

# One-step Ionothermal Synthesis of $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Mesoporous Nanoflakes at Low Temperature

## Supplementary Information

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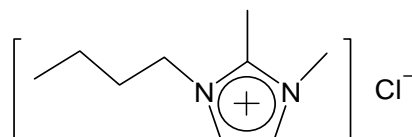
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## Experimental Section

*Materials:* The sodium amide was analytical grade and used without further purification. The aluminum chloride was purified by the sublimation of a commercial analytical grade reagent. The ionic liquid 1-butyl-2, 3-dimethylimidazolium chloride ([bdmim][Cl]) was prepared according to the literature (I. B. Malham, P. Letellier, M. Turmine, *J. Phys. Chem. B* **2006**, *110*, 14212) and its general structural feature was shown below:

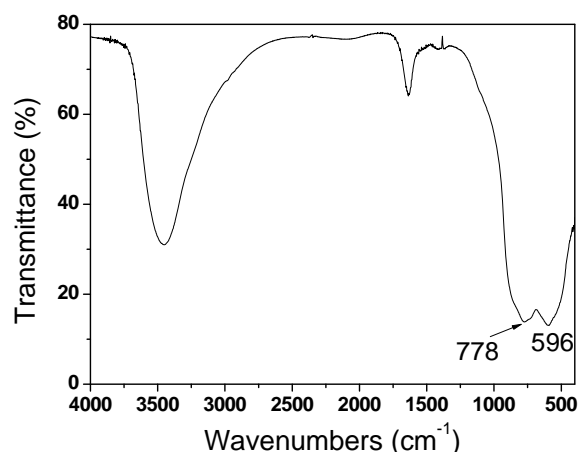


1-butyl-2, 3-dimethylimidazolium chloride

*One-step synthesis of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes:* In a typical synthesis of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes, 5 mmol of AlCl<sub>3</sub> and 15 mL of the ionic liquid [bdmim][Cl] were put into a Teflon-lined autoclave with a capacity of 30 mL to form a complex solution. Subsequently, 15 mmol of NaNH<sub>2</sub> was added into the above solution. All the manipulations were carried out in a dry glove box in order to prevent hydration of reactants by air humidity. Then, the autoclave was sealed and heated at 150 °C for 10 h. When the reaction was completed, the autoclave was cooled to room temperature naturally. The resultant product was collected and washed with deionized water, and anhydrous ethanol for several times until the solution was neutral. The final product was dried in a vacuum at 80 °C for 3 h.

*Instruments and Characterizations:* XRD measurements were performed on a Rigaku D/max 2500 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.154056$  nm) at V = 40 kV and I = 150 mA, the scanning speed was 8°/min. XPS measurement was performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an exciting source of Mg K $\alpha$  X-rays. The FTIR spectroscopy of the sample was conducted at room temperature with a KBr pellet on a VECTOR-22 (Bruker) spectrometer ranging from 400 to 4000 cm<sup>-1</sup>. Morphology observations were performed on a JEOLJSM-6700F field emission scanning electron microscope (FE-SEM). TEM and HRTEM images were recorded with a Tecnai G<sup>2</sup> 20S-Twin transmission electron microscope operating at an accelerating voltage of 120 and 200 kV, respectively. Nitrogen adsorption–desorption isotherms were obtained on an ASAP 2020 nitrogen adsorption apparatus. The Brunauer–Emmett–Teller (BET) specific surface areas ( $S_{\text{BET}}$ ) were calculated using the BET equation. Desorption isotherm was used to determine the pore size distribution using the Barret–Joyner–Halender (BJH) method.

