Metal–Organic Framework Films

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Lithographic Deposition of Patterned Metal–Organic Framework Coatings Using a Photobase Generator**

*Benjamin K. Keitz, Chung Jui Yu, Jeffrey R. Long, and Rob Ameloot**

Abstract: *A photobase generator was used to induce metal–organic framework (MOF) nucleation upon UV irradiation. This method was further developed into a simple, one-step method for depositing patterned MOF films. Furthermore, the ability of our method to coat a single substrate with MOF films having different chemical compositions is illustrated. The method is an important step towards integrating MOF deposition with existing lithographic techniques and the incorporation of these materials into sensors and other electronic devices.*

Metal–organic frameworks (MOFs) are a class of three-dimensional permanently porous materials consisting of metal ion nodes bridged by multitopic organic ligands. The ability to tune the pore structure, surface area, metal ion, and the organic linker has positioned these materials at the forefront of research in gas storage, catalysis, and separations.[1–3] The aforementioned attributes have also increased interest in the use of MOFs as sensors or as low-κ dielectrics in microelectronic devices.[4,5] Integration into devices for these applications requires materials to be obtained as patterned thin films, which is challenging to achieve with MOFs since they are generally synthesized as microcrystalline powders or single crystals. Thus, there is significant interest in developing methods for both producing and patterning MOF thin films and coatings.

Current strategies for obtaining patterned films of MOFs have been recently reviewed.[6] These methods include patterned deposition of precursors that are subsequently converted to MOFs,[7–12] selective substrate functionalization followed by patterned framework surface growth when exposed to a synthesis mixture,[13–16] and lithographic techniques that generate patterns in a subtractive manner from a continuous MOF coating.[17–19] Among the above techniques, those that utilize either soft lithography or photolithography are the most promising, as they can take advantage of the mature state of lithographic technologies. However, current lithographic approaches to patterning MOFs are typically time-consuming multistep processes that begin with the deposition of a homogeneous coating.[19] Herein, we describe an operationally simpler one-step method that takes advantage of a photobase generator (PBG) to deposit MOF films only in areas exposed to UV irradiation. This method is demonstrated for the MOF materials HKUST-1, HKUST-1 with incorporated Keggin polyoxometalates, and $\{Cu_2(\textit{trans}\text{-}1,4\text{-chdc})_2\}$ (chdc = cyclohexanedicarboxylate).

MOF formation occurs by deprotonation of an organic ligand, typically a carboxylic acid, followed by coordination of the deprotonated ligand to the metal ions in solution. Base introduced into the synthesis mixture, either intentionally or by spontaneous decomposition of dialkylforamide solvents, induces MOF nucleation by facilitating ligand deprotonation.[20–22] For example, it has been shown that electrochemical generation of a base can confine framework growth to the surface of an electrode.[23] Inspired by these reports, we explored the possibility of generating base equivalents by irradiation of a PBG to initiate MOF formation and whether this same chemistry could be used to generate patterned MOF films.

As an initial proof of concept, we targeted the MOF HKUST-1, which is composed of Cu^{2+} paddlewheels bridged by 1,3,5-benzenetricarboxylate (trimesate) ligands. This hydrophilic framework can be prepared solvothermally or through the addition of exogenous base at room temperature.[24] As the PBG, we chose $NaBPh_4$, which is known to generate basic species in aqueous and organic solutions upon UV irradiation.[25] To verify the ability of $NaBPh_4$ to serve as a suitable PBG, it was combined with trimesic acid in a solution of $[D_6]$DMSO and the kinetics of the acidic protons disappearance upon exposure to UV irradiation were monitored using ^{1}H NMR spectroscopy (Supporting Information, Figures S2–S4, Table S1). Within 6 min of irradiation under our conditions, almost all of the trimesic acid was consumed, which is consistent with the known quantum yield of $NaBPh_4$ ($\Phi_{H_2O} = 0.22 \pm 0.03$) and the flux of our irradiation setup[26,27] (details on the irradiation setup and power are listed in the Experimental Section). Note that deprotonation occurs directly by $NaBPh_4$ upon irradiation and not through the formation of intermediate hydroxyl species. Next, $Cu(NO_3)_2 \cdot 3H_2O$ was combined with trimesic acid in DMSO to give a synthesis solution in which MOF nucleation does not take place spontaneously at room temperature. A stoichiometric amount of $NaBPh_4$ was added to this solution (1 equivalent per carboxylic acid group). Irradiating the

