Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Hierarchical Porous Metal-Organic Framework Monoliths

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Experimental Details

Chemicals and Reagents. 1,3,5-benzenetricarboxylic acid (BTC, 95%), styrene (≥ 99%), ethylbenzene, Basolite C300, $Cu(CH_3COO)_2.H_2O$, $Cu(NO_3)_2.3H_2O$, $Cr(NO_3)_3.9H_2O$, absolute ethanol, and all the solvents were purchased from Sigma-Aldrich and used as received. The HPLC grade solvents were used for HPLC tests.

Powder-packing synthesis of HKUST-1 monoliths. $Cu(CH_3COO)_2{\cdot}H_2O$ (1.0 mmol) and BTC (0.7 mmol) were directly used or ground separately using a pestle and mortar before use. The ground powders were combined in a glass vial with a 1 cm diameter and mixed thoroughly on an Agitator IKA® KS130 for 10 minutes. Ethanol/H_2O (3:4 v/v, 0.3 cm^3) was added to the powder dropwise and the vial was sealed. The reaction was left for 24 hours at room temperature. The resulting HKUST-1 monolith was dried under vacuum at room temperature for 24 hours.

For post-treatment, 0.1 g monolith was placed in a glass vial containing ethanol (10 cm^3) which was then placed in a Teflon liner within an autoclave. The autoclave was heated in a furnace at 120 ^oC for 24 hours. The sample was then filtered and ethanol was removed from the soaked monolith under vacuum at room temperature. When the monolith was in a stainless steel column, the column was soaked in ethanol, sealed and then placed in a furnace for the treatment.

For the synthesis of MIL-101(Cr) monolith, $Cr(NO_3)_3.9H_2O$ (1.25 mmol) and terephthalic acid (1.7 mmol) were ground separately using a pestle and mortar. The ground powders were combined in a glass vial with a 2 cm diameter and mixed on an Agitator IKA® KS130 for 10 minutes. H_2O (0.5 cm^3) was then added to the powder and the vial was sealed inside an autoclave. The reaction was left for 16 hours at 218 ^oC in a furnace. The resulting MIL-101(Cr) monolith was dried under vacuum at room temperature for 24 hours.

As comparison, HKUST-1 monolith was also prepared by slurry packing and compression of HKUST-1 particles. These HKUST-1 particles were prepared solvothermally using $Cu(NO_3)_2.3H_2O$ (0.3 mmol) and BTC (0.6 mmol) in 1:1 ethanol/H_2O (8 cm^3) in a Teflon liner in a sealed autoclave at 120 ^oC for 12 hours. For the slurry packing, the HKUST-1 slurry in methanol was poured into a column using the in-house packing method at 350 bars with Knauer K-1900. The packed column was also tested for the separation of styrene and ethylbenzene. For the compression approach, the HKUST-1 particles were compressed into a disc by a manual hydraulic press at the pressure of 566 MPa.

The slurry packing procedure was also to pack Basolite C300 particles into a column for HPLC test.

HPLC tests. The column was fitted into an Agilent 1200 series HPLC, comprising of a vacuum degasser, quaternary pump, ALS auto-sampler, heated column compartment and UV-Vis detector. All the tests were carried out at 25 ^oC unless otherwise stated. All signals were UV detected at 254 nm. Data analysis was performed using Agilent Chemstation software, version B.02.01 (Agilent Technologies, USA).

Sample Characterizations. The morphologies were observed by a Hitachi S-4800 SEM equipped with an EDX detector. The samples were coated with gold using a sputter-coater (EMITECH K550X) for 2 minutes at 25 mA before imaging. The BET surface area and pore size by N_2 sorption at 77 K were measured using a Micromeritics ASAP 2420 adsorption analyzer. The micropore size distributions were calculated by the NLDFT method which is typically used for micropores. Mesopore size distributions were calculated by the BJH method from the desorption data. Samples were degassed for 10 h at 120 °C for HKUST-1 samples before N_2 sorption analysis. For the cage and PIM samples, the degassing was performed at 100 ^{o}C for 48 hours. The pore volume and macropore distribution were determined using Hg intrusion porosimetry (Micromeritics Autopore IV 9500) in the pressure range of 0.10- 60000 psia. PXRD data were collected on a Panalytical X'Pert Pro Multi-Purpose Diffractometer in high-throughput transmission geometry. Cu anode operated at 40 kV and 40 mA. Samples were pressed into the well of aluminium plate. The PXRD patterns were collected over 5-50° 2θ with a scan time of 40 minutes. Compression test was conducted using an Instron 4204 with a 1 kN loading cell and cylindrical samples (30 mm height × 4.6 mm diameter). Sonication was performed using a Fisher Scientific FB15048 sonication bath.

