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Advanced fabrication method for the preparation of MOF thin films: Liquid-phase epitaxy approach meets spin coating method.

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ABSTRACT: Here we report a new and advanced method for the fabrication of highly oriented/polycrystalline metal-organic framework (MOF) thin films. Building on the attractive features of the liquid-phase epitaxy (LPE) approach, a facile spin coating method was implemented to generate MOF thin films in a high-throughput fashion. Advantageously, this approach offers a great prospective to cost-effectively construct thin-films with a significantly shortened preparation time and a lessened chemicals and solvents consumption, as compared to the conventional LPE-process. Certainly, this new spin-coating approach has been implemented

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3 successfully to construct various MOF thin films, ranging in thickness from a few micrometers
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5 down to the nanometer scale, spanning 2-D and 3-D benchmark MOF materials including
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7 $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$, $\text{Zn}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$, HKUST-1 and ZIF-8. This method was appraised and proved
8
9 effective on a variety of substrates comprising functionalized gold, silicon, glass, porous
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11 stainless steel and aluminum oxide. The facile, high-throughput and cost-effective nature of this
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13 approach, coupled with the successful thin film growth and substrate versatility, represents the
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15 next generation of methods for MOF thin film fabrication. Thereby paving the way for these
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17 unique MOF materials to address a wide range of challenges in the areas of sensing devices and
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19 membrane technology.
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24 25 26 27 ■ INTRODUCTION

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29 A number of strategic applications including sensor devices and membranes depend on the
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31 effective fabrication and deployment of desired porous materials as thin films. Metal-organic
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33 frameworks (MOFs),¹⁻³ an emerging class of crystalline porous materials, constructed from the
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35 assembly of metal ions or metal clusters bridged by organic ligands, have attracted considerable
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37 attention in the past two decades primarily due to their immense diversity, tunability and
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39 porosity. In particular, the hybrid organic-inorganic nature of MOFs permits the successful
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41 practice of reticular chemistry, whereby pre-designed molecular building blocks (MBBs),
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43 possessing the desired built-in functionality, connectivity and geometry, can be selected to target
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45 MOFs with given topologies, pore system and functionality suitable for a particular application.
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47 Additionally, many types of MOFs can also be further functionalized by post-synthetic
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49 modification.⁴⁻⁶ Therefore, the versatile properties of MOFs pave the way for their use in many
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51 applications ranging from gas storage and separation to catalysis, sensing, and solar cells.^{1-3,7-8}
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One of the ongoing challenges for the wide spread use of MOFs in other dynamic research areas is to control their growth and/or deposition as thin films on desired substrates.⁹⁻¹¹ Markedly, MOF thin films prepared on a functional surface, e.g. interdigitated capacitive or quartz crystal electrodes, would permit the introduction of numerous sensory transduction mechanisms in response to the interactions between the sorbed gas and the deposited host porous material.¹² Specifically, in the aforementioned cases, detecting and quantifying the adsorbed gases by monitoring the resultant changes in capacitance¹³ or frequency (mass change).⁹ Appropriately, controlled growth of porous materials on highly permeable substrates, i.e. development of composite membranes,¹⁴ offers potential to deposit a relatively thinner MOF membrane with the requisite working layer mechanical strength. Perceptively, there exists a need to develop effective and efficient methods for the controlled growth of MOFs on surfaces, and subsequently the attainment of MOF thin films with the desired orientation, thickness and mechanical stability. The plausible attainment of such controlled growth is of paramount importance for the success of using MOFs in membrane and sensor-based applications. Noticeably, the deployment of such advanced methods would allow for the effective integration of the unique chemical and physical properties of MOFs, e.g. pore space, functionality, charge, etc.,⁹⁻¹¹ into state-of-the-art devices leading to new electronic, photonic, and catalytic systems. It is to mention that several research groups, including ours, had recognized the potential of MOF thin films in many key applications and thus the ongoing development of different MOFs thin film fabrication methods.^{9,14-16}

