Size and Morphology Controlled Synthesis of Boehmite Nanoplates and Crystal Growth Mechanisms

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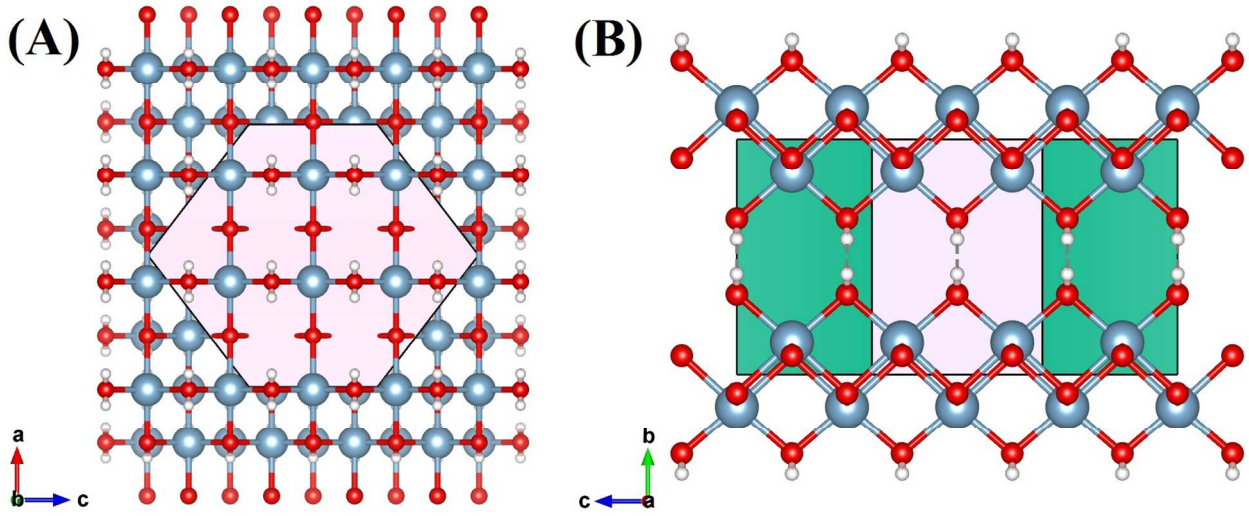
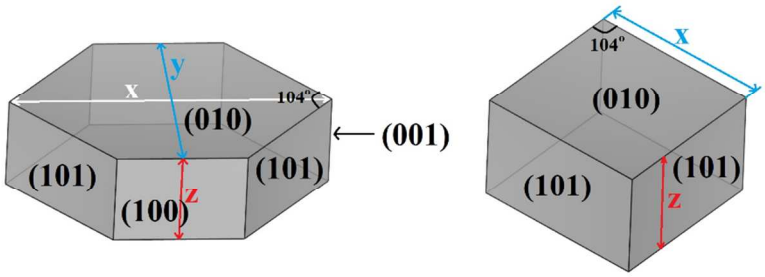
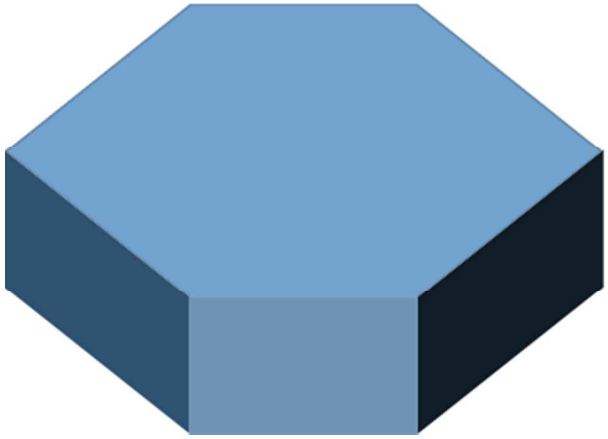


