High-Throughput Fabrication of Uniform and Homogenous MOF Coatings
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We describe a novel method to produce monolithic, oriented, crystalline and highly porous coatings on solid substrates. By adopting the recently described liquid-phase epitaxy (LPE) process developed to grow metal-organic framework coatings (MOFs) on modified Au-substrates to the spray method, we have prepared thick (μm) layers of several MOF types on modified Au-substrates, including HKUST-I and layer-pillar MOFs. The spray method not only allows such SURMOFs to be grown much faster than with the LPE-process but the dependence of layer thickness on the number of immersion cycles also provides valuable insights into the mechanism governing the layer-by-layer MOF formation process.

1. Introduction
With regard to a highly flexible functionalization of surfaces, e.g. in the context of interfacial systems chemistry,[5] the deposition of oriented porous materials on appropriately functionalized substrates offers a number of attractive options.[6] In particular, metal organic frameworks (MOFs)[2–4] are very well suited for such a surface modification, the rendering of specific functions to a coating can be either achieved by loading the MOF material after deposition with functional molecules or by a post-synthesis modification of the MOF-constituents.[5,6] The potential of such a surface functionalization has been realized by a number of groups and several synthesis schemes ranging in complexity and straightforwardness to rather sophisticated have been proposed.[7]

With regard to applications of such porous, coatings, however, it is not only important to have robust methods which can be used to generate very homogeneous, crack-free films with a well-defined thickness. In addition, a high degree of orientation is beneficial, in particular with regard to the growth of highly anisotropic MOFs like the so-called layer-pillar-systems.[8] In this context the recently introduced liquid phase epitaxy (LPE) process to obtain crystalline, highly oriented layers of MOFs on modified Au-substrates, also referred to as SURMOFs, is very attractive.[8,9]

A major drawback of this layer-by-layer method, however, is the fact that due to the sequential, time-consuming deposition process the thickness of the deposited MOF layers has so far been limited to a thickness of about 100 layers. The 400 different immersion cycles necessary for a film with this thickness require a time period on the order of 3 days.

With regard to a number of applications including storage and separation of small molecules (gas phase chromatography, liquid phase chromatography) thicker layers of dense, homogenous MOF-coatings are urgently required. This need is particularly pressing with regard to applications where MOFs are being used as membranes. The mechanical strength of layers with thicknesses of 100 layers (corresponding to about 100 nm) is simply not sufficient and thicknesses of at least a μm are required.

Here we present a completely new high-throughput approach to grow MOF thin layers on solid substrates using a spray method. Here, high-throughput denotes the reduction of the time needed to prepare SURMOFs by more than two orders of magnitude. The spray method, which has been successfully used in connection with other layer-by-layer fabrication schemes for coating substrates with two (or more) component thin layers (e.g. polyelectrolyte multilayers,[10–12]) is based on a nozzle system (scheme 1). In the nozzles an aerosol is produced from the reactants and solutions required for the MOF synthesis. The droplets within the aerosol (with sizes down to the 10 μm region) impinge on the substrate and coat the surface with a thin film of the reactant. Material will then be deposited at the solid/liquid interface in a fashion similar to that occurring during the LPE process. In the LPE process, rinsing with a solvent has been shown to be a crucial step.[5,6] An oriented growth can only occur if the simultaneous presence of the two different reactants on the supporting substrate is strictly excluded. In the context of the spray process this rinsing step is replaced by exposing the substrate to an aerosol produced from the pure solvent.

2. Results and discussion
Figure 1 shows an XRD pattern recorded for an HKUST-1 MOF thin film fabricated using the spray method with 20 full cycles
Interestingly, although the time to grow this MOF thin film is two orders of magnitude faster than with the LPE-method, the degree of orientation and ordering is comparable. As in the case of the LPE process the XRD data displayed in Figure 2 clearly reveal that on an OH-terminated SAM the MOF grows only with a [111] orientation. The thickness of the deposited SURMOFs can be determined either by analyzing the width of the diffraction peaks recorded in the out-of-plane diffraction geometry or by using patterned substrates on which only selective growth takes place. In the latter case the height of the deposited films can be determined directly using atomic force microscopy (AFM).

In Figure 3 we present profiles of the (200) XRD peaks measured for a number of different SURMOFs grown using the spray method with an increasing number of deposition cycles. The peak width $\Delta$ clearly decreases with increasing number of cycles. Using the expression $\Delta = \lambda/(N d \cos \theta)$, with $\lambda$ denoting the wavelength of the X-ray radiation, $N$ the number of the MOF lattice planes, $d$ the interplanar distance, and $\theta$

on a MHDA substrate, after a careful optimization of operation parameters. The time required to deposit this film amounted to only 30 minutes compared to 48 hours using the conventional layer-by-layer process. The films are very stable upon drying and removing of solvent both on the macro and micro scale, any kind of delamination was found to be absent. Clearly, the diffraction peaks reveal the presence of a crystalline, highly ordered and oriented HKUST-I film. The positions of the diffraction peaks are identical to that observed for the bulk. Note, that in the $\theta$-2$\theta$-(or out-of-plane) geometry only the periodicity normal to the substrate surface is observed, the data recorded in the in-plane scattering geometry (see Figure 1) shows the peaks along the [111] direction which are not present in the $\theta$-2$\theta$ scans.
the diffraction angle. The results obtained using the present conditions ($\lambda = 0.154 \text{ nm}, d = 1.3 \text{ nm}$ for HKUST-I along the [001]-direction) are shown in Figure 3a.

AFM-measurements for selectively grown MOF platelets on a patterned SAM substrate yield results consistent with those obtained from the XRD profile analysis, namely a thickness of 200 nm for 20 deposition cycles.