The relative performance of MOF thin films, e.g. as a membrane for gas separation, is critically dependent on the film thickness and crystal orientation since the permeation of gases can vary along different crystallographic directions.^{9,14} The adapted liquid phase epitaxy (LPE) process (or layer-by layer approach) introduced in 2007 for the synthesis and growth of highly

oriented MOFs layers on modified Au-substrates, represents a significant development for the fabrication of MOF thin films over the previous used in-situ crystallization methods.¹⁵ Nevertheless, the first introduced LPE dipping method^{9,15} suffers from several shortcomings. These include: i) prolonged growth process, e.g. it takes approximately one day to grow 100 layers, which is the result of 400 different immersion steps; and ii) increased cost as a large quantity of chemicals and solvents are needed to complete the process.¹⁵⁻¹⁶ These drawbacks will certainly hinder the scale up of this method for some important applications, specifically membrane-based technology where homogeneous MOF-coatings consisting of dense, defect free thick layers, measuring at least 0.5 μm , are required.^{9,14}

In an attempt to address this limitation, the first successful high-throughput approach was recently introduced to grow MOF thin layers on solid substrates using a spray method.¹⁶⁻¹⁷ Here, “high-throughput” was used to express the time frame needed to prepare the MOF thin films, which was reduced by at least two orders of magnitude. The spray method is based on applying a nozzle system, through which the reactants solutions and solvents, are deposited onto the targeted surface in the form of an aerosol. The main principle of this approach is governed by the fact that the droplets within the aerosol ($<10\text{ }\mu\text{m}$) are impinged on the substrate and thereby coat the surface with a thin film comprised of the desired reactant. The reactant (either metal precursor or organic ligand) will then be deposited at the solid/liquid interface in a similar manner as was done during the LPE process. In the typical LPE process, rinsing with a solvent proved to be an important step in removing the residual unreacted starting material.¹⁵ Accordingly, this rinsing step was replaced by spraying the surface with the pure solvent. Nevertheless, using the spray method, it is difficult to produce homogeneous coatings on a large-

scale due to the limitation of the nozzle size adjustment and the substantial amounts of consumed chemicals and solvents.

In this work, we introduce a new facile approach for the high-throughput fabrication of homogeneous and highly crystalline MOFs coatings as demonstrated using versatile substrates with a minimum amount of chemicals, by adapting for the first time the LPE approach to the spin coating method.

▪ EXPERIMENTAL

All chemicals and solvents were purchased from Sigma-Aldrich and used without further purification, unless otherwise noted. The spin coating process for all the thin films fabricated in this work was conducted at room temperature. Notably, the success of the spin coating procedure is governed by several critical parameters; that is, the spin coating speed, spinning time and injection volume/concentration. In this work, each parameter was systematically fine-tuned to obtain high-purity MOF thin films in a timely fashion. Accordingly, typical values for these parameters were found to be 500 rpm, 5-10 seconds, and 50 μ l, respectively.

Fabrication of $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ MOF thin films: In this case, a variety of substrates including glass, functionalized Au (with $-\text{COOH}$ groups), silicon wafer and stainless steel served as a support for thin film growth. The supports were first rinsed with ethanol and, then dried at 150°C to remove any contaminants from the surface. The gold substrates (i.e. 200-nm Au/2-nm Ti evaporated on Si wafers) were functionalized with self-assembled monolayers (SAMs),¹⁸ consisting of 16-Mercaptohexadecanoic acid (MHDA), according to a published procedure.¹⁹ The pre-treated substrates were placed on a vacuum chuck and subsequently spin coated in a continuous mode during the addition of 50 μ l of a 0.1 mM of $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot x\text{H}_2\text{O}$ ethanolic

