Electronic Supplementary Information

Selective Formation of Biphasic Thin Films of Metal-Organic Frameworks by Potential-

Controlled Cathodic Electrodeposition

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Reference

Experimental Methods

Materials. Zn(NO₃)₂•xH₂O (99%, metal basis) was obtained from Alfa Aesar. Batches were dried under vacuum at room temperature for 1 day before use. The degree of hydration was tested by CHN analyses and consistently gave x = 5. Terephthalic acid (H₂BDC, 98%), NaNO₃ (99.995% trace metal basis), and ferrocenium hexafluorophosphate (FcPF₆) were obtained from Sigma-Aldrich and used without further purification. H₂BDC used for reactions in an N₂ atmosphere was dried in a vacuum oven at 120 °C for over 12 hours. Triethylamine hydrochloride (Et₃NHCl, \geq 99.0%) was obtained from Sigma-Aldrich and recrystallized from absolute ethanol three times, then dried in a vacuum oven at 120 °C for over 12 hours. Tetrabutylammonium hexafluorophosphate (TBAPF₆, \geq 99.0%) and tetrabutylammonium perchlorate (TBAP, \geq 99.0%) were used as received from Fluka. Pt gauze (100 mesh, 99.9% metal basis) and wires ($\phi = 0.404$ mm, annealed, 99.9% metal basis, and $\phi = 0.5$ mm dia, hard, 99.95% metal basis) were obtained from Alfa Aesar. C, H, and N elemental analyses were performed by Midwest Microlab, LLC and Complete Analysis Laboratories, Inc.

Electrochemical Experiments. *N*,*N*-dimethylformamide (DMF, J.T. Baker, ACS Grade) was dried and deaerated through a solvent purification system using Al_2O_3 drying columns (SG Water USA, LLC). The electrolyte solution, designated as DMF*, was obtained by dissolving TBAPF₆ (19.4 g, 50.1 mmol) in 500 mL of DMF in a 500 mL volumetric flask to form a 0.1 M solution and stored in a sealed bottle over 4 Å molecular sieves (Alfa Aesar) inside of a N₂-filled glovebox. The water content was measured at 6.8 mg/kg with a Mettler Toledo C20 compact Karl Fischer coulometer.

Cyclic voltammetry (CV) and bulk electrolysis experiments were carried out on CH Instrument 600D, using Pt gauze as working electrode. All bulk electrolysis (electrodeposition) reactions were carried out on Pt gauze working electrodes, unless noted otherwise. For CVs carried out in the glovebox, a BioLogic SP200 potentiostat/galvanostat was used. CVs were carried out in standard three-electrode single-cell setups (Pt button working electrode, Ag/Ag(cryptand)⁺ reference electrode, and Pt wire counter electrode).

All depositions on Pt electrodes were performed in N₂-purged custom H-cells and kept under flowing N₂. The two sides of the electrochemical H-cells used for electrodeposition (compartments, diameter × height, 2.5 cm × 6 cm; total width, 8.5 cm) were connected through a fritted glass disk (diameter = 1.25 cm) to avoid cross-contamination of the analytes produced at the working (cathode) and auxiliary (anode) electrodes. The working, auxiliary, and reference electrodes were suspended with custom PTFE caps that fit to the H-cell compartments. The distance between the working electrode and the reference electrode is approximately 1 cm. All experimental potentials are referenced to the Ag/Ag(cryptand)⁺ couple. The Ag/Ag(cryptand)⁺ reference electrode was prepared according to previously described procedures.¹⁻³ Its standard potential, $E^{\circ}_{Ag/Ag(cryptand)+} = -0.526$ V, was measured against the Fc/Fc⁺. The working electrodes