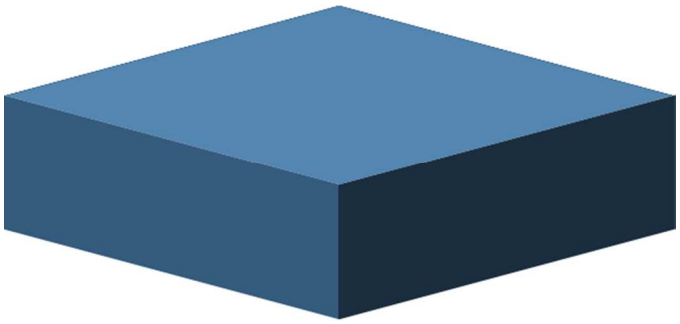
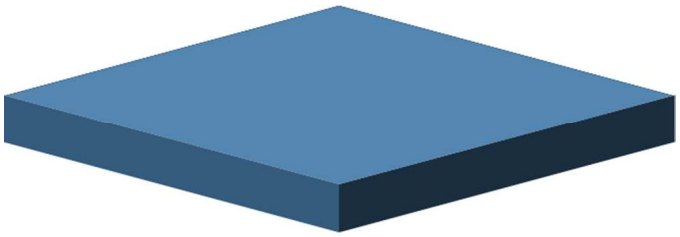
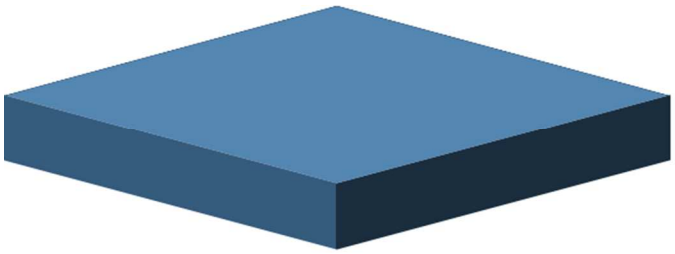
Figure S1. Crystal structure of boehmite β-AlOOH. (a) Top view along (010); and (b) side view along (100).

Figure S2. The morphology and size of boehmite samples measured from the SEM and TEM images.



For the hexagonal shaped boehmite (x≠y≠z), the x, y, and z means the distance along the (001), (100), and (010) direction, respectively; for the rhombic shaped boehmite (x=y≠z), the x and z means the size of the (101) edge and the distance along the (010) direction, respectively.

Sample	Morphology	Size (x × y × z)
1		136.5 × 32.9 ×25.8
2		94.8 × 45.7 × 10.3
3		78.6 × 60.1 × 22.2

Sample	Morphology	Size (x × y × z)
4		79.6 × 79.6 × 25.3
5		88.5 × 88.5 × 10.0
7		75.4 × 41.1 × 13.2
8		78.3 × 78.3 × 12.4
10		30.3 × 30.3 × 6.2
11		32.3 × 32.3 × 8.4