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3 solution for 5 seconds followed by 50 μl of a 0.1 mM of terephthalic acid (H_2bdc) solution for 8
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5 seconds. The substrates were washed with 50 μl of pure solvent (ethanol) between each step.
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8 ***Fabrication of ZIF-8 thin films:*** thin films were grown on a commercial alumina substrate,
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10 which was firstly washed with water and dried at 150°C for 24 hours. The cleaned substrate was
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12 placed on a vacuum chuck and subsequently spin coated with 50 μl of a 0.2 mM of $\text{Zn}(\text{NO}_3)_2 \cdot 6$
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14 H_2O methanol solution for 5 seconds and then with a 50 μl of a 0.4 mM of 2-Methylimidazole
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16 (2-MeImi) methanol solution for 8 seconds at room temperature.
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20 ***Fabrication of HKUST-1 thin films:*** the films were grown on a commercial alumina substrate,
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22 analogous to the method described above for ZIF-8. The substrates were placed on a vacuum
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24 chuck and subsequently spin coated with 50 μl of a 1.5 mM of $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot x\text{H}_2\text{O}$ ethanol
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26 solution for 5 seconds and then with a 50 μl of a 3 mM of 1,3,5-benzenetricarboxylic acid
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28 (H_3btc) ethanol solution for 10 seconds.
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32 After a given number of cycles, the samples were characterized using X-ray diffraction (XRD)
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34 and scanning electron microscope (SEM). For further details, refer to the supplementary
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36 material.²⁰
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39 The variable pressure-continuous permeate composition analysis technique was used to test the
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41 permeation of the gas mixture for the fabricated membrane. The permeate gas composition was
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43 monitored continuously until steady-state was achieved, as indicated when no change in the
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45 Mass spectrometer (MS) signal is observed. The membrane was activated for permeation studies
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47 using vacuum and flushing with helium gas until no residual gases were detected downstream
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49 using MS. The binary gas mixture, having a desired composition a_{up} , b_{up} of $\text{CO}_2:\text{H}_2$ (20:80), was
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51 applied upstream with a maintained flux at 40-50 cc/min. This was performed all the while
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53 monitoring the composition of the permeate downstream, i.e. a_{down} , b_{down} .
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Quartz crystal microbalance (QCM) measurements were completed using a Q-Sense E4 instrument from LOT Quantum Design.

■ RESULTS AND DISCUSSION

The spin coating process is a fast and easy method, which was used to generate thin and homogeneous organic films out of solutions on flat substrates.²¹ Here, we take advantage of the facile and uniform fabrication of coatings using the spin process to adapt it, for the first time, to the LPE approach to fabricate highly oriented, crystalline and homogeneous MOF thin films. Importantly, this will allow the thickness of the fabricated thin films to be controlled by the number of cycles. This new facile approach is based on using a fully automated spin coating machine equipped with 4 micro syringes, through which micro-drops of a metal cation precursor solution is placed for a certain duration of time on the substrate, while spinning at a speed of 500 rpm in a continuous mode. The centrifugal force will allow all of the fluid to spread homogeneously on the substrate. Next, the substrate is cleaned via the injection of micro-drops of solvent. The same procedure is repeated for the organic ligand solution and washing step. The described procedure, consisting of four steps, is considered one cycle and is repeated to generate thicker thin films (see scheme 1).

Scheme 1. Schematic representation of the setup employed for the fabrication of MOF thin films using the LPE approach adapted to the spin coating method. The substrate is placed on a vacuum chuck and subjected to a spin coating at a speed of 500 rpm. In order to grow the MOF thin film, the selected substrate is spin coated at room temperature with 50 μl of metal precursor solution for 5 seconds (1) followed by 50 μl of a ligand solution for 5 seconds and between each step the substrates were washed with 50 μl pure solvent (2 & 4).

Fig. 1 shows an X-Ray diffraction (XRD) pattern recorded for a $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ MOF thin film with 20 to 60 growth cycles which was fabricated on a gold substrate (1.5 x 1.5 cm) functionalized with 16-MHDA SAM.^{9,19} The growth and presence of $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ MOF thin film is confirmed from the out-of-plane diffraction scan, as evidenced by the excellent agreement between the peak positions in the experimental and calculated XRD patterns. The film is

preferentially oriented along the [100] faces in a parallel orientation relative to the COOH-terminated surface.²²

Figure 1. Out-of-plane XRD patterns (background-corrected) of $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ SURMOF grown on a COOH- terminated SAM by applying up to 60 growth cycles. Calculated data for $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ is shown for comparison (black line).

The homogeneity and thickness of the deposited SURMOFs were also investigated using scanning electron microscopy (SEM). The top-view and cross-sectional images (Fig. 2 a and b) show the formation of a homogeneous and continuous coating of a closed thin film having very small crystals of the $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ MOF over a large area (see depicted area $50 \times 50 \mu\text{m}$ in Fig. 2a). The cross-sectional image (Fig. 2b) reveal the formation of a thin film with a thickness measuring approximately 140 nm for 10 cycles, which notably is almost the same obtained using the spray coating method under analogous conditions.^{23,24} To study the rate of the MOF thin film growth by spin coating, the thickness of the $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ MOF thin film was estimated from the SEM cross-section images after a different number of growth cycles (Fig. 2c). Interestingly,