[*] Dr. B. K. Keitz, C. J. Yu, Prof. J. R. Long, Dr. R. Ameloot
Department of Chemistry, University of California, Berkeley
Materials Science Division, Lawrence Berkeley National Laboratory
Berkeley, CA 94720 (USA)
E-mail: rob.ameloot@biw.kuleuven.be

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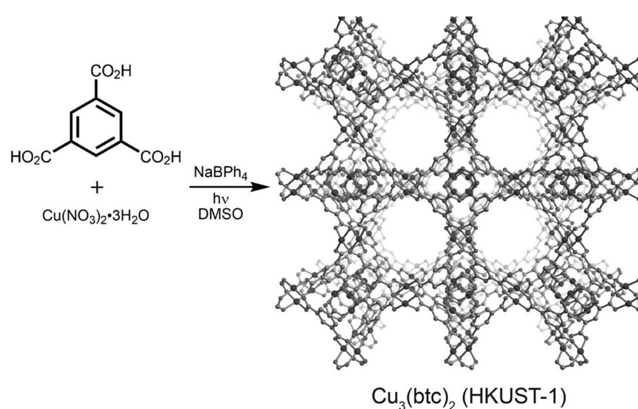

Figure 1. Synthesis of HKUST-1 at room temperature using a photobase generator (PBG) $NaBPh_4$ and exposure to UV light.

PBG-containing synthesis solution with UV light for about 15 min produced the desired HKUST-1 phase (Figure 1), as confirmed by powder X-ray diffraction (PXRD; Supporting Information, Figure S1).[28] In line with the kinetic data, shorter irradiation times (ca. 5 min) could also be used, but these reactions only displayed framework formation after standing at room temperature for several hours following UV exposure. Nitrogen physisorption measurements taken after activation yielded Langmuir and BET surface areas of $1697\ m^2 g^{-1}$ and $1304\ m^2 g^{-1}$, respectively (Supporting Information, Figure S5). Together with a micropore volume of $0.4\ cm^3 g^{-1}$, these data indicate the high quality of the HKUST-1 prepared by photoinitiated crystallization.[29,30] Control experiments without PBG failed to produce framework nucleation even after hours of UV irradiation. Similarly, a synthesis solution containing metal source, ligand, and PBG did not produce any HKUST-1 after sitting in the dark for several weeks.

Having demonstrated the bulk formation of HKUST-1 using a PBG, we explored the use of this chemistry as a means of generating patterned films of MOFs. The general setup for our patterned deposition experiments is shown in Figure 2A. Briefly, a small volume of $NaBPh_4$-containing HKUST-1 synthesis solution was sandwiched in between a microscope cover glass and a glass support plate, which were separated by a thin spacer. The cover glass surface was functionalized by silanization and subsequent oxidation of terminal vinyl groups to improve the adhesion of HKUST-1 particles to the surface. A similar functionalization could be applied to the glass support plate, but we chose to deposit MOF onto an upside-down substrate (the cover glass) to demonstrate that pattern formation was not simply a result of particles in the bulk settling onto the surface.[31] To deposit the MOF pattern, a photomask was placed on top of the assembly, which was followed by irradiation of the synthesis solution through both the mask and cover glass. As $NaBPh_4$ absorbs most strongly in the UV region (< 350 nm), a quartz photomask with chromium patterning was used to guarantee transmission in this range, while the thin borosilicate cover glass substrates were found to let sufficient UV light through (Supporting Information, Figure S6).

