Reductive electrosynthesis of crystalline metal-organic frameworks

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Reductive Electrosynthesis of Crystalline Metal-Organic Frameworks

Minyuan Li and Mircea Dincă∗
Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA, 02139, United States
mdinca@mit.edu

Electroreduction of oxoanions affords hydroxide equivalents that induce selective deposition of crystalline metal-organic frameworks on conductive surfaces. The method is illustrated by cathodic electrodeposition of $\text{Zn}_3\text{O(BDC)}_3$ (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 $\text{Zn}^{2+}$/BDC$^{2-}$ system, MOF-5 is the only observed crystalline MOF phase under these conditions. This fast and mild method of synthesizing metal-organic frameworks is amenable to direct surface functionalization and could impact applications requiring conformal coatings of microporous MOFs, such as gas separation membranes and electrochemical sensors.

Owing to 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 require that MOFs be deposited on various surfaces as, for instance, in membranes for gas separation,5 or thin films in luminescent sensing devices.6

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 been adapted to MOFs recently.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 the 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 metal ion concentration, solution pH, and reaction temperature, it is difficult to predict the rate at which a given MOF is assembled. As such, reaction times required to form various frameworks vary widely from case to case,12 and the search for appropriate crystallization conditions often becomes the bottleneck in the material discovery process.13

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

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

A convenient means to provide Brønsted base equivalents is the electrochemical generation of hydroxide anions by the reduction of water or oxoanions such as $\text{NO}_3^-$ and $\text{ClO}_4^-$.

Cathodic generation of $\text{HO}^-$ creates a pH gradient near the electrode surface, which has traditionally been used for electrodepositing metal oxide and hydroxide films.14 In certain cases, however, this method can also be utilized to electrodeposit non-oxide materials such as CaHPO$_4$ and CaCO$_3$.15 Inspired by these reports, we surmised that cathodic generation of $\text{HO}^-$ 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 $\text{HO}^-$, 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 $\text{Zn}_3\text{O(BDC)}_3$ (MOF-5), arguably one of the most iconic MOF materials.10

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The expected patterns identifying SnO that was deposited on the FTO electrode during the 15 min MOF-5 synthesis, NO reduction was subsequently probed using the Griess reagent, which tested positive for the presence of NO as required for instance for MOF-5 deposition, the overpotential for NO reduction would occur below -1.5 V.

Accordingly, a deposition bath was prepared by dissolving Zn(NO3)2 and H2BDC in a DMF:H2O (100:1, v/v) solvent mixture containing (NBu4)PF6 electrolyte, and an FTO electrode immersed in this solution was polarized at a constant potential of -1.6 V (vs. Ag/Ag(cryptand))2+. To this cathodic electrodeposition affords crystalline material in only 15 min at room temperature. In contrast to the traditional preparation of this framework, which involves high temperature and prolonged reaction time, 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.

The foregoing results introduce cathodic generation of base as a new method to grow crystalline MOF materials directly on conductive surfaces. The method allows 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 by extending the method to more electropositive metal ions such as Al2+ and Mg2+. To this end, parallel studies using conductive surfaces that display better catalytic properties towards nitrate reduction are ongoing.

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intensity of the Zn peaks relative to those of MOF-5 (see Figure S5). We tentatively assign this to the reduction of intra-framework Zn3+ ions, as observed for instance for Cu23 in composite films of Cu3(1,3,5-benzenetricarboxylate)22.

Scanning electron micrographs (SEMs, Figure S8) showed that a 15 minute electrodeposition produces rough films whose thickness varies from 20 to 40 μm due to electric field gradients on the FTO plate. Deposition of such thick films in only 15 minutes attests to a much faster growth rate than available with most other MOF surface deposition techniques. In line with this observation, SEM images of films grown for times as short as 30 seconds display large nuclei, indicative of growth rates 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 Zn2+ and BDC2- are reported, MOF-5 is the only observed MOF phase under these conditions. In contrast to the traditional preparation of this framework, which involves high temperature and prolonged reaction time, 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.

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![](image)

**Figure 4.** Powder X-ray diffraction patterns observed for an FTO electrode subjected to a constant potential of -1.6 V (vs. Ag/Ag(cryptand))2+ for 15 min in a deposition bath obtained by dissolving Zn(NO3)2 and H2BDC in DMF:H2O (100:1 v/v), and simulated for MOF-5, SnO2, and Zn.

**Figure 3.** CVs of DMF:H2O (100:1 v/v) solutions of NaNO3 (red) and ZnCl2 (blue) using FTO working electrodes and (NBu4)PF6 supporting electrolyte obtained at scan rates of 100 mV/s. The inset shows a CV of a NaNO3 solution using a Zn working electrode in DMF:H2O (100:1 v/v). Dashed traces represent background CV scans.