Electronic Supporting Information

Enhanced moisture sorption through regulated MIL-101(Cr) synthesis and its integration onto heat exchangers

Mei Gui Vanessa Wee,[1,2] Amutha Chinnappan,[2]* Runxin Shang,[3] Poh Seng Lee[3] and Seeram Ramakrishna[1,2]*

[1] Integrative Sciences and Engineering Programme, NUS Graduate School, National University of Singapore, Singapore 119077, Singapore
[2] Department of Mechanical Engineering: College of Design and Engineering: Centre for Nanotechnology and Sustainability, National University of Singapore, Singapore 117576, Singapore
[3] Department of Mechanical Engineering: College of Design and Engineering: Cooling Energy Science Technology Laboratory, National University of Singapore, Singapore, 117576, Singapore
E-mail: wee.mei.gui.vanessa@u.nus.edu, mpecam@nus.edu.sg, seeram@nus.edu.sg

1. Materials and methods

Materials: All chemicals were used as received from the commercial sources listed below. Chromium(III) nitrate nonahydrate (99%, Sigma-Aldrich), terephthalic acid (98%, Sigma-Aldrich), tetramethylammonium hydroxide solution (40 wt% in H_2O, Sigma-Aldrich), tetraethylammonium hydroxide solution (40% in H_2O, Sigma-Aldrich), tetrapropylammonium hydroxide solution (1.0 M in H_2O, Sigma-Aldrich), tetrabutylammonium hydroxide solution (40 wt% in H_2O, Sigma-Aldrich), *N,N*-dimethylformamide (99.8%, Sigma-Aldrich or 99.5% Tokyo Chemical Industries), ethanol (96%, QRëC), polyvinyl alcohol (average MW 85 000 – 124 000, 87 – 89% hydrolyzed, Sigma-Aldrich), colloidal silica (LUDOX®, 40 wt% in H_2O, Sigma-Aldrich), hydroxyethyl cellulose (average MW 90 000, Sigma-Aldrich), silica gel (Shanghai Lingyi Industry and Trade Co.) and calcium chloride dihydrate (99%, Sigma-Aldrich).

ATR-FTIR: The VERTEX 70 FT-IR spectrometer was used to identify functional groups present in the samples via ATR-FTIR between 4000 – 400 cm^{-1}.

PXRD: When screening samples, PXRD patterns were obtained on a Rigaku Miniflex 600 X-ray powder diffractometer equipped with a Cu-sealed tube (λ = 1.540598 Å) at a scan rate of 4 deg/min. For slow scans, PXRD patterns were collected on a Bruker D8 Advance PXRD (λ = 1.54060 A) at a scan rate of 2 deg/min.

NMR: NMR samples were prepared according to the method described by Ko et al.[1] ^{1}H-NMR measurement was then carried out using a 600 MHz NMR spectrometer.

FESEM: The samples were gold-coated using a Cressington Sputter Coater before characterizing their morphology via FESEM in the Hitachi Model S-4300.

TEM: TEM images were collected using the JEOL JEM-2010F to further ascertain the sample's morphology. The samples were prepared by adding ethanolic dispersions of MIL-101(Cr) dropwise to a carbon film-coated copper grid before air-drying overnight. ImageJ was then used to study the particle size distribution from these TEM images.

N_2 sorption: The NOVAtouch 4LX was used to quantify the samples' porosities based on methods previously reported by Elsayed et al.[2] Firstly, the samples were degassed overnight *in vacuo* at 393 K before the N_2 sorption isotherms were collected at 77 K. The S_{BET} was derived between p/p_0 = 0.03 – 0.3, the V_{pore} was calculated at p/p_0 = 0.98, and the DFT method was used for determining the pore size distribution.

