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ARTICLE TYPE

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

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A facile *in situ* nanoparticle seeding method is reported to prepare MIL-101(Cr) films on alumina supports. The *in situ* seeding of MIL-101(Cr) nanoparticles was promoted by use of dimethylacetamide (DMA). The generality of this approach is further demonstrated for $\text{Cu}_3(\text{btc})_2$ films by using a (poly)acrylate promoter.

Metal-organic frameworks (MOFs) are a relatively new class of crystalline solid-state material consisting of metal ions or aggregates that are connected by organic bridging linkers to form one-, two- or three-dimensional network structures.¹ Many MOFs have permanent porosity, and as such they have attracted considerable attention for a wide range of applications including gas storage, selective separations and heterogeneous catalysis.² Processing MOF powders into films is particularly important for their practical use as smart separation membranes and other related nanodevices.³ It is, however, difficult to synthesise continuous MOF films on unmodified supports. Several modification strategies have been developed to allow MOF films to be grown, and quartz crystal microbalances have recently been used to investigate this.⁴ Putting a conductive layer on the support has been reported for membranes of $\text{Zn}_4\text{O}(\text{bdc})_3$ (MOF-5, $\text{bdc} = 1,4\text{-benzenedicarboxylate}$) formed using microwave irradiation.⁵ Functionalising the support surface with organic molecules has been also found to be effective,⁶ and a gel-layer approach has been used to prepare thin films onto functionalised gold surfaces.⁷ Using metal slides as both the support and the metal source has allowed $\text{Cu}_3(\text{btc})_2$ (HKUST-1, $\text{btc} = 1,3,5\text{-benzenetricarboxylate}$) and $\text{Zn}_3(\text{btc})_2$ membranes to be prepared.⁸ Coating MOF seed crystals onto a support by dip-coating, spin-coating or thermal coating following by film growth (the secondary seeded growth method), is another commonly used route to MOF films.^{9, 10} However, these methods typically involve laborious multi-processing steps before the MOF films can be deposited.

For the secondary seeded growth method, the processes of MOF seed crystal preparation, coating of these seed crystals onto the support and film growth are separated. Recently, Jin and co-workers reported the preparation of MIL-53(Al) films via a secondary seeded growth method involving reactive seeding¹¹ in which the alumina support itself acts as the aluminium source reacting with the organic precursor to grow a seeding layer. This procedure enables some of the steps to be combined thus simplifying film formation, but the generality of this approach has yet to be determined.

With high surface energies and thus potentially enhanced interaction with supports, MOF nanoparticles have been used as seeding crystals in the secondary seeded growth method. Recent studies demonstrated that in addition to the presence of the MOF nanoparticles, high temperatures and the presence of both metal and ligand sources remaining in solution were vital for the formation of continuous films.¹⁰ If high concentrations of MOF nanoparticles could be induced, *in situ*, on the surface of the support during the synthesis of the MOF film, the continuous film could be formed without complex pre-modifications of supports. At first sight, this approach appears problematic since the high concentrations of metal ions and ligands required to form the films are not compatible with nanoparticle formation. It has, however, been reported that the MOF nanoparticles can be formed by supplying chemical additives such as monocarboxylic acids or functional polymers into the reaction mixture.^{12, 13, 14} Hence the problem could be solved by introducing an appropriate chemical additive into the MOF film reaction mixture.

Among MOF materials, $\text{Cr}_3\text{X}(\text{H}_2\text{O})_2\text{O}(\text{bdc})_3 \cdot n\text{H}_2\text{O}$ (MIL-101(Cr), $\text{X} = \text{F}, \text{OH}; n \sim 25$), first reported by Férey *et al.*,¹⁵ is an excellent candidate due to its extremely high surface area (up to $5000 \text{ m}^2 \text{ g}^{-1}$) and pore volume (up to $2.1 \text{ cm}^3 \text{ g}^{-1}$). It has two types of zeotypic mesoporous pores with free diameters of *ca.* 2.9 and 3.4 nm accessible through two microporous windows of *ca.* 1.2 and $1.6 \times 1.45 \text{ nm}$. In addition to the high mesoporosity and surface area, MIL-101(Cr) also has high hydrothermal/thermal stability, making it very promising for practical applications such as catalysis and separations.¹⁶ Recently, Férey and co-workers prepared MIL-101(Cr) optical thin films with thickness of up to 160 nm on silica wafers by dip coating from colloidal solutions generated through microwave heating.¹⁷ In addition, Ramos-Fernandez *et al.* reported dense coatings of MIL-101(Cr) on porous alumina and cordierite monoliths by the secondary seeded method.¹⁸ Herein, we present a facile *in situ* nanoparticle seeding method for the formation of MIL-101(Cr) films on alumina plates using dimethylacetamide (DMA) as the chemical additive. To the best of our knowledge, this is the first report of continuous MIL-101(Cr) films formed on alumina plates.