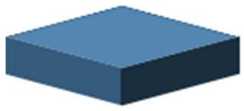
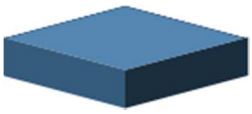
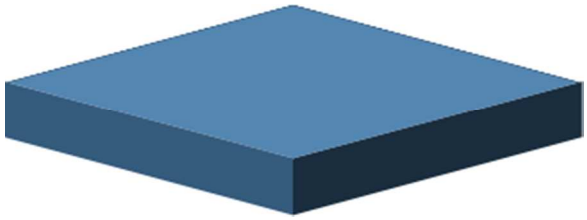
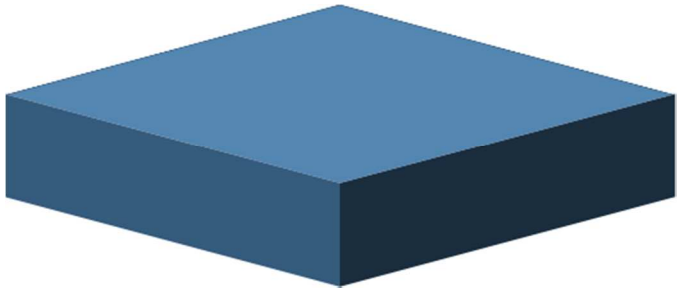
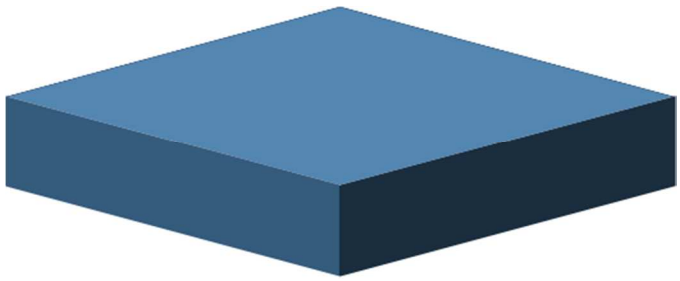
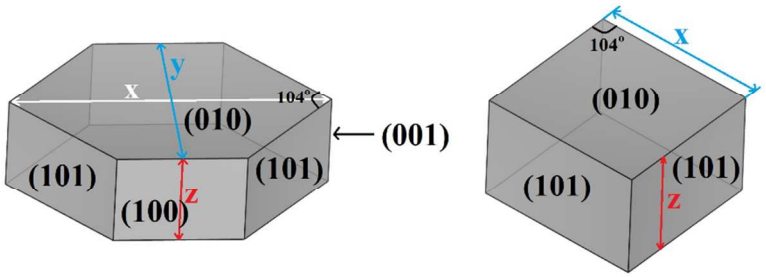
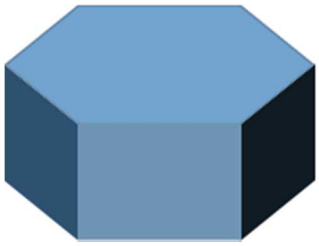
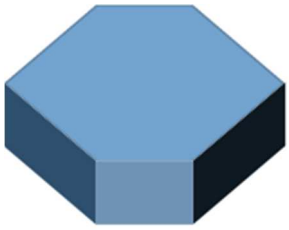
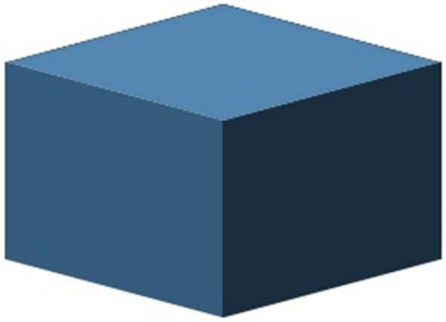
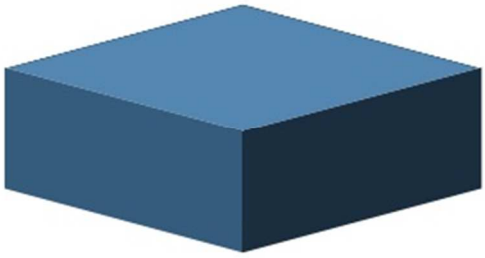
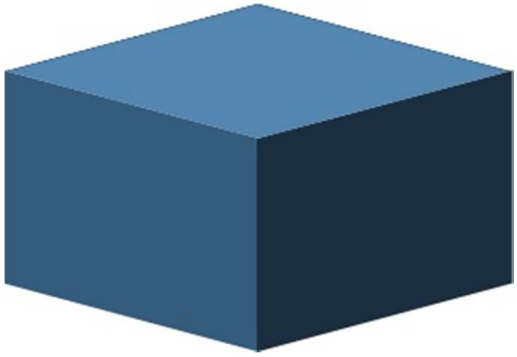
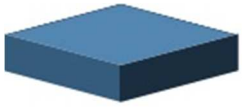
Sample	Morphology	Size (x × y × z)
12		19.2 × 19.2 × 4.0
13		20.1 × 20.1 × 5.1
14		37.5 × 37.5 × 7.5
15		21.4 × 12.7 × 4.2
16		26.7 × 14.8 × 3.7
17		68.4 × 68.4 × 16.8
18		71.3 × 71.3 × 15.3

Figure S3. The morphology and size of boehmite samples based on the fitting of XRD data.



For the Elliptical cylinder model (x≠y≠z), the x, y, and z means the distance along the (001), (100), and (010) direction, respectively; For the Cuboid model (x=y≠z), the x and z means the size of the (101) edge and the distance along the (010) direction, respectively.

Sample	Morphology	Size (x × y × z)
1		40.6 × 24.3 × 18.9
2		36.6 × 31.7 × 10.3
3		23.3 × 28.6 × 21.9

Sample	Morphology	Size (x × y × z)
4		36.3 × 36.3 × 26.2
5		39.5 × 39.5 × 16.1
7		24.7 × 31.2 × 23.7
8		42.2 × 42.2 × 28.3
10		19.2 × 19.2 × 4.9

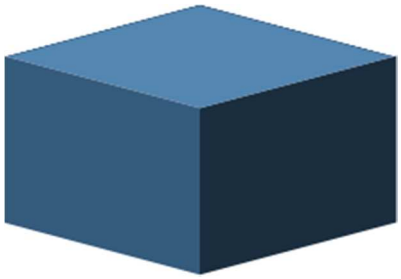
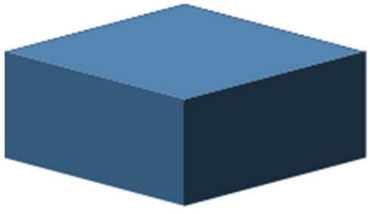
Sample	Morphology	Size (x × y × z)
11		17.1 × 17.1 × 6.3
12		15.7 × 15.7 × 4.1
13		19.0 × 19.0 × 5.3
14		27.4 × 27.4 × 8.6
15		16.8 × 15.1 × 2.9
16		13 × 11.4 × 3.0
17		32.4 × 32.4 × 22.1
18		29.9 × 29.9 × 14.1

Table S1. The size of the boehmite samples synthesized in different conditions measured via using SEM and TEM images. The sample number same as the number in **Table 1**.

