Supplementary information for: Probing electrosynthetic reactions with furfural on copper surfaces

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Materials and methods:

Cu synthesis:

Rough Cu foil was obtained by an electrochemical roughening method. Commercial Cu foil was cut to a suitable size as the precursor, and polished with Al powder. Then the Cu foil was washed by DI water and ultrasonic to remove the impurities on the surface. After this procedure, the Cu foil was used as working electrode in a three-electrode system (Ag/AgCl as reference, carbon rod as counter), with CO₂-saturated KHCO₃ as electrolyte, 6 cyclic voltammetry cycles were conducted in the range of 0 to -1.6 V (vs. Ag/AgCl), with a scan rate at 50 mV/s. Subsequently, chronoamperometry was carried out at +0.9 V for 1 min to oxidize the Cu foil, followed by the reduction process at -0.3 V for 10 mins. The illustration of the roughening scheme is shown in Figure 2.

Single crystal Cu substrates were purchased from MTI corporation and used as received after making electrical contact to a substrate holder. The crystallinity and orientation is confirmed through XRD measurements and through the acquisition of rocking curve data that shows peak FWHMs on the order of $0.6 - 0.7^{\circ}$.

Physical characterization:

X-ray diffraction (XRD) patterns were measured on a Bruker D8 Advance diffractometer with a Cu K α radiation source ($\lambda = 1.5418$ Å). High-resolution x-ray photoelectron spectroscopy (XPS) measurements were conducted on a Vacuum Generator Escalab 220i XL x-ray photoelectron spectrometer, calibrated by using carbon (C1s 284.6 eV). A Jeol, JSM -840A was used for scanning electron microscopy (SEM) measurements. Transmission electron microscopic (TEM) images were performed on JEOL JEM-2100F FEG-TEM, operated at 200 kV. The sample was scratched from rough Cu foil on to carbon film.

Electrochemistry and product quantification:

Cyclic voltammetry (CV) and other electrochemical techniques were performed using a Bio-Logic SP-150 Potentiostat (BioLogic Science Instruments, France). A three-electrode system has been employed by applying the above rough Cu foil as the working electrode, Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. K_2SO_4 solution (1 M, with added H₂SO₄ to adjust to pH 3) was used as the electrolyte in the measurements. The CVs were measured in the range of $0\sim-0.526$ V (vs. RHE) at a sweep rate of 20 mV s⁻¹. Potentiostatic electrolysis was conducted in a two-compartment custom built glass H-cell reactor.

The anode and cathode chambers were separated by a glass frit. Before each electrolysis experiment, 20 ml electrolyte was added into the reactor and purged with N_2 for 15 mins to remove dissolved gases. The reactor was sealed and the electrolyte was stirred at 500 rpm during the reaction. All reactions were carried out at room temperature.

In order to analyze the products of the reaction, gas chromatography (GC, SRI 8610C, Mandel) and NMR (Bruker AVANCE II 400 se) were performed to reveal the content and composition of the gas and liquid products respectively. After 3 hs electrolysis, 10 mL gas was extracted from the reactor by syringe and injected into GC to test the content of hydrogen. 400 μ L liquid product was mixed with 100 μ L D₂O to test the NMR and investigate the content of furfural alcohol (FA) and 2-methylfuran (MF). The faradaic efficiency (FE) was calculated by using the following formula:

$$\varepsilon_{\rm FE} = \frac{\alpha n F}{Q}$$

where α is electron transfer numbers (for the formation of H₂ and FA is 2, MF is 4), n is the moles of the products, F is faraday constant (96485 C mol⁻¹), Q is the charge passed in total during the reaction.

The pH of the solution did not change by more than 0.3 pH units throughout each catalytic run, as calculated from the total charge passed through the circuit.

Raman spectroscopy:

A three-electrode electrochemical cell was used for in-situ Raman experiment. Titanium foil was used as the counter electrode, Ag/AgCl was used as reference, and rough Cu foil as working electrode in a custom-built Teflon spectroelectrochemical cell. The scheme was shown in the main text Figure 1. The electrolyte is $1M K_2SO_4$ (with H_2SO_4 , pH3), which is also bubbled with N_2 for 15 mins to remove the dissolved gas. Raman spectroscopy were recorded on a Renishaw InVia Raman Microscope and excited with 633 nm excitation laser.

Potential (V vs. RHE)	2-MF(%)	FA(%)
-0.426	0.75	1.12
-0.526	0.77	1.62
-0.626	0.90	1.97
-0.726	1.18	1.19
-0.826	0.88	1.53

Table S1: Yields of the reaction, corresponding to Figure 3 in the main text.



Figure S1. TEM images of rough Cu foil.



Figure S2. CV curves of (a) rough Cu foil with different amount of furfural; (b) single crystal Cu foil with 59 mM furfural.



Figure S3. Operando SER spectra on R-Cu surface without adding furfural in the (a) low frequency (b) medium frequency and (c) high frequency regions. A zoomed in spectra of the R-Cu at open circuit potentials is also illustrated to clearly show the spectrum corresponding to the CuO_x surface.



Figure S4. CV curves of single crystal Cu (a) Cu (111); (b) Cu (110); (c) Cu (100) with (dark green) and without furfural (light green).



Figure S5. Faradaic efficiency of roughen single crystal Cu under with 59 mM furfural at different applied potential (a) -0.526 V; (b) -0.726 V vs. RHE.



Figure S6: Low-magnification XRD patterns of rough Cu and single crystal Cu electrodes



Figure S7: Zoomed-in XRD patterns of single crystal Cu electrodes after roughening show the appearance of weak peaks and a broadening at the base of the main peaks, indicating the onset of the formation of a polycrystalline surface structure.