Supporting Information

Environment-friendly Synthesis of Highly Hydrophobic and Stable MIL-53 MOF Nanomaterials

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Experimental Section

1. *Chemicals*

$AlCl_3$•$6H_2O$ and $Al(NO_3)_3$•$9H_2O$ (aladdin reagent, Co., Ltd, Shanghai, China, 99%), terephthalic acid (H_2BDC, Sigma Aldrich, 98%), ionic liquid of 1-ethyl-3-methyl-imidazolium bromine (Shanghai Cheng Jie Chemical Co. Ltd, 99%), ethanol and deionized water were used as received.

2. *Synthesis of MIL-53(Al)*

The typical preparation procedure involves firstly dissolving 0.0432 g H_2BDC into 1 g melted 1-ethyl-3-methyl-imidazolium bromine at 100 °C under stirring until a clear solution was obtained; subsequently adding 0.126 g $AlCl_3$•$6H_2O$ into the solution above. The resulted clear precursor in a 10 mL closed glass vessel was heated at 150 °C for 7 days in a preheated oven. After cooling down, the product was cleaned with repeated centrifugations for 5 times using ethanol as solvent. The collected powder was dried at 85 °C, and this sample is designated as MIL-53(Al)$_{it}$. The decanted ionic liquid was collected *via* rotary evaporation at 50 °C for next uses. The reference sample (designated as MIL-53(Al)$_{ht}$) was hydrothermally synthesized according to the previous report with half-reduced concentration of the precursor.[9b]

3. *Characterizations*

The crystalline structures of MIL-53(Al) crystals were determined by X-ray Diffraction (XRD) measurements using Riguku D/MAX2550 diffractometer with Cu-Kα radiation (λ = 1.5418 Å) running at a voltage of 50 kV and a current of 200

mA. Both samples were also characterized on field emission scanning electron microscope (FE-SEM: JEOS JSM6700F). Water vapor adsorption-desorption measurements on the MIL-53(Al)$_{it}$ and MIL-53(Al)$_{ht}$ powders were carried out using an Autosorb iQ2 adsorptometer, Quantachrome Instruments. Prior to the tests, as-synthesized MIL-53(Al) samples were calcined at 330 °C for 3 days with a heating rate of 1 °C min^{-1}. And then, the MIL-53(Al) powders were degassed under vacuum overnight at 150 °C. The measurements were carried out at 298 K. Nitrogen adsorption-desorption measurements were carried out at 77 K. Specific surface areas were determined using the Brunauer-Emmett-Teller (BET) equation; and the pore size distribution and pore volume were calculated by applying the nonlocal density functional theory (NLDFT) method. Fourier transform infrared spectra (FTIR) were collected on a Nicolet Impact 410 FTIR spectrometer at room temperature in the range of 400-4000 cm^{-1}, with potassium bromide pellets. Solid-state ^{27}Al CP/MAS NMR measurement was carried out on a Bruker Avance III model 400 MHz NMR spectrometer at a MAS rate of 5 kHz. Thermal gravimetric analysis (TGA) was performed on MIL-53(Al) samples in air (5 °C min^{-1}) (Netzch Sta 449c thermal analyzer). Elemental analysis was performed using a Perkin-Elmer 240 analyzer.