Table S1. Effect of different solvents on the formation of HKUST-1 monoliths

Solvent	**Observations**
DMSO	Monolith formed
Ethanol	Monolith formed
Ethanol/H_2O	Monolith formed
Water	Crystalline particles formed

Note: Water was found to only produce MOF powders. Ethanol, DMSO and ethanol/H_2O (3:4 v/v) were found to yield monoliths with characteristic HKUST-1 PXRD pattern. Due to its effectiveness and its less toxic nature compared to DMSO, ethanol/H_2O was chosen as the solvent for the preparation of HKUST-1 monoliths. In this study, the precursor powder mixture is always 0.2 g (1.0 mmol) $Cu(CH_3COO)_2$ + 0.14 g (0.7 mmol) BTC.

Table S2. Effect of solvent volume on the formation of monoliths.

Solvent volume (cm^3)	**cm^3 g^{-1}**	**Observations**
0.1	0.29	No reaction
0.2	0.59	Monolith formed (unreacted areas present)
0.3	0.88	Monolith formed
0.4	1.18	Monolith formed (brittle)
0.5	1.47	Crystals formed
0.6	1.76	Crystals formed

Note: Different volumes of solvent ethanol/H_2O (3:4 v/v) were added dropwise to the fixed amount of powder precursors 0.2 g $Cu(CH_3COO)_2$ + 0.14 g BTC. Initial observations showed that the monolithic structure was greatly impacted by solvent volume. When too little solvent was present the reaction failed to initiate and the monolith was not formed (0.29 cm^3g^{-1}) or only partially formed (0.59 cm^3g^{-1}). Too much solvent resulted in the monolith becoming brittle (1.18 cm^3g^{-1}) and as the volume increased further only powder/crystals were formed.

The preparation of monoliths relied on closely the formation and aggregation of HKUST-1 crystals in the packing powders during the reaction. When too much solvent was added, this caused the dissolution of the precursors (copper acetate/BTC) to a larger extent and individual HKUST crystalline particles were formed rather than a monolith.

