# Supplementary Data

# Facile synthesis of crack-free metal-organic framework films on alumina by a dip-coating route in the presence of polyethylenimine

Dongmei Jiang, Andrew D. Burrows,\* Yuli Xiong and Karen J. Edler

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK. E-mail:a.d.burrows@bath.ac.uk

#### **Experimental**

#### **Chemicals**

Chromium nitrate nonahydrate [Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 99%], Whatman Anodisc 25, and stearic acid were purchased from Fisher Scientific. 1.4-Benzenedicarboxylic acid (H<sub>2</sub>bdc, 98%) was purchased from Lancaster Synthesis. 2-Amino-1,4-benzenedicarboxylate, branched polyethylenimine (PEI;  $M_r$ : 750 000; 50% in water), butyric acid (99%), hexanoic acid (99%), Octanoic acid (98%), decanoic acid (98%), octadecanoic acid (98.5%) and octylamine (99%) were purchased from Aldrich Chemical Co.

#### Synthesis of the nanoparticles of MIL-101(Cr)-NH<sub>2</sub>

The nanoparticles of MIL-101(Cr)-NH<sub>2</sub> were synthesised according to the previously reported method.<sup>1</sup> In a typical experiment, H<sub>2</sub>bdc-NH<sub>2</sub> (0.23 g, 1.26 mmol) and Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.50 g, 1.25 mmol) were added to water (7 cm<sup>3</sup>). The resulting suspension was stirred for 3 h at room temperature then heated under autogeneous pressure at 130 °C for 24 h in a Teflon-lined autoclave. After cooling to room temperature, the solid product was isolated from the filtrate as a green powder by centrifugation at 11000 rpm and washed five times with ethanol. For analyses, the particles were dried under N<sub>2</sub> flowing gas at room temperature and for the elaboration of thin films, the particles were suspended in absolute EtOH (50 mL).

The average particle size of the nanoparticles of MIL-101(Cr)-NH<sub>2</sub> is  $16 \pm 4$  nm. The detailed characterisation is described in reference 1.

#### Formation of MIL-101(Cr)-NH<sub>2</sub>-PEI films

The colloidal solution for the films was first prepared by mixing the abovementioned MIL-101(Cr)-NH<sub>2</sub> ethanol solution (30 mL) with an ethanolic PEI solution (0.4572 g 50% PEI; 20 cm<sup>3</sup> EtOH). Thin films were fabricated by dip-coating the colloidal solution at room temperature and under ambient atmospheric conditions, using the Anodiscs as substrates and a withdrawal speed of 40 mm min<sup>-1</sup> using a KSV Nima DC516 dip coater. The thickness of the film was controlled through a multiple

deposition process using the same conditions. During the multiple deposition process, the film was kept for 30 seconds at the top and bottom of the dip-coating cycle respectively. The resulting film was denoted as MIL-101(Cr)-NH<sub>2</sub>-PEI-n, with n equal to the number of dip-coating cycles employed.

For characterisation, the PEI-decorated MIL-101(Cr)-NH<sub>2</sub> solid material was separated from the colloidal solution and no further washing was taken. The solid material was denoted as MIL-101(Cr)-NH<sub>2</sub>-PEI. Elemental analysis (%): C, 44.9; H, 8.11; N, 17.1.

#### Formation of MIL-101(Cr)-NH<sub>2</sub> films

The fabrication of the MIL-101(Cr)-NH<sub>2</sub> films was similar to that of the MIL-101(Cr)-NH<sub>2</sub>-PEI films, except that the colloidal solution for the films was prepared by diluting the ethanolic solution of MIL-101(Cr)-NH<sub>2</sub> (30 cm<sup>3</sup>) into 50 cm<sup>3</sup>. The resulting film was denoted as MIL-101(Cr)-NH<sub>2</sub>-*n*, with *n* equal to the number of dip-coating cycles employed.

