

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

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A facile polyethylenimine (PEI)-assisted dip-coating method allows crack-free films of MIL-101(Cr) and MIL-101(Cr)-NH<sub>2</sub> to be prepared on alumina supports. The presence of PEI enhances the selectivity of the films for CO<sub>2</sub> with respect to N<sub>2</sub>. The film surfaces can be made hydrophobic by further dip-coating with an aliphatic monocarboxylic acid.

Metal–organic frameworks (MOFs) are an important class of hybrid crystalline materials that consist of metal ions or aggregates that are linked together by bridging organic linkers to form extended network structures.<sup>1</sup> MOFs are currently attracting considerable attention as new materials for a range of applications including gas storage,<sup>2</sup> separations<sup>3</sup> and heterogeneous catalysis,<sup>4</sup> with their activity due to the porosity that many of these materials exhibit after activation to remove included solvent molecules.

Fabricating MOF materials as films or membranes is particularly important for their practical use as smart separation membranes, chemical sensors and other related nanodevices.<sup>5–7</sup> MOF film synthesis is currently dominated by *in situ* synthetic methods, which involve the growth of MOF films onto solid supports from solvothermal reaction mixtures. In these processes, surface functionalisation of the support is usually crucial for successful film formation. For example, putting a conductive layer on the support<sup>8</sup> or functionalising it using a polymer such as poly(methylmethacrylate), PMMA,<sup>9</sup> are effective in specific syntheses. However, these *in situ* methods typically involve laborious multi-processing steps to prepare MOF films. Recently, we reported a facile one step synthesis method *via in situ* seeding of nanoparticles for the synthesis of MIL-101(Cr) films, in which MIL-101(Cr) nanoparticles were formed on or near to the surface of the support under the assistance of

dimethylacetamide which in turn promoted continuous MIL-101(Cr) film formation.<sup>10</sup> Although this method simplifies the synthesis of the MOF, the seeding procedure, and the film growth into one step, the utilisation of MIL-101(Cr) is relatively low, with most of the MIL-101(Cr) material precipitating as a solid powder away from the support during the synthesis. This problem is apparent in other *in situ* synthetic methods, and leads to a waste of feedstock, which impedes practical applications of these methods, and limits scale up of the film synthesis.

An alternative strategy, which can greatly improve the utilisation of the MOF feedstock and simplify the film synthesis, is to fabricate the films or membranes by depositing MOF nanoparticles onto the supports by dip-coating or spin-coating. The dip-coating route provides the possibility of controlling the thickness of MOF films by adjusting the number of dip-coating cycles or controlling the MOF concentration in the nanoparticle suspension employed. The resulting films possess a hierarchical structure consisting of the microporosity from the MOF itself and the mesoporosity from the self-assembly of MOF nanoparticles, and this can lead to faster diffusion and permeation of guest molecules through MOF thin films. One prerequisite for the dip-coating method is the availability of nanoparticles of the desired MOFs. Size control of MOF particles has been achieved by several methods including use of microwaves or ultrasound, addition of a modulator such as a polymer or a monocarboxylic acid, and simple dilution of the reaction mixture.<sup>11,12</sup> The other, more difficult, prerequisite for this approach is the need to match and enhance the attractive interactions between the MOF nanoparticles and the support surface and to homogenise the stress forces between the particles in order to avoid crack formation.

The chromium(III) MOF [Cr<sub>3</sub>O(F,OH)(H<sub>2</sub>O)<sub>2</sub>(bdc)<sub>3</sub>]·*n*H<sub>2</sub>O, MIL-101(Cr) (*n* ~ 25), first reported by Férey *et al.*, has a large surface area due to the presence of zeotypic mesoporous cages in the structure, and possesses high chemical/hydrothermal stability.<sup>13</sup> These features, in addition to the potential for generation of unsaturated chromium(III) sites in the framework

