Unraveling a two-step oxidation mechanism in electrochemical Cu-MOF synthesis
Supporting Information

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Electrochemical synthesis of CuBTC An electrochemical cell was filled with the electrolyte consisting of 3 g of 1,3,5-benzene-tricarboxylic acid (BTC, Santa Cruz Biotechnology, >98%) and 1 g of Methyl-tributyl-methyl ammoniumsulfate (MTBS, Sigma Aldrich, 95%) in 100 mL of absolute ethanol (Sigma Aldrich, 99.9%). For experiments under oxygen exclusion the electrolyte was degassed by bubbling with 6N Argon for 20 minutes. A 1x1cm piece of copper foil (99,99%+, Mateck GmbH, thickness 0,5 mm) with a 0.5mm hole drilled into one corner was hung into the electrochemical cell by a copper wire. As counter electrode a flame annealed Pt/Ir wire (0.25 mm thickness) wound into a coil was used. The reference electrode was a silver/silver chloride electrode with an inner electrolyte of 3M aqueous KCl. A potential of 1V was applied between the copper foil and the reference electrode for 20 minutes to synthesize CuBTC. The plates were rinsed with ethanol and investigated as received via SEM, XRD and Raman.

Electrochemical surface oxidation of CuBTC The procedure for the surface oxidation of the Cu-foil was the same as for the electrochemical CuBTC synthesis with the exception of the electrolyte composition. The electrolyte consisted of 1 g of methyl-tributyl-methyl ammonium sulfate (MTBS) in 100 mL of ethanol.

Electrolyte degassing Solutions were degassed by bubbling with Argon for 20 minutes. The experimental setup was kept in an Argon atmosphere afterwards.

Deoxygenation of Cu foil To get rid of copper oxides on the surface of the copper foil prior to the synthesis the copper foil was immersed in 25% nitric acid for 3 minutes, rinsed with MilliQ-H_2O, immersed in 25% hydrochloric acid for 3 minutes, rinsed with MilliQ, rinsed with ethanol and immediately inserted into the electrochemical cell, following a procedure by Hall et al.[1]

Electroless synthesis of CuBTC from copper oxides 200 mg of Cu_2O (Sigma Aldrich, 99.99%+) or CuO (Sigma Aldrich, 99.999%) where dispersed in ~7 mL of a solution of 30 g/L 1,3,5-benzene-tricarboxylic acid in ethanol. After 16 hours the dispersion was centrifuged at 6000 rpm for 10 minutes. After removal of the supernatant the residue was resuspended in ethanol and centrifuged at 6000 rpm for 10 minutes. The supernatant was discarded and the resuspension/centrifugation procedure repeated. After drying in nitrogen stream the powder product was used for XRD as received, dispersed on carbon tape for investigation with SEM, and was spread on a glass slide for Raman measurements.

Raman spectra acquisition Raman spectra for Samples A-F were measured on a homebuilt Raman setup with a 35 mW 633 nm HeNe cw-laser as excitation source. Signal collection was done in backscattering by a long WD air objective (Olympus LMPlan FL N, 50x, NA 0.5) at a 55° angle from the sample normal. The laser power in the sample plane was around 0.1 mW. All reported Raman spectra are normalized to one second acquisition times. Spikes from cosmic rays have been removed by hand. Spectra from samples A, B and C were taken directly at the surface of the anode used to synthesize CuBTC. The Raman map for the patterning experiment was taken on a Bruker Senterra Raman microscope. The excitation wavelength was 488 nm and the laser power 2 mW in the sample plane.

Fabrication of a patterned MOF device A copper plate was deoxidized as detailed above. The plate was afterwards electrochemically oxidized in 0.1 M for 10 minutes at -0.1 V NaOH vs Ag/AgCl/3 M KCl. The counter electrode was a flame annealed Pt/Ir wire. A ~10 µL drop of 10% HCl was pipetted on the center of the plate and removed with the pipette after 15 seconds. After rinsing, the copper plate was used for electrochemical synthesis of CuBTC as detailed above in a degassed solution.

