

Liquid-Phase Quasi-Epitaxial Growth of Highly Stable, Monolithic UiO-66-NH₂ MOF thin Films on Solid Substrates

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High quality, monolithic UiO-66-NH₂ thin films on diverse solid substrates have been prepared via a low temperature liquid phase epitaxy method. The achievement of continuous films with low defect densities and great stability against high temperatures and hot water is proven, clearly outperforming other reported types of MOF thin films.

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) represent a class of highly functional solid materials assembled from metal or metal/oxo nodes and di- or higher-topic organic linkers,^[1,2] that continue to receive enormous attention. Due to their modular composition and the ability to access large number of topologies,^[3] a huge number of different types of these porous materials, covering a broad spectrum of functionalities, has become available. In addition, combination of different types of Hetero-MOFs fabricated by employing heteroepitaxy via layer-by-layer procedures^[4] allows the integration of several different functionalities in these materials, including electrical conductivity,^[5] optical up-conversion,^[6] luminescent properties, and the ability to modulate electrical properties upon illumination with light.^[7]

For numerous usages of MOFs, the commonly isolated powder-form, consisting of μm-sized particles, is well suited, e.g. for gas storage^[8] and water treatment applications.^[9]

However, a number of other emerging applications exploiting electrical and optical properties of MOFs^[5] require high quality monolithic, pinhole-free thin films supported on solid substrates,^[4] including coatings on fibers.^[10] Well-defined thin films are also required for the fabrication of membranes for gas-phase or liquid separation,^[11] the construction of sensor devices,^[12] the fabrication of optical, photovoltaic, and electronic devices,^[13] as well as the use of MOF thin films in electrochemical applications. In order to meet the demand for such thin films, in recent years a number of different fabrication methods have been introduced. So far, when it comes to the fabrication of high quality, pinhole-free films of uniform thickness, the liquid-phase epitaxy (LPE) method has been most successful.^[14] Using this approach, a large number of different types of MOF materials and synthesis procedures have been developed.^[15]

Two crucial points have to be considered in the context of the LPE method. The first is the appropriate functionalization of the substrate, facilitating MOF nucleation, and subsequent preferential growth of crystallites on areas where suitable functional groups are expressed. To this end, a number of methods have been developed, as described in the literature.^[16] The second important point is the fact that the LPE process is carried out at low temperature under kinetic control. Therefore, the solvothermal procedures developed for conventional bulk synthesis often needs to be modified, including the choices of solvent and metal-source. In addition, concentrations and deposition temperatures have to be optimized. Finally, for metal/oxo nodes, the temperatures in the LPE process may be too low to form the clusters serving as secondary building units in the conventional solvothermal process.^[4]

Though MOF thin films and, in particular Surface-supported Metal-Organic Frameworks (SURMOFs), fabricated using the LPE method have been used successfully in a number of applications, their stability, in particular that with respect to water, represents a formidable problem. For example, HKUST-1 films, for which the LPE method was first demonstrated,^[14] are highly unstable in aqueous environments, just like the bulk material.^[17] Substantial progress with regards to improving MOF thin film stability was obtained when Shekhah *et al.* reported a method to grow thin films from ZIF-8, a member of the zeolitic imidazolate frameworks (ZIFs) on solid substrates using the LPE method.^[18] In particular, they were able to grow high quality monolithic thin films on porous substrates, thus opening the doors to important applications in gas phase separation.^[11] When it comes to applications in aqueous environment, however, it has to be noted that ZIF-8 MOF thin films are highly

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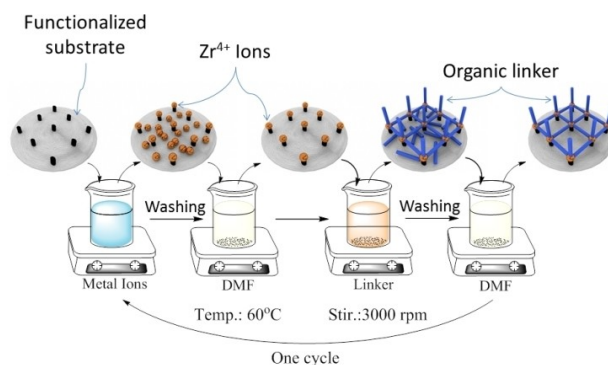
unstable (see below), in contrast to the bulk material.^[19] To further expand the application of SURMOF films, for instance in electrochemical and photoelectrocatalytic applications, in liquid-phase separations, as well as in the integration in battery devices, the availability of MOF thin films with higher stability in aqueous and more aggressive liquid environments is still required.