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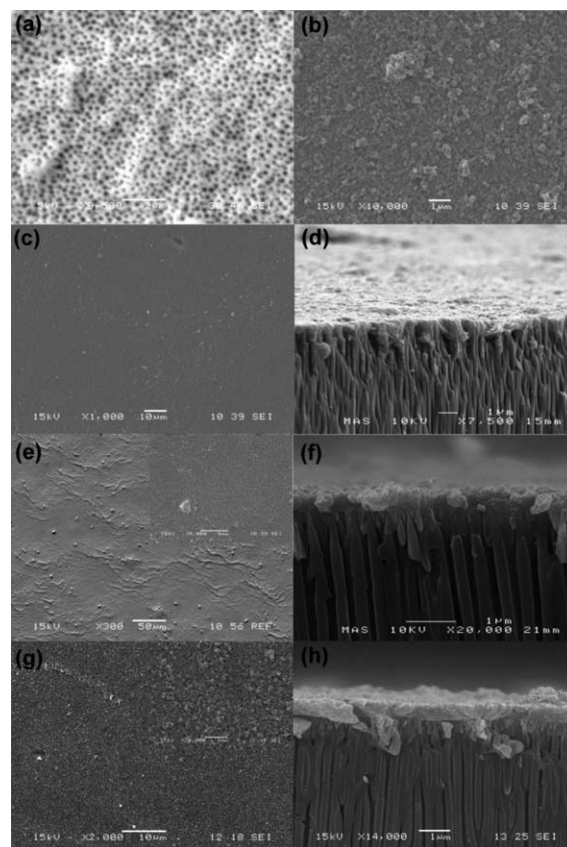
on activation, make MIL-101(Cr) particularly attractive for practical applications involving selective gas adsorption, separation and heterogeneous catalysis. We have previously reported the synthesis of MIL-101(Cr) films on alumina supports with thickness of up to 2.5  $\mu\text{m}$  *via* an *in situ* method,<sup>10</sup> whereas Férey and co-workers reported the preparation of thin films on silicon wafers with the thickness of up to 160 nm by a dip-coating method.<sup>14</sup> Ramos-Fernandez and co-workers prepared MIL-101(Cr) films on alumina disks using a secondary seeding approach whereby the disks were dip- or spin-coated with MIL-101(Cr) seeds, then a conventional solvothermal approach was used to produce the films.<sup>15</sup>

Despite these successes, films of functionalised MIL-101 materials have yet to be reported. MIL-101(Cr)-NH<sub>2</sub>, containing 2-amino-1,4-benzenedicarboxylate (bdc-NH<sub>2</sub>) instead of bdc, is particularly attractive for a number of reasons. The amine group on the linker helps to improve the affinity for particular gases such as CO<sub>2</sub>.<sup>16</sup> Furthermore, it provides a platform for developing further functionalised MOFs *via* post-synthetic modifications.<sup>17</sup> Indeed, a wide range of functionalities have been incorporated into MOFs following reaction with an amine group on the pore wall. Recently, we reported the direct synthesis of MIL-101(Cr)-NH<sub>2</sub>, with the product formed as nanoparticles with a particle size of  $16 \pm 4$  nm.<sup>18</sup> Herein, we present the fabrication of crack-free MIL-101(Cr) and MIL-101(Cr)-NH<sub>2</sub> films by dip-coating of the nanoparticles in the presence of the polymer poly-ethylenimine (PEI). This approach is somewhat different from that previously reported whereby MOF nanoparticles are embedded within polymer membranes,<sup>19,20</sup> as the films reported herein are essentially those of the crystalline MOFs.

As a first step for preparing the films, nanoparticulate suspensions of MIL-101(Cr) and MIL-101(Cr)-NH<sub>2</sub> were prepared by dispersing the previously prepared nanoparticles into ethanol in the presence of PEI. Only a single dipping solution was required, and no washing steps were needed between depositions. The films were prepared by dip-coating Anodiscs (anopore alumina) into the nanoparticulate suspension a number of times, with the speed maintained at 40 mm min<sup>-1</sup>. The prepared films are denoted MIL-101(Cr)-PEI-*n* and MIL-101(Cr)-NH<sub>2</sub>-PEI-*n*, where *n* is the number of dip-coating cycles employed. The detailed preparation procedures are described in the ESI.†

For MIL-101(Cr)-PEI-*n*, good coverage of the Anodisc was observed for *n* = 10 (Fig. S1a and b†), and for MIL-101(Cr)-PEI-30, crack-free films with a thickness of 310 nm were obtained (Fig. S1c–f†). SEM images of the samples MIL-101(Cr)-NH<sub>2</sub>-PEI-*n* (*n* = 10, 30, 60) are shown in Fig. 1. Fig. 1b and c show that the surface of the Anodisc is well covered with the MIL-101-NH<sub>2</sub>-PEI-10 film, with no bare surfaces observed (compare Fig. 1a). From the cross-section view (Fig. 1d) it can be seen that the film is very thin (<100 nm) though the thickness is readily increased by employing more dip-coating cycles. Thus, MIL-101-NH<sub>2</sub>-PEI-30 has a thickness of 255 nm (Fig. 1f), whereas MIL-101-NH<sub>2</sub>-PEI-60 has a thickness of 545 nm (Fig. 1h). Importantly, no cracks were observed as the film thickness increased.