Scanning Electron Microscopy SEM images were taken on a Zeiss 1530 Gemini Leo (Figures 4,5,7) or on a Hitachi SU8000 (Figures 1&3) at varying voltages. For samples A, B and C the images were taken directly from the surface of the anode used to synthesize CuBTC

X-Ray Diffraction (XRD) XRD diffractograms of Samples A-C were taken directly on the copper anodes after synthesis on a Bruker-AXS D5005 using a CoKα source. Sample D was analyzed as an isolated powder on a Philips PW1820 diffractometer with CuKα source. The data for sample D was converted to CoKα equivalent diffraction angles Θ_2 through:

$$\Theta_2 = \sin^{-1}\left(\frac{E_1}{E_2}\sin\Theta_1\right)$$

With E_1 the energy of CuKα (8047 eV), E_2 the energy of CoKα (6930 eV) and Θ_1 the angles measured with CuKα source.
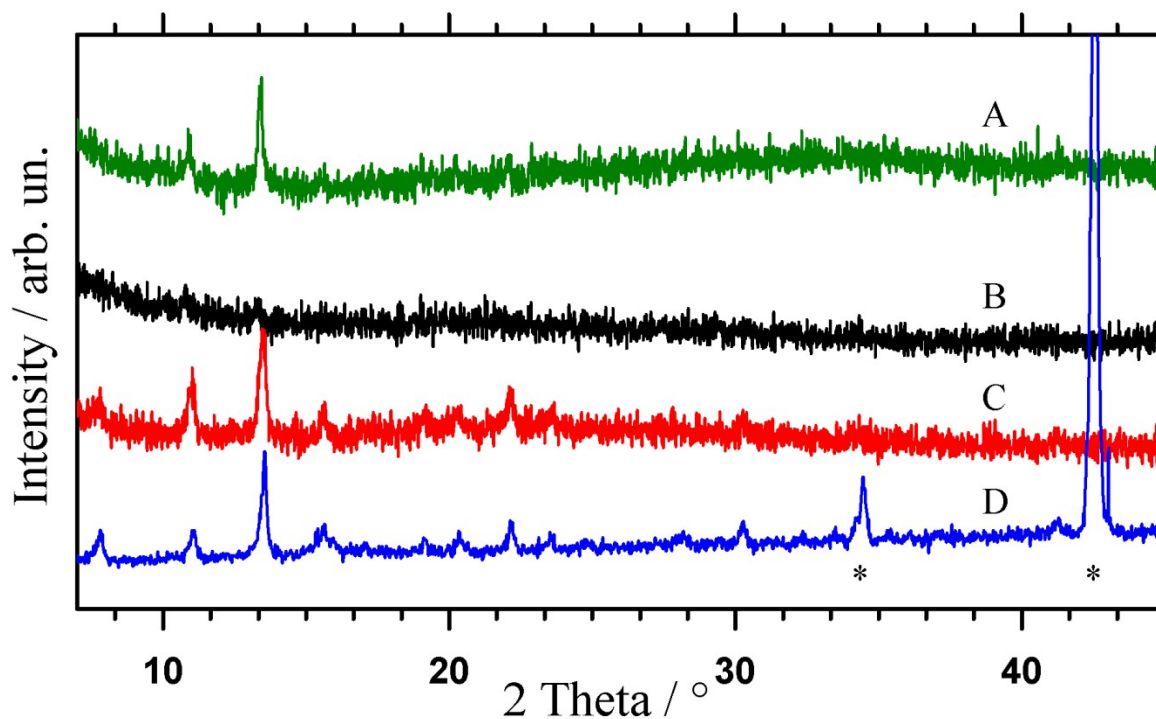
SI 1. XRD diffractograms of Samples A-D. The data of Sample D was converted from Cu Kα_1 excitation to Co Kα_1 excitation to match the source of the other data sets. All observed reflexes match with the known diffractogram of CuBTC with the exception of the 42.5° and 34.4° reflexes (marked with an asterisk) in Sample D which can be attributed to Cu_2O. Samples A-C were measured on the copper anodes directly while Sample D was measured as a powder diffractogram from the isolated product.
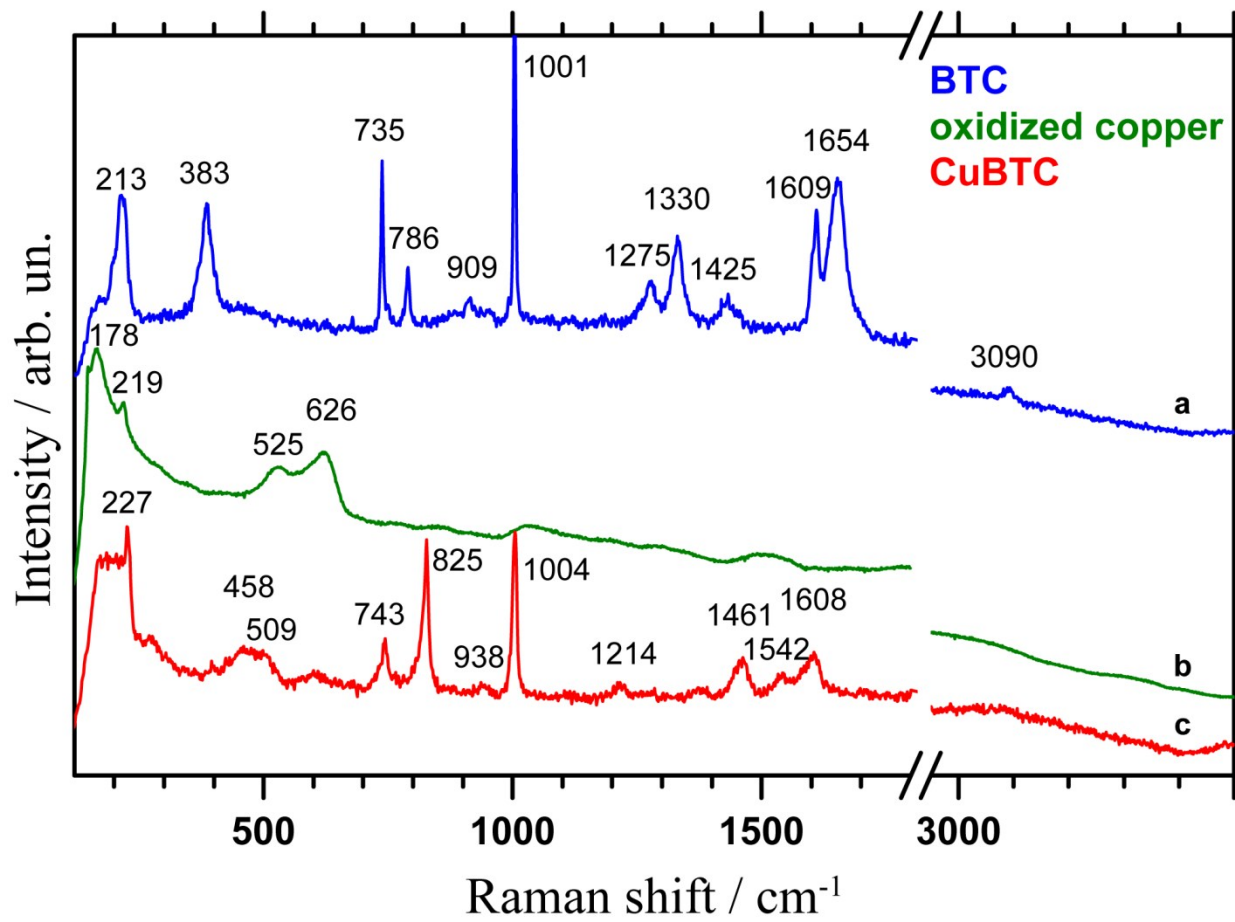
SI 2. Raman spectra of 1,3,5-Benzenetricarboxylate (a, blue), an oxidized copper surface (b, green) and CuBTC (c, red). The spectral region from 1800 to 3000 cm^{-1} contains no features and was therefore omitted.