In fact, one of the most promising candidates among the huge family of MOF compounds in this respect are UiO-type MOFs.^[20] In this framework material, the nodes consisting of $Zr_6(O)_4(OH)_4$ -clusters are extended in 3D through the ditopic terephthalate linkers. Because of the high oxidation state of Zr^{4+} , the strength of carboxylate- Zr^{4+} -bonds result in a pronounced stability of the UiO (and also NU1000) bulk compound in boiling water and even in strongly basic conditions.^[21] Unfortunately, the rather complicated secondary building unit (SBU) required for the fabrication of such UiO-type materials has prohibited the straightforward application of the liquid-phase epitaxy method.

In a recent paper, Fischer and co-workers proposed a procedure using pre-synthesized $Zr_6O_4(OH)_4(OMc)_{12}$ SBUs instead of the $ZrCl_4$ metal source used in conventional synthesis in combination with growth modulators.^[22] Using the LPE method, they were able to deposit UiO-66 material. However, the crystallinity of these films is much inferior compared to the corresponding bulk material, and the large width of the diffraction peaks reveals an average domain size in the deposited MOF thin films of below 3 nm.

Herein we report the successful implementation of the LPE approach for the synthesis of UiO-66-NH₂ thin films on solid substrates. The most important parameter in the liquid-phase epitaxial synthesis of the UiO thin films reported here is the choice of a suitable solvent, DMF, together with an -OH functionalization of the substrate.^[14] Flat gold films supported on Si-wafers were first functionalized by immersion in an ethanolic solution of 11-mercapto-undecanol (MUD) resulting in the formation of a self-assembled monolayer (SAM) exposing an -OH terminated stem. The functionalized gold coated substrates were then immersed in a DMF solution of $ZrCl_4$ in presence of HCl,^[23] subsequently washed with DMF, and finally immersed in a solution of the organic linker, 2-aminoterephthalic acid in DMF as shown in Scheme 1. The deposition cycle was completed by washing again with the pure DMF solvent. The overall thickness of the deposited thin films was adjusted by the number of growth cycles. Figure S1 shows the calculated XRD patterns for UiO-66-NH₂ powder synthesized using the solvothermal method, calculated XRD pattern for the reported UiO-66-NH₂ crystal structure, and that for the UiO-66-NH₂ SURMOF deposited on a flat gold-coated substrate. The XRD pattern recorded confirmed the crystallinity of the film. The pattern revealed better results than the ones reported in a previous work (Semrau et al.),^[22] but showed a lower degree of crystallinity when compared to the material's bulk form.

Evaluation of the integral breadths of the (111) and (200) out-of-plane peaks applying the Scherrer-equation under the consideration of the instrumental contribution to the line



Scheme 1. Schematic diagram for the synthesis of UiO-66-NH₂ SURMOF through LPE

broadening yields domain sizes of 29 nm and 39 nm, respectively.

Since no additional stress/strain broadening was assumed, these values are lower estimates for the domain sizes. Notably, these values are substantially larger than the values reported for the previously reported UiO-66 thin films.^[22] Note also that the relative intensities of (111) and (200) diffraction peaks are slightly different for the SURMOF than for the MOF powder, indicating the presence of a preferential growth direction. However, the growth is not unidirectional as in the case of reported ZIF-8 SURMOFs.^[18] It is argued that the polar nature of the surface equally favored the growth of the two polar directions of the crystallites. Further modification of the surface chemistry and/or further optimization of growth conditions is expected to allow a higher degree of preferred growth orientation in these UiO-66-NH₂ thin films.