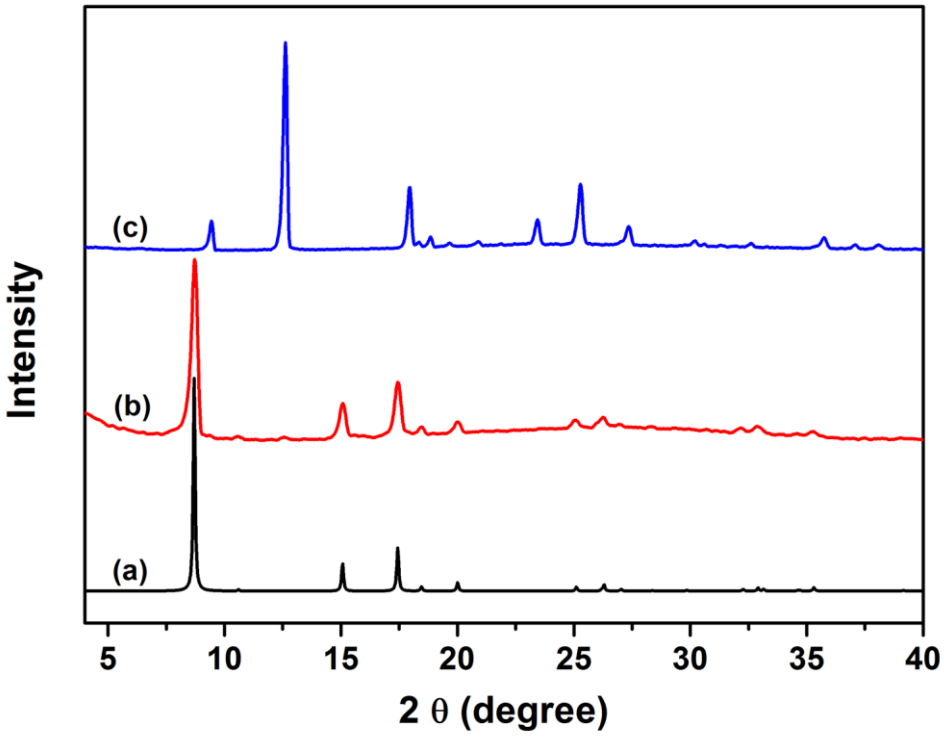

Fig. S1 XRD patterns of (a) large-pore form of MIL-53(Al), (b) calcined MIL-53(Al)$_{it}$ after 30 days and (c) calcined MIL-53(Al)$_{ht}$.

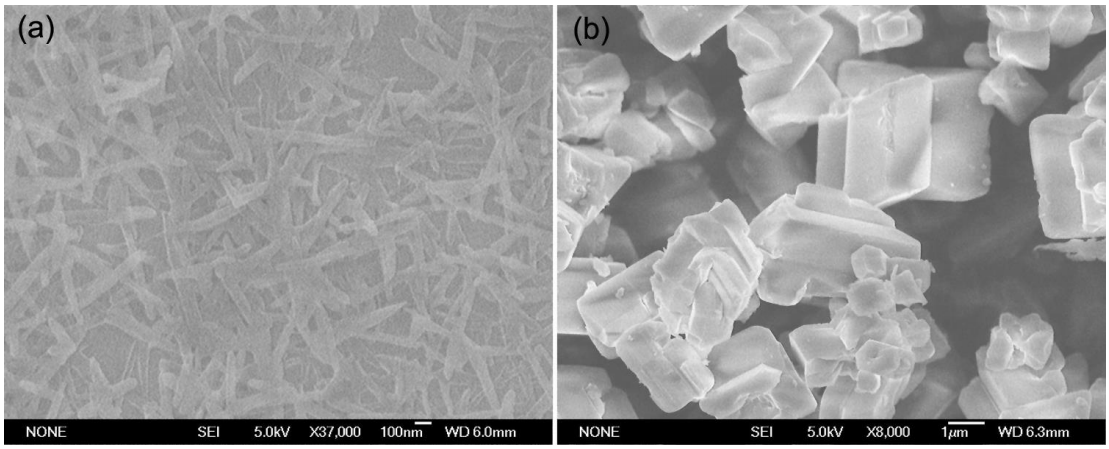

Fig. S2 SEM pictures of (a) MIL-53(Al)$_{it}$ and (b) MIL-53(Al)$_{ht}$ samples.