An interesting result of this analysis is that the increase of HKUST-I SURMOF thickness per deposition cycle is clearly larger than that reported for the normal LPE deposition process of HKUST-I SURMOFs on COOH-terminated SAMs, namely 1.3 nm.\textsuperscript{[13]} Obviously, employing the spray method results in a growth mode, which is more complex than the growth mode which was originally proposed in connection with the LPE process.\textsuperscript{[13]}

On an acetate-terminated (100) surface of an HKUST-I SURMOF (see Figure 22 in Ref. 6) the most naïve growth model would assume that the acetate-groups exposed at the SURMOF surface are replaced by btc-units, leading to a btc-terminated surface. When rinsing with Cu\textsuperscript{2+}(ac)\textsubscript{2} in the next step, (Cu\textsuperscript{2+})\textsubscript{2} dimers bound below to the btc-units will form by an btc/ac exchange. The upward termination will be by the remaining ac groups, thus again yielding an acetated-terminated surface, see Figure 2. Such a growth mode would, however, imply an increase in thickness corresponding to a quarter of a unit cell, 0.65 nm, per deposition cycle only, see Figure 2.

The fact that for the LPE-method the increase in thickness is twice as large\textsuperscript{[13]} suggests the presence of additional amounts of the other reactant. Since both reactants, Cu\textsuperscript{2+}(ac)\textsubscript{2} and H\textsubscript{2}btc, fit into the pores of HKUST-I, the most straightforward explanation is that these additional amounts are still stored in the already deposited SURMOF as a result of an incomplete rinsing process. On the basis of these considerations we explain the fact that for the spray method a much larger thickness per cycle is observed by the less effective rinsing. Obviously, the amount of material which can be removed by coating the surface with a thin layer of solvent is substantially smaller than when immersing the substrate in the pure solvent. To better understand the mechanism governing the LPE-process urgently theoretical modeling is required, e.g. along the line of the work by R. Schmid and coworkers as reported in.\textsuperscript{[6]}

We have also employed the spray method for substrates on which the SAMs had been laterally patterned via micro-contact printing (µCP). The corresponding AFM data shown in Figure 4 demonstrate that the growth of MOF thin films obtained via the spray is also highly selective, as in the case of the LPE method.\textsuperscript{[8]} Deposition is only obtained on the COOH-terminated squares, whereas the amount of material present on the CH\textsubscript{3}-terminated stripes is almost negligible.

Scanning electron microscopy (SEM) cross section images (see Figure 5) demonstrate also the thickness and the homogeneity of the deposited layers.

We have successfully applied the spray method not only for HKUST-1 but also for two dimensional (2D) layer systems of the type $\{[M_2(L)_2(H_2O)]\}$, namely $\{[Zn_2(bdc)_2(H_2O)]\}$ and $\{[Cu_2(bdc)_2(H_2O)]\}$, and for layer-pillar-type $\{[M_2(L)_2(P)]\}$ MOFs, namely $\{[Cu_2(ndc)(dabco)]\}$.\textsuperscript{[15,16]} The corresponding results shown in the supporting information section suggest that all MOF-types suitable for the LPE-process are also suited for the spray method.

Figure 4. AFM image of HKUST-1 SURMOF (20 cycles) grown on a SAM laterally patterned by microcontact printing (µCP) consisting of COOH-terminated squares and CH\textsubscript{3}-terminated stripes (left). Height profile of the selected area (white line) (right).

Figure 5. A cross-section scanning electron micrograph of HKUST-1 SURMOF grown on a COOH functionalized gold substrate, the thickness was estimated to be 1000 nm.
3. Conclusions

The novel spray process developed to grow highly oriented, crystalline MOF-coatings with thicknesses in the μm-regime on modified solid substrates carries a huge potential, since the deposition time is substantially smaller than with the previously used liquid phase epitaxy (LPE) method. The already fairly large number of applications of SURMOF thin films(21) will further increase due to the larger versatility of the spray method. Despite the larger deposition rate the structural quality appears to exceed that of LPE-grown SURMOFs. In particular with appropriate delamination strategies(17) we expect SURMOFs prepared with the spray method to have a substantial impact on membrane technology.

4. Experimental Section

The HKUST-1 MOFs were grown on Au substrates (200-nm Au/2-nm Ti evaporated on Si wafers) that were at first functionalized by self assembled monolayers, SAMs, of 16 mercaptohexadecanoc acid MHDA, 11 mercaptoundecanol that were prepared as described in.9, 14 These substrates were then placed on a sample holder and subsequently sprayed with a 1 mM of Cu₂(CH₃COO)₄·H₂O ethanol solution for 10 seconds and then with a 0.2 mM of BTC solution for 20 seconds at room temperature. Critical parameters of the spray procedure are carrier gas pressure, liquid pressure, flow rate, and distance between the nozzle and the target. Typical values of these parameters are 1.5 bar, 0.2 bar, 0.25 ml/s and 0.1 m. Between each step the substrates were sprayed with ethanol. After a given number of cycles the samples were characterized with Infra-Red Reflection Absorption Spectroscopy (IRRAS) and X-ray diffraction (XRD). Scanning electron microscope (SEM) data were obtained using a LEO 1530 Gemini scanning microscope. Atomic force microscopy (AFM) data were recorded with Digital Instruments NanoScope MultiMode with NanoScope IIIa control unit.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. XRD spectra recorded for HKUST-1, [(M⊂(L)⊂(2•H•O)] and [(M⊂(L)⊂(3•P)] MOFs samples prepared by spray method are shown in the Supporting Information.

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