Sample	x		y		z		z/x	z/y	y/x
1	136.5	54.4	32.9	4.7	25.8	8.7	0.2	0.8	0.2
2	94.8	37.4	45.7	11.1	10.3	1.9	0.1	0.2	0.5
3	78.6	27.2	60.1	14.8	22.2	7.6	0.3	0.4	0.8
4	79.6	15.9			25.3	3.3	0.3		
5	88.5	39.1			10.0	1.9	0.1		
7	75.4	27.3	41.1	7.3	13.2	4.1	0.2	0.3	0.5
8	78.3	18.6			12.4	3.1	0.2		
10	30.3	11.3			6.2	1.9	0.2		
11	32.3	6.7			8.4	1.4	0.3		
12	19.2	4.0			4.9	1.3	0.3		
13	20.1	3.9			5.1	0.9	0.3		
14	37.5	11.1			7.5	1.2	0.2		
15	21.4	4.5	12.7	2.6	4.2	1.3	0.2	0.3	0.6
16	26.7	10.7	14.8	2.1	3.7	0.9	0.1	0.2	0.6
17	68.4	22.7			16.8	7.6	0.2		
18	71.3	16.6			15.3	3.3	0.2		

Table S2. The size of the boehmite samples synthesized in different conditions based on the fitting of XRD data. The sample number same as the number in **Table 1**.

Boehmite crystallite size												
Sample	Isotropic		Aniso. Model	x		y		z		z/x	z/y	y/x
1	33.6	±0.3	Elliptical Cyl.	40.6	±1.5	24.3	±0.5	18.9	±0.4	0.5	0.78	0.6
2	24.5	±0.2	Elliptical Cyl.	36.6	±1.5	31.7	±0.9	10.3	±0.1	0.3	0.32	0.9
3	33.2	±0.4	Elliptical Cyl.	23.3	±0.6	28.6	±0.8	21.9	±0.5	0.9	0.77	1.2
4	42.3	±0.5	Cuboid	36.3	±0.8			26.2	±0.7	0.7		
5	34	±0.4	Cuboid	39.5	±1.0			16.1	±0.3	0.4		
7	35.7	±0.4	Elliptical Cyl.	24.7	±0.7	31.2	±0.9	23.7	±0.6	1	0.76	1.3
8	47.3	±0.6	Cuboid	42.2	±1.0			28.3	±0.7	0.7		
10	11.55	±0.09	Cuboid	19.2	±0.4			4.86	±0.04	0.3		
11	13.49	±0.08	Cuboid	17.1	±0.3			6.3	±0.06	0.4		
12	9.98	±0.10	Cuboid	15.7	±0.4			4.09	±0.06	0.3		
13	12.6	±0.07	Cuboid	19	±0.2			5.26	±0.04	0.3		
14	19.94	±0.18	Cuboid	27.4	±0.6			8.61	±0.12	0.3		
15	7.96	±0.09	Elliptical Cyl.	16.8	±0.7	15.1	0.4	2.9	±0.03	0.2	0.19	0.9
16	7.61	±0.08	Elliptical Cyl.	13	±0.5	11.4	0.3	3.02	±0.04	0.2	0.27	0.9
17	36.7	±0.4	Cuboid	32.4	±0.8			22.1	±0.5	0.7		
18	27.8	±0.3	Cuboid	29.9	±0.7			14.1	±0.3	0.5		

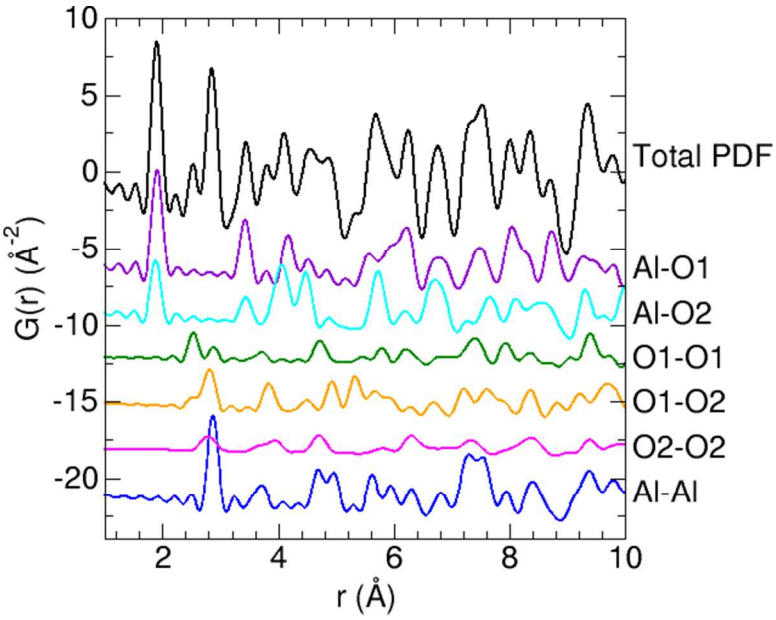


Figure S4: Partial pair correlations (labeled colored lines) contributing to the total PDF of crystalline boehmite (black line). The model used in calculation is based on the *Cmcm* boehmite crystal structure[1].