Water sorption analyses: The samples' water sorption characteristics were studied in the Surface Measurements System Dynamic Vapor Sorption (DVS). The isotherms were collected at 298 K. For the cyclic tests, the adsorption (90 min) and desorption (65 min) durations were adapted from previous work by Entezari et al.[3]

TGA: Using the Shimadzu DSC-60 differential scanning calorimeter, TGA data were collected based on the method reported by Elsayed et al. from 298 – 873 K, 10 K/min and argon flow at 60 mL/min.[2]

2. Experimental data

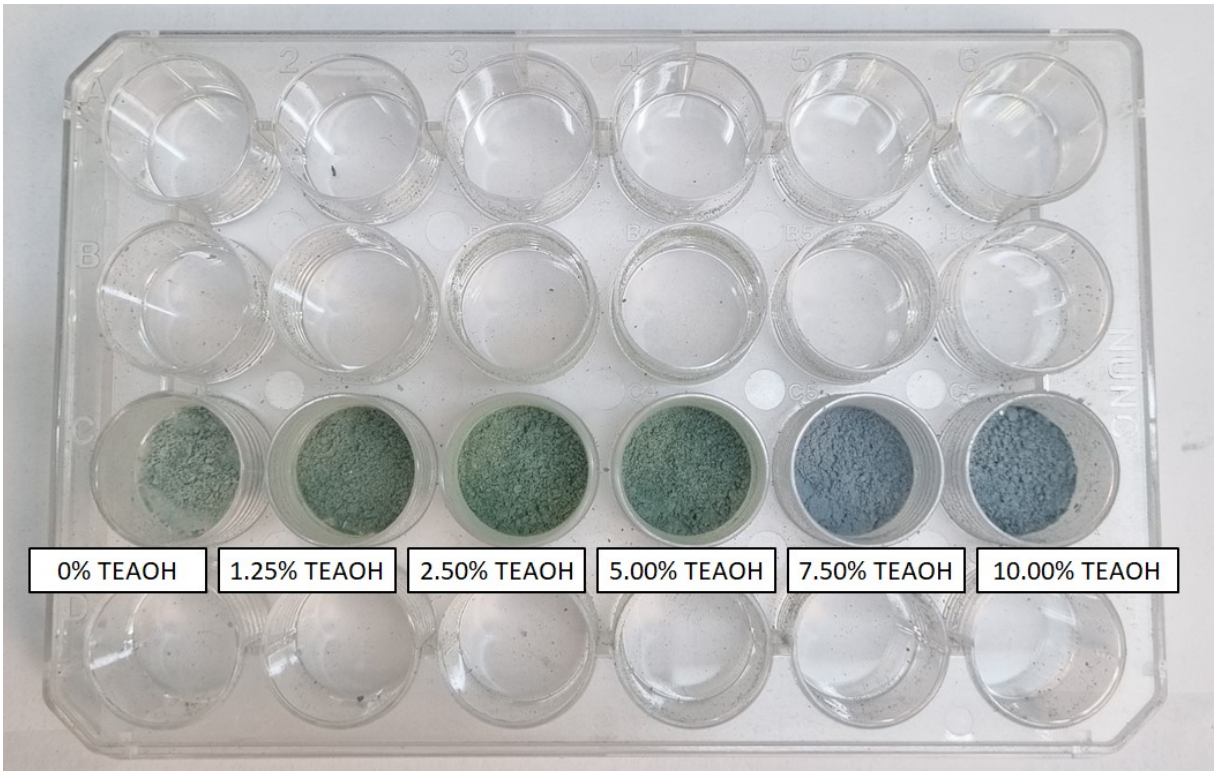

Figure S1. Digital photograph of samples prepared from 0, 1.25, 2.50, 5.00, 7.50 and 10.00% TEAOH solutions.