The presence of PEI in the nanoparticulate suspension is essential for successful film formation. For both MIL-101(Cr)



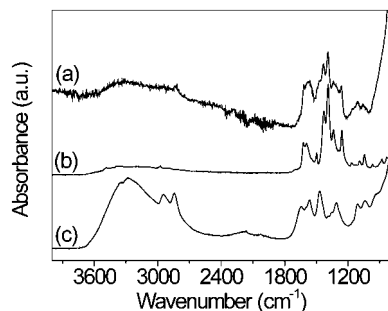
**Fig. 1** SEM images of the samples: (a) the Anodisc, (b), (c) and (d) MIL-101(Cr)-NH<sub>2</sub>-PEI-10, (e) and (f) MIL-101(Cr)-NH<sub>2</sub>-PEI-30, (g) and (h) MIL-101(Cr)-NH<sub>2</sub>-PEI-60 (top views: (a, b, c, e, g) and cross-section views: (d, f, h)).

and MIL-101(Cr)-NH<sub>2</sub>, dip-coating the Anodisc into the nanoparticulate suspension 10 times in the absence of PEI led to very poor surface coverage (Fig. S2a and b; S3a and b†). Increasing the number of dip-coating cycles to 30 led to better coverage, but large cracks were observed in the films produced (Fig. S2c; S3c and d†). These results confirm the importance of PEI in crack-free film formation. Firstly, PEI enhances the interaction of the MOF nanoparticles with the surface of Anodisc through hydrogen bonding,<sup>21</sup> which helps the MOF nanoparticles to be homogeneously adsorbed on the surface during the dip-coating. Secondly, the presence of the PEI on the MOF nanoparticles reduces and homogenises the stress forces between the MOF nanoparticles, which contributes to the crack-free film formation as the film thickness increased.

The structures of the films were further characterised by ATR-IR spectroscopy. The ATR-IR spectrum of the MIL-101(Cr)-NH<sub>2</sub>-PEI-30 film shows the characteristic peaks of MIL-101(Cr)-NH<sub>2</sub> in the region of 1000–1800 cm<sup>-1</sup> (Fig. 2a and b). There are also PEI peaks within this region (Fig. 2c), though the presence of a peak at 2833 cm<sup>-1</sup>, attributed to the  $\nu(\text{C-H})$  vibration of PEI, confirms the presence of PEI in the MIL-101(Cr)-NH<sub>2</sub>-PEI-*n* films.

For further investigation of the effect of PEI on the MIL-101(Cr) and MIL-101(Cr)-NH<sub>2</sub> structures, the nanoparticles from the suspensions in the presence of PEI were isolated and





**Fig. 2** ATR-IR spectra of (a) MIL-101(Cr)-NH<sub>2</sub>-PEI-30 film on the Anodisc, (b) MIL-101(Cr)-NH<sub>2</sub> powder, and (c) PEI.

investigated by powder X-ray diffraction, gas adsorption and elemental analysis. These materials, denoted MIL-101(Cr)-PEI and MIL-101(Cr)-NH<sub>2</sub>-PEI respectively, exhibited similar PXRD patterns to MIL-101(Cr) and MIL-101(Cr)-NH<sub>2</sub> (Fig. S4†), demonstrating the MIL-101 framework was maintained. Elemental analysis demonstrated the presence of PEI with considerably enhanced nitrogen content with respect to the materials formed in the absence of PEI. Thus, for MIL-101(Cr), the nitrogen content increases from trace amounts to 7.7%, whereas for MIL-101(Cr)-NH<sub>2</sub> it increases from 5.5% to 17.1%.