Data were fit in the program PDFgui[2]. Both single and two phase models were applied during refinement, based on the *Cmcm* boehmite crystal structure[1], and the monoclinic $P12_1/n1$ gibbsite crystal structure[3]. Lattice parameters, isotropic atomic displacement parameters, fractional coordinates of the atoms, and a parameter for correlated motion (δ_2) were refined for the boehmite phase models, but gibbsite fractional coordinates were held fixed to the values reported by Megaw[3] in order to reduce the number of free parameters in the multi-phase fits. PDF data were initially fit between 1 and 100 Å, to refine a spherical particle form factor (as an approximation of average structural coherence length) and a gibbsite phase fraction (for select samples). These values were held fixed while fitting crystallographic model parameters to the local structure data (between 1 and 10 Å). The resulting fits and boehmite model parameters are given in **Figure S5** and **Table S3**, respectively, for the two series of data.

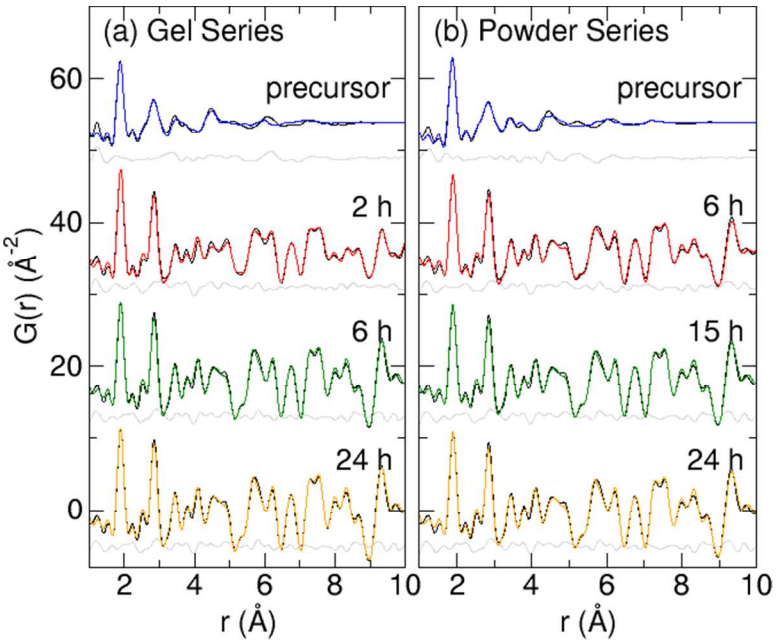


Figure S5: 1 Å to 10 Å PDF fits to the (a) gel and (b) amorphous powder precursor evolution series. Data are shown as black lines, fits as colored lines, and difference curves are shown below the data and fits as grey lines. Models used for the 2 h sample in (a) and the 6 h sample in (b) include both gibbsite and boehmite phases, while pure boehmite models were used in all other fits. Refined crystallographic parameters from analysis are reported in **Table S3**.

Table S3: PDF refinement parameters for the boehmite structural models (*Cmcm* Space Group, with $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^{\circ}$, Al at (0,*y*,¼), O1 at (0,*y*,¼), and O2 (hydrogen bearing O) at (0,*y*,¼)) in the gel and amorphous powder precursor study. Correlation length scale (estimated with a spherical particle diameter model) and gibbsite phase fraction were determined with refinement of the PDF data between 1 and 100 Å in real space, while all other reported values are those determined from 1 to 10 Å refinements (with correlation length scale and phase fractions held fixed during refinement). Values in parentheses are estimated standard deviation reported from refinement.