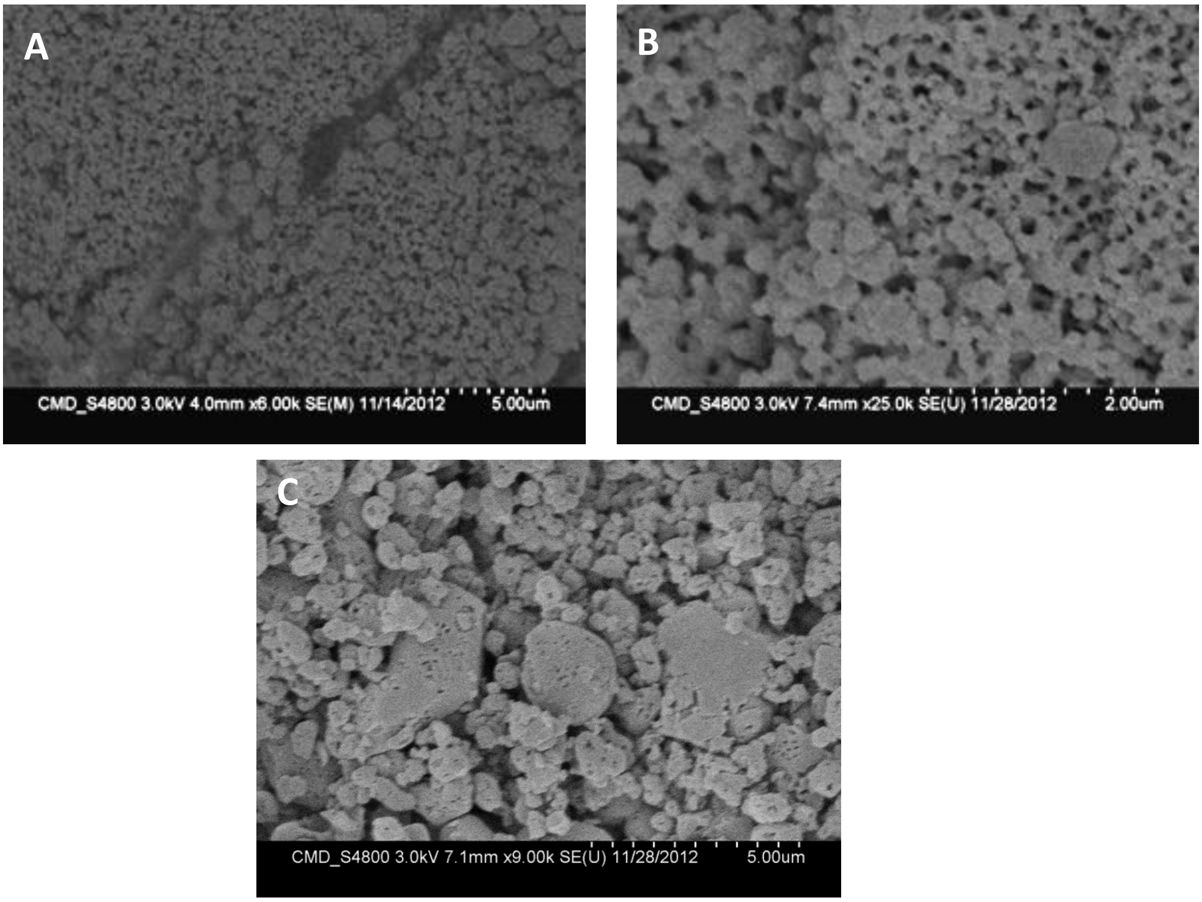

Fig. S1. The SEM images show the macroporous structure of the monoliths prepared with ethanol:water (3:4 v/v) at room temperature (A), 60 °C (B), and 90 °C (C). The particles-based macroporous structures are retained for all the samples. However, with the increasing reaction temperature, some larger porous particles are formed and the particles look more discrete from each other.

$Cu(CH_3COO)_2$ (0.2 g, 1.0 mmol) and Benzene-1,3,5-tricarboxylic acid (0.140 g, 0.7 mmol) ground separately and dry mixed in a glass vial (1 cm diameter) followed by the addition of 0.88 cm^3 g^{-1} of ethanol/H_2O (3:4 v/v) to initiate the reaction which was then left for 24 hours.

