

Supporting Information for Formation of Ordered Microporous Aluminum-Based  
Material Mediated by Phthalic Acid

*Wei Zhang,<sup>a,b</sup>Jian-Hua Cai,<sup>a,b</sup>Pei-Pei Huang,<sup>a,b</sup>Lin-Lin Hu,<sup>a,b</sup> An-Min Cao<sup>\*a,b</sup> and Li-  
Jun Wan<sup>\*a,b</sup>*

a Key Laboratory of Molecular Nanostructure and Nanotechnology and Beijing  
National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese  
Academy of Sciences (CAS), Beijing 100190, P. R. China.

b University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

Corresponding authors

\* E-mail: [anmin\\_cao@iccas.ac.cn](mailto:anmin_cao@iccas.ac.cn). (A.-M. C.)

\* E-mail: [wanlijun@iccas.ac.cn](mailto:wanlijun@iccas.ac.cn). (L.-J. W.)

## EXPERIMENTAL SECTION

**Materials.** Aluminum nitrate, formic acid, ammonium formate, phthalic acid, benzoic acid, isophthalic acid, terephthalic acid, aluminium sulfate and sodium hydroxide were of analytical pure were purchased from Sinopharm Chemical Reagent Co.,Ltd. All chemicals were used as received without further purification. Milli-Q water (typically  $18.2 \text{ M}\Omega\cdot\text{cm}$  at  $25 \text{ }^\circ\text{C}$ ) was used for all experiments.

**Preparation of ordered microporous aluminum-based material.** 0.2733 g phthalic acid was first dissolved in 50 mL 0.2 M formic acid-ammonium formate buffer solution and the pH value was precisely adjusted to 4.4. Then 0.1352 g  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  was added and the mixed solution was further incubated at  $70 \text{ }^\circ\text{C}$  for 2 h under vigorously stirring. The white precipitation was collected through continuous washing-and-centrifugation cycles and oven-dried at  $80 \text{ }^\circ\text{C}$  overnight. The sample was further annealed at  $300 \text{ }^\circ\text{C}$  for 4 h to obtain the target product m-ABM.

### **Controlled experiments of preparation of ordered microporous aluminum-based material.**

*NaOH-induced precipitation:* 0.2733 g phthalic acid and 0.1352 g  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  were first dissolved in 50 mL water. Then dilute solutions of NaOH were added dropwise under vigorously stirring. The white precipitation was collected through continuous washing-and-centrifugation cycles and oven-dried at  $80 \text{ }^\circ\text{C}$  overnight.

*In the absence of phthalic acid:* 0.1352 g inorganic aluminum salt was dissolved in 50 mL 0.2 M formic acid-ammonium formate buffer solution at the pH 4.4. Then the mixed solution was further incubated at  $70 \text{ }^\circ\text{C}$  for 2 h under vigorously stirring. The white precipitation was collected for further characterization.

**Characterization.** Scanning electron microscopy (SEM) experiments were collected on Field Emission Scanning Electron Microscopy (JSM-6701F, JEOL). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy

(HRTEM) images were recorded on a JEOL-2100F operated at 200 kV. X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-2500 with Cu K $\alpha$  radiation at 50 kV and 250 mA. N<sub>2</sub> sorption isotherms were carried out on Micromeritics ASAP 2020 with samples pre-degassed at 150 °C for 12 h. Ultraviolet-visible (UV-Vis) spectra were collected on Shimadzu UV-2550. Raman spectroscopy was performed on DXR Raman Microscope (Thermo Scientific). The concentration of fluoride was measured by ion chromatography (IC Dionex ICS-900) equipped with a Dionex AS 14A analytical column and a DS5 conductivity detector. The eluent is the mixed solution of 3.5 mM of Na<sub>2</sub>CO<sub>3</sub> and 1 mM of NaHCO<sub>3</sub> and at a flow rate of 1 mL min<sup>-1</sup>.

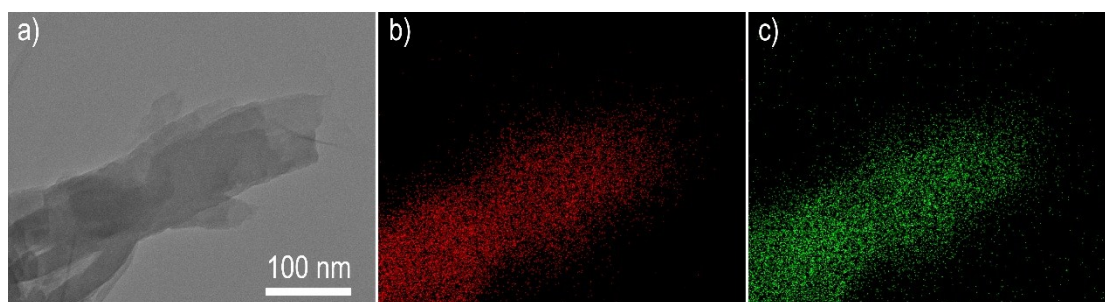


Fig. S1 STEM characterization of randomly-picked m-ABM: (a) morphology mode of STEM image, (b-c) elemental mappings of (b) Al and (c) O on the sample. These demonstrate the obtained ordered microporous sample was aluminum-based material.

