

Reductive Electrosynthesis of Crystalline Metal-Organic Frameworks

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Electroreduction of oxoanions affords hydroxide equivalents that induce selective deposition of crystalline metal-organic frameworks on conductive surfaces. The method is illustrated by cathodic electroreduction 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 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

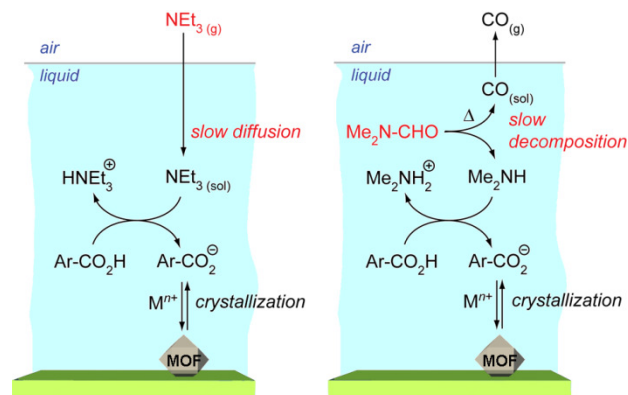


Figure 1. Typical crystallization routes for the synthesis of metal-organic frameworks: slow vapor diffusion of triethylamine (left), and slow thermal decomposition of *N,N*-dimethylformamide (right).

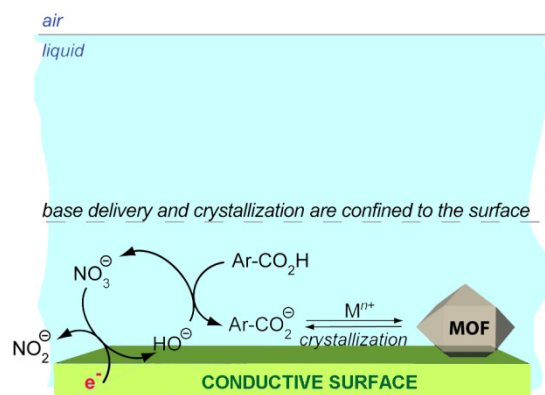


Figure 2. Mechanism for the cathodic electroreposition of crystalline MOFs. In contrast with other methods, cathodic electroreposition should allow accumulation of HO^- anions near the conductive surface, thus confining MOF crystallization to the electrode.

A convenient means to provide Brønsted base equivalents is the electrochemical generation of hydroxide anions by the reduction of water or oxoanions such as NO_3^- and ClO_4^- . Cathodic generation of 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 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 electroreposition of $Zn_4O(BDC)_3$ (MOF-5), arguably one of the most iconic MOF materials.¹⁰

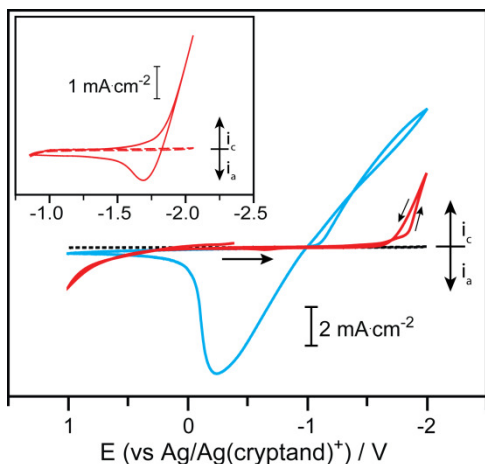


Figure 3. CVs of DMF:H₂O (100:1 v/v) solutions of NaNO₃ (red) and ZnCl₂ (blue) using FTO working electrodes and (NBu₄)PF₆ supporting electrolyte obtained at scan rates of 100 mV/s. The inset shows a CV of a NaNO₃ solution using a Zn working electrode in DMF:H₂O (100:1 v/v). Dashed traces represent background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

Cyclic voltammograms (CVs) of NaNO₃ and ZnCl₂ solutions in DMF:H₂O (100:1 v/v)¹⁷ mixtures were obtained using inert fluorine-doped tin oxide (FTO) working electrodes and were 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 ZnCl₂ solution is observed at -1.00 V. In contrast, onset of NO₃⁻ reduction does not occur until approximately -1.75 V on FTO, as anticipated for uncatalyzed multielectron redox processes, which usually require large overpotentials.¹⁹ Owing to the more anodic Zn plating potential compared to NO₃⁻ reduction on FTO, we projected that in a mixed solution containing both Zn²⁺ and NO₃⁻, as required for instance for MOF-5 deposition, the overpotential for NO₃⁻ reduction would be somewhat reduced by the catalytic effect of the electroplated metal deposit.²⁰ Indeed, a CV of a solution of NaNO₃ in DMF:H₂O (100:1 v/v) using Zn as a working electrode shows that the onset of NO₃⁻ reduction on Zn is anodically shifted by approximately 250 mV relative to FTO (Figure 3, inset). This suggested that in a deposition bath containing Zn(NO₃)₂ and H₂BDC, the two ingredients required for MOF-5 synthesis, NO₃⁻ 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 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). Nitrate reduction was subsequently probed using the Griess reagent, which tested positive for the presence of NO₂⁻ in the post-electrolytic deposition bath.²¹

Figure 4 shows the powder X-ray diffraction pattern of the film that was deposited on the FTO electrode during the 15 min electrolysis. The expected patterns identifying SnO₂ and Zn metal account for the diffraction peaks at $2\theta = 26.4^\circ$, 33.7° , and 37.7° and $2\theta = 36.4^\circ$, 39.0° , and 43.2° , respectively. Remarkably, MOF-5 accounts for all the remaining crystalline peaks from the electrodeposited film. Indeed, all peaks below $2\theta = 25^\circ$ match a powder X-ray diffraction 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 increases the

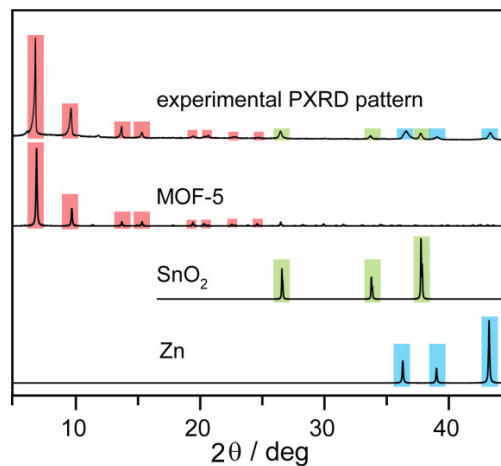


Figure 4. Powder X-ray diffraction patterns observed for an FTO electrode subjected to a constant potential of -1.6 V (vs. Ag/Ag(cryptand)⁺) for 15 min in a deposition bath obtained by dissolving Zn(NO₃)₂ and H₂BDC in DMF:H₂O (100:1 v/v), and simulated for MOF-5, SnO₂, and Zn.

intensity of the Zn peaks relative to those of MOF-5 (see Figure S5). We tentatively assign this to the reduction of intra-framework Zn²⁺ ions, as observed for instance for Cu²⁺ in composite films of Cu₃(1,3,5-benzenetricarboxylate)₂.²²

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,²³ 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,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 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 Al³⁺ and Mg²⁺. To this end, parallel studies using conductive surfaces that display better catalytic properties towards nitrate reduction are ongoing.

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Supporting Information Available: Detailed experimental procedures, additional CVs and powder X-ray diffraction patterns, a current-time deposition trace, and scanning electron micrographs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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