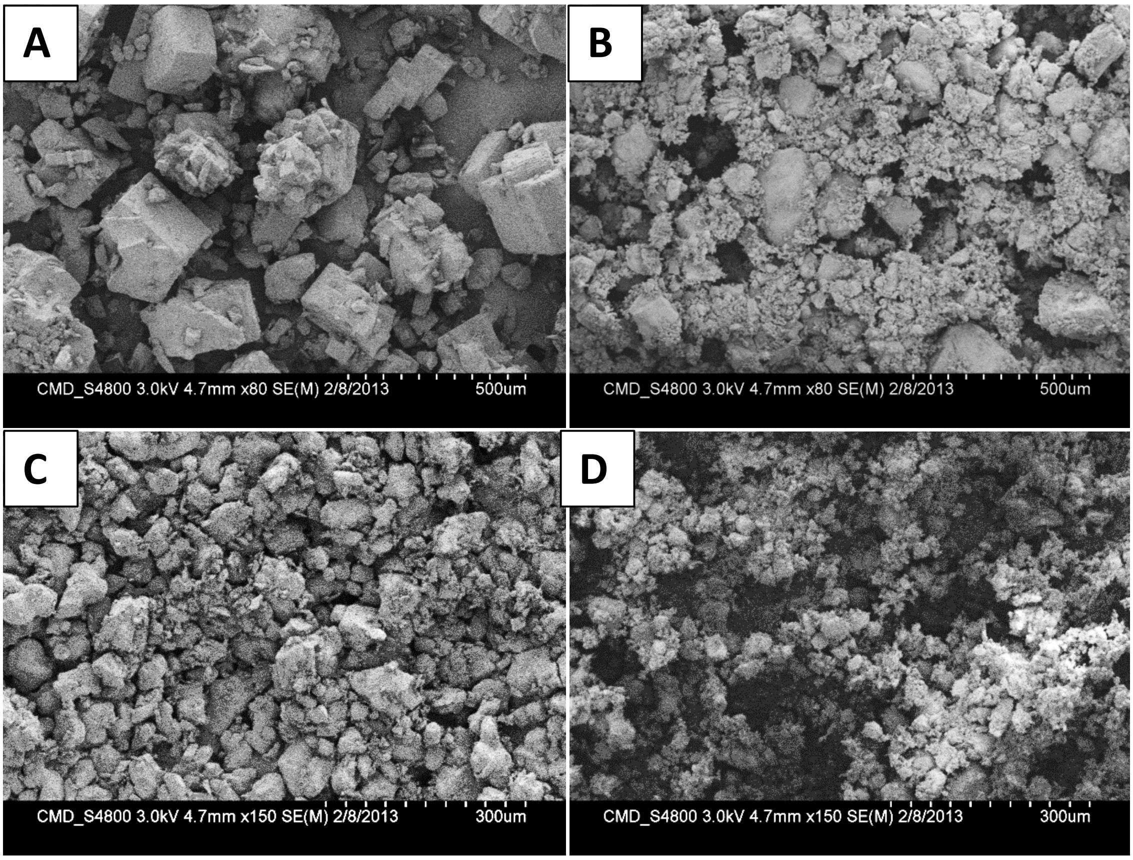

Fig. S2. SEM images of BTC powder before grinding **(A)** and after grinding **(B)**, and those of Cu(OAc)$_2$.H$_2$O before grinding **(C)** and after grinding **(D)**. Grinding the starting powers reduces the particle sizes and improves the monolith synthesis.

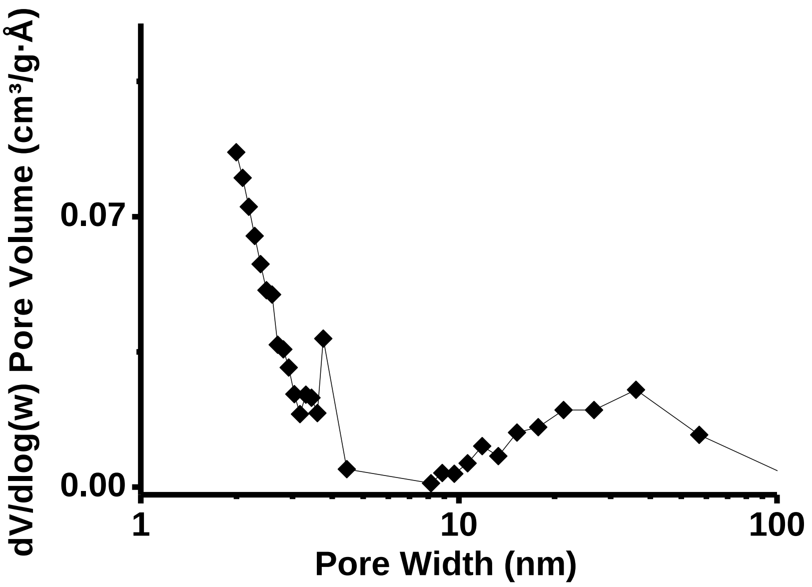

Fig. S3. The mesopore size distribution calculated by the BJH method from the desorption data for the ethanol-treated HKUST-1 monolith.

