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# Reductive Electrosynthesis of Crystalline Metal–Organic Frameworks

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S Supporting Information

**ABSTRACT:** Electroreduction of oxoanions affords hydroxide equivalents that induce selective deposition of crystalline metal–organic frameworks (MOFs) on conductive surfaces. The method is illustrated by cathodic electrodeposition of $Zn_4O(BDC)_3$ (MOF-5; BDC = 1,4-benzenedicarboxylate), which is deposited at room temperature in only 15 min under cathodic potential. Although many crystalline phases are known in the $Zn^{2+}/BDC^{2-}$ system, MOF-5 is the only observed crystalline MOF phase under these conditions. This fast and mild method of synthesizing MOFs is amenable to direct surface functionalization and could impact applications requiring conformal coatings of microporous MOFs, such as gas separation membranes and electrochemical sensors.

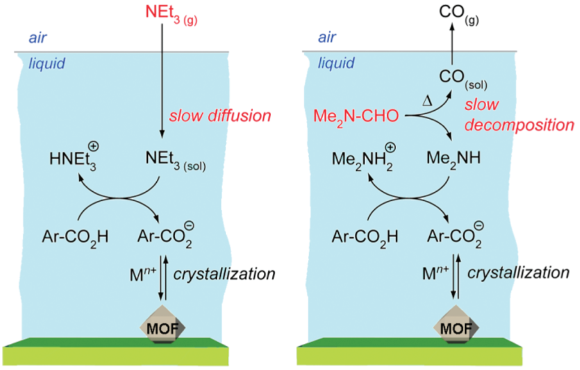

**Figure 1.** Typical crystallization routes for the synthesis of metal–organic frameworks: (left) slow vapor diffusion of triethylamine and (right) slow thermal decomposition of *N*,*N*-dimethylformamide.

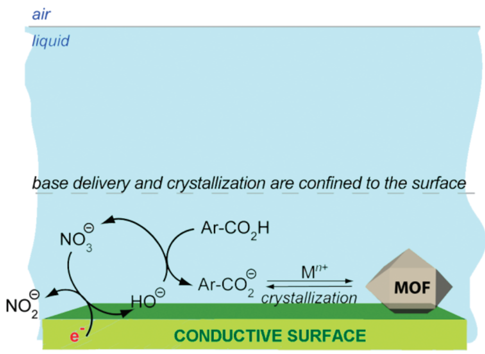

**Figure 2.** Mechanism of cathodic electrodeposition of crystalline MOFs. In contrast to other methods, cathodic electrodeposition should allow accumulation of $HO^-$ anions near the conductive surface, thus confining MOF crystallization to the electrode.

Because of their high surface areas, regular pore sizes and pore shapes, and potential for chemical tunability, metal–organic frameworks (MOFs) have enjoyed tremendous popularity in recent years. Most prominent among many proposed applications for these materials are their uses in gas storage,[1] gas separation,[2] catalysis,[3] and luminescent sensors,[4] for instance. Importantly, many of the anticipated applications, such as membranes for gas separation[5] or thin films in luminescent sensing devices,[6] require that MOFs be deposited on various surfaces. This requirement poses significant difficulties, however, because bulk MOFs are made as brittle crystals or insoluble powders that are not amenable to common surface-processing techniques.[7] To address this, membrane or thin-film growth techniques initially developed for zeolites and molecular materials, such as seeded and epitaxial growth, have also recently been adapted to MOFs.[8] However, the development of more facile and generally applicable methods of growing crystalline MOFs on surfaces remains an open challenge with significant potential implications in gas separation and electrochemical sensing, among others.

In trying to develop new methods for interfacing MOFs with surfaces, we noted that in situ deprotonation of neutral ligands is a key requirement for crystallizing materials based on anionic ligands. Indeed, the synthesis of virtually all frameworks containing carboxylates or azolates, for instance, starts from the respective carboxylic acids or azoles.[9] To optimize crystal growth, base equivalents must be introduced very slowly either by vapor diffusion, as in the original synthesis of MOF-5,[10] or by in situ formation of dialkylamines from dialkylformamides, the more common current technique (see Figure 1).[9,11] Importantly, because ligand deprotonation in these cases takes place in the bulk reaction medium, nucleation and growth of MOF crystals occur indiscriminately on any surface exposed to this medium. Moreover, because the rate of formamide decomposition depends on many factors, including the metal ion concentration, solution pH, and reaction temperature, it is difficult to predict the rate at which a given MOF would be assembled. Thus, the reaction time required to form various frameworks varies widely from case to case,[12] and the search for appropriate crystallization conditions often becomes the bottleneck in the material discovery process.[13]