Infrared (IR) spectroscopy of UiO-66-NH₂@gold coated substrate (see Supporting Information, S.I.) confirmed the presence of the carboxylate peaks at 1576 cm⁻¹ and at 1658 cm⁻¹, characteristic for carboxylate groups bonded to the Zr^{4+} ions in the ZrO_4 SBUs.^[24] Note, that the frequencies of the carboxylate stretching are red-shifted when compared to the corresponding carboxylate vibrations in HKUST-1, which are located at 1556 cm⁻¹ and 1621 cm⁻¹.^[25] This is a result of much stronger carboxylate-zirconium bondings in UiO-66-NH₂ than in the Cu⁺²-carboxylate bonds present in HKUST-1. Finally, the characteristic NH₂-vibrations resulting from the amino-functionalized ligands can be clearly seen at 3430 cm⁻¹.

Moreover, the stability of the hereby presented UiO-66-NH₂ thin films in boiling water considerably excels that of any other previously reported MOF thin film.^[26] Figure 1 shows a comparison of XRD patterns recorded before and after immersing a ZIF-8 (thickness approx. 500 nm) and a UiO-66-NH₂ thin film (thickness approx. 110 nm) for one hour in boiling water. Whereas for the ZIF-8 SURMOF (synthesized for 200 deposition cycles following the procedure described in Reference [27]) contact with hot water resulted in a complete removal of the thin film, no change in XRD intensities was observed for the UiO-66-NH₂ sample. Moreover, Figure S6 in the SI file shows the SEM images for the UiO-66-NH₂@gold coated substrate before and after boiling stability study. This confirmed not only the

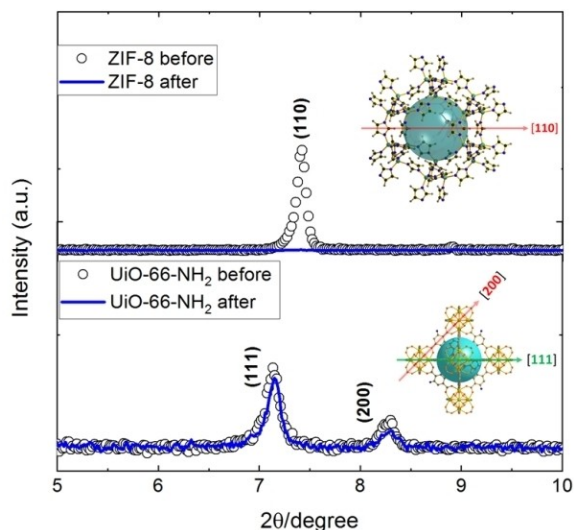


Figure 1. XRD pattern of ZIF-8@gold-coated Al_2O_3 substrate and UiO-66- NH_2 @gold coated substrate before (black circles) and after (blue line) boiling for one hour.

known high stability of this material in aqueous environments, but also the strong adhesion of the synthesized thin film to the substrate even at elevated temperatures.

Top-view and cross-sectional SEM images of the films were also obtained and shown in Figure 2. The corresponding data reveal that the UiO-66- NH_2 film obtained after 30 cycles exhibits an average thickness of ~ 110 nm and confirms the presence of

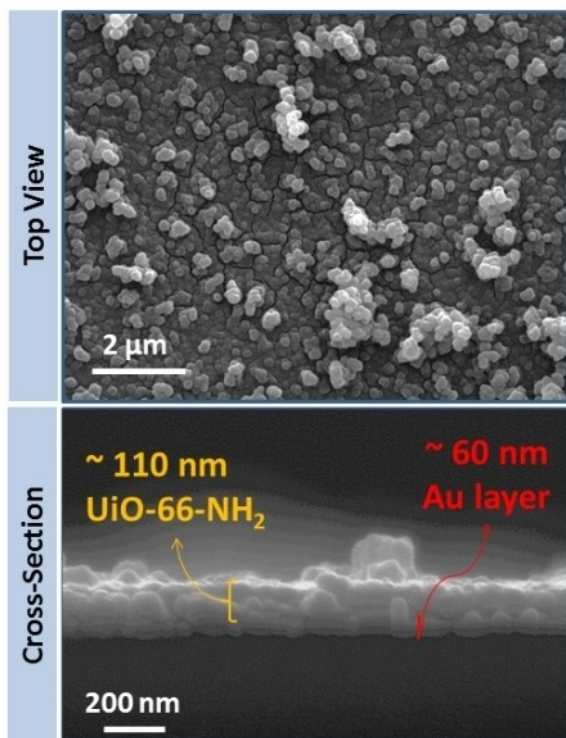


Figure 2. SEM images of UiO-66- NH_2 @gold coated substrate top view and cross section.