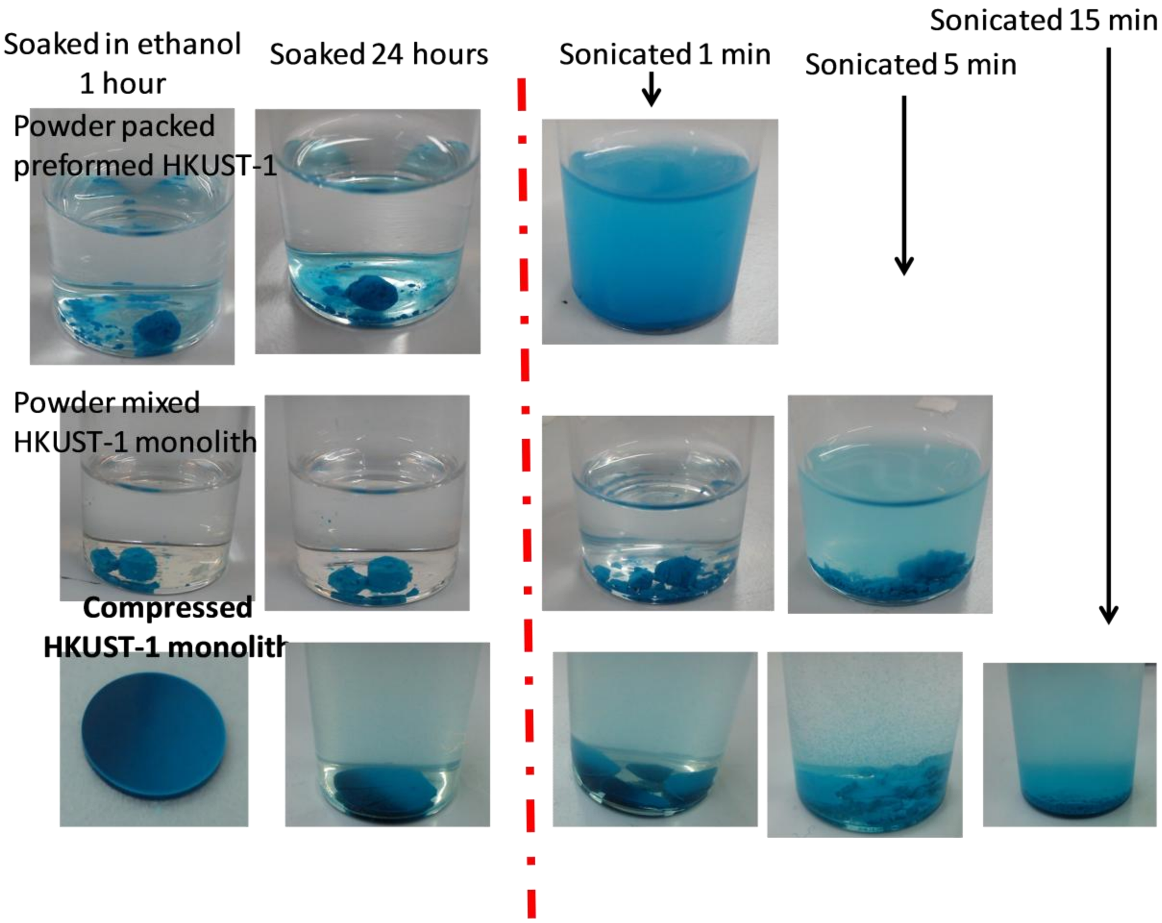

Fig. S4. Photos to show the comparison of monolith stability by soaking and sonicating in ethanol. The monolith prepared by compression with a manual hydraulic press seemed more stable. See further data & discussion in Figure S5 for the compressed monolith.

