L^{-1} (pH = 5.5)).

Fig. S10 shows the FT-IR spectra of α-HH synthesized without and with the existence of

DPA-PEI. The bands at 1154, 1096, 662 and 600 cm^{-1} can be assigned to SO_4^{2-} stretches and the

bands at 3607 and 3551 cm^{-1} can be assigned to O-H stretching. The bands at 3445 cm^{-1} can be

assigned to N-H stretching, which increases in width with an increase in the concentration of

DPA-PEI (Figure S9b-d). Two bands are observed in the region of 2800-3000 cm^{-1}, which are

assigned to the asymmetric (2932 cm^{-1}) and symmetric (2850 cm^{-1}) stretching vibrations of CH_2.

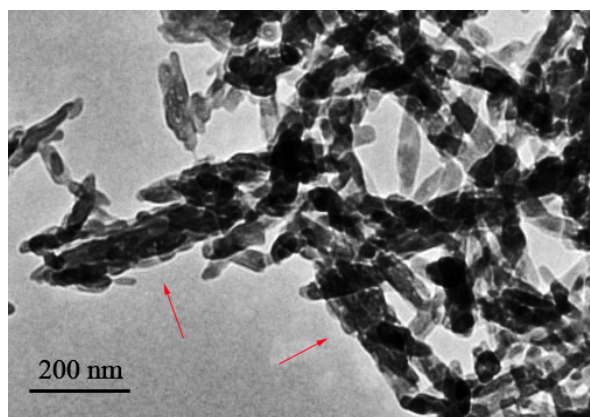The data indicate the presence of DPA-PEI on crystal surface.

Figure S11. TEM image of the oriented aggregation state of nanorods after growth for 1 h. (at DPA-PEI 1.0 g L^{-1} and pH 5.5. Red arrows highlight the co-oriented nanorods in the aggregates).
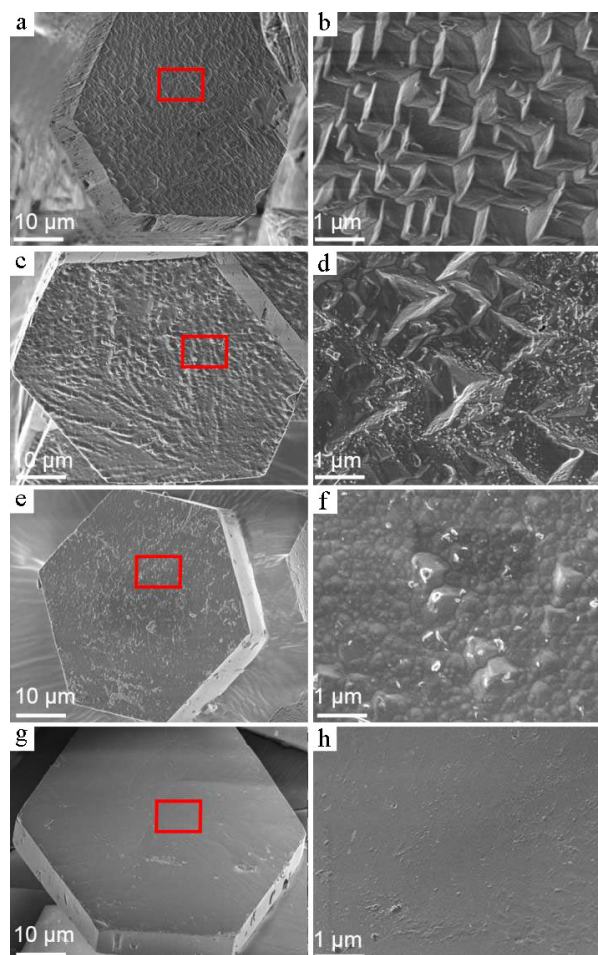

Fig. S12 {002} facets evolution of α-HH crystals revealed by SEM in full-view and high-resolution SEM images with different time.

((a,b) 4.0 h; (c,d) 4.5 h; (e,f) 5.5 h; (g,h) 7.0 h, $C_{DPA-PEI}$ = 5.0 g L^{-1}, pH = 5.5).
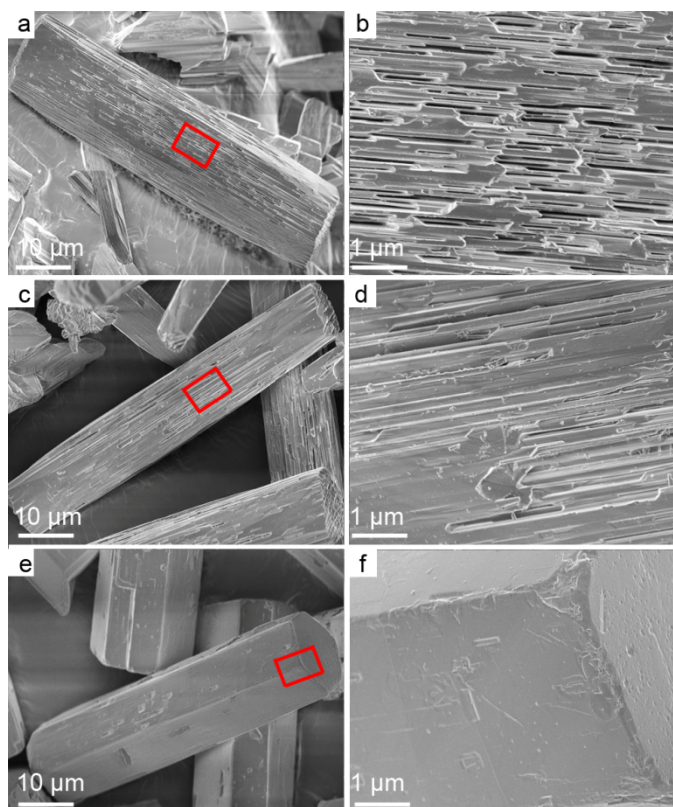
Fig. S13 (110)/(010) face evolution of α-HH crystals revealed by SEM in full-view and high-resolution SEM images with different time.

((a,b) 2.0 h; (c,d) 2.5 h; (e,f) 3.5 h, $C_{DPA\text{-}PEI}$ = 2.0 g L^{-1}, pH = 5.5).

Table S1. Data of Molecular weights of DPA-PEI with 30% DPA measured with GPC in triplicate.

test 1	test 2	test 3	average
M_n = 12063.39	M_n = 8686.82	M_n = 9507.49	M_n = 10085.9
M_w = 26177.56	M_w = 26581.68	M_w = 26335.76	M_w = 26365.00
M_w/M_n = 2.17	M_w/M_n = 3.06	M_w/M_n = 2.77	M_w/M_n = 2.61

References

(1) Lee, H. S.; Lee, Y. H.; Statz, A. R.; Rho, J. S.; Park, T. G. Messersmith, P. B. *Adv. Mater*. **2008**, *20*, 1619-1623.

(2) Prochazkova, S.; Vårum, K. M.; Østgaard, K. *Carbohydr. Polym*. **1999**, *38*, 115-122.

(3) Goodridge, L.; Goodridge, C.; Wu, J.; Griffiths, M.; Pawliszyn, J. *Anal. Chem.* **2004**, *76*, 48-52.

(4) Guan, B. H.; Yang, L. C.; Wu, Z. B.; Shen, Z. X. Ma, X. F. Ye, Q. Q. *Fuel* **2009**, *88*,1286-1293.