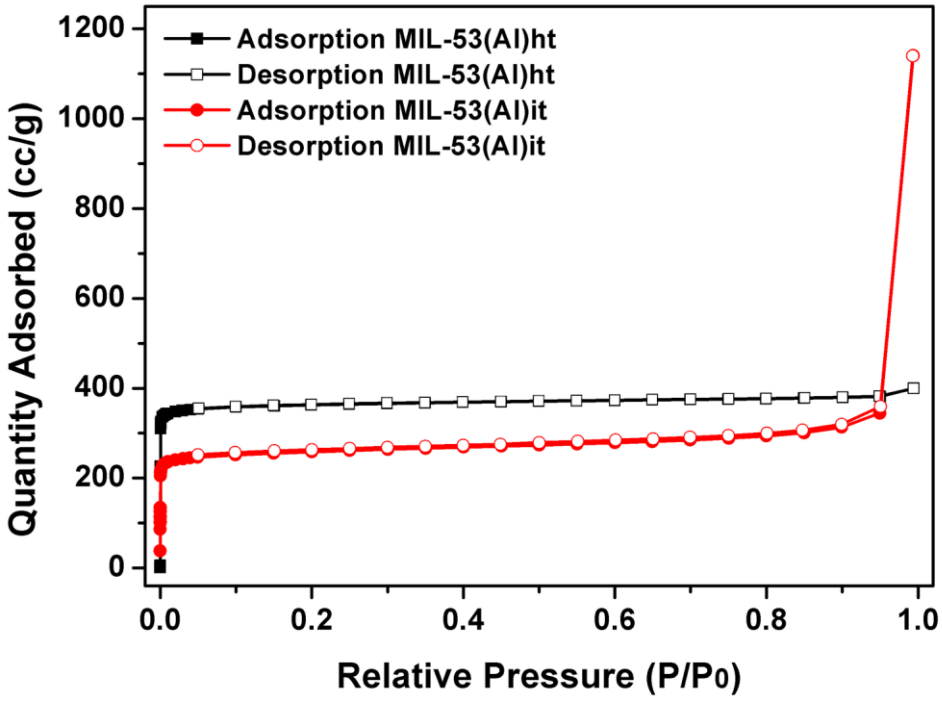

Fig. S3 N_2 adsorption isotherms of MIL-53(Al)$_{it}$ and MIL-53(Al)$_{ht}$ samples.

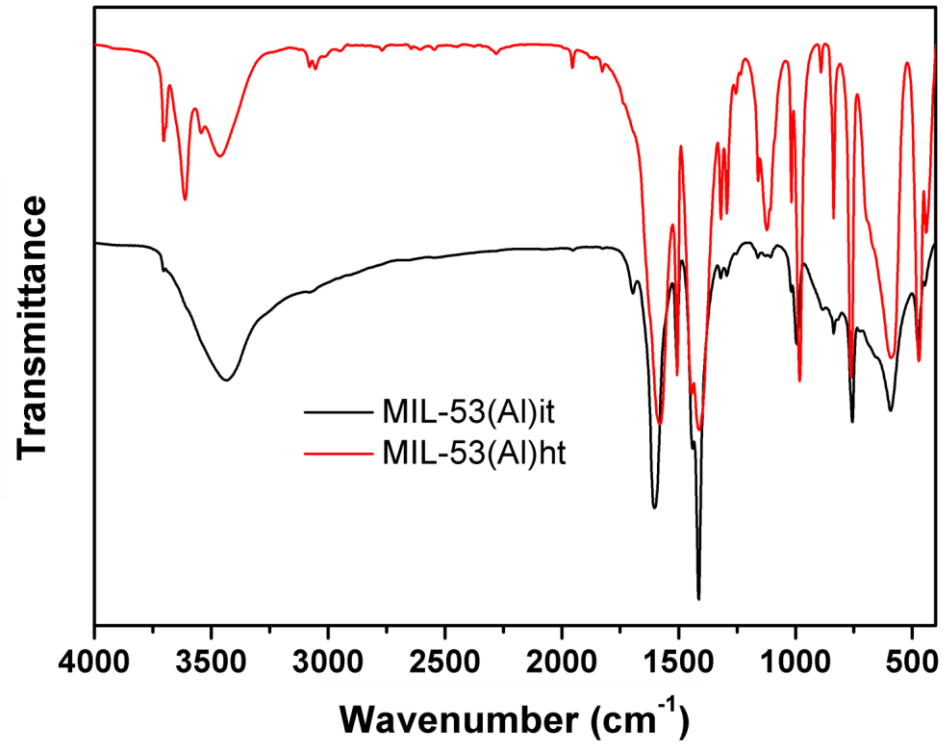

Fig. S4 IR spectra of MIL-53(Al)$_{it}$ and MIL-53(Al)$_{ht}$ samples.