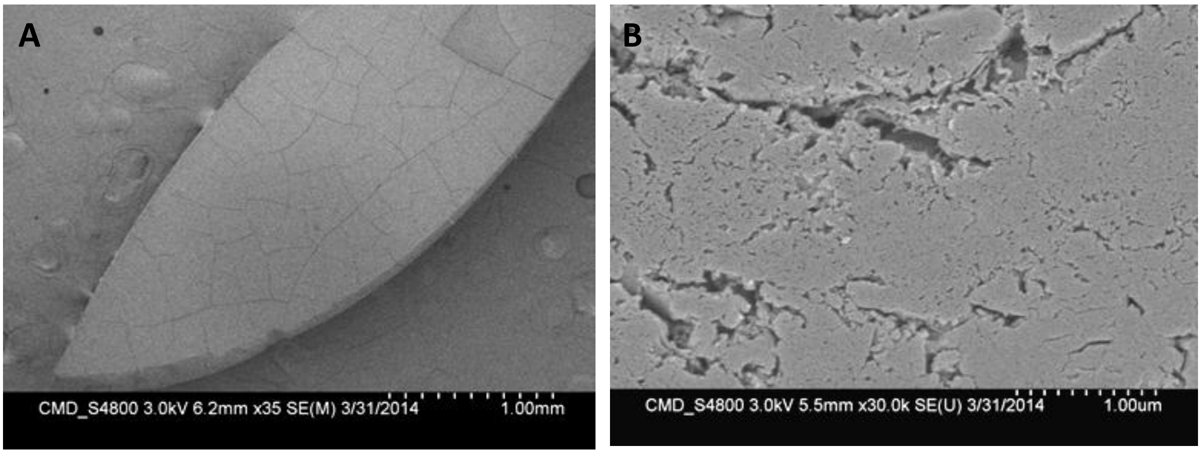

Fig. S5. The SEM images of the HKUST-1 monolith prepared by a manual hydraulic press at the pressure of 566 MPa. The monolith was formed by compressing the pre-formed HKUST-1 crystalline microparticles (prepared by a solvothermal method using water/ethanol as solvent) for 1 minute. The monolith seemed very stable. However, cracks were developed on the surface. And a skin dense surface was formed as well. These features are not good for separation applications. Also it may not be possible to prepare a monolithic column by this approach.

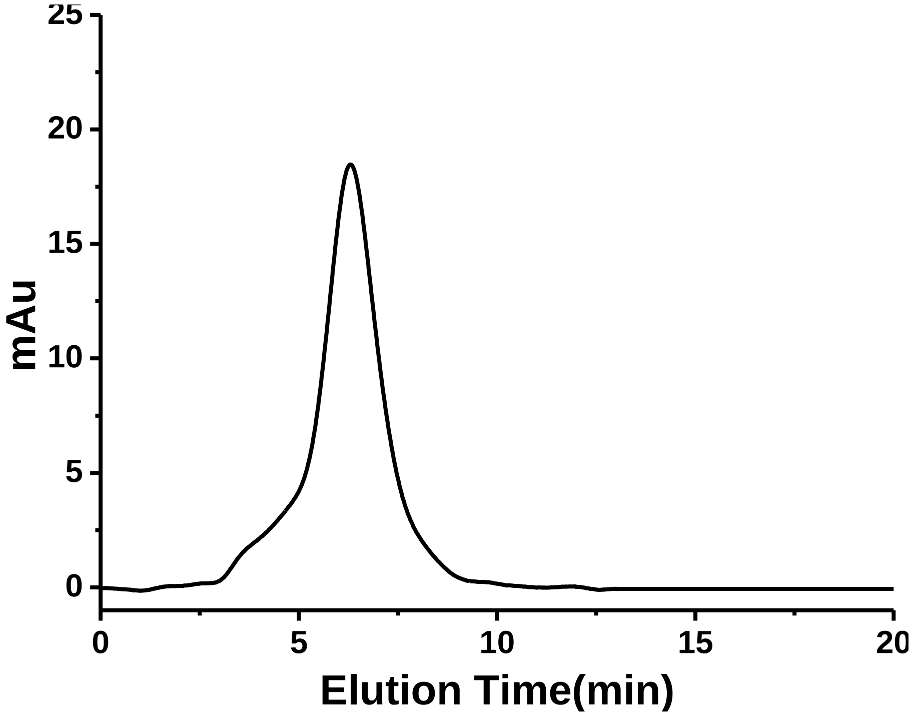

Fig. S6. HPLC chromatogram for the separation of ethylbenzene (1) and styrene (2) with Basolite C300-packed column. Condition: injection 1µL, flow rate using heptane:DCM 98:2 v/v as the mobile phase 1 cm^3 min^{-1}.

