

Electronic Supplementary Information (ESI) for ChemComm.

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## **Promoted electrocatalytic hydrogenation of furfural in a bi-phasic system**

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## **Experimental procedures:**

### **ER-Cu synthesis:**

A copper foil (99.9% metals basis, Macklin) was cut to a suitable size as the precursor. An ultrasonic cleaning of the copper foil was performed sequentially with acetone and 2 M hydrochloric acid for 10 minutes. A two-electrode system consisting of a copper foil and a carbon rod was applied with a voltage of 3.0 V for 500 s in 85 wt% phosphoric acid (Macklin) solution to obtain electrochemically polished Cu (EP-Cu), according to a previously reported method.<sup>1</sup> The EP-Cu was immediately put into deionized water saturated with nitrogen and sonicated for 10 minutes to wash away the residual phosphoric acid and phosphate. ER-Cu was obtained by an electrochemical roughening method. The EP-Cu was used as the working electrode in a three-electrode system consisting of a Ag/AgCl (3.5 M KCl) and a carbon rod as the reference and counter electrodes, respectively. Within 0.1 M KHCO<sub>3</sub> electrolyte, CVs were conducted in the range of -0.51 to 0.99 V (vs. RHE), with a scan rate of 20 mV/s.

### **Physical characterization:**

XRD patterns were measured on a Bruker D8 Advance diffractometer with a Cu K $\alpha$  radiation source ( $\lambda = 1.54056 \text{ \AA}$ ). The morphology of samples was observed by scanning electron microscopy (SEM) on a ZEISS ULTRA55. X-ray photoelectron spectroscopy (XPS) measurements were conducted on Thermo scientific (Escalab250Xi), using C 1s (284.6 eV) as a reference. <sup>1</sup>HNMR analysis was carried out on a Bruker 300 MHz spectrometer (DRX300).

### **Electrochemistry and product quantification:**

Electrochemical tests were conducted on a CHI650E electrochemical workstation utilizing an H-type electrolytic cell with a Nafion membrane (Nafion 117, Sigma-Aldrich) separator. ER-Cu, a graphite rod, and a Ag/AgCl (3.5 M KCl) electrode were the working, counter, and reference electrodes, respectively. All the potentials measured were converted to reversible hydrogen electrode (RHE) according to the Nernst equation  $E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.210 + 0.059 \times \text{pH}$ . K<sub>2</sub>SO<sub>4</sub> solution (0.5 M, with an appropriate amount of H<sub>2</sub>SO<sub>4</sub> to adjust pH 1~3) was used as the electrolyte in measurements for aqueous and bi-phasic electrolysis, both containing 35

mM FAL. But the cathodic electrolyte of the bi-phasic electrolytic systems consisted of 25 mL K<sub>2</sub>SO<sub>4</sub> (0.5 M) solution and 20 mL different organic solvents. All electrochemical tests were carried out under a nitrogen atmosphere and at room temperature.

Excessive 1,2-dichloroethane solvent was introduced into the bi-phasic system for extraction prior to product analysis. As for the emulsion-promoted electrocatalysis, the addition of 1,2-dichloroethane would lead to demulsification, and the encapsulated products by emulsions could be extracted and subsequently quantified by high performance liquid chromatography.

### **Product analysis:**

Quantitative analysis of products was conducted on high performance liquid chromatography (HPLC). Liquid products were collected from the cathode chamber and analyzed by HPLC (SHIMADZU LC-2030 Plus) equipped with a UV detector at 216 and 240 nm. The column (Shim-pack GIST C18) was operated at 40 °C with a low-pressure gradient method including H<sub>2</sub>O and CH<sub>3</sub>OH at a flow rate of 1 mL min<sup>-1</sup>. The CH<sub>3</sub>OH fraction is 20% in the first 12 min, rises from 20% to 80% in 12-18 min, and stays 80% in 18-25 min. The conversion (%) of FAL, the yield (%) and FE (%) of hydrogenation products were calculated based on the following equations (Eqs. (1)-(3)):

$$\text{Conversion (\%)} = \frac{\text{moles of substrate consumed}}{\text{moles of initial substrate}} \times 100\% \quad (1)$$