Our first attempts at forming MIL-101(Cr) films on alumina plates used the reactive seeding method of Jin and co-workers.¹¹ Only a very pale green colour derived from MIL-101(Cr) was observed on the alumina plates using this method (Fig. S1b), suggesting that the MIL-53(Al) seeding layer does not well support MIL-101(Cr) growth.

We then moved to studying the direct reaction between chromium(III) and bdc in the presence of the support. The mother solution for the MIL-101(Cr) film syntheses contained $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, H_2bdc and water, and was identical to that used for bulk samples of MIL-101(Cr)¹⁵ with the exception that no HF was added. On using untreated alumina supports, only very poor coverage with MIL-101(Cr) was observed, as determined by the very pale green colour of the plates after treatment (Fig. S1c). In contrast, using DMA-wetted alumina supports gave a uniform green colour after 8 h at 220 °C (Fig. S1d). The SEM images of the sample (MIL-101(Cr)-A) are shown in Fig. 1. The top view (Fig. 1b and c) shows that the surface of the alumina plate is well covered with the MOF film. The particle sizes on the surface of the film are less than 1 μm , which is much smaller than that of bulk powder MIL-101(Cr) prepared under the same synthetic conditions in the absence of DMA (up to 2 μm ; Fig. S3). From the cross section view it can be seen that the film is very thin (in the nanoscale region; Fig. 1d) and the thickness could not be accurately measured due to the rough surface of the alumina support (Fig. 1a). The thickness of the film was increased by returning the sample to the synthesis solution and heating for another 8 h at 220 °C. After this time the film thickness was 1.6 μm (MIL-101(Cr)-B, Fig. 1f), and following an additional 8 h at 220 °C it had increased further to 2.5 μm (MIL-101(Cr)-C, Fig. 1h).

The structure of the films was examined by X-ray diffraction and ATR-IR spectroscopy. Fig. 2 shows the XRD patterns of the MIL-101(Cr)-C film, together with the pattern for powdered MIL-101(Cr) and the simulated powder diffraction pattern for

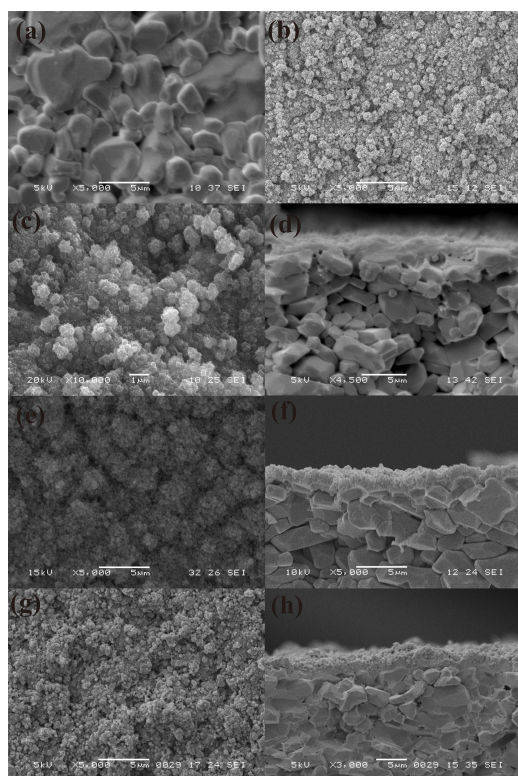


Fig. 1 SEM images of the samples: (a) alumina plate, (b, c, d) MIL-101(Cr)-A film on alumina plate, (e, f) MIL-101(Cr)-B film on alumina plate, (g, h) MIL-101(Cr)-C film on alumina plate (top view: a, b, c, e, g; cross section view: d, f, h).

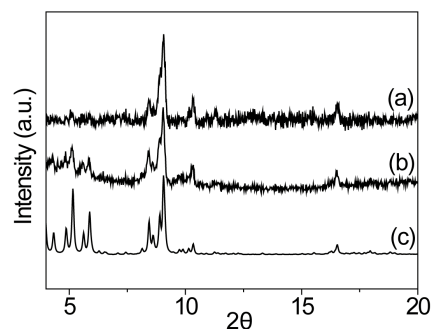


Fig. 2 X-ray diffraction patterns of (a) MIL-101(Cr)-C film on alumina plate, (b) powder MIL-101(Cr), (c) simulated MIL-101(Cr).

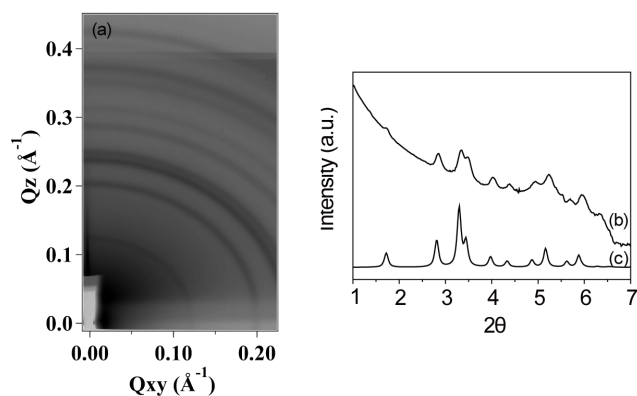


Fig. 3 Grazing incidence X-ray diffraction patterns of (a) MIL-101(Cr) film on alumina film/silica wafer, (b) line profile through the GIXD pattern at $Q_{xy} = 0$, (c) simulated MIL-101(Cr).