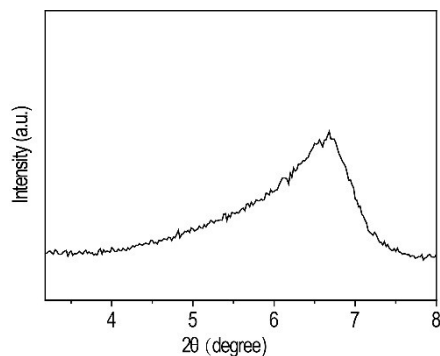


Fig. S2 SAXS pattern of the prepared aluminum-based material. The diffraction peak at  $2\theta$   $6.7^\circ$  is attributed to the reflection from the ordered aluminum-based wall.

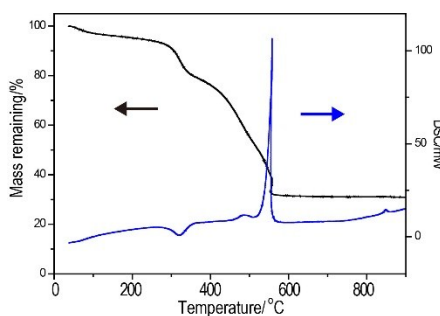


Fig. S3 Thermogravimetric analysis of the prepared sample measured with a heating rate of 10 K/min under oxygen atmosphere. The weight loss at about 100 °C is attributed to the removal of water. The second step of weight loss occurs at slightly less than 300 °C, which is probably because of the melting or decomposition of PA molecule and the dehydration of aluminum hydroxide. The third step at about 550 °C represents the complete removal of residual carbon.

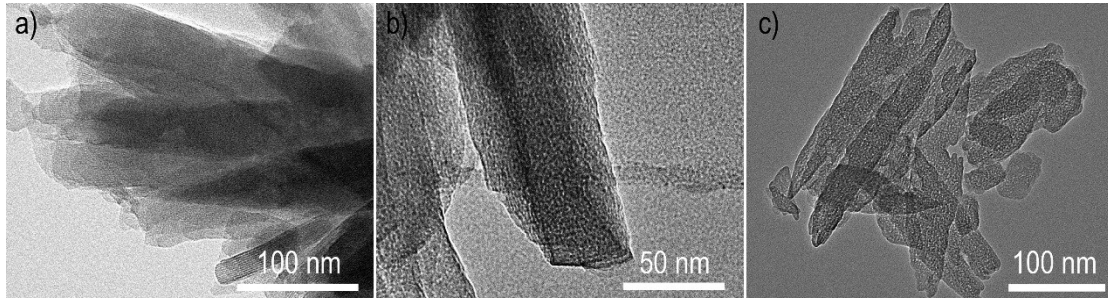


Fig. S4 TEM images of the obtained sample annealed at different temperature, (a) 400, (b) 500 and (c) 550 °C. The microporous structure survived the heating at 400 °C. However, a higher temperature of 500 °C or even 550 °C can seriously damage the channels.

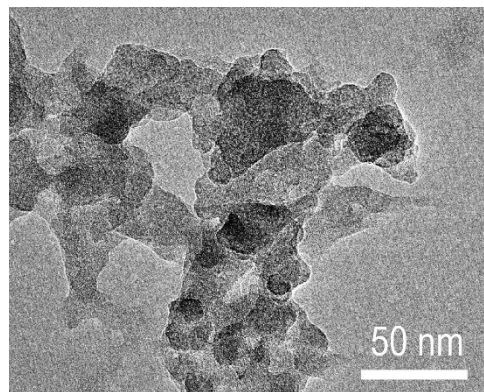


Fig. S5 TEM image of the obtained aluminum oxide prepared by using NaOH as precipitant in the presence of PA molecule. The fast precipitation of  $\text{Al}^{3+}$  form irregular-shaped particles with no ordered pore.