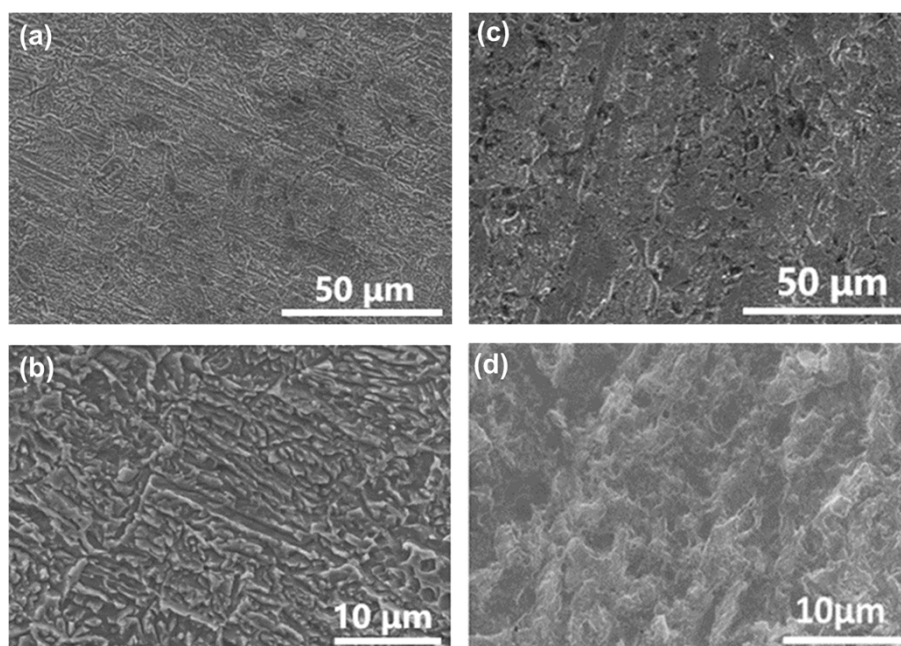
$$\text{Yield (\%)} = \frac{\text{moles of product}}{\text{moles of initial substrate}} \times 100\% \quad (2)$$

$$\text{FE (\%)} = \frac{\text{moles of product} \times z \times F}{\text{total charge passed}} \times 100\% \quad (3)$$

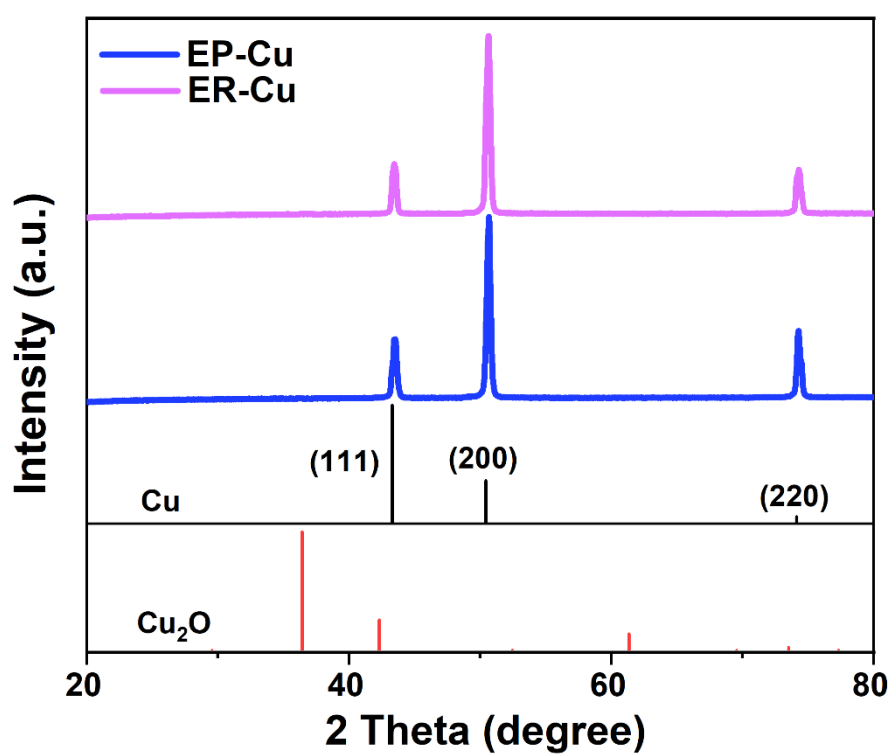
Where *z*, the number of transferred electrons, was 2 for FOL and 4 for 2-MF, respectively. Owing the systematical errors involved in HPLC and electrochemical measurements, there would be some errors in the total FEs. The similar situation has been identified in previous reports.<sup>2-4</sup>