were cleaned by sonication in aqueous 3 M HNO₃ for 15 minutes, washed with deionized water, then dried in an N₂ stream. They were suspended with Pt wire such that the entire mesh (1 cm \times 1 cm) was submerged and exposed to the electrolysis bath. Similarly, Pt mesh ($2 \text{ cm} \times 2 \text{ cm}$), suspended by a Pt wire, was used as an auxiliary electrode in all deposition experiments. For a typical deposition experiment, reagent powders and a pre-dried stir bar were added to an empty dry cell. The cell was quickly capped, sealed with Parafilm, and purged with N₂ for 30 minutes. Each compartment was then charged with 10 mL of DMF* using a syringe. The auxiliary electrode compartment was sealed with Parafilm[®] under N₂, while the working side was sparged with N₂ and stirred until complete dissolution of the MOF precursors. A typical deposition solution consists of $[Et_3NHC] = [Zn(NO_3)_2 \cdot 5H_2O] = 100 \text{ mM}$ and $[H_2BDC] = 50 \text{ mM}$, unless noted otherwise. All cathodic electrodeposition reactions were carried out on Pt mesh working electrodes, unless noted otherwise. For a typical CV experiment, a three-electrode setup was used: a Pt button working electrode (area = 0.0314 cm²) from CH Instruments, a Ag/Ag(cryptand)⁺ reference electrode, and Pt wire auxiliary electrode. All CVs were recorded at a 100 mV/s scan rate unless otherwise noted. Stable background scans were achieved before any CV experiments.

Preparation of the Hydrated Electrolyte Solvent Solution (DMF-hyd). The hydratred electrolyte solution was prepared by first dissolving TBAPF₆ (19.4 g, 50.1 mmol) in 100 mL of DMF in a 500-mL storage vessel inside the glovebox. The storage vessel was then kept under high nitrogen flow, while distilled and deionized water (5 mL, Ricca, ASTM Type I, 18 MW resistance) was added with a syringe to provide a 1:20 (v/v) volumetric content of water. This solution was then subjected to three freeze-pump-thaw cycles to remove dissolved oxygen and diluted to 500 mL with dry DMF inside the glovebox to form a 1%, or 1:99 (v/v) volumetric content, water solution in DMF with 0.1 M TBAPF₆. A Mettler Toledo C20 compact Karl Fischer coulometer was used to measure the water content of dry DMF (37.6 ppm) and its solutions. The water content of DMF* was 6.8 ppm, and that of DMF-hyd was 10,053 ppm.

Powder X-Ray Diffraction (PXRD). PXRD patterns were measured on a Bruker D8 Discover diffractometer with a Göbel mirror, rotating sample stage, LynxEye detector, and Cu K_{α} (λ = 1.5405 Å) X-ray source. Anti-scattering incident source slit (typically 1 mm) and an exchangeable steckblende detector slit (typically 8 mm) were used. Top-loading PMMA specimen holder rings were loaded into a universal sample cup. Powder samples or substrate-mounted samples were loaded on top of glass slides or silicon low-background plates. Knife-edge attachments were used to remove scattering at low angles. A low-background sample cup was also used for powder samples, and patterns were obtained while rotating at 15 rev/min. Experimental patterns were adjusted to an internal standard (shifting the experimental value to that published for Pt, ICSD Collection Code 76153,⁴ at 39.76°, or Zn, ICSD Collection Code 421014,⁵ at 43.24°). Backgrounds were subtracted with the enhanced background option in

Bruker EVA software. Patterns of single crystal structures were simulated in Mercury 3.0 with default parameters.

Scanning Electron Microscopy (SEM). Scanning electron micrographs were obtained with a JSM-5910 microscope or a FEI XL-30 microscope under high vacuum mode. Typical acceleration voltage varied between 1.5 and 15 kV. Substrate-mounted samples were immobilized with carbon adhesive tape to the sample holder. The original imagines were processed in Adobe Photoshop for increased brightness and contrast only. No other modifications were applied.

Nuclear Magnetic Resonance (NMR). ¹H NMR spectra were obtained on a Varian Inova 500 NMR spectrometer with an Oxford Instruments Ltd. superconducting magnet. Deposited samples were digested in deuterated trifluoroacetic acid (F_3C -COOD) under sonication and then diluted with DMSO-d₆.

