Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


Supporting Information for

# Large-scale synthesis and formation mechanism study of basic aluminium sulfate microcubic crystals

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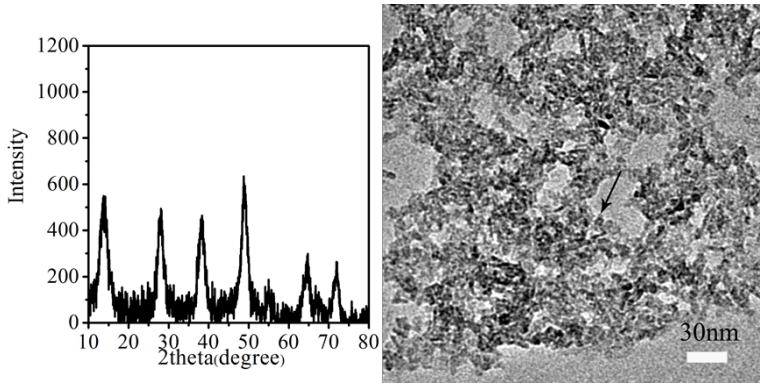
**Figure S1.** XRD pattern and TEM image of raw materials




Low crystalline γ-AlOOH nanoparticles with a size of ca.5 nm as directed by the arrow were used as the raw material, and the corresponding XRD pattern and TEM image are shown in Figure S1.

**Figure S2.** Unit cell of boehmite bulk.

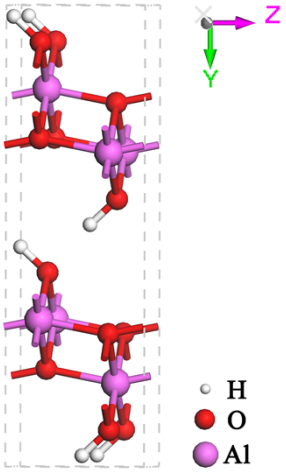
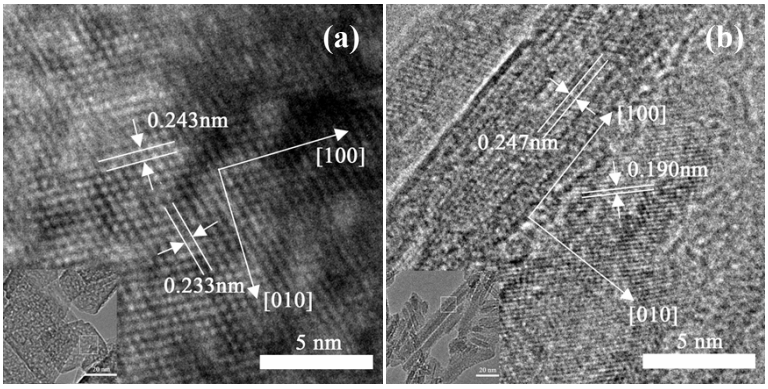
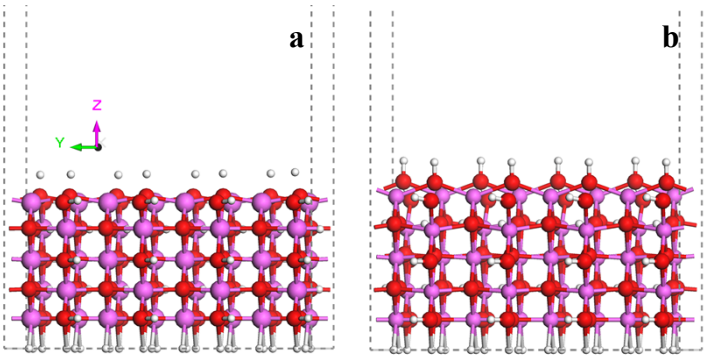


**Figure S3.** HR-TEM images of products under (a) 10 mmol $Na_2SO_4$, (b) 10 mmol $H_2SO_4$.




As shown in the HRTEM images of prepared nanoplate and nanorod, only (100), (010) and (001) planes are involved in this system.

**Figure S4.** Fully protonated (100) plane of γ-AlOOH and corresponding electronic property.




| Atom | Charge | Bond | Length/Å | Population | $E_{ads}^{total}$ / eV | $E_{ads}$ / eV |
|---|---|---|---|---|---|---|
| O | -1.05 | O-H | 1.006 | 0.53 | -91.53 | -11.44 |
| Al | 1.95/1.95 | Al-O | 1.993/2.002 | 0.35/0.34 | | |

Note: $E_{ads}^{total}$ is the total adsorption energy for fully protonated surface and $E_{ads}$ is the average adsorption energy for per $H^+$.

**Figure S5.** XRD patterns for the products obtained in time-depended experiments at 240 °C for different time: 30 min (a), 45 min (b), 60 min (c), 75 min (d), 90 min (e) and 120 min (f).