In order to quantify the hydrofuroin after ECH, we synthesized hydrofuroin

according to the previous report,<sup>5</sup> and then subjected it to HPLC to obtain a quantitative calibration curve. The hydrofuroin was reduced from 1,2-di(furan-2-yl)ethane-1,2-dione by NaBH<sub>4</sub> in the presence of MoCl<sub>5</sub>. The obtained mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried in vacuum. It was further refined using an HPLC (Shanghai Xuancheng, LC3000) equipped with column (COSMOSIL, C<sup>18</sup>-MS-II), and reconstituted in acetonitrile d<sub>3</sub> (99.8%) and dimethyl sulfoxide (DMSO, 99.9%) for <sup>1</sup>HNMR analysis (Fig. S10). DMSO was the internal standard to determine the hydrofuroin content. The hydrofuroin was subjected to HPLC for quantitative calibration that was used to quantify the hydrofuroin in the ECH.



**Fig. S1** SEM images of (a and b) EP-Cu and (c and d) ER-Cu.



**Fig. S2** XRD patterns of EP-Cu (blue) and ER-Cu (pink), along with the standard ones of Cu (PDF#04-0836) and Cu<sub>2</sub>O (PDF#05-0667).

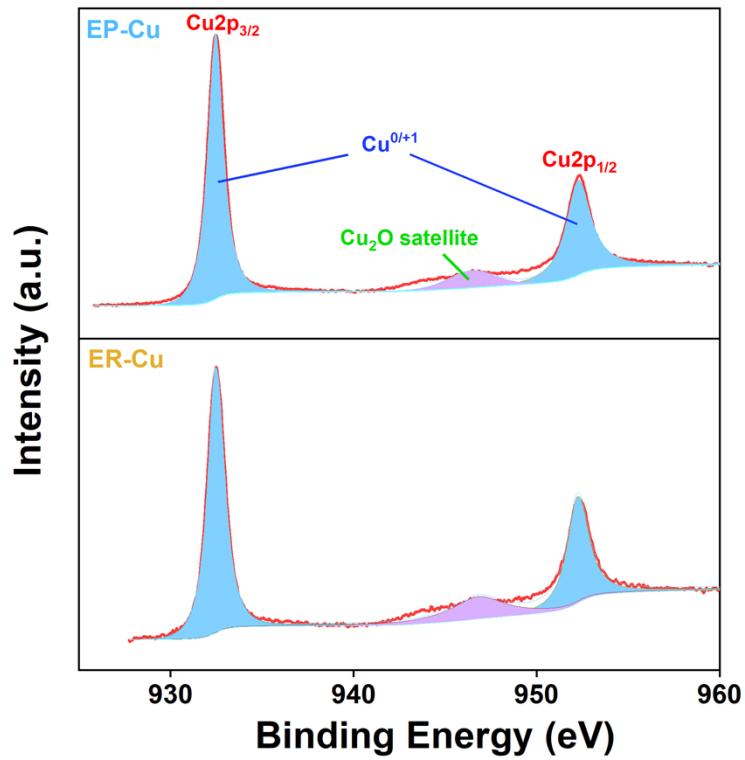


Fig. S3 Cu 2p XPS spectra of EP-Cu and ER-Cu.