	Gel Series			
	Precursor	**2 h**	**6 h**	**24 h**
Spherical Particle Diameter (Å)	8.9(5)	67(3)	81(2)	94(3)
Gibbsite Phase Fraction (%)	-	31(1)	-	-
scale	1.7(1)	1.55(4)	1.21(2)	1.25(2)
***a* (Å)**	2.83(3)	2.864(3)	2.868(2)	2.867(2)
***b* (Å)**	11.2(1)	12.21(1)	12.209(7)	12.206(7)
***c* (Å)**	4.09(4)	3.693(4)	3.692(2)	3.690(2)
u_{iso}(Al) (Å^2)	0.017(7)	0.0031(5)	0.0030(3)	0.0030(3)
u_{iso}(O1) (Å^2)	0.01(1)	0.004(1)	0.0053(6)	0.0053(6)
u_{iso}(O2) (Å^2)	0.019(7)	0.007(1)	0.0059(6)	0.0058(6)
***y* (Al)**	0.682(1)	0.6810(5)	0.6813(2)	0.6814(2)
***y* (O1)**	0.295(2)	0.2900(7)	0.2911(4)	0.2910(4)
***y* (O2)**	0.073(2)	0.0836(7)	0.0822(4)	0.0821(3)
δ_2 (Å^{-2})	3.49(5)	3.06(6)	3.15(4)	3.13(4)
R_{wp} (%)	24.5	14.8	12.5	12
	Powder Series			
	Precursor	**6 h**	**15 h**	**24 h**
Spherical Particle Diameter (Å)	8.6(4)	63(2)	77(2)	76(2)
Gibbsite Phase Fraction (%)	-	12(1)	-	-
scale	1.95(9)	1.32(3)	1.16(2)	1.21(2)
***a* (Å)**	2.80(2)	2.870(2)	2.870(2)	2.870(2)
***b* (Å)**	11.9(1)	12.22(1)	12.210(7)	12.210(7)
***c* (Å)**	3.77(2)	3.691(3)	3.692(2)	3.691(2)
u_{iso}(Al) (Å^2)	0.0103(3)	0.0029(4)	0.0030(3)	0.0030(3)
u_{iso}(O1) (Å^2)	0.014(5)	0.0052(8)	0.0052(7)	0.0053(6)
u_{iso}(O2) (Å^2)	0.068(2)	0.0062(7)	0.0060(6)	0.0060(6)
***y* (Al)**	0.673(1)	0.6809(3)	0.6814(3)	0.6814(3)
***y* (O1)**	0.305(2)	0.2910(5)	0.2910(4)	0.2910(4)
***y* (O2)**	0.067(2)	0.0825(5)	0.0823(4)	0.0823(4)
δ_2 (Å^{-2})	3.52(2)	3.11(5)	3.15(4)	3.15(4)
R_{wp} (%)	21.12	14.34	13.04	13.45

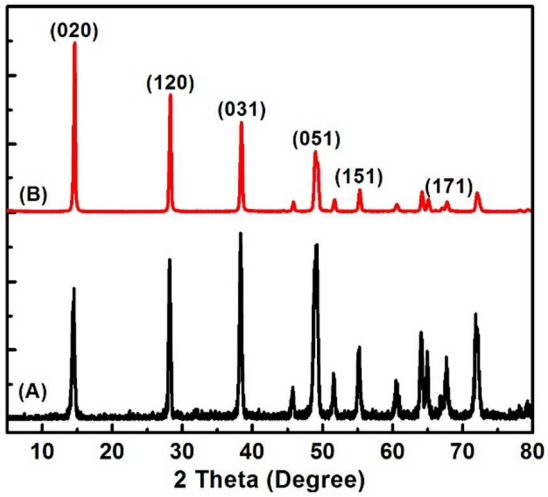


Figure S6. XRD patterns of boehmite synthesized at (A) 1.0 M amorphous powder precursor and (B) 1.0 M gel precursor. The temperature and reaction time for all reactions were 200 ^{o}C and 48 h, respectively. The pH of all reaction was 14.

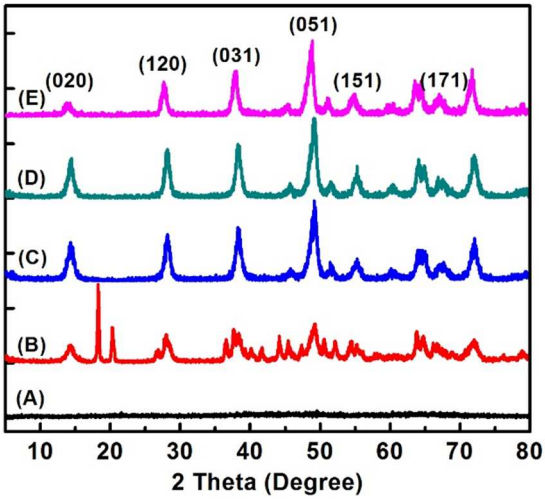


Figure S7. XRD patterns of (A) original $Al(OH)_3$ gel and samples synthesized using 0.25 M gel at 120 ^{o}C for different reaction times: (B) 2h, (C) 6h; (D) 12 h and (E) 24 h. The pH of all reaction was 13.3.