Table S1. Band assignment for the Raman spectra of 1,3,5-Benzenetricarboxylic acid (BTC), an oxidized copper surface and CuBTC (see SI2 for spectra)

BTC	Oxidized Copper	CuBTC	Assignment
	178		-
213			-
	219		Cu_2O $(2\,\Gamma_{12})$ [2]
		227	$\nu CuCu$ [3]
383			-
		458	$\nu Cu\text{-}O$, $\nu Cu_2(\mu\text{-}O)_2$ [3]
		509	$\nu Cu\text{-}O$, $\nu Cu_2(\mu\text{-}O)_2$ [3]
	525		Cu_2O (Γ_{25}^+) [2]
	626		Cu_2O $(\Gamma_{15}^{(2)})$ [2]
735			δCO, δCC [4]
		743	γCH_{ring} [3]
786			δCO, δCC [4]
		825	γCH_{ring} [3]
909			-
		938	-
1001		1004	νCC_{ring} [4]
		1214	-
1275			δCH, νCC, δOH [4]
1330			νCO, νCC [4]
1425			νCC, δCH [4]
		1461	$\nu_{asym}C\text{-}O_2$ [3]
		1542	$\nu_{sym}C\text{-}O_2$ [3]
1609		1608	νCC_{ring} [3]
1654			$\nu C=O$ [5]
3090			νCH [4]

ν: stretching, δ: in-plane bending, γ: out-of-plane bending

The vibrations between 450 and 1500 cm^{-1} are most likely combination bands. The vibrations most likely contributing are listed.
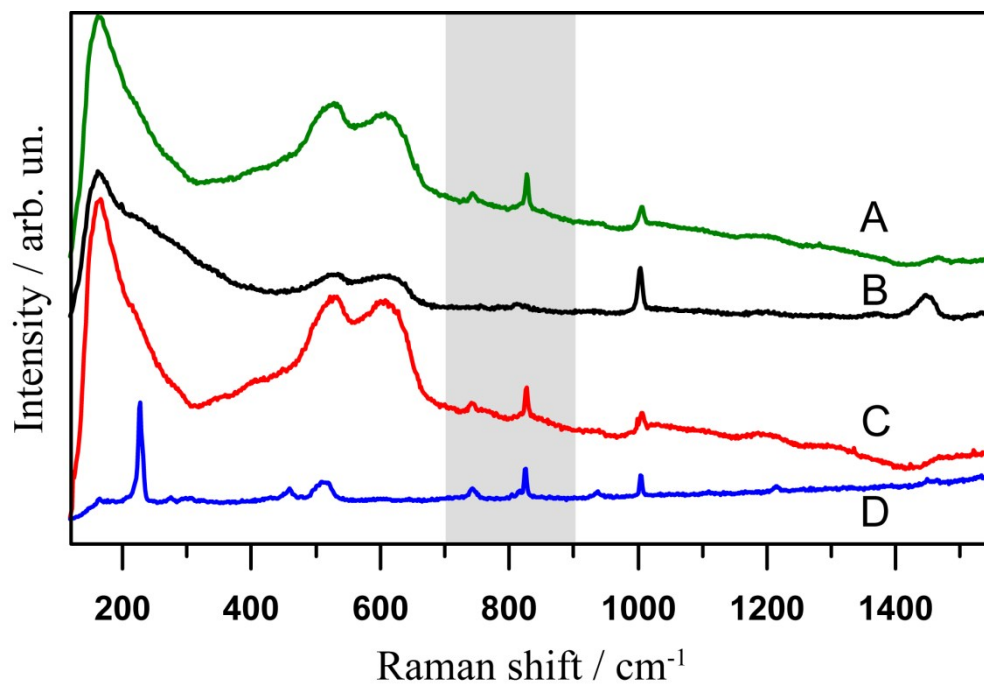
SI 3. Large range Raman spectra of Samples A-D. The area marked in grey is the For Samples A-C the spectra were taken directly on top of the copper anode used in the respective synthesis. The sample for Sample D was taken from the isolated powder. The grey area indicates the out of plane ring bending vibrations at 743 cm-1 and 825 cm-1 used for identification of CuBTC in the main paper. Excitation wavelength: 633 nm.