we found that the time needed to successfully deposit this thin film consisting of 100 cycles is only 50 minutes, which is significantly shorter in comparison to 25 hours needed when employing the conventional LPE process. Yet, it is very close to the time needed by the spray method, which was 30 minutes.^{8-10, 12} Furthermore, the films were found to be very robust upon rinsing and drying, where no washing out or delamination was observed. Interestingly, although the time needed to grow this MOF thin film was found to be much more faster than the conventional LPE-method, the high degree of film orientation is still comparable to previously reported results.²⁰ Therefore, the spin coating method has many advantages over the conventional dipping LPE method, i.e. shorter preparation time, greatly reduced amount of consumed chemicals (precursors solution and solvents), and the possibility to easily coat larger surfaces up to 3x3 cm (Fig. S1-4).

It is evident from the thickness analysis (Fig. 2c), that the increase of $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ film thickness per deposition cycle is larger than that reported for the conventional LPE deposition process of $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ film on COOH-terminated SAMs.²² However, employing the spin method results in a growth mode similar to the spray method, which is more complex than the growth mode originally proposed in connection to the LPE process, i.e. a much faster growth rate per cycle.¹⁶ This suggests, as was claimed in the case of the spray method, the presence of additional amounts of other reactants. Since both reactants, copper acetate $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot x\text{H}_2\text{O}$ and H_2bdc , fit into the pores of $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$, the additional amounts can be stored in the already deposited MOF due to inadequate solvent rinsing. On this basis, it is possible to explain the larger thin film thickness per cycle observed for the spin coating method, by the less effective rinsing. Noticeably, the amount of material which can be removed by spin coating the surface

with a thin layer of solvent is substantially smaller than immersion of the substrate in the pure solvent.

Figure 2. (a) Top view SEM image of Cu₂(bdc)₂·xH₂O MOF thin film (60 cycles) and (b) cross-section SEM images of Cu₂(bdc)₂·xH₂O MOF thin film grown 16-MHDA SAM after different cycles (10, 20), with the thickness estimated. (c) Height profile of the Cu₂(bdc)₂·xH₂O MOF thin film for different numbers of deposition cycles. (d) SEM image of Cu₂(bdc)₂·xH₂O MOF thin film (20 cycles) grown on a SAM laterally patterned by μCP consisting of -COOH (terminated squares and -CH₃ terminated stripes).

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3 In order to prove that this growth process is also selective, we employed the spin coating
4 method for the growth of MOF thin films on pre-patterned substrates, on which the MHDA
5 SAMs had been laterally patterned via micro-contact printing (μ CP) process.²⁴ Fig. 2d shows the
6 SEM data of $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ MOF thin films grown via the LPE-spin method on a pre-patterned
7 substrate consisting of COOH-terminated squares and CH_3 -terminated stripes, which will serve
8 to demonstrate that the growth is highly selective, as in the case of the LPE and spray methods.¹²
9 The SEM images clearly show that the deposition of the MOF thin film was achieved on the
10 COOH-terminated squares, whereas the amount of material present on the CH_3 -terminated
11 stripes is almost negligible.^{15,24}

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13 The spin coating method was not only applied to functionalized gold substrates and alumina
14 but also to other types of substrates like silicon wafer, glass and porous stainless steel. Figure S1
15 shows optical images for a range of substrates both before and after the growth of
16 $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ MOF thin film using this new approach. This was also followed and confirmed
17 using XRD analysis (Figures S2-4). The optical images confirm the formation of a homogeneous
18 coating on all substrates with sizes measuring up to 3 x 3 cm.

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20 We have successfully applied the spin coating method not only for $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ (Fig. S5-
21 6), but also for its isostructural analogue -namely $\text{Zn}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ (Fig. S7-8).⁹ The power of the
22 spin coating method for the fabrication of MOF thin films was further extended to include three-
23 dimensional (3D) materials. Markedly, we utilized this approach for the growth of 3D MOFs
24 including ZIF-8 (Fig. 3 and Fig. S9) and HKUST-1 (Fig. S10-11) MOFs thin films on alumina
25 supports.^{25,26} The corresponding results (refer to the supporting information section) suggest that
26 many MOF-types suitable for the LPE-process are also uniquely suited for the adapted spin
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coating method and can be readily grown up to few micrometers thick by careful optimization of the critical growth parameters.