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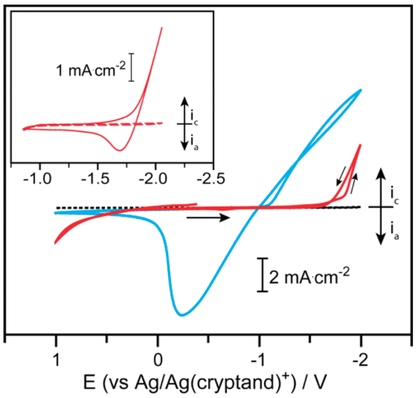

**Figure 3.** CVs of solutions of $NaNO_3$ (red) and $ZnCl_2$ (blue) in 100:1 (v/v) DMF/$H_2O$ obtained using FTO working electrodes and $(NBu_4)PF_6$ as the supporting electrolyte at scan rates of 100 mV/s. The inset shows a CV of a $NaNO_3$ solution using a Zn working electrode in 100:1 (v/v) DMF/$H_2O$. Dashed traces represent background CV scans.

A convenient means of providing Brønsted base equivalents is the electrochemical generation of hydroxide anions by the reduction of water or oxoanions such as $NO_3^-$ and $ClO_4^-$. Cathodic generation of $HO^-$ creates a pH gradient near the electrode surface, which has traditionally been used for electrodeposition of metal oxide and hydroxide films.[14] In certain cases, however, this method can also be utilized for electrodeposition of non-oxide materials such as $CaHPO_4$ and $CaCO_3$.[15] Inspired by these reports, we surmised that cathodic generation of $HO^-$ in the presence of neutral bridging ligands and metal ions should cause ligand deprotonation and consequent growth of MOFs directly on the electrode surface, as shown in Figure 2. Moreover, because the only electrochemically generated species relevant to MOF synthesis is $HO^-$, we anticipated that the method should be amenable to many metal—ligand combinations. This approach contrasts with anodic deposition methods that rely on anode corrosion for the formation of metal cations.[16] Proof-of-principle experiments were therefore conducted on the cathodic electrodeposition of $Zn_4O(BDC)_3$ (MOF-5; BDC = 1, 4-benzenedicarboxylate), which is arguably one of the most iconic MOF materials.[10]

Cyclic voltammograms (CVs) of $NaNO_3$ and $ZnCl_2$ solutions in 100:1 (v/v) DMF/$H_2O$[17] mixtures were obtained using inert fluorine-doped tin oxide (FTO) working electrodes and referenced against a Ag/Ag(cryptand)$^+$ couple.[18] As shown in Figure 3, at a scan rate of 100 mV/s, Zn plating from the $ZnCl_2$ solution was observed at −1.00 V. In contrast, the onset of $NO_3^-$ reduction did not occur until approximately −1.75 V on FTO, as anticipated for uncatalyzed multielectron redox processes, which usually require large overpotentials.[19] Because of the more anodic Zn plating potential relative to $NO_3^-$ reduction on FTO, we projected that in a mixed solution containing both $Zn^{2+}$ and $NO_3^-$, as required for instance for MOF-5 deposition, the overpotential for $NO_3^-$ reduction would be somewhat reduced by the catalytic effect of the electroplated metal deposit.[20] Indeed, a CV of a solution of $NaNO_3$ in 100:1 (v/v) DMF/$H_2O$ using Zn as a working electrode showed that the onset of $NO_3^-$ reduction on Zn was anodically shifted by approximately 250 mV relative to FTO (Figure 3 inset). This suggested that in a deposition bath containing $Zn(NO_3)_2$ and $H_2BDC$, the two ingredients required for MOF-5 synthesis, $NO_3^-$ reduction would occur below −1.5 V. Accordingly, a deposition bath was prepared by dissolving $Zn(NO_3)_2$ and $H_2BDC$ in a 100:1 (v/v) DMF/$H_2O$ solvent mixture containing $(NBu_4)PF_6$ electrolyte, and an FTO electrode immersed in this solution was polarized at a constant potential of −1.6 V for 15 min. The steady-state current density during the electrodeposition reached a value of −6.6 mA cm$^{-2}$ under these conditions (Figure S4 in the Supporting Information). Nitrate reduction was subsequently probed using the Griess reagent, which tested positive for the presence of $NO_2^-$ in the postelectrolytic deposition bath.[21]