**Fig. S1.** FTIR spectrum of the as-prepared  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes.

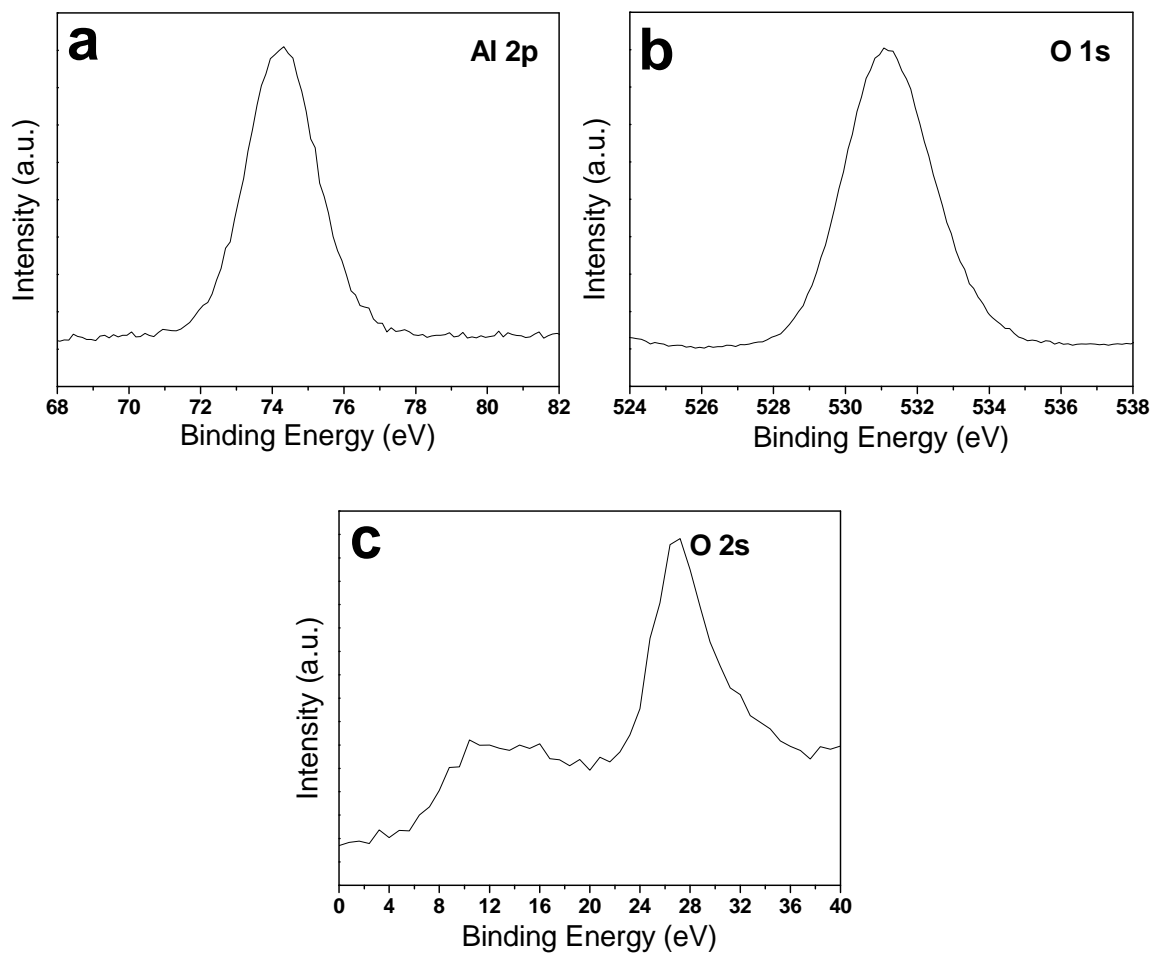


In the above FTIR spectrum, the intensive bands at 778 and 596 cm<sup>-1</sup> ascribed to Al-O stretching vibrations, are the principal feature of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>[1]</sup> The intensive band centered at 3442 cm<sup>-1</sup> and weak band at 1638 cm<sup>-1</sup> are attributed to the stretching and bending vibrations of physically adsorbed water, respectively. There are no characteristics of AlOOH observed in the FTIR spectrum, such as the bands of the  $\nu$ (Al)O-H stretching vibrations between 3000 and 3200 cm<sup>-1</sup>, the bands of  $\delta$ Al-O-H modes between 1000 and 1200 cm<sup>-1</sup>.<sup>[2]</sup> The results indicate that the as-prepared sample is pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> without any impurities, such as boehmite.

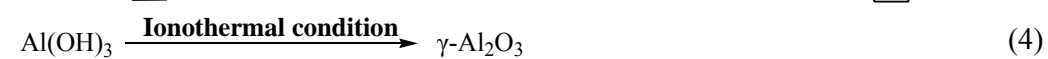
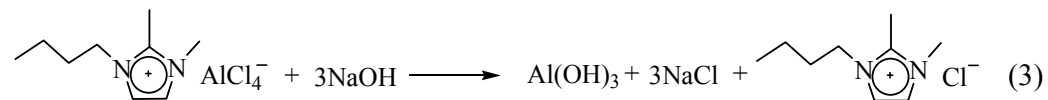
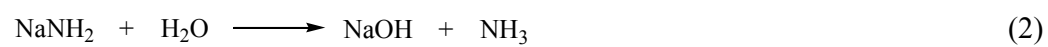
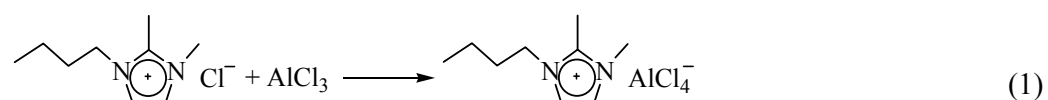
[1]. T. M. H. Costa, M. R. Gallas, E. V. Benvenuti, and J. A. H. da Jornada. *J. Phys. Chem. B* **1999**, *103*, 4278–4284.