#### Synthesis of the nanoparticles of MIL-101(Cr)

Nanoparticulate MIL-101(Cr) with the particle sizes of 50 nm was synthesized according to the previous published method.<sup>2</sup> In a typical experiment, H<sub>2</sub>bdc (0.275 g; 1.65 mmol) and Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.66g; 1.65 mmol) were added to water (50 cm<sup>3</sup>, 2775 mmol). The resulting suspension was stirred for 1 h at room temperature then heated under autogeneous pressure at 180 °C for 4 h in a Teflon-lined autoclave. After cooling to room temperature, the mixture was filtered with Whatman filter paper to remove the recrystallised H<sub>2</sub>bdc. The product was isolated from the filtrate as a green powder following centrifugation at 11000 rpm, and then washed three times with EtOH. The MIL-101(Cr) nanoparticles were further dispersed in 25 cm<sup>3</sup> ethanol, heated at 80 °C for 4 h, then separated by centrifugation with three times water washing. The obtained nanoparticles were dispersed in 25 cm<sup>3</sup> water and 0.025 g NH<sub>4</sub>F was added. The mixture was stirred at 60 °C for 5 h, then separated by centrifugation and washed five times with hot water to remove traces of NH<sub>4</sub>F. For

analyses, the particles were dried under  $N_2$  flowing gas at room temperature and for the elaboration of thin films, the particles were left in absolute EtOH (50 cm<sup>3</sup>).

The detailed characterisation is described in reference 2.

#### Formation of MIL-101(Cr)-PEI films

The colloidal solution for the films was first prepared by mixing the MIL-101(Cr) ethanolic suspension (30 cm<sup>3</sup>) and ethanolic PEI solution (0.4572 g 50% PEI; 20 cm<sup>3</sup> EtOH). Thin films were fabricated by dip-coating the colloidal solution under ambient conditions, using the Anodiscs as substrates and a withdrawal speed of 40 mm min<sup>-1</sup> using a KSV Nima DC516 dip coater. The thickness of the film was controlled through a multiple deposition process using the same conditions. During the multiple deposition process, the film was kept for 30 seconds at the top and bottom of the dip-coating cycle respectively. The resulting film was denoted as MIL-101(Cr)-PEI-*n*, with *n* equal to the number of dip-coating cycles employed.

For characterisation, the PEI-decorated MIL-101(Cr) solid material was separated from the colloidal solution with no further washing. The solid material was denoted MIL-101(Cr)-PEI. Elemental analysis (%): C, 43.0; H, 6.9; N, 7.71.

## Formation of MIL-101(Cr) films

The fabrication of the MIL-101(Cr) films was similar to that of the MIL-101(Cr)-PEI films, except that the colloidal solution for the films was prepared by diluting 30 cm<sup>3</sup> of the MIL-101(Cr) ethanol solution into 50 cm<sup>3</sup> ethanol, and no PEI was employed. The resulting film was denoted as MIL-101(Cr)-n, with n equal to the number of dip-coating cycles employed.

#### **Characterisation**

Powder X-ray diffraction (XRD) patterns of the materials were recorded on a Bruker D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.542$  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. The sorption isotherms of N<sub>2</sub> at 77 K / 273 K and CO<sub>2</sub> at 273 K under medium relative pressure were carried out on BELSORP Mini-II (BEL Japan) instrument. The sample was degassed at 150 °C for 4 h prior to sorption. The specific surface areas of the samples were calculated by the Brunauer-Emmett-Teller method in the  $P/P_0$  range of 0.05-0.1. The total volume was obtained by calculating the data at the relative pressure of 0.99. The selectivities of the materials for CO<sub>2</sub> were calculated from the single gas isotherms by dividing the CO<sub>2</sub> adsorption capacity by that of N<sub>2</sub> at the relative pressure of 1. Water contact angle measurements were carried out using a VSM-004 400x USB Microscope with a lamp is positioned behind the sample to make the image processing. For a typical measurement, 0.5 µL of deionised water was vertically dropped onto the film sample and the image was immediately taken by the MicroCapture software. The image was further analysed by using the ImageJ software to determine the water contact angle of the sample.

### References

- D. Jiang, L. L. Keenan, A. D. Burrows and K. J. Edler, *Chem. Commun.*, 2012, 48, 12053.
- 2. D. Jiang, A. D. Burrows and K. J. Edler, CrystEngComm, 2011, 13, 6916.