The N<sub>2</sub> adsorption measurements on MIL-101(Cr)-PEI and MIL-101(Cr)-NH<sub>2</sub>-PEI (Fig. S5†) at 77 K show that the presence of PEI leads to decreased N<sub>2</sub> capacities. The pore size distribution revealed that the pore sizes of MIL-101(Cr)-PEI decreased from 1.7 and 2.2 nm to 1.6 and 2.0 nm whereas the pore sizes of the MIL-101(Cr)-NH<sub>2</sub>-PEI decreased from 1.6 and 2.0 nm to 1.1 and 1.6 nm, confirming that PEI penetrated into the pores. The presence of PEI within the materials has an important influence on the gas sorption properties of the resulting films. CO<sub>2</sub> sorption measurements revealed that MIL-101(Cr)-NH<sub>2</sub>-PEI shows enhanced CO<sub>2</sub> capacity over MIL-101(Cr)-NH<sub>2</sub> in the whole pressure region of 0 to 1 atm at 273 K, though in contrast MIL-101(Cr)-PEI exhibits decreased CO<sub>2</sub> capacity compared to MIL-101(Cr). Further comparison studies with N<sub>2</sub> sorption shows that both MIL-101(Cr)-PEI and MIL-101(Cr)-NH<sub>2</sub>-PEI possess enhanced CO<sub>2</sub>/N<sub>2</sub> selectivities over their analogues without PEI (Fig. S6†). MIL-101(Cr)-PEI exhibited a CO<sub>2</sub>/N<sub>2</sub> selectivity of 24 at 1 atm, while MIL-101(Cr)-NH<sub>2</sub>-PEI showed a selectivity of 123 under the same conditions. The selectivity for CO<sub>2</sub> is increased by factors of 3.5 and 4.9 for MIL-101(Cr)-PEI and MIL-101(Cr)-NH<sub>2</sub>-PEI respectively (Table S2†). This demonstrates that PEI not only helps the formation of crack-free films, but also greatly enhances the selectivity of the films towards CO<sub>2</sub>.

In order to prepare a film for separation of CO<sub>2</sub> from N<sub>2</sub>, high selectivity for CO<sub>2</sub> over N<sub>2</sub> as well as high CO<sub>2</sub> capacity is important. However, the hydrophobicity of the film is also significant for practical use as the moisture in real gas mixtures may decrease separation efficiency due to competition between water and CO<sub>2</sub> molecules for the adsorption sites. Hydrophobic films reduce this competition, and may also increase the life of a MOF film in cases where the film is moisture sensitive. For the MIL-101(Cr)-PEI-*n* and MIL-101(Cr)-NH<sub>2</sub>-PEI-*n* films, water

**Table 1** Water contact angle data of the films

Carboxylic acid modifier	Film	
	MIL-101-NH <sub>2</sub> -PEI-30	MIL-101-PEI-30
None	— <sup>a</sup>	— <sup>a</sup>
Butyric acid	— <sup>a</sup>	— <sup>a</sup>
Hexanoic acid	34°	32°
Octanoic acid	60°	63°
Decanoic acid	72°	74°
Octadecanoic acid	104°	101°
Octylamine	28°	— <sup>a</sup>

<sup>a</sup> Water drop absorbed into the film.

drops are immediately adsorbed into the films, with no water contact angle observable, demonstrating the films to be hydrophilic. By simply dip-coating the MIL-101(Cr)-NH<sub>2</sub>-PEI-30 film once into an ethanolic long chain aliphatic monocarboxylic acid solution (0.05 M), the film becomes hydrophobic. The hydrophobicity increases with the length of the aliphatic chain, as evidenced by increases in observed water contact angles (Table 1, Fig. S7 and S8†). The carboxylic acid group itself is also important in this treatment protocol. On using octylamine as the modifier, the MIL-101(Cr)-NH<sub>2</sub>-PEI-30 film shows much lower hydrophobicity than that with octanoic acid (Table 1; 28° vs. 60°). For the MIL-101(Cr)-PEI-30 film, the hydrophilicity does not change at all on treatment with octylamine. These differences can be attributed to the weaker interactions present between the amine group of the octylamine and the amine groups on the film in comparison with the hydrogen bonding present between the carboxylic acid groups and the amines.

In summary, a facile and effective PEI-assisted dip-coating method has been developed to fabricate crack-free MIL-101(Cr) and MIL-101(Cr)-NH<sub>2</sub> films with controlled thickness on alumina Anodiscs, with the nature of the product confirmed by SEM, XRD and ATR-IR spectroscopy. The PEI additive not only contributes to the film formation, but also enhances the CO<sub>2</sub> sorption capacity and selectivity of the MOF material in the films. The hydrophilic nature of the films can be easily adjusted to hydrophobic by layering aliphatic monocarboxylic acids onto the surface *via* dip-coating. The PEI-assisted dip-coating method itself is cost-efficient, providing a better utilisation of MOF material than *in situ* approaches and has a good potential for scale up. Due to the potential for both hydrogen bonding and coordination, PEI has strong affinities to both MOFs and inorganic supports, suggesting this approach to MOF films will have broad applicability.

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