Facile and Rapid Room-Temperature Electrosynthesis and Controlled Surface Growth of Fe-MIL-101 and Fe-MIL-101-NH₂

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Experimental Procedures and Details

General Considerations
No unexpected or unusualy high safety hazards were encountered. All reagents were obtained from commercial vendors and used without purification, excluding solvents. For electrochemical experiments, dimethylformamide (DMF) was obtained from a solvent drying system and stored in a glove box under 4Å sieves. TBAPF₆ was recrystallized from hot ethanol and dried under vacuum overnight prior to use. Indium tin oxide (ITO) plates were purchased from nanocs, in 1” x 3” sheets with resistances of 100 ohms.

PXRD measurements were performed with a Bruker D8 XRD (LynxEye position sensitive detector) operating with a Cu Kα x-ray generator (λ = 1.54 Å) with a 40 kV beam voltage and 40 mA current. Low-pressure adsorption measurements were obtained on a Micromeritics 3Flex. Electrochemistry was performed using either a CHI-620D potentiostat/galvanostat or a CHI-760D bipotentiostat.

All XPS spectra were acquired using a Thermo Fisher K-alpha+ spectrometer equipped with a monochromator and a 128 channel CCD detector plate. The X-rays used were monochromatic Al Kα X-Rays (1486.7 eV) with a power of 72 W (12 kV, 6 mA) at a takeoff angle normal to the surface and a base pressure lower than 1 x 10⁻⁸ mBar. The X-Ray spot size was elliptical in shape with a semi-major axis of 400.0 µm. The intense C 1s peak at 284.8 eV was used to calibrate all spectra. Initial XPS survey scans were collected at a pass energy of 50 eV using a step size of 1.0 eV. High-resolution XPS spectra were collected at a pass energy of 20 eV using a step size of 0.1 eV. Reported values for average atomic surface composition were taken by integration of the high-resolution spectra using the Scofield cross sections for the relative sensitivity factors. Atomic percentages determined by XPS do not include hydrogen.

Scanning electron microscopy images, high resolution FIBing and energy dispersive X-ray (EDX) spectra were acquired with a JSM-7400F high resolution scanning electron microscope (SEM) or Auriga 60 CrossBeam high resolution focused ion beam & scanning electron microscope.

Electrochemical Measurements
Cyclic voltammetry was performed using a standard three-electrode configuration in a nitrogen-filled glovebox. A glassy carbon disk electrode (GCE, 3.0 mm diameter) was polished with a slurry of 0.05-micron alumina powder in Millipore water. Residual alumina was rinsed from the GCE surface with Millipore water, and the electrode was then sonicated in Millipore water for three minutes and transferred into the glovebox as the working electrode. A piece of platinum gauze was used as the counter electrode. All potentials were measured against a Ag wire reference electrode. Cyclic voltammograms were recorded at 100 mV/s with IR drop compensation in a solution of dry DMF containing 1.0 mM FeCl₂, 1.0 mM 2,6-lutidine, 1.0 mM terephthalic acid and 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Controlled potential electrolysis (CPE) experiments were performed in a nitrogen-filled glovebox using a standard three-electrode configuration in which a 2 x 1 cm² ITO plate was used as the working electrode, a piece of platinum gauze as the counter electrode, and a Ag wire as the reference electrode. CPE experiments employing a single compartment cell were carried out within a 20-mL vial. For CPE experiments performed in two-compartment cells, a piece of sintered glass was used to separate the anodic and cathodic compartments.
Cleaning and Preparation of ITO Electrodes

Indium tin oxide (ITO) plates were cut into 2 x 1 cm² pieces and were cleaned by treatment with NaOH. The ITO plates were sonicated in a 10 wt % solution of NaOH for 10 min twice, and then sonicated for an additional 10 min in Millipore water to remove any excess NaOH. The ITO plate was then rinsed with additional Millipore water and then immediately used MOF electrosynthesis or subjected to electrografting with 4-diazobenzoic acid.

Solvothermal Synthesis of Fe-MIL-101

The following synthesis has been modified from a previously published method. FeCl₃•6H₂O (0.675 g, 2.45 mmol) and terephthalic acid (0.205 g, 1.24 mmol) were dissolved in DMF (15 mL). The resulting suspension was sonicated until it was translucent and then heated at 110 °C for 20 hours. After cooling the reaction to room temperature, the desired product was isolated via centrifugation and was washed three times with DMF (20 mL) and three times with MeOH (20 mL).

Electrosynthesis of Fe-MIL-101 using Unmodified ITO Electrodes

This electrosynthesis was carried out in a two-compartment cell. FeCl₂ (0.528 g, 4.17 mmol), terephthalic acid (0.694 g, 4.18 mmol), and TBAPF₆ (2.154 g, 5.56 mmol) were dissolved in 20 mL of DMF. The resulting clear, light-yellow solution was added to the working compartment of the electrolysis cell. TBAPF₆ (2.177 g, 5.62 mmol) was dissolved in 20 mL of DMF, and the clear, colorless solution was added to the adjacent compartment. The working, reference, and counter electrodes were an unmodified ITO electrode, Ag wire, and Pt mesh, respectively. Once the electrodes were set up, a 487 μL aliquot of 2,6-lutidine (4.18 mmol) was added to the working compartment, and the CPE was immediately run at 0.75 V for 14 hours, resulting in a brown, cloudy solution.