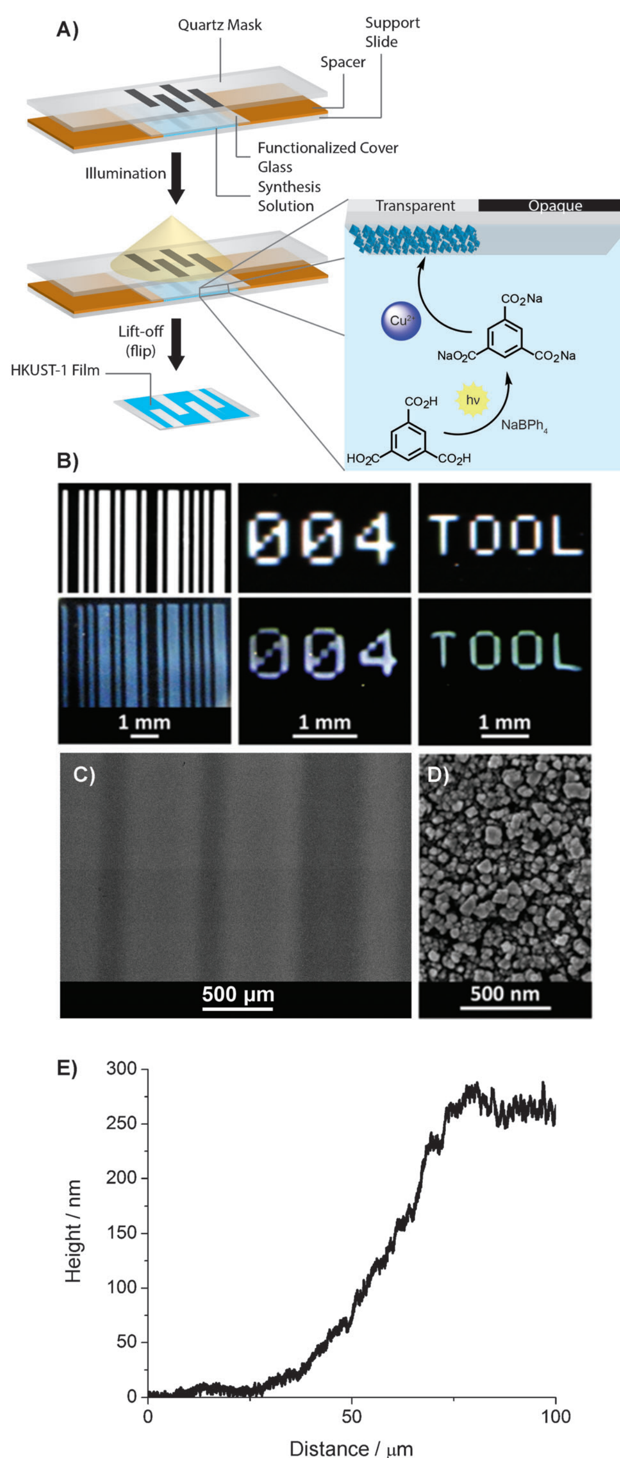

Figure 2. A) Illustration of HKUST-1 photodeposition by excitation of a PBG-containing synthesis solution. B) Optical photographs of photomask (top) and as-deposited HKUST-1 patterns after 15 min of irradition (bottom). C) Low-magnification SEM micrograph of HKUST-1 coating (light areas) following sputter coating with carbon. D) High-magnification SEM micrograph of photodeposited HKUST-1. E) Height profile of the edge of deposited HKUST-1 from profilometry.

Examples of photomasks and corresponding HKUST-1 patterns deposited after 15 min of irradiation are shown in Figure 2B. From these images, it is clear that the features of

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the photomasks are transferred to the deposited MOFs patterns with high fidelity, even though the PBG is able to diffuse freely throughout the solution. Film thicknesses of about 250 nm were obtained from profilometry and scanning electron micrographs (SEM) of the deposited films showed closely packed crystallites with an average diameter of less than 100 nm (Figure 2C,E). A high-magnification SEM image of the line edge was consistent with the gradual increase in film thickness observed by profilometry (Supporting Information, Figure S7). The relatively long exposure times (minutes) required to generate the base necessary for MOF formation also results in diffusion of the photogenerated base, which limits the resolution of our technique to micrometer-scale features. Although features of this size would be unacceptable in photolithography aimed at state-of-the-art microelectronics fabrication, they compare favorably with other methods of patterning MOFs.[6] Additionally, in sensors, the active sensing surface typically covers an area in the μm^2 to mm^2 range, which is a feature size range compatible with the photodeposition method demonstrated herein.[32,33] Note that the alternative experimental setup consisting of a functionalized bottom substrate (as opposed to the cover glass) also provided patterned MOF films.