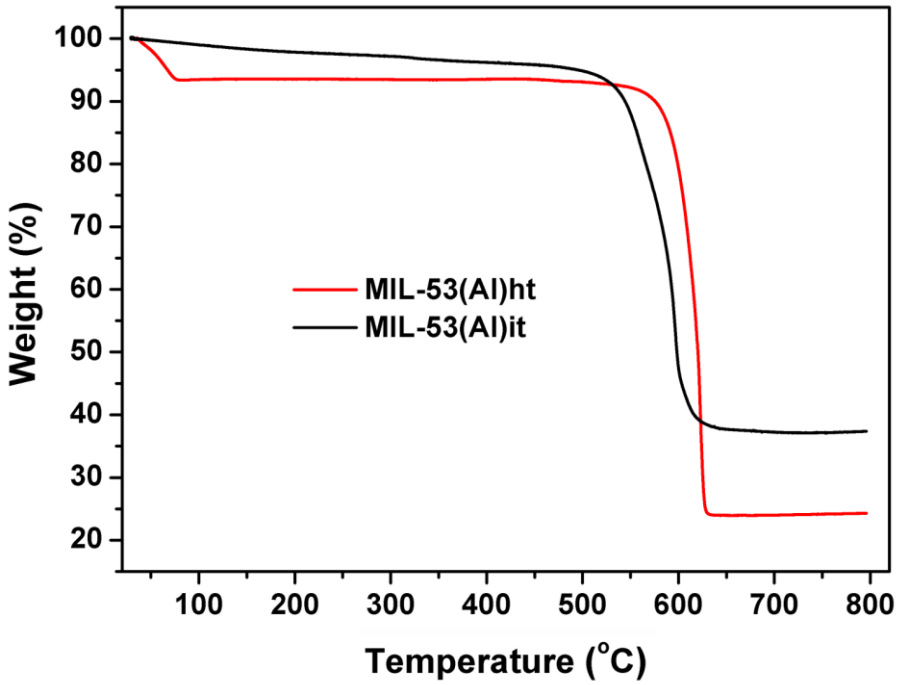

Fig. S5 TG curves of MIL-53(Al)$_{it}$ and MIL-53(Al)$_{ht}$ samples.

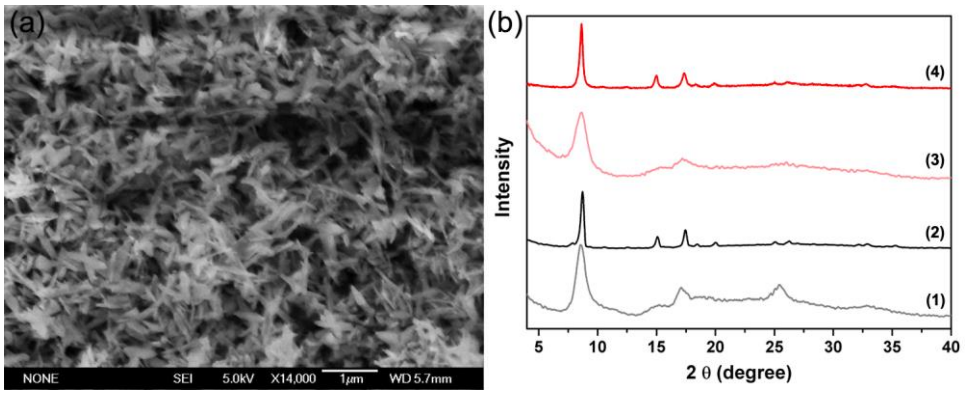

Fig. S6 SEM image (a) and XRD patterns (b) of as-synthesized (3) and calcined MIL-53(Al)$_{it}$ (4) using recycled ionic liquid (the corresponding XRD patterns of initially prepared sample in fresh ionic liquid are shown in (1) and (2)).

Table S1 Results from the N_2-sorption measurements for MIL-53(Al)$_{it}$ and MIL-53(Al)$_{ht}$ samples.

Sample	S_{BET} (m^2 g^{-1})	Pore size (nm)	Micropore volume (cm^3 g^{-1})	Total pore volume (cm^3 g^{-1})
MIL-53(Al)$_{ht}$	1489	0.85	0.49	0.56
MIL-53(Al)$_{it}$	1031	0.83, 3.4	0.36	0.72

Table S2 Elemental analysis of as-synthesized MIL-53(Al)$_{it}$ (designated as MIL-53$_{as}$(Al)$_{it}$), calcined MIL-53(Al)$_{it}$ and MIL-53(Al)$_{ht}$ samples.

Sample	N (wt.%)	C (wt.%)	H (wt.%)	S (wt.%)	C/N molar ratio	C/H molar ratio
MIL-53$_{as}$(Al)$_{it}$	4.39	34.50	4.065	0.142	9.169	0.707
MIL-53(Al)$_{it}$	0.05	33.38	2.807	0.028	778.9	0.991
MIL-53(Al)$_{ht}$	0.04	42.92	3.147	0.053	1251.8	1.137