Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information for

Synthesis of γ-AlOOH nanocrystals with different morphologies due to the effect of sulfate ions and the corresponding formation mechanism study

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Figure S1. Unit cell of boehmite bulk .

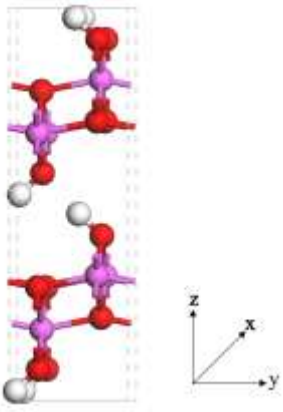


Table S1. Parameters used for the calculation of the adsorption energy.

Crystal plane	100	010	001
Number of atoms	80+(12)[a]	68	80+ (8)[a]
Slab thickness (Å)	15	15	15
Surface areas (Å^2)	92.4	43.6	71.8
Surface periodicity	$1\vec{b}\times 2\vec{c}$	$2\vec{a}\times 2\vec{c}$	$2\vec{a}\times 1\vec{b}$
k-mesh	2×3×1	4×1×3	4×2×1

[a] corresponding to the H atoms.

On the basis of the optimized geometry, the γ-AlOOH crystal cell was cleaved along the (100), (010) and (001) Miller planes to create γ-AlOOH slabs. To simulate the reactions occurring on (100), (010) and (001) planes in contact with sulfate ion, (1×2), (2×2) and (2×1) surfaces were modeled by periodically replicated slabs to construct the adsorption configuration corresponding to (100), (010) and (001), respectively. After constructing the elemental slabs, the interlayer interactions were minimized by allowing a vacuum width of 15 Å normal to the layers. Additionally, the unsaturated atoms in the bottoms were coordinated with hydrogen to eliminate the polarization effect. It was found that a slab of 7 atomic layers in thickness, in which the top three layers were unconstrained to the bulk lattice parameter, was sufficient to obtain a converged system within a rational calculation time. The detailed structure parameters were listed in Table S3, and rationality of the k-mesh and atoms layers chosen for relaxation were tested as provided in our pervious study of chloride ion on AlOOH sufaces.[23]

Figure S2. EDS images of S1 (a) and S2 (b). The detailed element content was listed in the table.

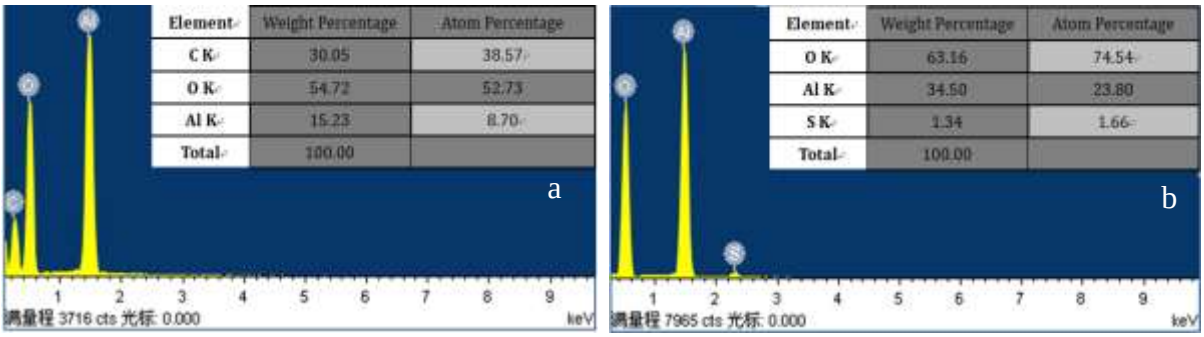
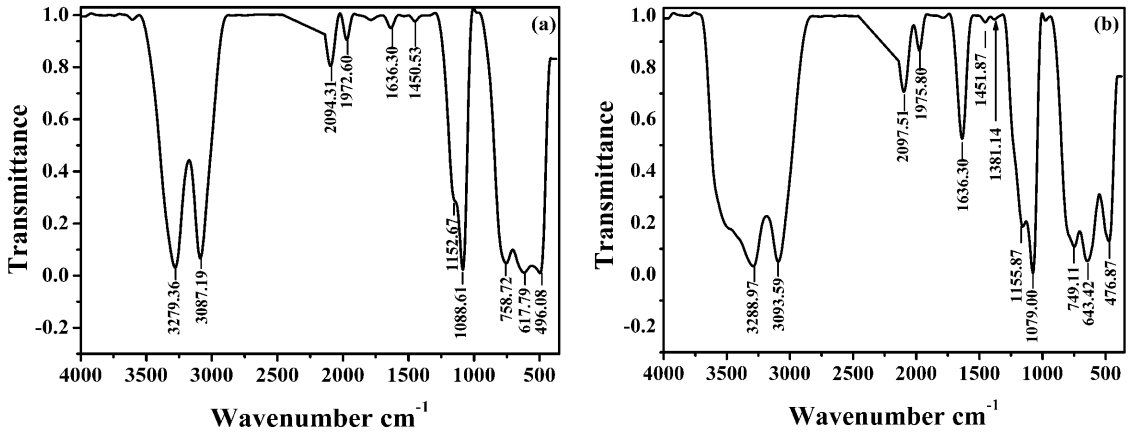


Figure S3. IR spectra of the hydrothermal products. (a) S1, (b) S2.