In contrast to the conventional LPE method in case of the ZIF-8, the newly adapted spin coating method on alumina support reveals the formation of a closed ZIF-8 thin film solely on top of the alumina support with no evident growth inside the support, as evidenced by the associated SEM images depicted in Fig. 3. Distinctively, the adapted spin coating method proffers a more efficient and effective pathway for the fabrication of MOF thin films. In point of fact, comparison of the thin films grown using the conventional LPE approach and the adapted spin coating method revealed the fabrication of a MOF thin film with a thickness of 2.9-3.0 μm in a total preparation time of approximately 80 minutes and only 200 cycles. Whereas, in the case of the conventional dipping LPE method 300 cycles generated a thickness of 2.5 μm with a total time of about 30 hours (the speed is 6 min/cycle), taking into consideration that the same concentration for both the metal precursor and ligand solutions was used.²⁵ In order to confirm that the fabricated ZIF-8 thin film using the spin coating approach is continuous and defect free, it was tested as a membrane for gas separation application. For the purpose of this study, a mixture comprised of H_2/CO_2 was chosen (Fig.4). The gas mixture permeation study shows that the ZIF-8 thin film is selective towards H_2 by approximately 4.6, which is in a very good agreement with previously reported studies.^{14,25}

Figure 3. (a) Top view and (b) cross-section SEM image of ZIF-8 membrane grown on alumina support using the spin coating approach.

Figure 4. CO₂/H₂: 20/80 mixture permeation tested using variable pressure-continuous permeate composition analysis technique at 308 K with 2.0 bar as a feed pressure.

In a final proof-of-concept, quartz crystal microbalance (QCM) substrates were coated with Cu₂(bdc)₂•xH₂O MOF using the LPE spin method in order to test MOF thin film fabricated using this new method for sensing application. The coated Cu₂(bdc)₂•xH₂O MOF on QCM substrate

was washed extensively with pure ethanol and then tested for the sensing of NH_3 in humid conditions. The mass uptake for the pure H_2O feed was first measured as a reference (Fig. 5), where slow mass uptake is observed. However, in case of 1% NH_3 in water solution a very rapid uptake was detected on the QCM, which indicates the high selectivity of this MOF for the NH_3 gas. Despite being similar in size, exposure of the thin film to NH_3 revealed a much faster uptake which can be explained by the stronger affinity of the nitrogen atoms towards the copper centers in the $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ MOF framework.²⁷⁻²⁹

Figure 5. QCM for mass uptake of H_2O (black) and 1% NH_3 (magenta) uptake over the $\text{Cu}_2(\text{bdc})_2 \cdot x\text{H}_2\text{O}$ MOF grown using the spin coating method over a COOH functionalized QCM substrate.

CONCLUSIONS

A new facile approach for the growth of MOF thin films was successfully developed based on adapting the LPE approach to the spin coating method. Studies confirmed this approach was effective in growing homogeneous, crystalline MOF-coatings, as exemplified using both 2D and 3D benchmark MOFs, on solid substrates yielding thin films with controllable thickness from nm

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3 to μm -regime. This new approach offers substantial advantages and a great prospective due to its
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5 associated shorter growth time and lessened chemicals consumption over the previously
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7 employed conventional LPE approaches. The fabricated thin films using the adapted spin coating
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9 approach presented the same structural quality and homogeneity as in the previously reported
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11 analogous films grown using the conventional LPE-approach. The versatility and applicability of
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13 this new spin coating/LPE method to diverse MOF thin films paves the way to explore and
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15 deploy this approach in many key applications pertaining to energy and environmental
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3 ▪ **ASSOCIATED CONTENT**
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9 Detailed experimental section, optical images, SEM images and XRD patterns.
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21 ▪ **Author Contributions**
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■ REFERENCES