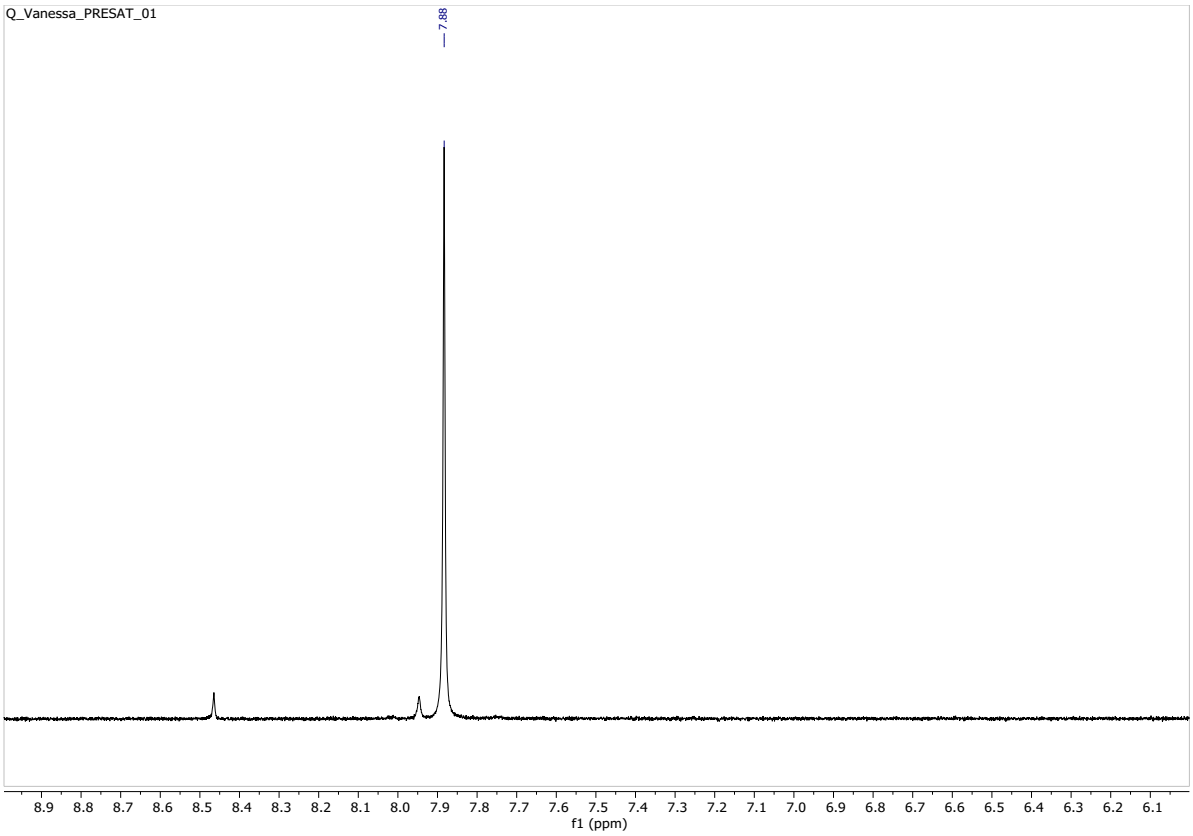

Figure S2. ^{1}H NMR spectrum of the linker extracted from the MIL-101(Cr) sample prepared using 1.25% TEAOH.