The capabilities of the photodeposition method were further demonstrated by patterning MOFs with different chemical compositions in adjacent regions on the same substrate. Thus, phosphotungstic acid hydrate, a Keggin-type heteropolyacid (HPA) known to incorporate into the pores of HKUST-1, was added to an HKUST-1 synthesis solution and a thin film of HPA-containing HKUST-1 was deposited onto a glass substrate.[34] No spontaneous nucleation of the HPA-containing synthesis mixture occurred at room temperature in the absence of UV irradiation. Following deposition, the substrate was washed, rotated, and exposed to a normal, HPA-free HKUST-1 synthesis solution to deposit a second MOF film in a different zone on the same substrate (Supporting Information, Figure S8). Energy-dispersive X-ray spectroscopy (EDX) confirmed the presence of HPA exclusively in the HKUST-1 layer deposited first (Figure 3), which demonstrates that migration of HPA does not take place during the second deposition step.

To further illustrate the potential of photoinduced crystallization in depositing a variety of MOFs, a synthetic procedure was developed to obtain Cu_2(trans-1,4-chdc)$_2$ as a bulk powder (Supporting Information, Figures S9, S10) and as thin films (Supporting Information, Figure S11) upon irradiation of a $NaBPh_4$-containing synthesis solution in which nucleation does not take place spontaneously at room temperature.[35] The measured BET surface area of 426 $m^2 g^{-1}$ and micropore volume of 0.15 $cm^3 g^{-1}$ for the bulk sample are in line with the crystallographic data for this material. These results, together with several reported synthetic procedures in which MOF formation is triggered by the introduction of base, clearly indicate the potential of photoinduced crystallization to deposit multiple patterned coatings of different MOFs on a single substrate. Arrays of chemically distinct MOF coatings could be applied as active sensing surfaces in multiplexed sensors that are used for the identification of complex mixtures. Particularly promising to explore this route

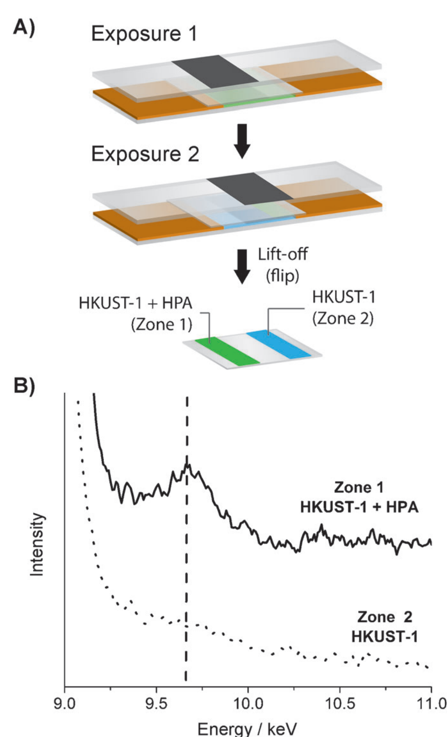

Figure 3. Multistep photodeposition of HKUST-1 coatings with different chemical compositions. A) Representation of the two-step deposition procedure. In the first step, HKUST-1 is deposited in Zone 1 from a synthesis solution containing HPA. Subsequently a second coating is deposited in Zone 2 from a synthesis solution without HPA. b) EDX analysis demonstrating the presence of the tungsten-containing HPA in Zone 1 but not in Zone 2. The tungsten L-emission line is indicated with a dotted line.

are arrays comprising MOF films with different adsorption preferences, such as hydrophilic HKUST-1 and hydrophobic {Cu_2(trans-1,4-chdc)$_2$}, which are both compatible with photodeposition. While water sensing based on a single MOF-coated sensor has already proven successful,[36,37] very few coating methods capable of depositing chemically distinct MOF films in close proximity to each other, which would extend the potential of this approach, have been reported to date.

In summary, we demonstrated that a photobase generator, such as $NaBPh_4$, can initiate the formation of MOFs upon UV irradiation. This chemistry was subsequently used as the basis for an operationally simple method of depositing patterned MOF films in a manner analogous to a photoresist. We also demonstrated the capability of this method to coat one substrate with MOF films having different chemical compositions. With further improvements in resolution, sensitivity, and access to more chemically diverse frameworks, this methodology should facilitate the incorporation of MOFs into sensors and other electronic devices.