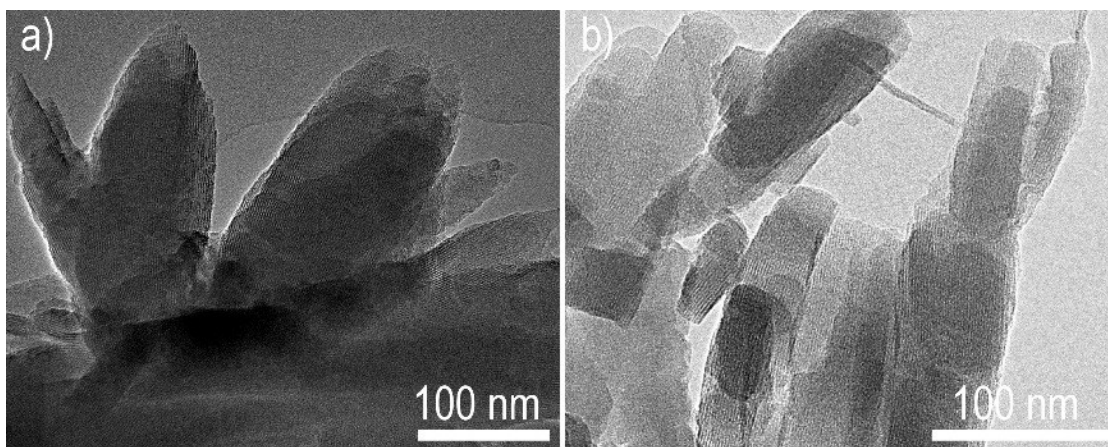


Fig. S6 Low-magnification TEM images of the obtained sample before (a) and after annealing (b) to demonstrate the presence of regular channels.

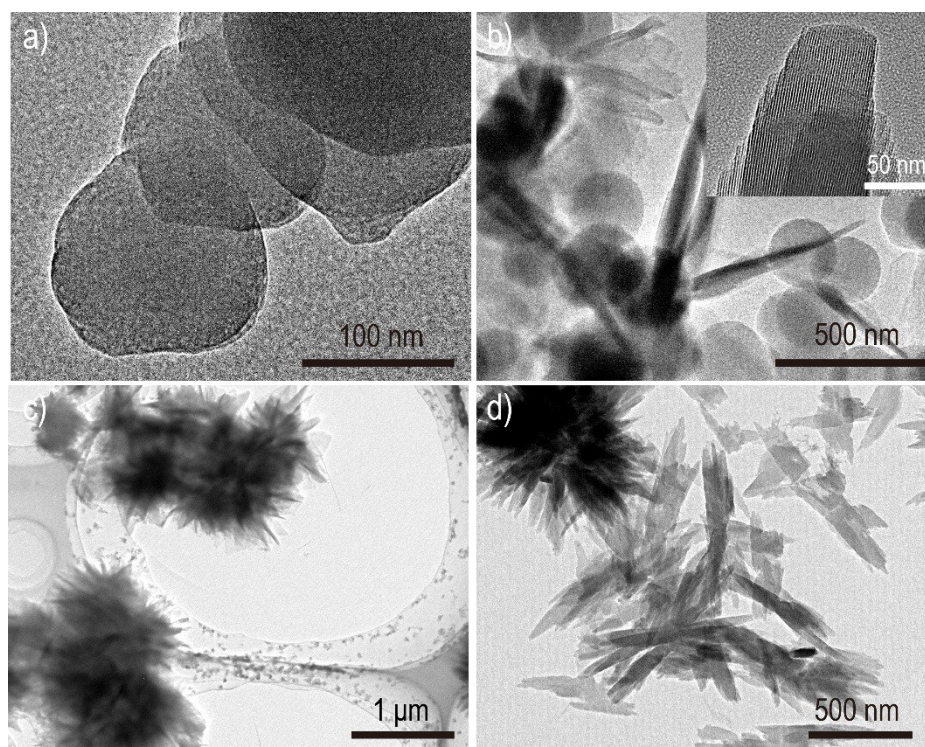


Fig. S7 TEM image of the obtained samples produced by changing the amount of PA molecule, (a) 0, (b) 3.2, (c) 6.4 and (d) 32 mM. In the absence of phthalic acid, only nanoparticles are obtained and there are no regular channels in the sample. When quite a small amount of PA was used, there was co-exist of both nanoparticles with no discernable ordered pore and plate-like materials with regular channels in the prepared samples. The ratio of plate-like materials to nanoparticles increased with the amount of PA used. In the presence of a large amount of PA, only plate-like samples with regular channels were obtained.