a closed thin film, with inter-grown domains with excellent adhesion to the functionalized, gold coated substrate. Particles seen in the SEM consist of several domains, this is why the particle size deduced from the SEM data (200–300 nm) is typically larger than the average domain size determined from the XRD results. Of particular relevance for applications of these monolithic thin films, e.g. in the context of membranes, is the fact that the SEM images show no evident pinholes or areas of reduced thickness. Additionally, the MOF thin films supported on the gold substrates resisted removal/detachment from the surface when rigorously washed with different types of solvents (ethanol, DMF, and water).

Furthermore, in order to demonstrate the versatility of the UiO-66- NH_2 deposition method presented in this work, membranes were prepared using the Layer-By-Layer (LBL) process to deposit SURMOFs on porous alpha alumina ($\alpha\text{-Al}_2\text{O}_3$) supports (Fraunhofer IKTS; $d=13$ mm, $h=1$ mm, support $d_{50}=2.5$ μm , membrane $d_{50}=70$ nm, $\varepsilon=0.4\text{--}0.55$). Using non-coated and Au-coated (coating applied via physical vapor deposition) supports, the successful synthesis of crystalline UiO-66- NH_2 thin films could be confirmed (see S.I.). Also a clear change in the transport behavior could be recognized when compared to the bare $\alpha\text{-Al}_2\text{O}_3$ support (Figure 3). Still, given the triangular narrow sized windows of this framework (ca. 0.6 nm)^[28,29] the H_2 permeance behavior should have exhibited a lower dependency with an increasing feed pressure. Therefore, the presence of micro defects, and/or small cracks is suggested. The achievement of an improved surface quality is currently under study, e.g., using a larger number of deposition steps. This would enable the further testing of highly stable and defect-free UiO-66- NH_2 SURMOF films for a vast number of applications, e.g. in gas separation or processes involving higher operation temperatures.

Finally, to fully demonstrate the applicability of the methodology developed here, a liquid phase separation experiment was conducted on a filter-paper substrate coated with a monolithic UiO-66- NH_2 SURMOF. The thin layer separator demonstrated excellent separation for a mixture of methylene

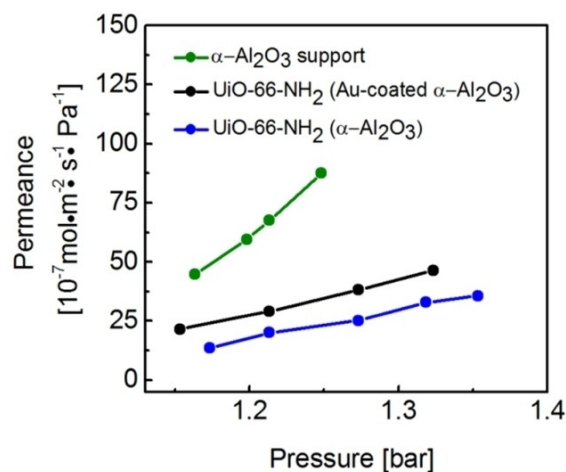


Figure 3. Hydrogen permeance as a function of increasing feed pressure for various UiO-66- NH_2 supported thin films.

blue and methyl orange aqueous solution, Figure S7. The availability of monolithic, pinhole-free MOF coatings on filaments is important for applications^[30] in the context of functionalized textiles, e.g. for medical applications and for the fabrication of coated membranes for filtration application.^[31] Membranes derived from MOF powders typically suffer from pinhole-related leakage.^[32]

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Keywords: metal-organic frameworks · liquid-phase separation · thin films · porous materials · UiO-66-NH₂ supported thin films

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