- (1) Kitagawa, S.; Kitaura, R.; Noro, S. Functional Porous Coordination Polymers. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334-2375.
- (2) Férey, G. Hybrid Porous Solids: Past, Present, Future. *Chem. Soc. Rev.* **2008**, *37*, 191-214.
- (3) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. Systematic Design of Pore Size and Functionality in Isorecticular MOFs and Their Application in Methane Storage. *Science* **2002**, *295*, 469-472.
- (4) Tanabe, K. K.; Cohen, S. M. Post-synthetic Modification of Metal-organic Frameworks-a Progress Report. *Chem. Soc. Rev.* **2011**, *40*, 498-519.
- (5) Shekhah, O.; Arslan, H. K.; Chen, K.; Schmittl, M.; Maul, R.; Wenzel W.; Wöll, C. Post-synthetic Modification of Epitaxially Grown, Highly Oriented Functionalized MOF Thin Films. *Chem. Comm.* **2011**, *47*, 11210 -11212.
- (6) Shekhah, O.; Cadiau, A.; Eddaoudi, M. Fabrication and Non-covalent Modification of Highly Oriented Thin Films of a Zeolite-like Metal-organic Framework (ZMOF) with rho Topology. *Cryst. Eng. Comm.* **2015**, *17*, 290-294.
- (7) Cui, Y.; Yue, Y.; Qian, G.; Chen, B. Metal-organic Frameworks for Separations. *Chem. Rev.* **2012**, *112*, 1126-1162.
- (8) Furukawa, H.; Cordova, K.E; O'Keeffe, M., Yaghi, O. M. The Chemistry and Applications of Metal-organic Frameworks. *Science* **2013**, *341*, 1230444-1-1230444-12.
- (9) Shekhah, O.; Liu, J.; Fischer, R. A.; Wöll, C. MOF Thin Films: Existing and Future Applications. *Chem. Soc. Rev.* **2011**, *40*, 1081-1106.

- (10) Zacher, D.; Schmid, R.; Wöll, C.; Fischer, R. A. Surface Chemistry of Metal–organic Frameworks at the Liquid–solid Interface. *Angew. Chem. Int. Ed.* **2011**, *50*, 176-199.
- (11) Falcaro, P.; Ricco, R.; Doherty, C. M.; Liang, K.; Hill, A. J.; Styles, M. J. MOF Positioning Technology and Device Fabrication. *Chem. Soc. Rev.* **2014**, *43*, 5513-5560.
- (12) Kreno, L. E.; Leong, K.; Farha, O.K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. Metal-organic Framework Materials as Chemical Sensors. *Chem. Rev.* **2012**, *112*, 1105-1125.
- (13) Sapsanis, C.; Omran, H.; Chernikova, V.; Shekhah, O.; Belmabkhout, Y.; Buttner, U.; Eddaoudi, M.; Salama, K. N. Insights on Capacitive Interdigitated Electrodes Coated with MOF Thin Films: Humidity and VOCs Sensing as a Case Study. *Sensors* **2015**, *15*, 18153-18166.
- (14) Qiu, S.; Xue, M.; Zhu, G. Metal–organic Framework Membranes: From Synthesis to Separation Application. *Chem. Soc. Rev.* **2014**, *43*, 6116-6140.
- (15) Shekhah, O. Layer-by-Layer Method for the Synthesis and Growth of Surface Mounted Metal-organic Frameworks (SURMOFs). *Materials* **2010**, *3*, 1302-1315.
- (16) Arslan, H.; Shekhah, O.; Wohlgemuth, J.; Franzreb, M.; Fischer R. A.; Wöll. C. High-Throughput Fabrication of Uniform and Homogenous MOF Coatings. *Adv. Funct. Mater.* **2011**, *21*, 4228-4231.
- (17) Izquierdo, A.; Ono, S. S.; Voegel, J. C.; Schaaf, P.; Decher. G. Dipping versus Spraying: Exploring the Deposition Conditions for Speeding up Layer-by-Layer Assembly. *Langmuir* **2005**, *21*, 7558-7567.

(18) Azzam, E. M. S.; Bashir, A.; Shekhah, O.; Alawady, A. R. E.; Birkner, A.; Grunwald, C.; Wöll C. Fabrication of a Surface Plasmon Resonance Biosensor Based on Gold nanoparticles Chemisorbed onto a 1, 10-Decanedithiol Self-Assembled Monolayer. *Thin Solid Films* **2009**, *518*, 387-391

(19) Shekhah, O.; Roques, N.; Mugnaini, V.; Munuera, C.; Ocal, C.; Veciana, J.; Wöll C. Grafting of Monocarboxylic Substituted Polychlorotriphenylmethyl Radicals onto a COOH-Functionalized Self-Assembled Monolayer Through Copper (II) Metal Ions. *Langmuir* **2008**, *24*, 6640-6648.