Electrochemical Grafting of 4-Diazobenzoic Acid

Modification of ITO was based on a previously published method. As small amount of 4-aminobenzoic acid (2.7 mg) and a small stir bar were added to a 20 mL via along with 19.1 mL of Millipore water and 0.9 mL of 12.0 M HCl. A 10 mL aliquot of the solution was combined with 200 μL of a 1.0 M solution on aqueous NaNO₂. The resulting solution was allowed to stir for 5 min. A cleaned 2 x 1 cm² ITO plate was used as the working electrode with 1 x 1 cm² area immersed in the NaNO₂ based solution. The ITO electrode was used as a working electrode and a cyclic voltammogram was then recorded from 0.6 V to –0.5 V versus Ag/AgCl at a scan rate of 0.4 V/s with iR drop compensation. Modification of the ITO substrate was confirmed by XPS spectroscopy.

Electrosynthesis of Fe-MIL-101 Films on Carboxy-Modified ITO Electrodes

This electrosynthesis was carried out in a single-compartment cell. FeCl₂ (0.1268 g, 1.0 mmol) and terephthalic acid (0.1661 g, 1.0 mmol) were fully dissolved in DMF (5 mL) in the glovebox, followed by the addition of 120 μL of 2,6-lutidine. Controlled potential electrolysis (CPE) was initiated using a carboxy-modified ITO plate as the working electrode in that solution with gentle stirring at either $E_{app} = 0.5, 0.75, 1.0$ or $1.25$ V versus Ag/Ag⁺ for 2, 6, 10, 14 or 18 hours. After electrolysis the ITO electrode appended with the MOF film, which was removed from the electrolysis cell and washed three times with DMF (20 mL) prior to detailed characterization.

Solvothermal Synthesis of Unknown Material from Electrolyte Solutions
FeCl₃ • 6H₂O (0.270 g, 1 mmol), terephthalic acid (0.166 g, 1 mmol), and 2,6-Lutidene (29 μL, 0.250 mmol) were dissolved in DMF (5 mL). The resulting suspension was sonicated until it was translucent and was then heated at 110 °C for 20 hours.

**Solvothermal Synthesis of Fe-MIL-101-NH₂**

The following synthesis has been modified from a previously published method.⁴ FeCl₃ • 6H₂O (0.720 g, 2.66 mmol) and 2-amino-terephthalic acid (0.242 g, 1.34 mmol) were dissolved in DMF (12 mL). The resulting suspension was sonicated until it was translucent and was then heated at 110 °C for 24 hours. After cooling the reaction to room temperature, the desired product was isolated via centrifugation and was washed three times with DMF (20 mL) and three times with CH₂Cl₂ (20 mL).

**Electrochemical Synthesis of Fe-MIL-101-NH₂ on Carboxy-Modified ITO Electrodes**

This electrosynthesis was carried out in a single-compartment cell. FeCl₂ (0.1268 g, 1.0 mmol), 2-aminoterephthalic acid (0.1811 g, 1.0 mmol) and tetrabutylammonium hexafluorophosphate (0.1937 g, 0.5 mmol) were fully dissolved in DMF (5 mL) in the glovebox. An aliquot of 120 μL 2,6-lutidine was then added to the solution. Controlled potential electrolysis (CPE) was initiated using a carboxy-modified ITO plate as the working electrode in that solution with gentle stirring at \( E_{app} = 0.75 \) V versus Ag/Ag⁺ for 8 hours. After electrolysis the ITO electrode appended with the MOF film was removed from the electrolysis cell and washed three times with DMF (20 mL) prior to detailed characterization.

**Electrochemical Synthesis of Fe-MIL-100 on Carboxy-Modified ITO Electrodes**

This electrosynthesis was carried out in a single-compartment cell. FeCl₂ (0.1268 g, 1.0 mmol) and trimesic acid (0.2101 g, 1.0 mmol) were fully dissolved in DMF (5 mL) in the glovebox, followed by the addition of 120 μL of 2,6-lutidine. Controlled potential electrolysis (CPE) was initiated using a carboxy-modified ITO plate as the working electrode in that solution with gentle stirring at \( E_{app} = 1.2 \) V versus Ag/Ag⁺ for 18 hours. After electrolysis the ITO electrode appended with the MOF film, was removed from the electrolysis cell and washed three times with DMF (20 mL) prior to detailed characterization.