Gas Sorption Measurements. The N₂ adsorption isotherm at 77K was obtained with a Micromeritics ASAP 2020 surface area and porosity analyzer. Entire pre-weighed FTO plates covered with electrodeposited Zn/MOF-5 composite were activated by soaking first in DMF (3 x 1 day), then in dichloromethane (3 x 1 day), followed by heating under vacuum (10^{-5} mmHg) at 150 °C. They were then transferred to a tared isotherm sample tube equipped with a TranSeal (Micromeritics) and heated again under high vacuum at 180 °C until the outgas rate was less than 2 mTorr/min. The tube with the plates was weighed again to determine sample mass. The surface area was calculated by fitting the isotherm data to the BET equation.



Figure S1. Cyclic voltammograms of 15 mM NaNO₃ solutions in DMF* (blue) and DMFhyd (green), and their associated backgrounds (black dashes) on a Pt button electrode (2 mm dia.). All traces shown represent the second potential sweep cycles.



Figure S2. Cyclic voltammograms of a DMF* solution (black) and after adding reagents sequentially, in the same solution, in the following order: H_2BDC , $Zn(NO_3)_2 \cdot 5H_2O$, and Et_3NHCl . All scans shown are from the second potential sweep cycles. (top) 12.5 mM H₂BDC (purple), showing the H⁺/H₂ redox couple ($E_{p,c} = -1.22$ V, $E_{p,a} = -0.54$ V); (middle) 12.5 mM H₂BDC and 25 mM Zn(NO₃)₂ \cdot 5H₂O (light blue); (bottom) 12.5 mM H₂BDC, 25 mM Zn(NO₃)₂ • 5H₂O, and 25 mM Et₃NHCl (orange).



Figure S3. SEMs of samples deposited at -1.00 V for 8 hours, in a solution of DMF (as opened, < 0.1% water) with 0.1 M TBAP as the supporting electrolyte and reagent concentrations of [Et₃NHCl] = 300 mM, [Zn(NO₃)₂•5H₂O] = 150 mM, and [H₂BDC] = 50 mM,. The average current density during the deposition was -0.29 mA•cm⁻².



Figure S4. Additional views of the X-ray crystal structure of $[Zn_3(BDC)_4]^{2^-,6}$ viewed normal to the (100) plane (left) and the (010) plane (right). Purple, red, and grey spheres represent Zn, O, and C atoms, respectively. Et₂NH₂⁺ and DEF species occupying the pore space, as well as H atoms, were removed for clarity. O atoms from the carboxylate groups that were not coordinated to zinc atoms are highlighted in yellow.



Figure S5. Simulated PXRD patterns for reported frameworks containing $[Zn_3(BDC)_4]^{2-}$, generated from solvated single-crystal structures obtained from the Cambridge Crystallographic Structural Database (CCSD) (top),⁶⁻⁸ and after removing charge-balancing ions and solvent molecules by directly editing the .cif files (bottom). The six letter codes are the structure codes in the CCSD.



Figure S6. PXRD patterns of samples deposited at -1.50 V, using DMF* with reagent concentrations of [Et₃NHCl] = 350 mM, [Zn(NO₃)₂•5H₂O] = 150 mM, and [H₂BDC] = 50 mM. The 5-min reaction was measured directly on the Pt substrate, while the rest were measured on the isolated powders that were scraped from the Pt substrates. Except for the 5-minute reaction pattern, all patterns showed strong diffraction signals of the anionic framework, (Et₃NH)₂Zn₃(BDC)₄.



Figure S7. SEMs of samples deposited at -1.50 V for 1 hour, in a DMF* solution with reagent concentrations of [Et₃NHCl] = 350 mM, [Zn(NO₃)₂•5H₂O] = 150 mM, and [H₂BDC] = 50 mM.



Figure S8. SEMs of samples deposited at -1.50 V for 4 hours, in a solution of DMF* with reagent concentrations of [Et₃NHCl] = 350 mM, [Zn(NO₃)₂•5H₂O] = 150 mM, and [H₂BDC] = 50 mM.