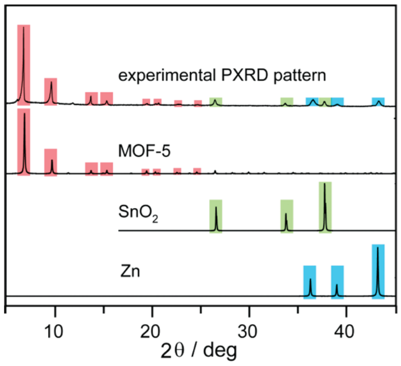

**Figure 4.** PXRD pattern observed for an FTO electrode subjected to a constant potential of −1.6 V vs Ag/Ag(cryptand)$^+$ for 15 min in a deposition bath obtained by dissolving $Zn(NO_3)_2$ and $H_2BDC$ in 100:1 (v/v) DMF/$H_2O$, along with simulated patterns for MOF-5, $SnO_2$, and Zn.

Figure 4 shows the powder X-ray diffraction (PXRD) pattern of the film that was deposited on the FTO electrode during the 15 min electrolysis. The expected patterns identifying $SnO_2$ and Zn metal account for the diffraction peaks at $2\theta$ = 26.4, 33.7, and 37.7° and $2\theta$ = 36.4, 39.0, and 43.2°, respectively. Remarkably, MOF-5 accounts for all of the remaining crystalline peaks from the electrodeposited film. Indeed, all of the peaks below $2\theta$ = 25° match the PXRD pattern simulated from the single-crystal X-ray structure of MOF-5. Crystallization of MOF-5 under these conditions demonstrates that cathodic electrodeposition is applicable to the functionalization of surfaces with MOFs. Intriguingly, extending the deposition time to 30 min increased the intensity of the Zn peaks relative to those of MOF-5 (Figure S5). We tentatively assign this to the reduction of intraframework $Zn^{2+}$ ions, as observed for instance for $Cu^{2+}$ in composite films of $Cu_3$(1,3,5-benzenetricarboxylate)$_2$.[22]

Scanning electron micrographs (SEMs) (Figure S8) showed that a 15 min electrodeposition produces rough films whose thickness varies from 20 to 40 $\mu$m as a result of electric field gradients on the FTO plate. Deposition of such thick films in only 15 min attests to a much faster growth rate than available with most other MOF surface deposition techniques. In line with this observation, SEMs of films grown for times as short as 30 s displayed large nuclei, indicative of growth rates that are significantly larger than nucleation rates. Overall, the electron microscopy analysis portends complex electrodeposition kinetics, which will be the subject of future studies.

Importantly, although 15 other phases that contain only $Zn^{2+}$ and $BDC^{2-}$ have been reported,[23] MOF-5 was the only MOF phase observed under these conditions. In contrast to the traditional preparation of this framework, which involves high temperatures and prolonged reaction times,[24] cathodic electrodeposition affords crystalline material in only 15 min at room temperature. Additionally, because $HO^-$ presumably accumulates at the conductive surface, crystallization of MOF-5 takes place preferentially on the electrode. We anticipate that this will be useful for patterning surfaces with MOF crystals.[16,25]

The foregoing results have introduced cathodic generation of base as a new method for growing crystalline MOF materials directly on conductive surfaces. The method allows the crystallization of desired materials in a single synthetic step in only minutes at room temperature. It therefore provides a potential alternative for accessing conformal coatings of MOFs, as required for gas separation membranes for instance. Future efforts will focus on further proving the generality of the approach and on eliminating codeposited metals by either reducing the cathodic potential required for electrodeposition or extending the method to more electropositive metal ions such as $Al^{3+}$ and $Mg^{2+}$. To this end, parallel studies using conductive surfaces that display better catalytic properties toward nitrate reduction are ongoing.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Detailed experimental procedures, additional CVs and PXRD patterns, a current−time deposition trace, and SEMs. This material is available free of charge via the Internet at http://pubs.acs.org.

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