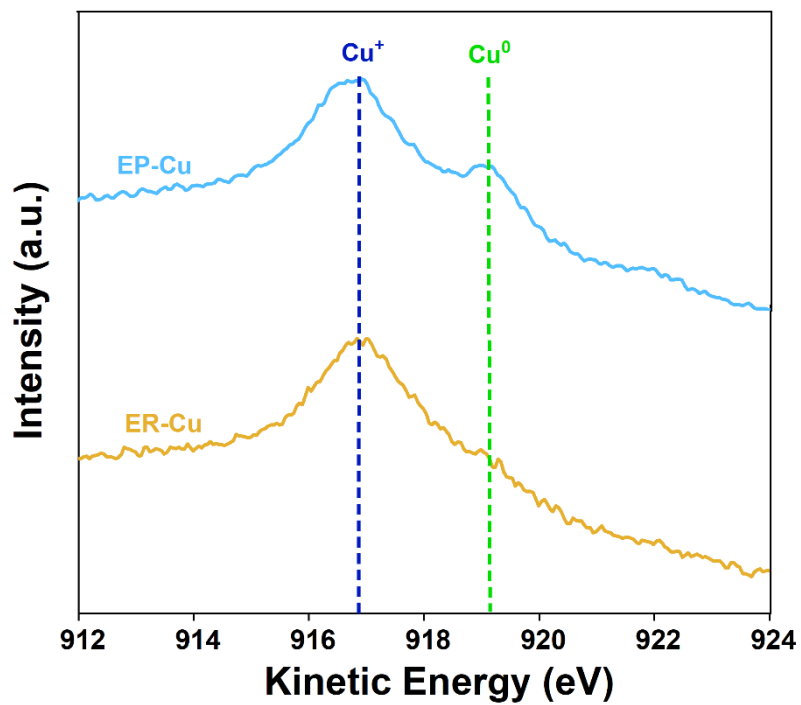
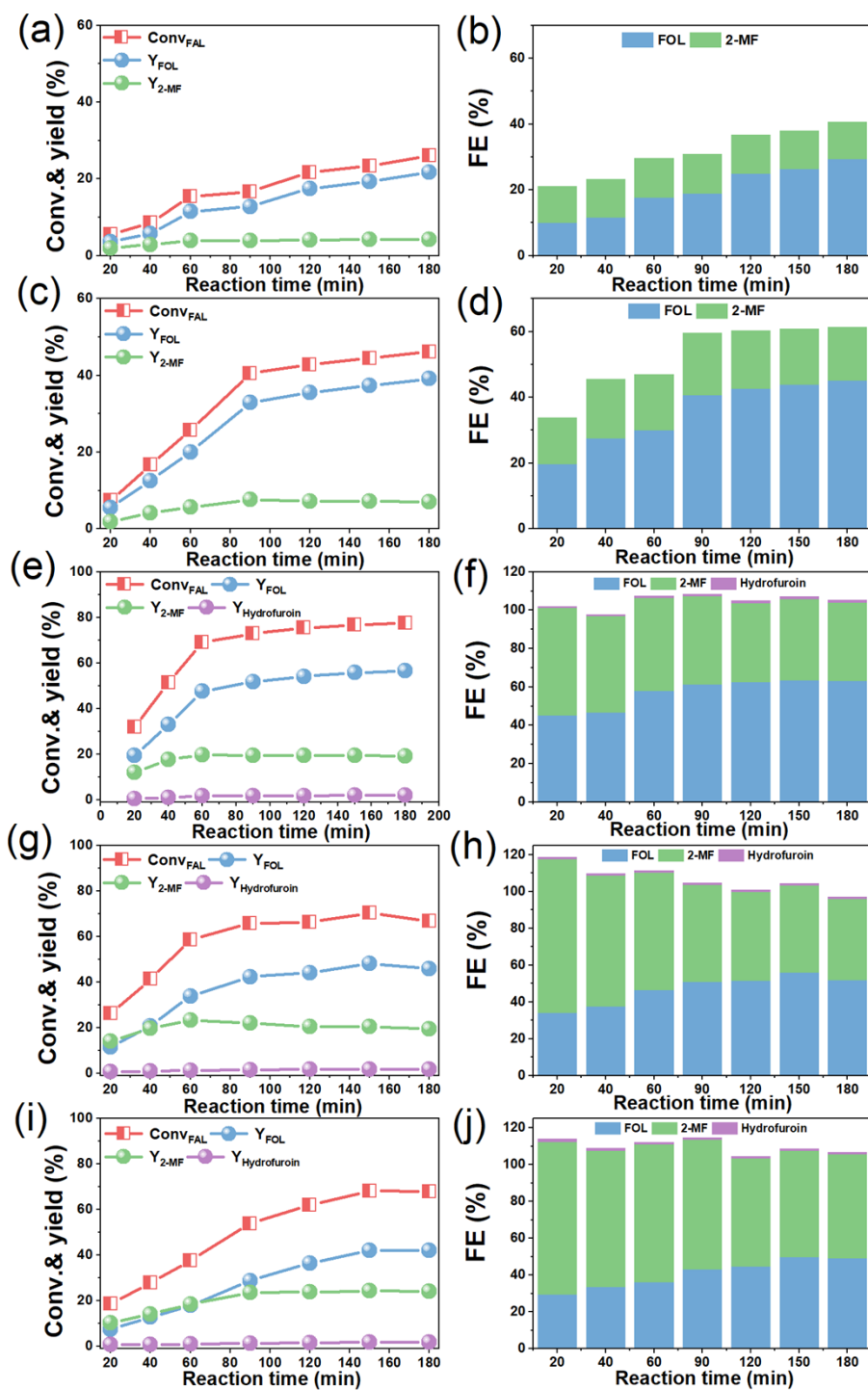