Experimental Section

All reagents were purchased from commercial vendors and used without further purification. A stock solution of $NaBPh_4$ (290 mg, 0.85 mmol), 1,3,5-benzenetricarboxylic acid (65 mg, 0.28 mmol), and

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1,3,5-trimethoxybenzene (65 mg, 0.39 mmol) as internal standard was prepared in [D_6]DMSO (8 mL). Aliquots (0.5 mL) of this stock solution were dispensed into 4 mL borosilicate vials, which were subsequently irradiated from above the vial for different amounts of time. Following irradiation, a ^{1}H NMR spectrum was immediately acquired using a Bruker Avance 400 NMR spectrometer.

Cover glasses (22 × 22 mm^2) were functionalized as described previously.[38] Briefly, cover glasses were cleaned with acetone (1 h) and 1M NaOH (1 h), rinsed with water and acetone and then contacted with 10-undecenyltrichlorosilane in hexanes for 24 h. Afterwards, the cover glasses were rinsed with hexanes and dried with compressed air. The terminal vinyl group of the silane functionalized slides was oxidized to a carboxylate group in an aqueous solution of $NaIO_4$, K_2CO_3 and $KMnO_4$ (24 h).

MOF formation: A stock solution of $Cu(NO_3)_2{\cdot}3H_2O$ (1.2 g; 4.9 mmol) and 1,3,5-benzenetricarboxylic acid (0.58 g; 2.8 mmol) in 4.6 mL (5 g) of DMSO was prepared and 0.1 mL of this solution was added to a solution of $NaBPh_4$ (62 mg, 0.18 mmol) in DMSO (0.9 mL) for the preparation of HKUST-1. To obtain bulk powder, the PBG-containing synthesis solution was placed in a quartz tube and irradiated for 15 min. The formed powder was isolated by centrifugation and subsequently washed with DMSO and ethanol. After washing with EtOH, the framework was activated under vacuum at 393 K. For photodeposition experiments a small volume (< 20 μL) of the $NaBPh_4$-containing mixture was sandwiched in between a microscope cover glass and a support plate in such a way that no air bubbles are trapped. The cover glass and the support plate were separated by 64 μm thick Kapton tape. After placing a quartz photomask on top of this assembly, the synthesis solution was irradiated for 15 min through the photomask with light from a 500 W Xe Arc lamp (Newport Model 66921 power source) guided through an optical fiber. The total irradiation power (visible and UV) on the solution, after passing the photomask and cover glass, was measured to be approximately 13 mW cm^{-2}. Approximately 10% of this power is in the 200–350 nm range (based on the lamp emission spectrum) and can be absorbed by the photobase generator to subsequently result in carboxylic acid deprotonation. After irradiation, cover glasses with MOF patterns were carefully removed and washed with DMSO and MeOH and dried in a stream of air. The photoinduced formation of {Cu_2(trans-1,4-chdc)$_2$} was carried out in a similar manner to above using $Cu(NO_3)_2{\cdot}3H_2O$ (24 mg, 0.1 mmol), trans-1,4-chdc (17 mg, 0.1 mmol), and $NaBPh_4$ (43 mg, 0.13 mmol) in DMSO (1 mL). To obtain bulk powder, the PBG-containing synthesis solution was placed in a quartz tube and irradiated for 2 h. The formed powder was isolated by centrifugation and washed subsequently with DMSO and ethanol. Coatings were deposited on non-functionalized glass cover slides (cleaned as above with acetone and 1M NaOH) by irradiation for 15 min and washed as above.

Powder XRD patterns were recorded on a Bruker Advance D8 diffractometer operating in reflection mode. Nitrogen physisorption measurements were performed on a Micromeretics ASAP 2420 instrument after activation at 393 K (ramping rate 1 degree min^{-1}) under vacuum for 24 h. Photographs and optical and scanning electron micrographs were acquired using a Canon D-450 DSLR camera, an Olympus BX60M microscope, and a FEI SEM instrument, respectively. SEM images were acquired after sputter coating the films with either carbon or gold. Height profiles of deposited coatings were recorded using a Veeco Dektak 150 profilometer.

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