Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Data

Facile Synthesis of Metal-Organic Framework Membranes via *In Situ* Seeding of Nanoparticles

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Experimental

Chemicals

Chromium nitrate nonahydrate [$Cr(NO_3)_3 \cdot 9H_2O$, 99%], copper nitrate hemi(pentahydrate) [$Cu(NO_3)_2 \cdot 2.5H_2O$], Whatman Anodisc 13 and benzene-1,3,5-tricarboxylic acid (H_3btc) were purchased from Fisher Scientific. 1.4-Benzenedicarboxylic acid (H_2bdc, 98%) was purchased from Lancaster Synthesis. *N*,*N*-Dimethylacetamide (DMA, 99%) was purchased from Alfa. Poly(acrylic acid) sodium salt (Mw:2100) were purchased from Aldrich. Alumina plates (Plate notched alumina 100 mm × 120 mm GE Healthcare) was purchased from Fisher Scientific and cut into 10 mm × 15 mm pieces for further use.

Synthesis of MIL-101 films on alumina plates

The alumina plate with size of 10 mm × 15 mm was cleaned with DMA in a teflon-lined autoclave at 220 °C for 8 h to remove any contaminants from the surface. After cooling, the alumina plate was taken out from the Teflon-line autoclave, and washed with fresh DMA. The DMA-wetted alumina plate was subsequently placed in a home-made teflon holder, immersed vertically inside a teflon insert containing the synthesis solution and heated in a stainless steel autoclave at 220 °C for 8 h. The synthesis solution contained 0.33 mmol $Cr(NO_3)_3 \cdot 9H_2O$, 0.33 mmol H_2bdc and 10 cm^3 H_2O. The resulting films were washed with water and then dried at room temperature.

Synthesis of $Cu_3(btc)_2$ films on anodisc

The anodisc was dipped into the poly(acrylic acid) sodium salt (PAA salt) aqueous solution (2g PAA salt /10 ml H_2O) for 30 min and taken out. The treated anodisc was subsequently placed in a home-made Teflon holder, immersed vertically inside a Teflon insert containing the synthesis solution and heated in a stainless steel autoclave at 100 °C for 24 h. The synthesis solution contains 1.5 mmol $Cu(NO_3)_2 \cdot 2.5H_2O$, 0.8 mmol H_3btc, 6 mL H_2O and 6 mL ethanol. The resulting films were washed with water by ultrasonication for 10 min and then dried at room temperature.

Characterisation

X-ray diffraction (XRD) patterns of the materials were recorded on Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.542 Å). Scanning Electron Microscopy (SEM) measurements were carried on a JEOL JSM6480LV instrument. Infrared spectra of the samples were measured using a PerkinElmer Spectrum 100 spectrometer equipped with an ATR sampling accessory.

Grazing incidence X-ray diffraction (GIXD)

The film for the grazing incidence X-ray diffraction experiments was grown onto a flat Al_2O_3 film coated on a silicon wafer of the size 15 mm × 15 mm. The GIXD experiments were carried out on Beamline I07 at the Diamond Light Source, UK using monochromatic X-ray radiation of energy 12.5 keV (λ = 0.1090 Å) and a Pilatus detector. The pattern was taken at an incident angle of 0.25^o with one second exposure and the image axes converted to angle using a silver behenate film as a calibrant.

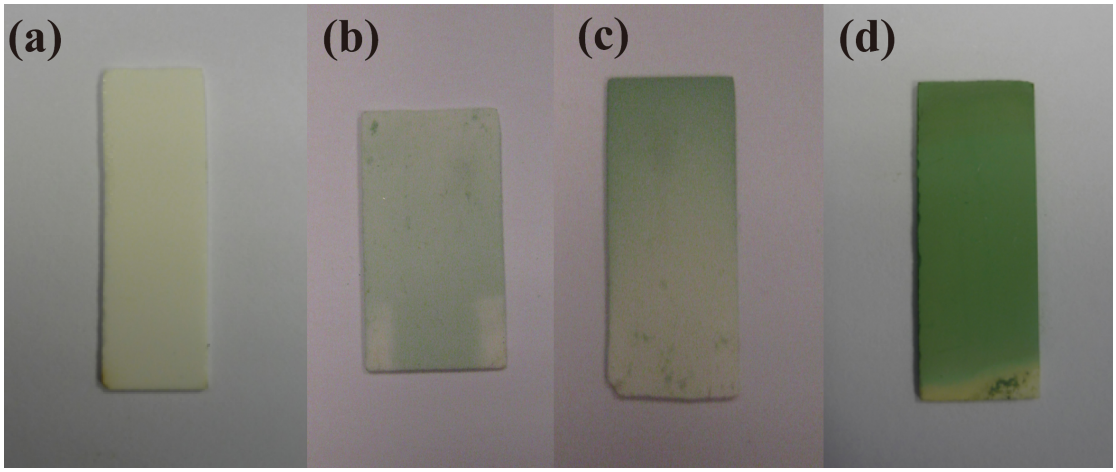

Fig. S1. Digital photographs of (a) alumina plate, (b) MIL-101(Cr) film synthesised via the 'reactive seeding' method, (c) MIL-101(Cr) synthesised without DMA wetting on the alumina plate and (d) MIL-101(Cr)-A film synthesised with DMA wetting on the alumina plate.