(20) Streit, H.; Adlung, M.; Shekhah, O.; Stammer, X.; Arslan, H. K.; Zybaylo, O.; Ladnorg, T.; Gliemann, H.; Franzreb, M.; Wöll, C.; Wickleder C. Surface-Anchored MOF-Based Photonic Antennae. *Chem. Phys. Chem.* **2012**, *11*, 2699-2702.

(21) Vozar, S.; Poh, Y-C.; Serbowicz, T.; Bachner, M.; Podsiadlo, P.; Qin, M.; Verploegen, E.; Kotov, N.; Hart. A. J. Automated Spin-Assisted Layer-by-Layer Assembly of Nanocomposites. *Rev. Sci. Instrum.* **2009**, *80*, 23903-1-23903-5. *Sci. rep.* **2012**, *2*, 1-5

(22) Wang, Z.; Liu, J.; Lukose, B.; Gu, Z.; Weidler, P.; Gliemann, H.; Heine, T.; Wöll. C. Nanoporous Designer Solids with Huge Lattice Constant Gradients: Multi-heteroepitaxy of Metal–Organic Frameworks. *Nano Lett.* **2014**, *14*, 1526-1529.

(23) Liu, J.; Lukose, B.; Shekhah, O.; Arslan, H.; Weidler, P.; Gliemann, H.; Bräse, S.; Grosjean, S.; Godt, A.; Feng, X.; Müllen, K.; Magdau, I.; Heine, T.; Wöll C. A Novel Series of Isorecticular Metal Organic Frameworks: Realizing Metastable Structures by Liquid Phase Epitaxy. *Sci. Rep.* **2012**, *2*, 921-925.

(24) Munuera, C.; Shekhah, O.; Wang, H.; Wöll, C.; Ocal, C. The Controlled Growth of Oriented Metal–Organic Frameworks on Functionalized Surfaces as Followed by Scanning Force Microscopy. *Phys. Chem. Chem. Phys.* **2008**, *10*, 7257-7261.

(25) Shekhah, O.; Swaidan, R.; Belmabkhout, Y.; du Plessis, M.; Jacobs, T.; Barbour, L. J.; Pinnau, I.; Eddaoudi, M. The Liquid Phase Epitaxy Approach for the Successful Construction of Ultra-thin and Defect-free ZIF-8 Membranes: Pure and Mixed Gas Transport Study. *Chem. Comm.* **2014**, *17*, 2089-2092.

(26) Shekhah, O.; Fu, L.; Sougrat, R.; Belmabkhout, Y.; Cairns, A. J.; Giannelis, E. P.; Eddaoudi, M. Successful Implementation of the stepwise Layer-by-Layer Growth of MOF Thin Films on Confined Surfaces: Mesoporous Silica Foam as a First Case Study. *Chem. Comm.* **2012**, *48*, 11434-11436.

(27) Zybaylo, O.; Shekhah, O.; Wang, H.; Tafipolsky, M.; Schmid, R.; Johannsmann, D.; Wöll, C. A Novel Method to Measure Diffusion Coefficients in Porous Metal–organic Frameworks. *Phys. Chem. Chem. Phys.* **2010**, *12*, 8092-8098.

(28) Kim, H.; Yun, W.; Kim, M. B.; Bae, Y.; Lee, J. D.; Jeong, N. C. A Chemical Route to Activation of Open Metal Sites in the Copper-based Metal-organic Framework Materials HKUST-1 and Cu-MOF-2. *J. Am. Chem. Soc.* **2015**, *137*, 10009-10015.

(29) Xue, D.-X.; Belmabkhout, Y.; Shekhah, O.; Jiang, H.; Adil, K.; Cairns, A. J.; Eddaoudi, M. Tunable Rare Earth fcu-MOF Platform: Access to Adsorption Kinetics Driven Gas/Vapor Separations via Pore Size Contraction. *J. Am. Chem. Soc.* **2015**, *137*, 5034-5040.

Table of Contents Graphic

Advanced fabrication method for the preparation of MOF thin films: Liquid-phase epitaxy approach meets spin coating method.

*Valeriya Chernikova, Osama Shekhah and Mohamed Eddaoudi**

A new facile and advanced method for the fabrication of highly oriented/polycrystalline metal-organic framework (MOF) thin films is reported here. Building on the attractive features of the liquid-phase epitaxy (LPE) approach, a facile spin coating method was implemented to generate MOF thin films in a high-throughput fashion.

TOC