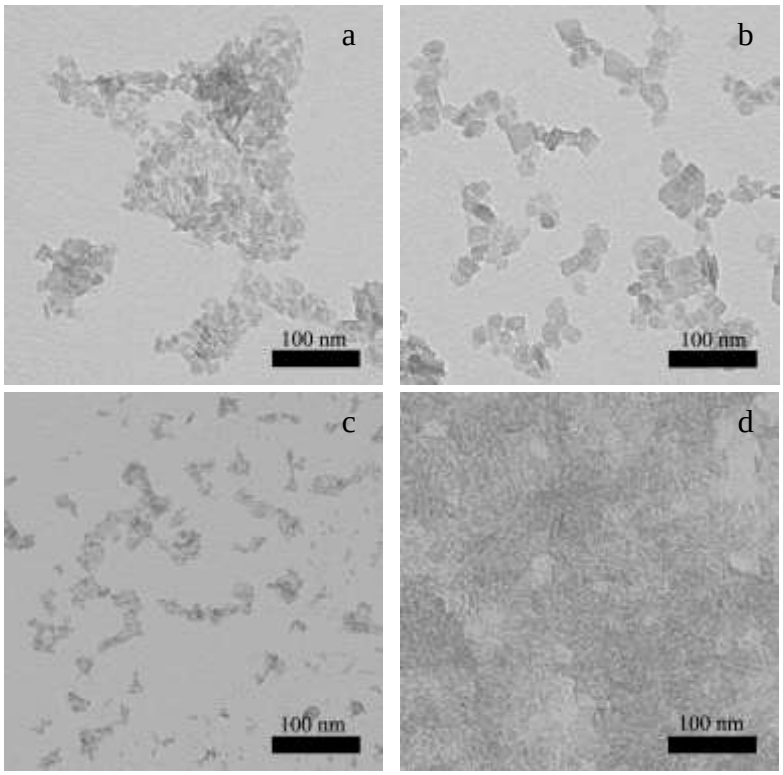
Herein, the IR spectra of products S1 and S2 are almost the same. No vibrations peaks of S-O-Al or S-Al bonds are found in IR. Take S1 as example. The broad absorptions at 3279.36 and 3087.19cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of -OH groups. Those at 2094.31, 1972.60, 1636.30 and 1450.53 cm^{-1} are attributed to the vibrational overtones of the surface -OH groups of γ-AlOOH. The five absorption bands around 1152.67, 1088.61, 758.72, 617.79 and 496.08 cm^{-1} are respectively assigned to the O-H bending, the (OH)-Al=O asymmetric stretching vibrations, the (AlO)-O-H angle bending, (OH)-Al=O angle bending and the O=Al-(OH) angle deformation (wagging) vibrations, and are the fundamental modes of vibrations of boehmite, because it is a nonlinear molecule with four atoms.

The only difference in IR is the vibrational peak at 1381.14 cm^{-1} for S2 which is the typical peak of S=O, demonstrating that sulfate ions adsorb on the surface of AlOOH particles formed in acidic environment.

Table S2. Mulliken Charge Population on the H, μ_1-O, Al atoms after protonation.

		Charge population		
Species		H	μ_1-O	Al
AlOOH	(010)	0.30	-0.91	1.89
	(001)	0.30	-0.91	1.79
$AlOOH/H^+$	(010)	0.29, 0.30	-0.65	1.88
	(001)	0.36, 0.35	-0.57	1.44

Figure S4. TEM images of the hydrothermal products. S1 in presence of 0.01 mol Na_2SO_4 for 1 h (a) and 2 h (b); S2 in presence of 0.01 mol H_2SO_4 for 1 h (c) and 2 h (d).

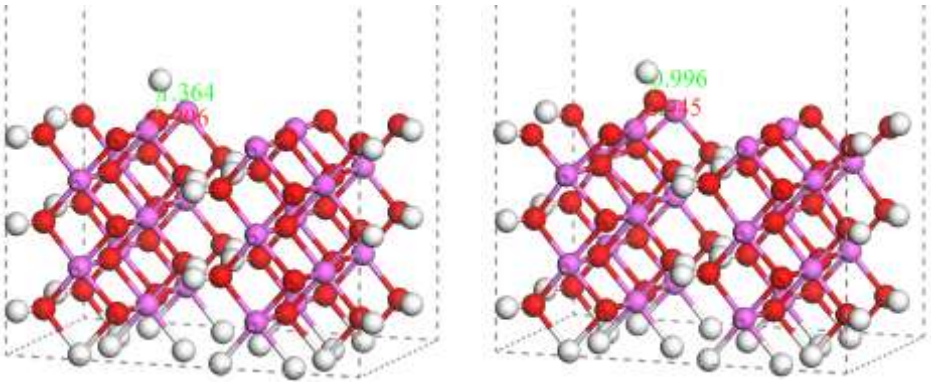


As shown in Figure S4, the sizes of nanosheets are ca.10 and 30 nm, while the lengths of nanorods are ca.10 and 40 nm after hydrothermal treatment for 1 and 2 h, respectively.

Table S3. Adsorption energies of H^+ on γ-AlOOH planes.

Planes	(100)	(010)	(001)
E_{AlOOH} /Ha	-7876.1522	-6296.4647	-7874.3878
$E_{AlOOH/H+}$ /Ha	-7875.7812	-6297.8860	-7875.7923
E_{ads} /eV	7.23	-9.65	-9.54

Figure S5. Adsorption structures of H^+ on (100) plane.



Starting conformation After optimazation

As shown in above figures, the Al-O bond length is elongated from 1.906 Å to 2.045 Å under the Columba attraction of single H^+, which indicates the tendency of surface structure reconstruction. The high concentration of H^+ corresponding to dissolution and recrytallization process of BAS will be given out in the following study.