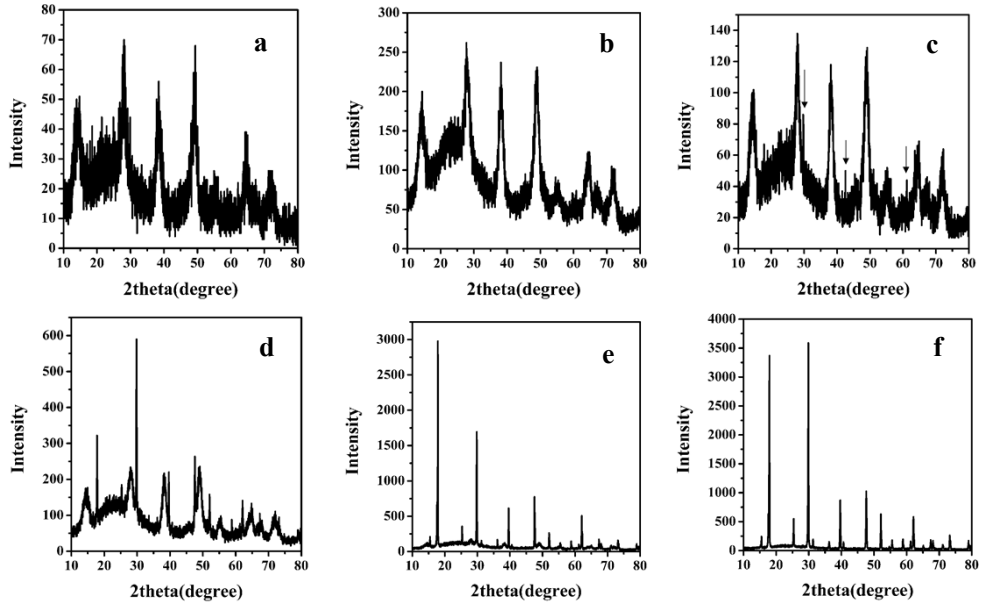



**Figure S6.** SEM images of products at 75 min. (a) TEM image, (b) SEM image of t surface of one cube.

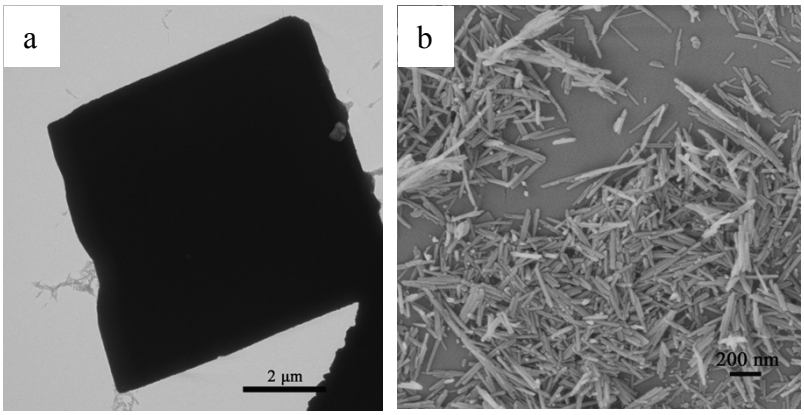


**Figure S7.** XRD pattern of final product with 0.133 mol $H^+$ added (a) and SEM image of product with 0.200 mol $H^+$ added (b).