Sample F

Sample F was produced under similar conditions as Sample D, in a non-degassed ethanolic solution of 0.15M BTC. As starting material we used CuO instead of Cu_2O. All other parameters were the same. As can be seen from the SEM image (SI 5), no growth of CuBTC could be observed. The Raman spectrum shows the vibrational fingerprint of CuO[6] and is free of all features in the Ring-bending region from 740-825 cm^{-1} indicating that no CuBTC was produced.
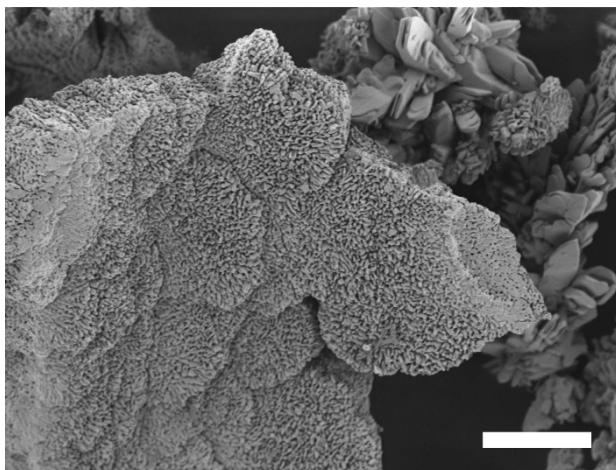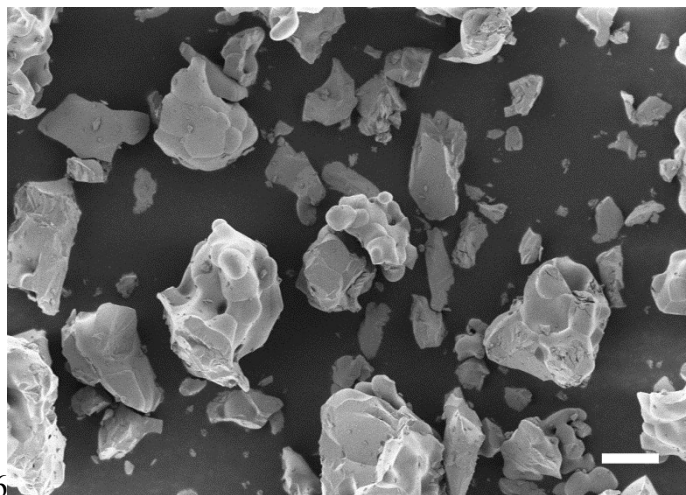

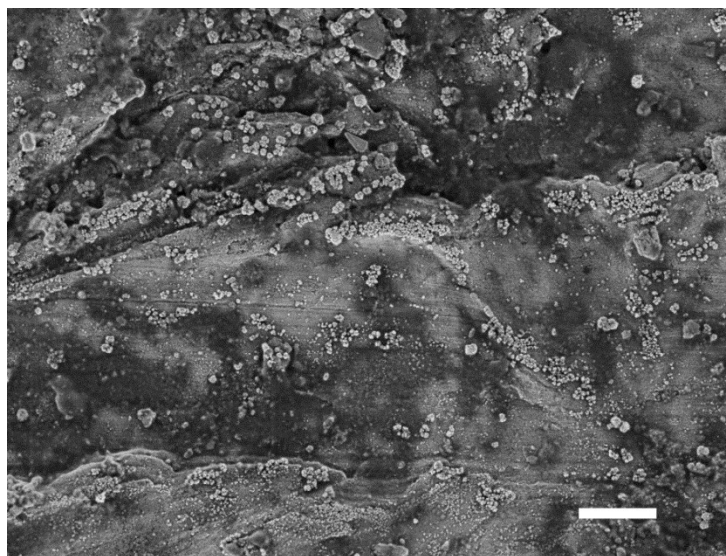**SI 4**. SEM image of Sample F. (scalebar 5 µm)
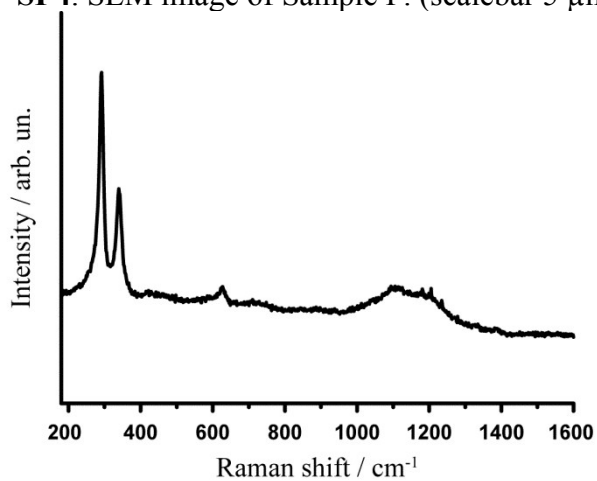
SI 5. Raman spectrum of Sample F.