[2]. Y. L. Feng, W. C. Lu, L. M. Zhang, X. H. Bao, B. H. Yue, Y. Lv, and X. F. Shang. *Cryst. Growth Des.*, **2008**, *8* (4), 1426–1429.

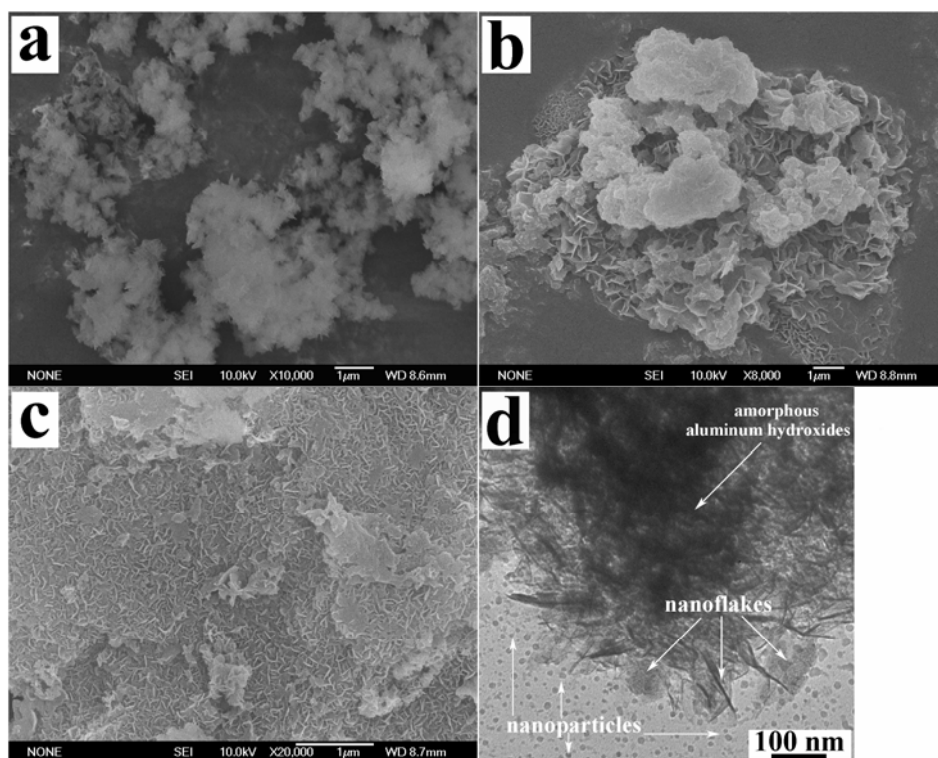
**Fig. S2.** XPS spectra of the as-prepared  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes.



**Fig. S3.** The possible reaction mechanism:

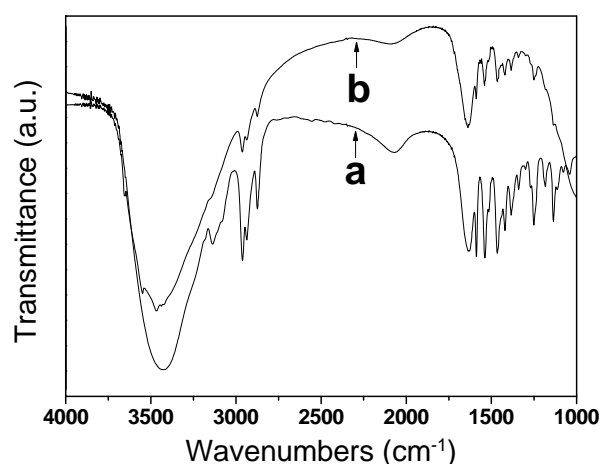


**Fig. S4.** FE-SEM images of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes assembled by nanoparticles obtained at reaction times of a) 1, b) 4, c) 7 h, and d) the corresponding TEM image of b).