**Electrochemical Synthesis of Fe-MIL-88B-NH₂ on Carboxy-Modified ITO Electrodes**

This electrosynthesis was carried out in a single-compartment cell. FeCl₂ (0.1268 g, 1.0 mmol), 2-aminoterephthalic acid (0.1811 g, 1.0 mmol) and tetrabutylammonium hexafluorophosphate (0.1937 g, 0.5 mmol) were fully dissolved in DMF (4 mL) in the glovebox, followed by the addition of 1 mL of degassed Milli-Q water and 120 μL of 2,6-lutidine. Controlled potential electrolysis (CPE) was initiated using a carboxy-modified ITO plate as the working electrode in that solution with gentle stirring at \( E_{app} = 0.4 \) V versus Ag/Ag⁺ for 2 hours. After electrolysis the ITO electrode appended with the MOF film was removed from the electrolysis cell and washed three times with DMF (20 mL) prior to detailed characterization.
**Figure S1.** (a) Cyclic voltammogram recorded for 1.0 mM FeCl$_2$, 1.0 mM 2,6-lutidine, and 1.0 mM terephthalic acid in DMF containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The CV was recorded at a scan rate of 100 mV/s. (b) Current versus time trace for an 18 hour electrolysis at 298 K using a two-compartment cell at $E_{\text{app}} = 0.75$ V using an ITO working electrode and the electrolyte conditions described under part (a). We note that CVs recorded for FeCl$_2$ dissolved in DMF containing 0.1 M tetrabutylammonium hexafluorophosphate appear identical to that shown in panel (a) following addition of 2,6-lutidine and terephthalic acid.

**Figure S2.** Cyclic voltammogram of 4-aminobenzoic acid in 0.5 M HCl with (black) and without (red) the addition of NaNO$_2$. 
Figure S3. High resolution XPS spectra of the C 1s region of carboxy-modified ITO (black) against an ITO plate treated in 4-aminobenzoic acid without the addition of NaNO₂ (red).
Figure S4. Powder X-ray diffraction pattern of Fe-MIL-101 that was either solvothermally prepared as a powder, or electrosynthesized on carboxy-modified ITO at $E_{\text{app}} = 0.75$ V for either 2, 6, 10, 14, or 18 hours, as compared to the simulated/predicted powder pattern. The diffraction patterns for the electrosynthesized materials were collected from MOF grown on the surface of the ITO electrode.
Figure S5. SEM image of Fe-MIL-101 electrosynthesized on carboxy-modified ITO at $E_{\text{app}} = 0.75$ V for either 2, 6, 10, or 14 hours.
Figure S6. Powder X-ray diffraction pattern of Fe-MIL-101 that was either solvothermally prepared as a powder, or electrosynthesized on carboxy-modified ITO at a potential of either $E_{app} = 0.5$ V, 0.75 V, 1.0 V, or 1.25 V over the course of 18 hours, as compared to the simulated/predicted powder pattern. The diffraction patterns for the electrosynthesized materials were collected from MOF grown on the surface of the ITO electrode.
Figure S7. FIB image and EDX characterization of Fe-MIL-101 electrosynthesized on carboxy-modified ITO.
Figure S8. Survey XPS spectrum (top) and high resolution XPS spectra of C 1s (middle left), O 1s (middle right), Fe 2p (bottom left), and Cl 2p (bottom right) of Fe-MIL-101 grown electrochemically on carboxy-modified ITO (red) and solvothermally synthesized Fe-MIL-101 powder (black).
Figure S9. Powder X-ray diffraction pattern of Fe-MIL-101-NH$_2$ that was either solvothermally grown as a powder, or electrosynthesized on carboxy-modified ITO at a potential of $E_{\text{app}} = 0.75$ V over the course of 8 hours in a one-compartment electrochemical cell. The simulated/predicted powder pattern of Fe-MIL-101 is also shown. The diffraction patterns for the electrosynthesized materials were collected from MOF grown on the surface of the ITO electrode.
Figure S10. Survey XPS spectrum (top left) and high resolution XPS spectra of O 1s (top middle), N 1s (top right), Fe 2p (bottom left), Cl 2p (bottom middle), and C 1s (bottom right) of Fe-MIL-101-NH$_2$ electrosynthesized on carboxy-modified ITO.
Figure S11. FIB image and EDX characterization of Fe-MIL-101-NH$_2$ electrosynthesized on carboxy-modified ITO.
Figure S12. Powder X-ray diffraction pattern of Fe-MIL-88B-NH₂ electrochemically grown on carboxy-modified ITO at $E_{\text{app}} = 0.4$ V for 2 h, as compared to the simulated/predicted powder pattern. The diffraction pattern was collected from material grown on the surface of the ITO electrode.
Figure S13. Powder X-ray diffraction pattern of Fe-MIL-100 electrosynthesized on carboxy-modified ITO at $E_{\text{app}} = 1.2$ V for 2 h, as compared to the simulated/predicted powder pattern. The diffraction pattern was collected from material grown on the surface of the ITO electrode.
Table S1 Summary of BET (Langmuir) surface areas (m$^2$/g)

|                       | MIL-101 in solution | MIL-101 plated | MIL-101-NH$_2$ plated |
|-----------------------|---------------------|----------------|------------------------|
| 1 Compartment         |                     | 1806 (3061)    | 1918 (2961)            |
| 2 Compartment         |                     |                |                        |
| Modified ITO          | 1905 (2840)         | 2313 (3434)    |                        |
| Unmodified ITO        |                     |                |                        |
| Solvothermal          | 2368 (3333)         |                |                        |
|                       | 2679 (3502)         |                |                        |
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