Figure S9. PXRD patterns of samples deposited for 30 minutes, in DMF* solutions with reagent concentrations of $[Et_3NHCl] = 100 \text{ mM}$, $[Zn(NO_3)_2 \cdot 5H_2O] = 100 \text{ mM}$, and $[H_2BDC] = 50 \text{ mM}$. The (*) peak at 8.4° corresponded to crystallized supporting electrolyte TBAPF₆. All patterns were measured on isolated powders scraped from the Pt substrates.



Figure S10. SEMs of films deposited at -1.50 V for 30 minutes, in DMF* solutions with reagent concentrations of [Et₃NHCl] = 100 mM, [Zn(NO₃)₂•5H₂O] = 100 mM, and [H₂BDC] = 50 mM. Both polyhedral and featherlike morphologies were observed, which we assign to Zn₄O(BDC)₃ and (Et₃NH)₂Zn₃(BDC)₄, respectively.



Figure S11. SEMs of films deposited at -1.70 V for 30 minutes, in DMF* solutions with reagent concentrations of [Et₃NHCl] = 100 mM, [Zn(NO₃)₂•5H₂O] = 100 mM, and [H₂BDC] = 50 mM.



Figure S12. N_2 adsorption isotherm collected at 77 K for a composite of MOF-5 and Zn deposited on FTO.³ FTO was chosen because it afforded larger quantities of the Zn/MOF-5 composite, necessary for the adsorption measurement and the subsequent NMR analysis. The surface area values were based on an evacuated sample mass of 11.5 ± 0.3 mg, obtained from combining the samples from six 0.5 cm × 2.5 cm × 0.2 cm FTO plates. Each plate had an electrochemically-active (film-covered) surface of approximately 0.5 cm × 1.25 cm.



Figure S13. ¹H NMR $\delta_{\rm H}(500 \text{ MHz}; \text{DMSO/F}_3\text{C-COOD})$ spectrum of a Zn/MOF-5 composite (approximately 9.2 ± 0.3 mg dry mass) digested in 0.4 mL of F₃C-COOD (residual at 15.43 ppm, not shown) and 1.2 mL of DMSO-d₆ (referenced to 2.50 ppm). The NMR sample was spiked with 50 µL (43.4 ± 0.1 mg) of mesitylene, 6.88 (3H, s, 6-H), 2.14 (9H, s, 6-Me), as an internal standard to determine the amount of H₂BDC, 8.00 (4H, s, 6-H). The singlets at 7.88 (1H, s, HCON), 2.69 (3H, s, NMe) and 2.82 (3H, s, NMe) correspond to DMF. Assuming that all H₂BDC was from Zn₄O(BDC)₃, the composite consisted of 43.0 ± 1.5 % w/w of MOF-5, giving a MOF-5 specific surface area of 2140(80) m²/g.



Figure S14. Experimental PXRD pattern of a samples deposited at -1.70 V for 30 minutes, in DMF* solutions with reagent concentrations of [Et₃NHCl] = 100 mM, [Zn(NO₃)₂•5H₂O] = 100 mM, and [H₂BDC] = 50 mM and expected patterns for Zn, MOF-5, and (Et₃NH)₂[Zn₃(BDC)₄]. Peaks corresponding to the diffraction pattern of metallic zinc could be observed.





Figure S16. PXRD patterns of samples deposited at -2.00 V, using DMF* with reagent concentrations of [Et₃NHCl] = 350 mM, [Zn(NO₃)₂•6H₂O] = 150 mM, and [H₂BDC] = 50 mM. The 4-hour reaction was measured directly on the Pt substrate. The experimental pattern showed diffraction patterns of zinc metal and the anionic framework, (Et₃NH)₂Zn₃(BDC)₄.



Figure S17. SEMs of films deposited at -1.10 V for 6 hours, then at -1.70 V for 5 minutes, in DMF* solutions with reagent concentrations of [Et₃NHCl] = 100 mM, [Zn(NO₃)₂•6H₂O] = 100 mM, and [H₂BDC] = 50 mM. The top right panel is a zoom-in of the central region of the top left panel.

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