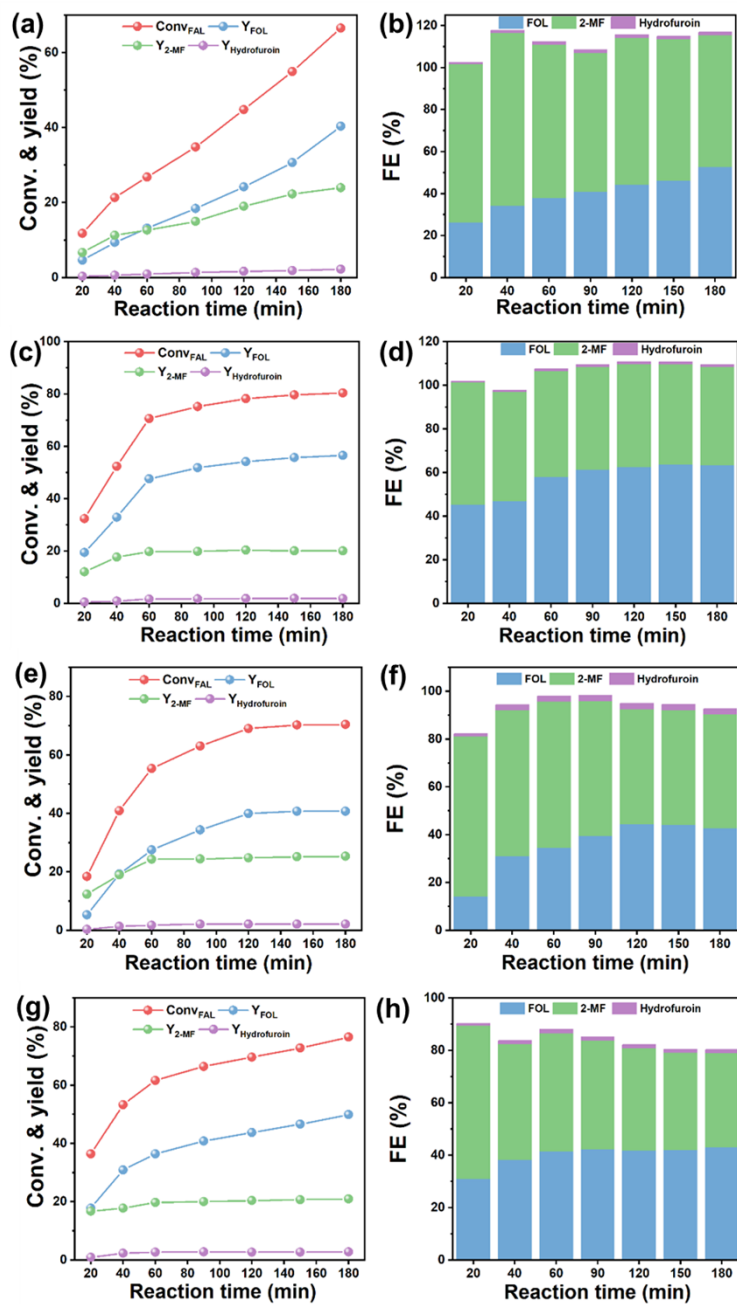