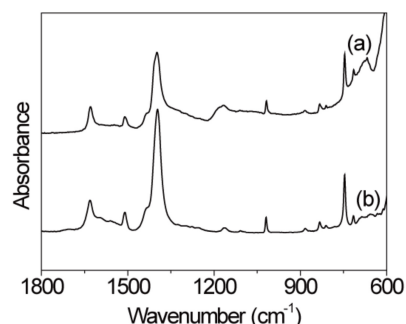
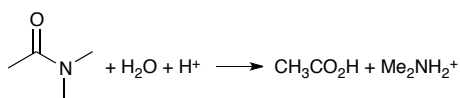


Fig. 4 ATR-IR spectra of (a) MIL-101(Cr)-C film on alumina plate, (b) powder MIL-101(Cr).

this material. The film (Fig. 2a) shows a similar XRD pattern as that of the powder (Fig. 2b), confirming that it has the MIL-101(Cr) structure. The bulk structure of the film was further investigated by grazing incidence X-ray diffraction (Fig. 3) confirming that the film has no preferential orientation of the crystallites on the support but forms a powder-like layer with diffraction rings corresponding to those seen in the simulated XRD patterns. GIXD patterns were taken at several positions across the film confirming identical structures over the entire surface. ATR-IR spectra (Fig. 4) confirm that the film on the alumina support has the same structure as MIL-101(Cr), and show no evidence for DMA. The bands in the region of 1300-1800 cm^{-1} are mainly from the carboxylate groups, and the peaks at 1017 and 749 cm^{-1} can be attributed to vibrations of the benzene rings.¹⁹

The presence of DMA on the support is crucial for the

formation of the MIL-101(Cr) films. Without wetting with DMA, very little MOF material is formed on the support (Fig. S1c vs Fig. S1d). DMA hydrolyses in the presence of acids as shown in Scheme 1 to produce acetic acid. The synthesis of MIL-101(Cr) is carried out in aqueous solution at 220 °C, and the high temperature and acidic conditions (pH < 3) are favourable for the decomposition of DMA.



Scheme 1 DMA decomposition under aqueous acidic conditions.

We presume that some of the adsorbed DMA on the alumina plate decomposes during the synthesis as shown in Scheme 1. We have previously demonstrated that monocarboxylic acids can promote the formation of MOF nanoparticles,¹³ so suggest that the acetic acid produced by the DMA hydrolysis induces the formation of MOF nanoparticles on or near to the surface of the alumina. These *in situ* formed MIL-101(Cr) nanoparticles further act as heterogeneous nucleation sites on the alumina plate and successfully promote the growth of continuous MIL-101(Cr) films.

In order to confirm the role of DMA in the formation of MIL-101(Cr) nanoparticles, we investigated the synthesis of bulk MIL-101(Cr) in the presence of DMA. The powder X-ray diffraction data confirmed that the addition of DMA does not change the nature of the product, with MIL-101(Cr) still observed (Fig. S2). However, SEM and TEM images demonstrate that the particle size of MIL-101(Cr) synthesised with DMA is significantly smaller than that of the product formed in its absence. Thus, in the presence of DMA the particle size is less than 200 nm (Fig. S3a,c), whereas without DMA the particle size is up to 2 µm (Fig. S3b,d).

Having demonstrated that chemical additives that promote MOF nanoparticle formation can be used to assist the synthesis of MOF films, we sought to assess the generality of this observation. DMA has little effect on the formation of Cu₃(btc)₂ films, so we sought another promoter. The sodium salt of poly(acrylic acid) has been used previously to form nanoparticles of Cu₃(btc)₂.¹⁴ Here, simply putting the alumina anodisc wetted with an aqueous solution of sodium poly(acrylate) into the synthesis solution for Cu₃(btc)₂, continuous Cu₃(btc)₂ films are formed after 24 h at 100 °C in one step as shown in SEM images (Fig. S4b,c). In the absence of sodium poly(acrylate), only discontinuous films were observed (Fig. S4a).

In summary, a facile and effective *in situ* MOF nanoparticle seeding method has been developed to fabricate MIL-101(Cr) thin films on alumina plates, with the nature of the product confirmed by SEM, XRD and ATR-IR spectroscopy. Dimethylacetamide has been shown to be an effective promoter for MIL-101(Cr) film production, since it supports nanoparticle formation near to the surface. By choosing suitable chemicals that can induce *in situ* the formation of MOF nanoparticles on the surface of supports, this facile *in situ* seeding MOF nanoparticles method is expected to have broad feasibility for various MOF film syntheses.

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