**Fig. S1.** SEM images of samples: (a, b) MIL-101(Cr)-PEI-10, (c, d, e, f) MIL-101(Cr)-PEI-30 (top view: a, b, c, d; cross section view: e. f).



**Fig. S2.** SEM images of samples: (a, b) MIL-101(Cr)-10, (c, d) MIL-101(Cr)-30 (top view: a, c; cross section view: d).



**Fig. S3.** SEM images of samples: (a, b) MIL-101(Cr)-NH<sub>2</sub>-10, (c, d, e, f) MIL-101(Cr)-NH<sub>2</sub>-30 (top view: a, b, c, d; cross section view: e, f).



**Fig. S4.** Powder XRD patterns of samples: (a)  $MIL-101(Cr)-NH_2$ , (b)  $MIL-101(Cr)-NH_2$ -PEI, (c) MIL-101(Cr), (d) MIL-101(Cr)-PEI, and (e) the simulated XRD pattern of MIL-101(Cr) from the crystal structure.



**Fig. S5.** N<sub>2</sub> adsorption-desorption isotherms (left) and the pore size distributions (right) of samples at 77 K: (a) MIL-101(Cr)-NH<sub>2</sub>, (b) MIL-101(Cr)-NH<sub>2</sub>-PEI, (c) MIL-101(Cr), (d) MIL-101(Cr)-PEI.



Fig. S6.  $CO_2$  (left) and  $N_2$  (right) adsorption isotherms of samples at 273 K: (a), MIL-101(Cr)-NH<sub>2</sub>-PEI, (b) MIL-101(Cr)-NH<sub>2</sub>, (c) MIL-101(Cr), (d) MIL-101(Cr)-PEI.



**Fig. S7.** Digital photos of water contact angle results for the MIL-101(Cr)-NH<sub>2</sub>-PEI-30 films with various modifiers: (a) without modifier, (b) butyric acid, (c) hexanoic acid, (d) octanoic acid, (e) decanoic acid, (f) octadecanoic acid, (g) after water treatment of the octadecanoic acid treated film, (h) after ethanol treatment of the octadecanoic acid treated film, (i) octylamine.



**Fig. S8.** Digital photos of water contact angle results for MIL-101(Cr)-PEI-30 films with various modifiers: (a) without modifier, (b) butyric acid, (c) hexanoic acid, (d) octanoic acid, (e) decanoic acid, (f) octadecanoic acid, (g) after water treatment of the octadecanoic acid treated film (h) after ethanol treatment of the octadecanoic acid treated film, (i) octylamine.

Sample	$\mathbf{S}_{\mathrm{BET}}{}^a$	$\mathbf{V}_{\mathrm{total}}{}^{b}$	Pore size <sup>c</sup>
	$(m^2g^{-1})$	$(\mathrm{cm}^3\mathrm{g}^{-1})$	(nm)
MIL-101(Cr)-NH <sub>2</sub>	2070	2.26	1.54/1.99
MIL-101(Cr)-NH <sub>2</sub> -PEI	735	1.28	1.14/1.63
MIL-101(Cr)	2944	2.57	1.72/2.22
MIL-101(Cr)-PEI	2296	2.31	1.55/1.97

Table S1. Physicochemical data for MOF samples

<sup>*a*</sup> Specific surface area was calculated in the  $P/P_0$  range of 0.05-0.1; <sup>*b*</sup> Total volume was calculated by taking the data at  $P/P_0$  0.99; <sup>*c*</sup> Pore size was calculated from BJH mode.

Sample	CO <sub>2</sub>	N <sub>2</sub>	Selectivity <sup>a</sup>
	/mmol g <sup>-1</sup>	/mmol g <sup>-1</sup>	
MIL-101(Cr)-NH <sub>2</sub>	3.02	0.12	25
MIL-101(Cr)-NH <sub>2</sub> -PEI	3.70	0.03	123
MIL-101(Cr)	5.28	0.71	7
MIL-101(Cr)-PEI	4.32	0.18	24

Table S2.  $CO_2$  and  $N_2$  adsorption data for MOF materials under 1 atm at 273 K

 $^{a}$  The selectivity was calculated from the single gas isotherms by dividing the CO<sub>2</sub> uptake by that of N<sub>2</sub>.