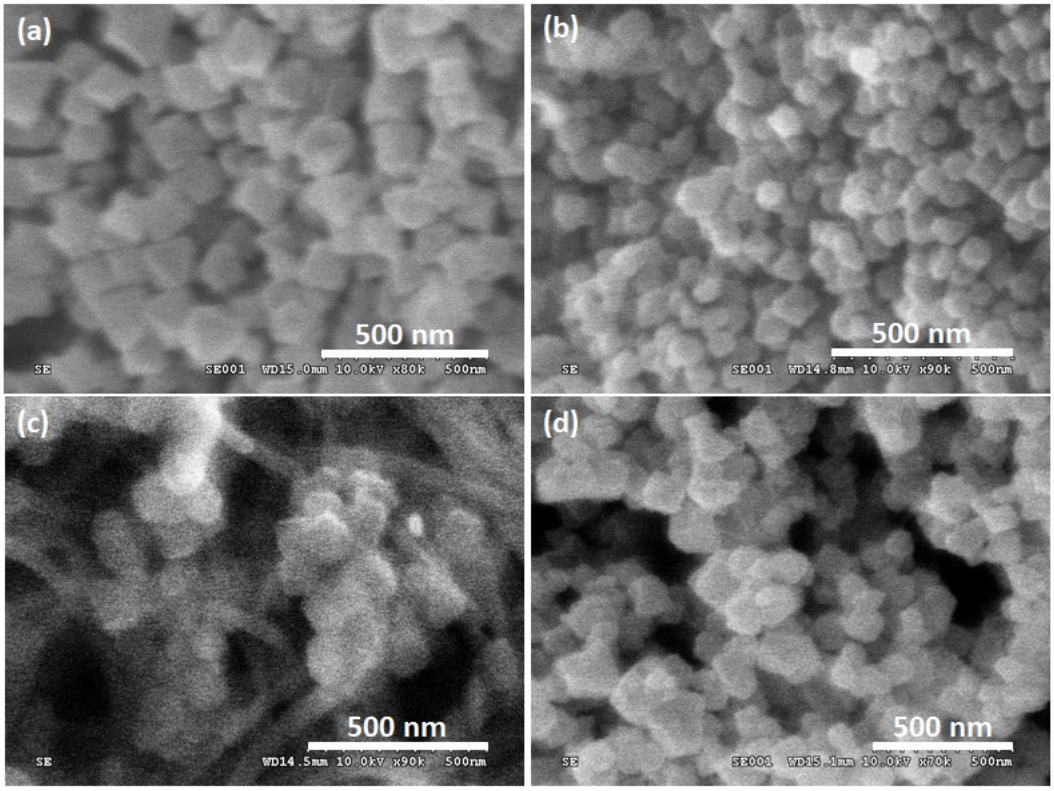

Figure S3. FESEM images of MIL-101(Cr) prepared from 1.25% quaternary alkylammonium hydroxide solutions from (a) TMAOH, (b) TEAOH, (c) TPAOH and (d) TBAOH with scale bars at 500 nm.

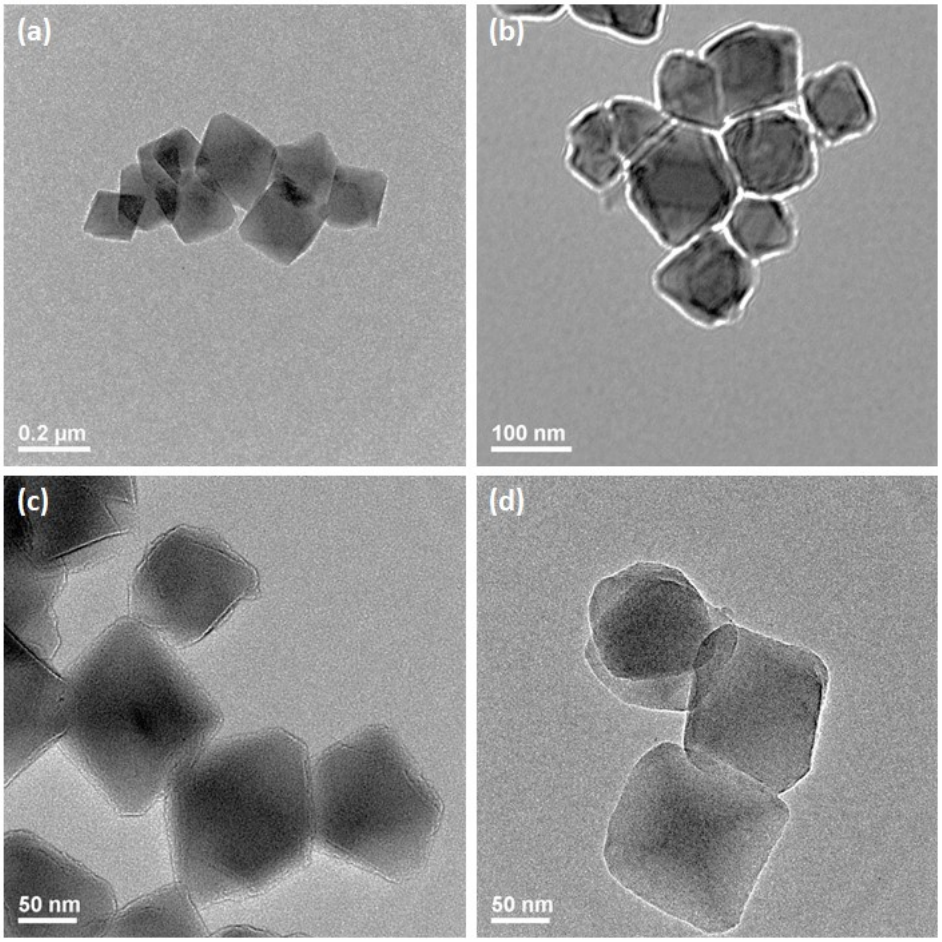

Figure S4. TEM images of samples prepared using 1.25% TMAOH solutions showing cuboctahedral particles and needlelike terephthalic acid crystals with scale bars at (a) 0.2 µm, (b) 100 nm and (c, d) 50 nm.