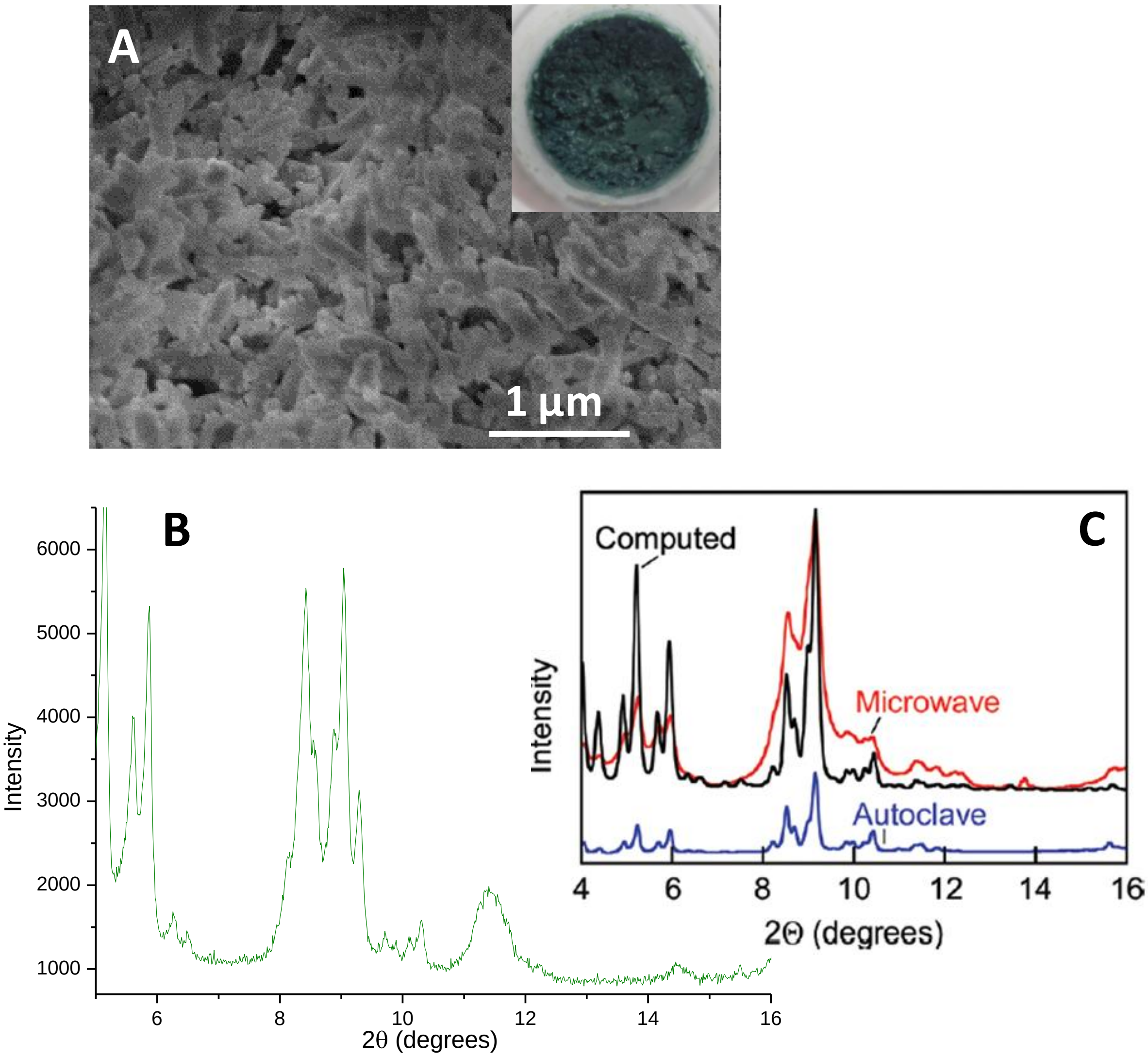

Fig. S7. (A) The SEM image and photo of the prepared MIL-101 (Cr) monolith. (B) The PXRD pattern of the MIL-101 (Cr) monolith and (C) the PXRD pattern of MIL-101 (Cr) crystals produced from the literature. (L. Bromberg, Y. Diao, H. M. Wu, S. A. Speakman and T. A. Hatton, *Chem. Mat.*, 2012, **24**, 1664-1675.) The PXRD patterns agree with each other.