Fig. S4 Cu LMM spectra of EP-Cu and ER-Cu.

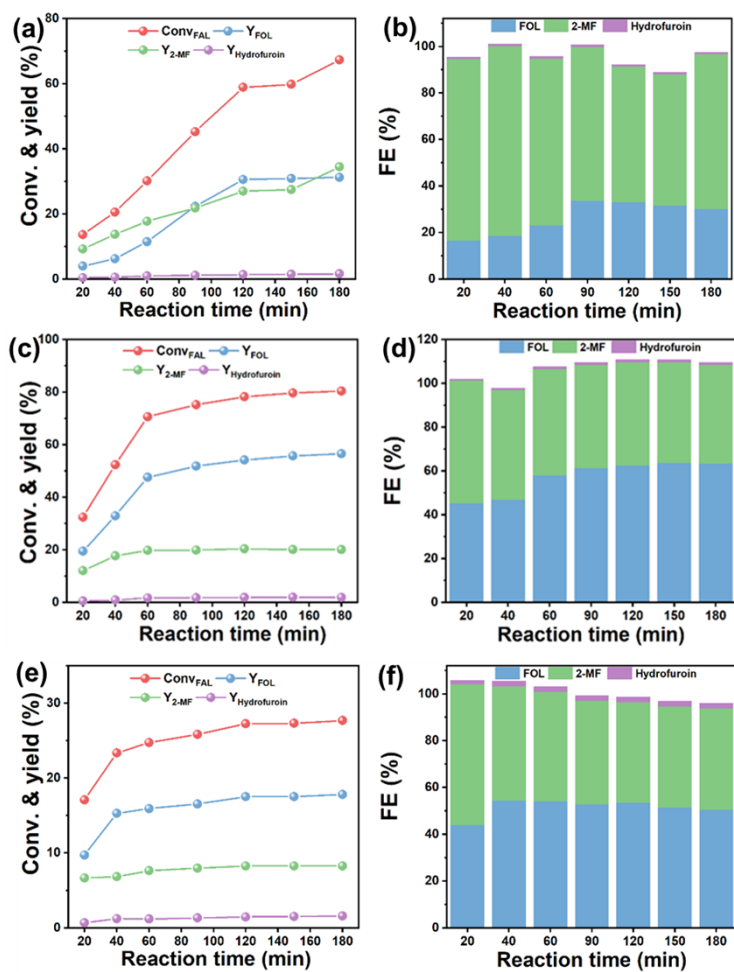


**Fig. S5** Time courses of FAL hydrogenation in bi-phasic systems. (a and b) 1,2-dichloroethane, (c and d) toluene, (e and f) cyclohexane, (g and h) petroleum ether, and (i and j) *n*-hexane.