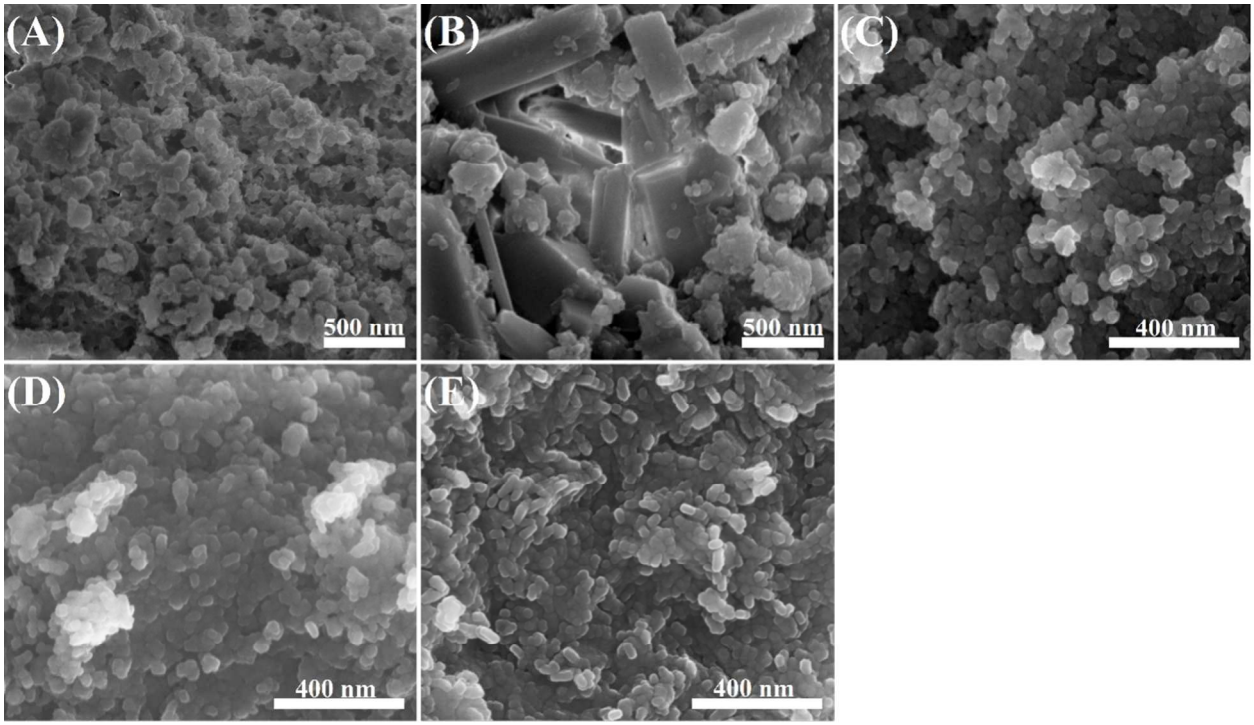


Figure S8. SEM images of (A) original $Al(OH)_3$ gel and samples synthesized using 0.25 M gel at 120 ^oC for different reaction times: (B) 2h, (C) 6h; (D) 12 h and (E) 24 h. The pH of all reaction was 13.3.

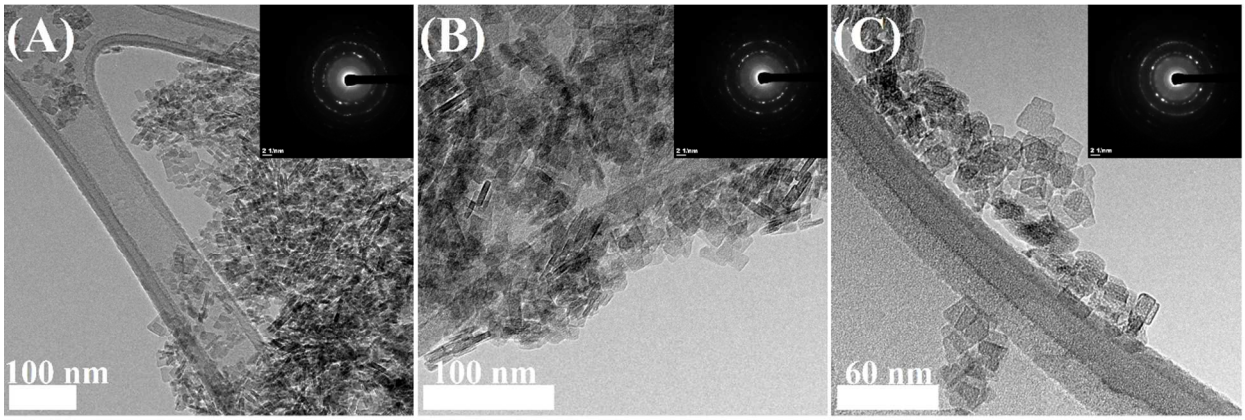


Figure S9. TEM images of samples synthesized using 0.25 M gel at 120 ^oC for different reaction times: (A) 6h; (B) 12 h and (C) 24 h. The pH of all reaction was 13.3.