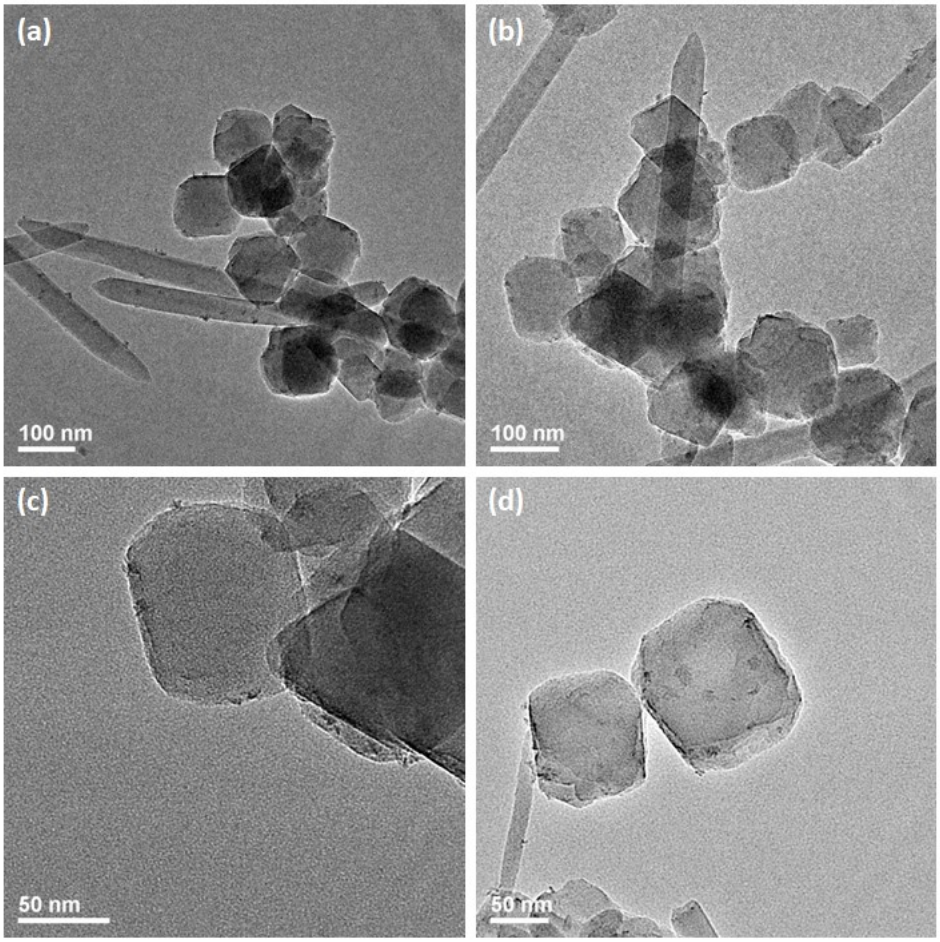

Figure S5. TEM images of samples prepared using 1.25% TPAOH solutions showing cuboctahedral particles and needlelike terephthalic acid crystals with scale bars at (a, b) 100 nm and (c, d) 50 nm.