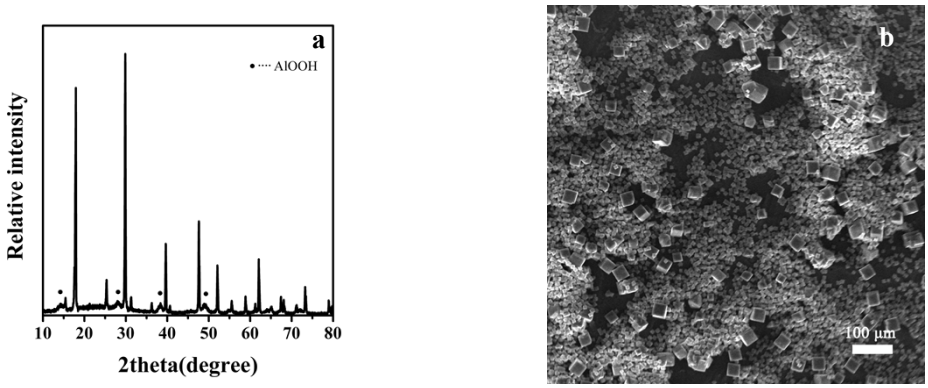



**Figure S8.** Status of mixture in typical synthesis (a) and standing for 30 min (b)

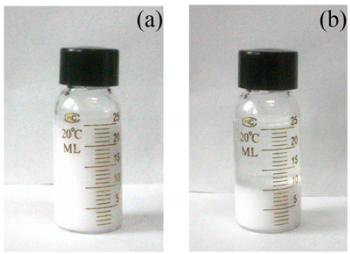



**Figure S9a.** XRD patterns of as-synthesized products at temperatures from 160 ºC to 300 ºC

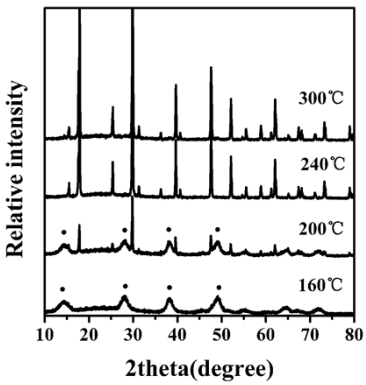


**Figure S9b**. SEM images of products formed at 160 ºC (a), 200 ºC (b), 240 ºC (c), 300 ºC (d)

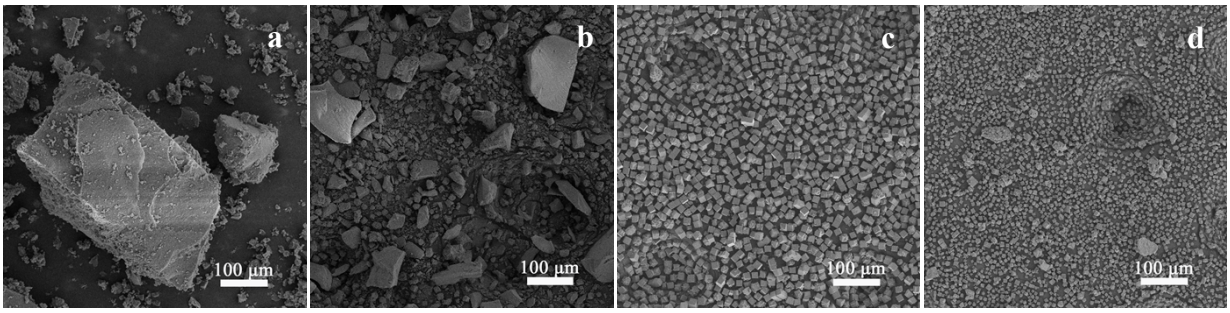



**Table S1.** Crystallographic Data for Basic Aluminium Sulfate.

| | |
|---|---|
| formula | $Al_3S_2O_{15}H_9$ |
| $M_r$ | 394.13 |
| crystal group | trigonal |
| space group | $R\bar{3}$ |
| *a* (Å) | 7.0135(9) |
| *b* (Å) | 7.0135(9) |
| *c* (Å) | 17.1580(2) |
| α (deg) | 90 |
| β (deg) | 90 |
| γ (deg) | 120 |
| *Z* | 3 |
| *V* (Å$^3$) | 730.915(16) |
| $D_c$ (g cm$^{-3}$) | 2.686 |
| $\mu$ (mm$^{-1}$) | 0.921 |
| *F* (000) | 600 |
| no. of unique reflns | 197 |
| no. of obsd reflns[I>2σ(I)] | 162 |
| parameters | 25 |
| GOF | 1.013 |
| final R | $R_1$=0.0447 |
| indices [$I>2\sigma(I)$][a,b] | $wR_2$=0.0963 |
| *R* indices | $R_1$=0.0367 |
| (all data) | $wR_2$=0.0935 |
| Largest difference peak and hole(e Å$^{-3}$) | 0.63 and -0.46 |
| [a]$R_1=\Sigma \|\|F_0\|-\|F_c\|\|/\Sigma \|F0\|$. [b]$wR_2=[\Sigma w (F_0^2-F_c^2)^2/\Sigma w (F_0^2)^2]^{0.5}$. | |

**Table S2.** Parameters used for calculation of the surface energy.

| Crystal plane | Bulk | 003 | 101 | 012 |
|---|---|---|---|---|
| Number of atoms | 78 | 156 | 156 | 156 |
| Slab thickness (Å) | | 15 | 15 | 15 |
| Surface areas ($Å^2$) | | 88.3 | 87.0 | 101.2 |
| Surface periodicity | | $1\vec{a} \times 2\vec{b}$ | $2\vec{a} \times 1\vec{b}$ | $2\vec{a} \times 1\vec{b}$ |
| K-point mesh | 4*4*2 | 4*2*1 | 2*4*1 | 2*4*1 |
| Surface energy ($mJ/m^2$) | | 1622.8 | 1767.2 | 860.44 |

Based on the above result, supposing the total quality (m) and the single volume ($V_0$) are the same in polyhedron and cube. The surface energy data of (012), (101) and (003) planes have been given in main text. The total surface energy can be calculated according to the following equations.

$$\sum E_p = (6\gamma_{101}S_{101} + 2\gamma_{003}S_{003} + 6\gamma_{012}S_{012}) \times (m/\rho V_o)$$

$$\sum E_c = 6\gamma_{012}S_{012} \times (m/\rho V_o)$$

The total volume of polyhedron predicted by BFDH method is 32835.554 $Å^3$. Take this value as $V_0$, and $\sum E_p$ is $8.37\times10^{-14} \times (m/\rho V_o)$ mJ and $\sum E_c$ is $1.65\times10^{-15} \times (m/\rho V_o)$ mJ, respectively, which illustrates that the surface energy of cube exposing {012} plane is much lower than that of polyhedron with same volume. Therefore, it is considered that the cube exposing {012} plane is the most stable morphology.