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SI 6. SEM image of pristine Cu_2O, as received (scalebar 10 µm)


SI 7. SEM image of a copper surface after electrochemical oxidation in ethanol (scalebar 5 µm)

Current transients

All current curves decrease during the first 200 to 300 s until reaching a plateau that is the same for all samples (within the experimental error). The lack of difference between the samples can be explained by the fact that the electrode processes themselves (charge transfer and diffusion) are not the current-limiting factor in ethanol-based electrosynthesis. As has been discussed by Martinez Joaristi et al. (ref 7 in the manuscript), the current limiting factor is the resistivity of the solution.

At the potentials used for synthesis, Cu oxidation to Cu_2O (and to a small extent to CuO) is not the only process taking place. Solvent oxidation as postulated by Stypuła et al. (Production of nanoparticles of copper compounds by anodic dissolution of copper in organic solvents J. Appl. Electrochem., 2006, 36, 1407-1414) is a significant side reaction which also explains the current efficiency of the synthesis of < 100 %. Thus, the same amount of current passes for all synthesis conditions, albeit it stems from different condition-dependent processes.
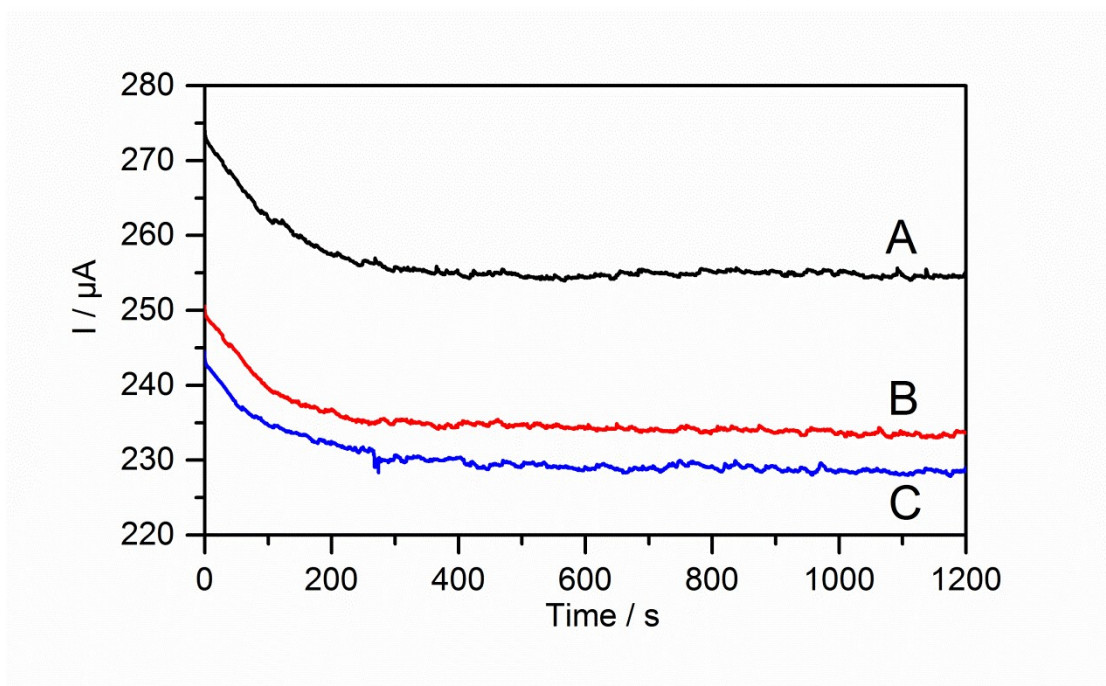
SI 8. Current transients for samples of type A, B & C

References
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