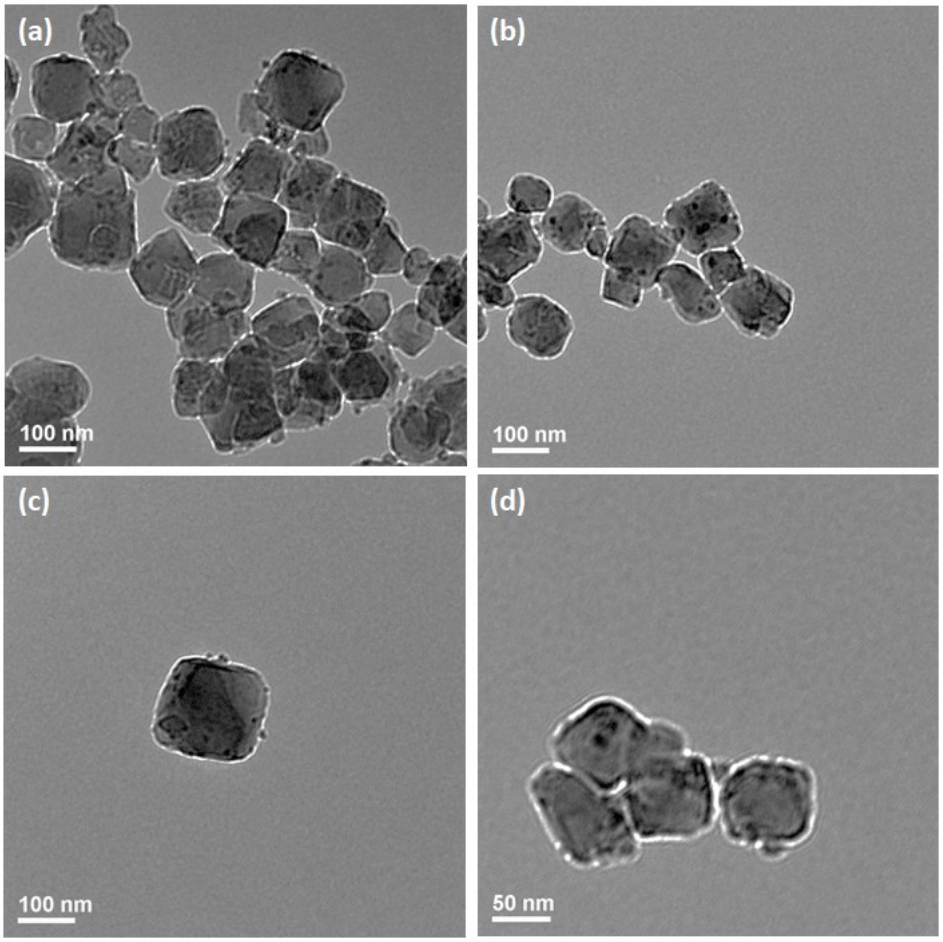

Figure S6. TEM images of samples prepared using 1.25% TBAOH solutions showing cuboctahedral particles and needlelike terephthalic acid crystals with scale bars at (a, b, c) 100 nm and (d) 50 nm.

Table S1. The mass of water uptake and the mass of water released in each adsorption-desorption half cycle for Tests 1 – 4.

	Cycle 1		Cycle 2		Cycle 3	
Test	**Water uptake/g**	**Water released/g**	**Water uptake/g**	**Water released/g**	**Water uptake/g**	**Water released/g**
1	0.61	0.48	0.60	0.47	0.59	0.46
2	0.69	0.53	0.78	0.56	0.83	0.61
3	0.73	0.42	0.91	0.51	0.91	0.53
4	0.27	0.16	0.27	0.17	0.25	0.15

Table S2. The mass of water uptake and the mass of water released in each adsorption-desorption half cycle for Test 5.

Cycle no.	**Water uptake/g**	**Water released/g**
1	0.33	0.31
2	0.37	0.35
3	0.37	0.34
4	0.35	0.33
5	0.36	0.33
6	0.36	0.34
7	0.34	0.32

3. References

[1] N. Ko, P. G. Choi, J. Hong, M. Yeo, S. Sung, K. E. Cordova, H. J. Park, J. K. Yang, J. Kim, *J Mater Chem A Mater* **2015**, *3*, 2057.

[2] E. Elsayed, H. Wang, P. A. Anderson, R. Al-Dadah, S. Mahmoud, H. Navarro, Y. Ding, J. Bowen, *Microporous and Mesoporous Materials* **2017**, *244*, 180.

[3] A. Entezari, M. Ejeian, R. Wang, *Appl Therm Eng* **2019**, *161*, DOI 10.1016/j.applthermaleng.2019.114109.