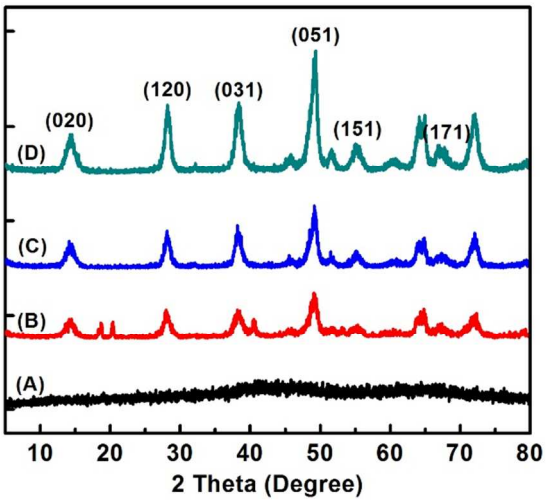


Figure S10. XRD patterns of (A) amorphous powder and samples synthesized using 0.25 M amorphous powder at 120 ^{o}C for different reaction times: (B) 6h, (C) 12h; and (D) 24 h. The pH of all reaction was 13.3.

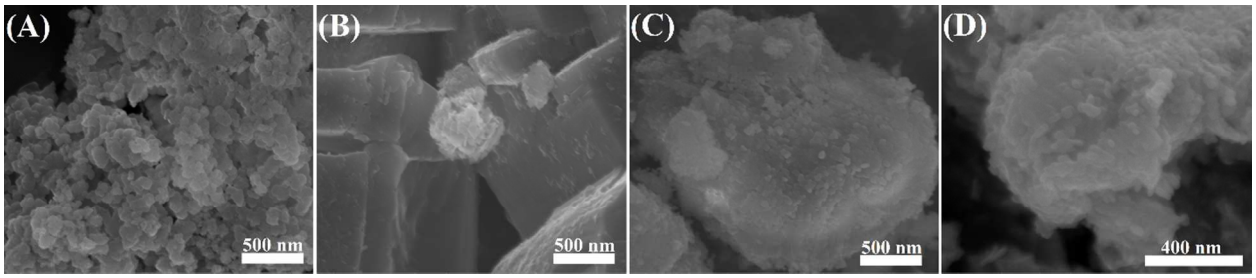


Figure S11. SEM images of samples synthesized using 0.25 M amorphous powders at 120 ^{o}C for different reaction times: (A) 6h; (B) 12 h and (C) 24 h. The pH of all reaction was 13.3.

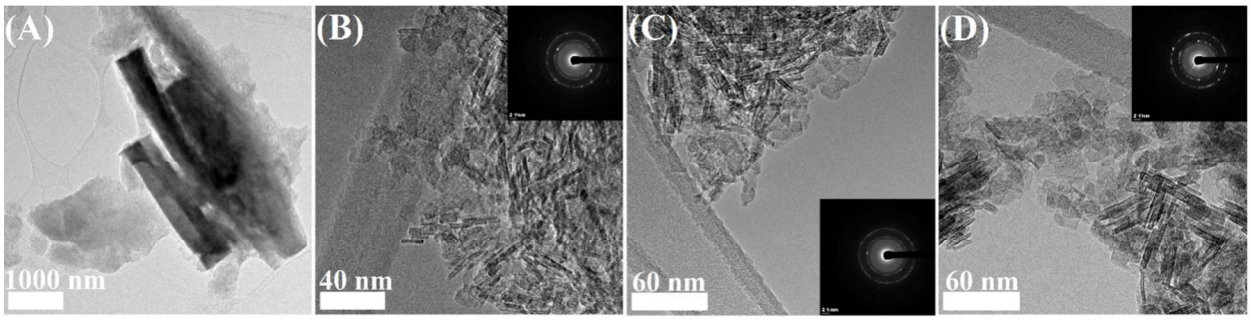


Figure S12. TEM images of samples synthesized using 0.25 M amorphous powder at 120 ^{o}C for different reaction times: (A) 6h; (B) 12 h and (C) 24 h. The pH of all reaction was 13.3.

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