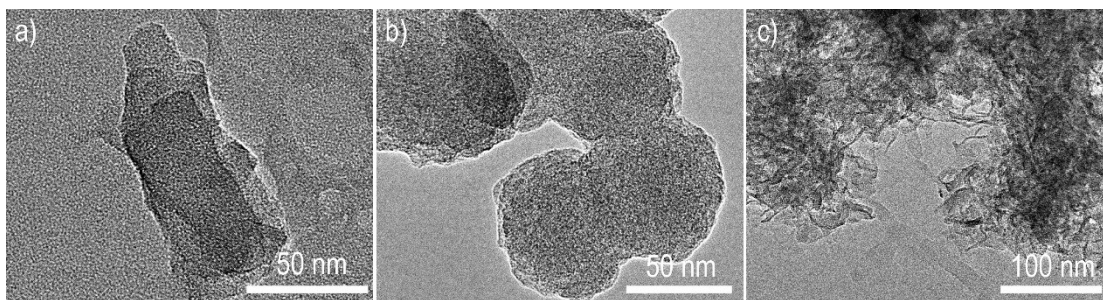


Fig. S8 TEM images of the samples prepared by using different acid containing benzene ring to replace PA molecules, (a) benzoic acid, (b) isophthalic acid, (c) terephthalic acid. Different shaped materials were achieved and no regular channels could be distinguished. These further demonstrate that the coordination interaction between ortho-dicarboxylic group and aluminum ions play a significant role in the formation of regular channels.

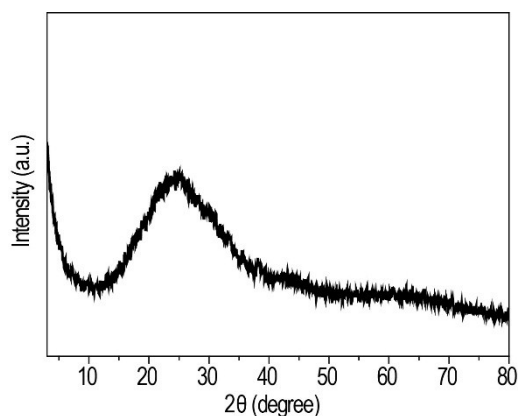


Fig. S9 XRD pattern of the obtained sample produced in the absence of PA molecule. No discernable peaks demonstrate the amorphous property of the precipitates.

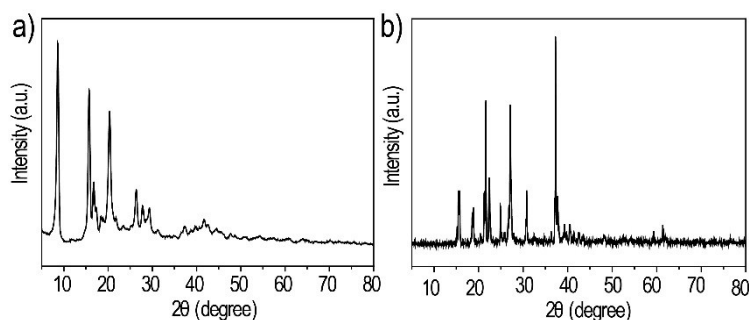


Fig. S10 XRD patterns of (a) prepared microporous material without heat treatment and (b) crystalline PA. The diffraction peaks of the prepared precursor are quite different with the crystalline PA, which demonstrates that the obtained microporous material is a new compound instead of a simple mixture of aluminum hydroxide and PA.

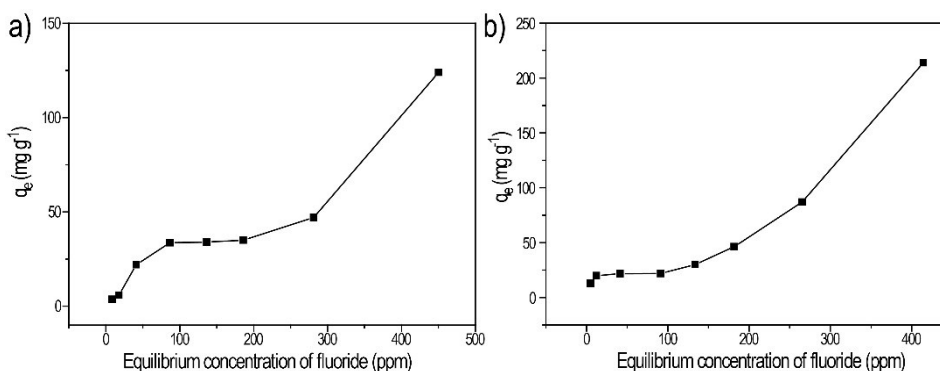


Fig. S11 Adsorption isotherms of fluoride over (a) amorphous  $\text{Al}_2\text{O}_3/\text{MWCNT}$  composite prepared according to the literature and (b)  $\gamma\text{-Al}_2\text{O}_3$  obtained by annealing the prepared microporous material at  $800\text{ }^\circ\text{C}$ . Our microporous sample showed a defluoridation capability  $50\text{ mg}\cdot\text{g}^{-1}$ , showing the advantage of such a microporous structure.

#### Reference.

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2. W. Li, C.-Y. Cao, L.-Y. Wu, M.-F. Ge and W.-G. Song, *J. Hazard. Mater.*, 2011, **198**, 143-150.