To disclose the formation mechanism of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes, the products obtained at different reaction durations have been analyzed through FE-SEM images, as shown above. Fig. S4a represents the FE-SEM image of the product obtained after 1 h, which indicates that there are some thin flakes, along with a majority of amorphous aluminum hydroxides in the product. The product obtained after 4 h is composed of much more thin flakes with amorphous substance decreasing, as is evident from Fig. S4b. When the reaction time prolonged to 7 h, the product was mainly composed of nanoflakes in Fig. S4c. When it finally came to 10 h, well-defined and uniform nanoflakes with 10 nm in thickness were obtained, as shown in Fig. 2a of the text. Fig. S4d shows the corresponding TEM image of the product obtained after 4 h, which is composed of amorphous substance, thin flakes and nanoparticles. The very small particles can easily be generated in the ionic liquid medium during further ionothermal process, due to their low interface tension.

**Fig. S5.** FT-IR spectra of (a) the pure [bdmim][Cl] and (b) the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoflakes/[bdmim][Cl].



**Table S1.** Frequencies of FTIR Absorption Bands for the Pure [bdmim][Cl] and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoflakes/[bdmim][Cl].

Frequencies of absorption bands (cm <sup>-1</sup> )		Assignments <sup>[1]</sup>
Pure [bdmim][Cl]	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> nanoflakes/[bdmim][Cl]	
3136	3136	CH...Cl hydrogen bonding between the anions and the 4,5-hydrogens of the imidazole ring
2961 2870	2961 2869	C-H bonds of alkyl chains stretching vibrations
1537 1460	1536 1460	imidazole ring skeleton stretching vibrations
1135	1133	C-N bonds of imidazole ring stretching vibration
3435 1635	3441 1636	the vibrations of the adsorbed water molecules

Compared with that of the pure [bdmim][Cl], the FTIR spectrum of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes/[bdmim][Cl] displays significant differences. The absorption band at 3136 cm<sup>-1</sup> which are attributed to the CH...Cl hydrogen bonding between the anions and the 4, 5-hydrogens of the imidazolium ring, becomes broadened and weakened after the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes are obtained in [bdmim][Cl]. The result indicates that there are strong interactions between ionic liquids and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes, that is, the existence of the strong hydrogen bonds between the Cl([bdmim][Cl])–H–O( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). Evidence for the contribution of  $\pi$ - $\pi$  stacking to self-assembly was also found in the FTIR spectra. Firstly, the change of peak of the C–N stretching vibration ( $\nu_{C-N}$ ) mode of the imidazolium ring at 1135 cm<sup>-1</sup> is an effective tool to examine the  $\pi$ - $\pi$  stack of the imidazolium ring. In the present case, it is easy to observe that the  $\nu_{C-N}$  mode in spectrum b becomes broadened and weakened, compared with the spectrum a. Moreover, the  $\nu_{C-H}$  mode of C–H of the alkyl chain of

[bdmim]<sup>+</sup> around 2961 and 2870 cm<sup>-1</sup> in spectrum a is also found to be influenced due to the mutual packing. The observed variation of the  $\nu_{\text{C-H}}$  mode of the alkyl chain can be explained in that the  $\pi$ - $\pi$  stacking interaction of the imidazolium ring may influence the nitrogen-alkyl carbon bond, changing the  $\nu_{\text{C-H}}$  mode. In addition, the reorganizing process of aluminum oxide crystallites via  $\pi$ - $\pi$  stacking as well as hydrogen bonding significantly influenced other peaks at 1537 and 1460 cm<sup>-1</sup> assigned to the skeleton stretching vibration of the imidazolium ring in the FTIR spectra. According to the discussions above and the literatures,<sup>[1]</sup> the proposed possible hydrogen bond-co- $\pi$ - $\pi$  stack mechanism is responsible for the formation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes assembled by nanoparticles.

[1]. (a) Y. Zhou, J. H. Schattka, M. Antonietti, *Nano Lett.* **2004**, *4*, 477–481; (b) H. S. Park, Y. S. Choi, Y. J. Kim, W. H. Hong, H. Song, *Adv. Funct. Mater.* **2007**, *17*, 2411–2418; (c) M. Yoshizawa, W. Xu, C. A. Angell, *J. Am. Chem. Soc.* **2003**, *125*, 15411–15419; (d) F. Shi, Q. Zhang, D. Li, Y. Deng, *Chem.-Eur. J.* **2005**, *11*, 5279–5288; (e) J. B. Lian, D. Kim, X. D. Liu, J. M. Ma, W. J. Zheng, *J. Phys. Chem. C* **2009**, *113*, 9135–9140.



**Fig. S6.** Room temperature UV-vis (a) and PL spectra (b) of the as-prepared  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes.