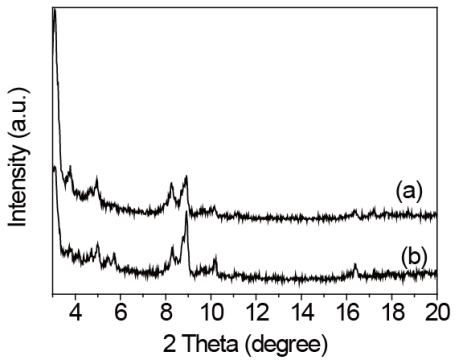

Fig. S2. XRD patterns of MIL-101(Cr) synthesised (a) with DMA and (b) without DMA.

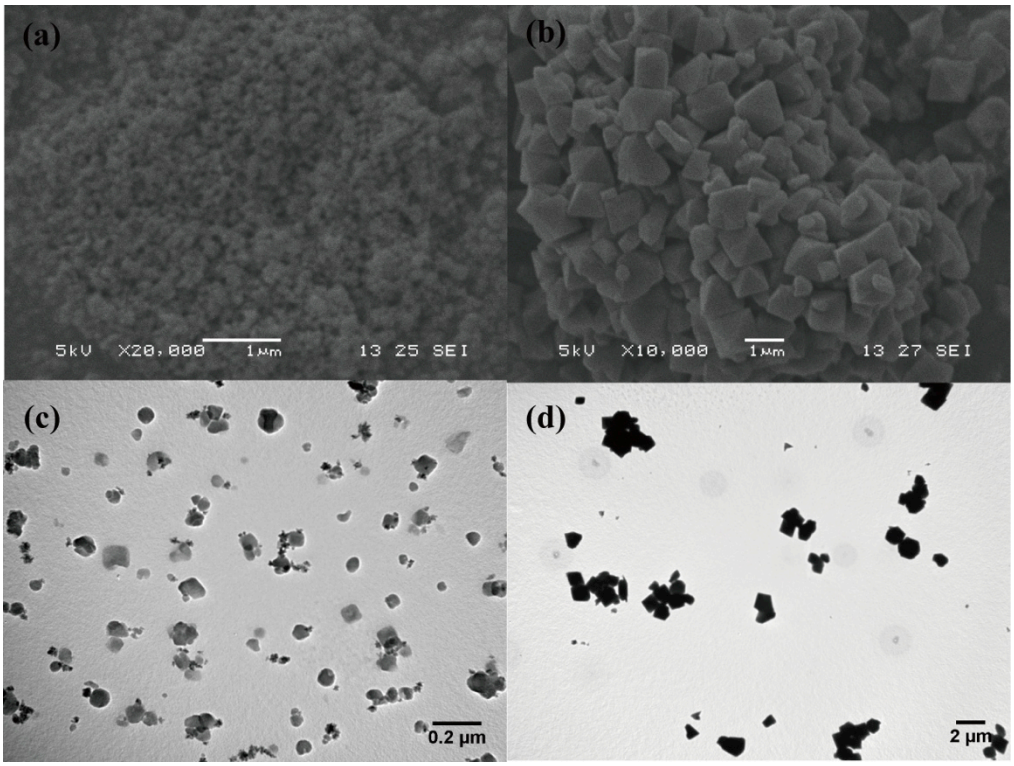

Fig. S3. SEM and TEM images of powder MIL-101(Cr) synthesised (a)/(c) with DMA and (b)/(d) without DMA.

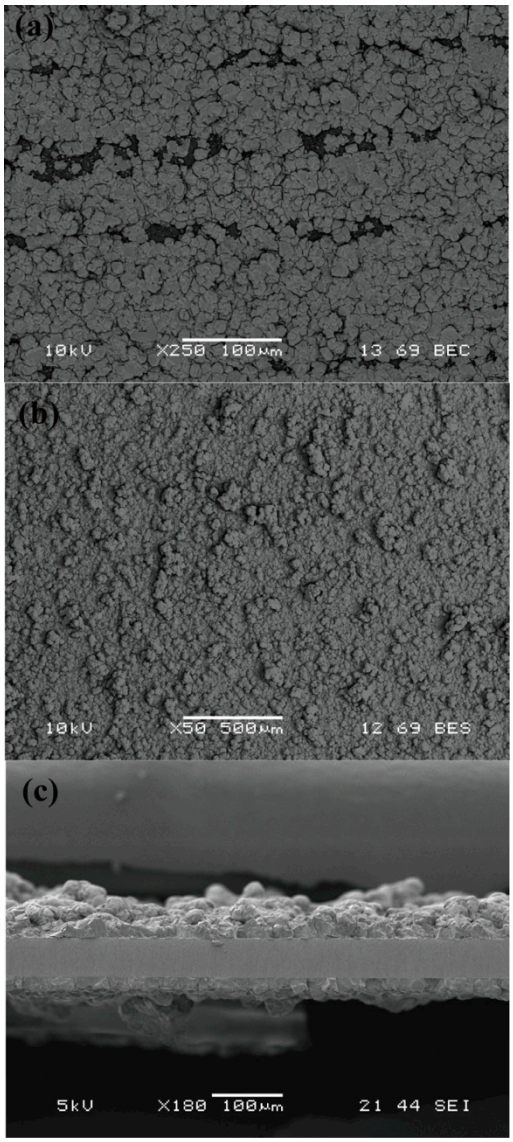

Fig. S4. SEM images of $Cu_2(btc)_3$ film on anodisc (a) without PAA sodium salt and (b)/(c) with PAA sodium salt [(a)/(b) top views, (c) cross section view].