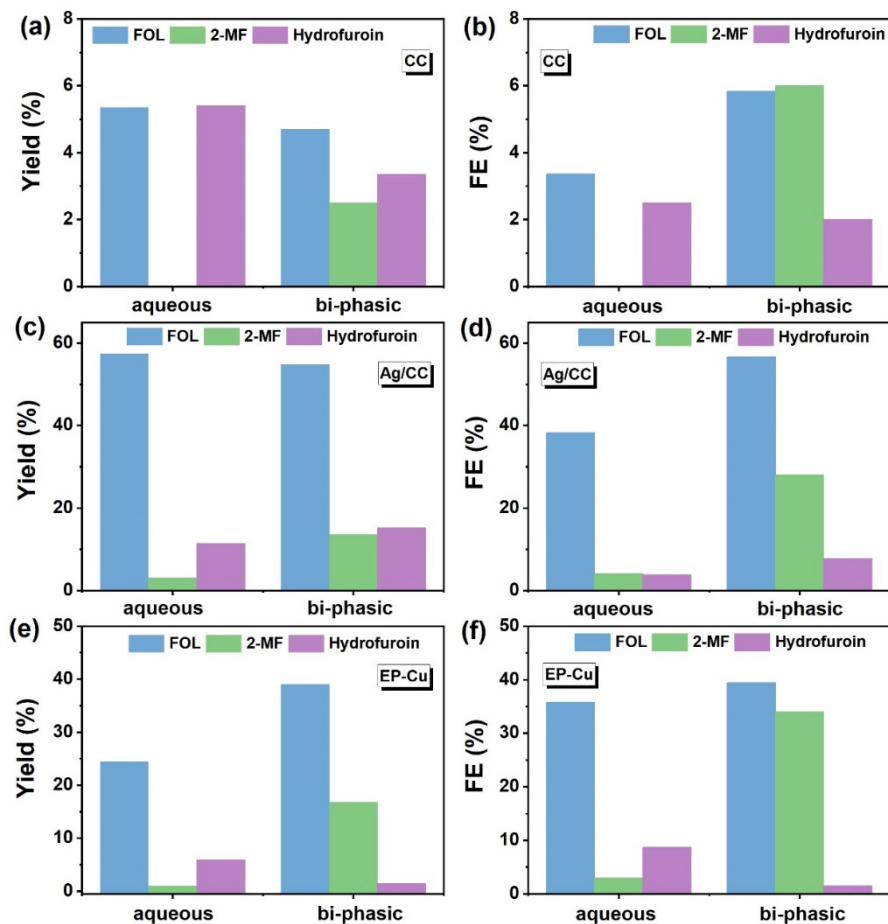


**Fig. S6** Electrochemical performance of ER-Cu at different applied potential (a and b) -0.63 V, (c and d) -0.73 V, (e and f) -0.83 V and (g and h) -0.93 V vs. RHE for 3 h in the cyclohexane bi-phasic system (pH 2).

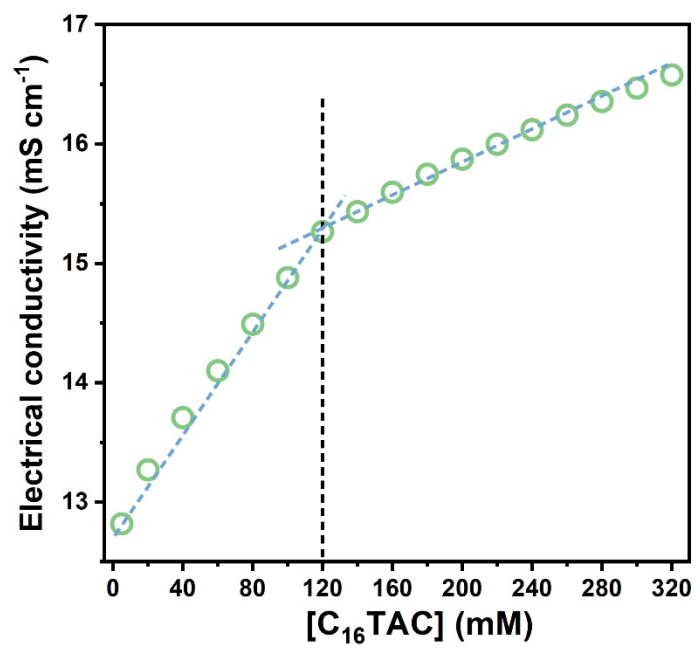




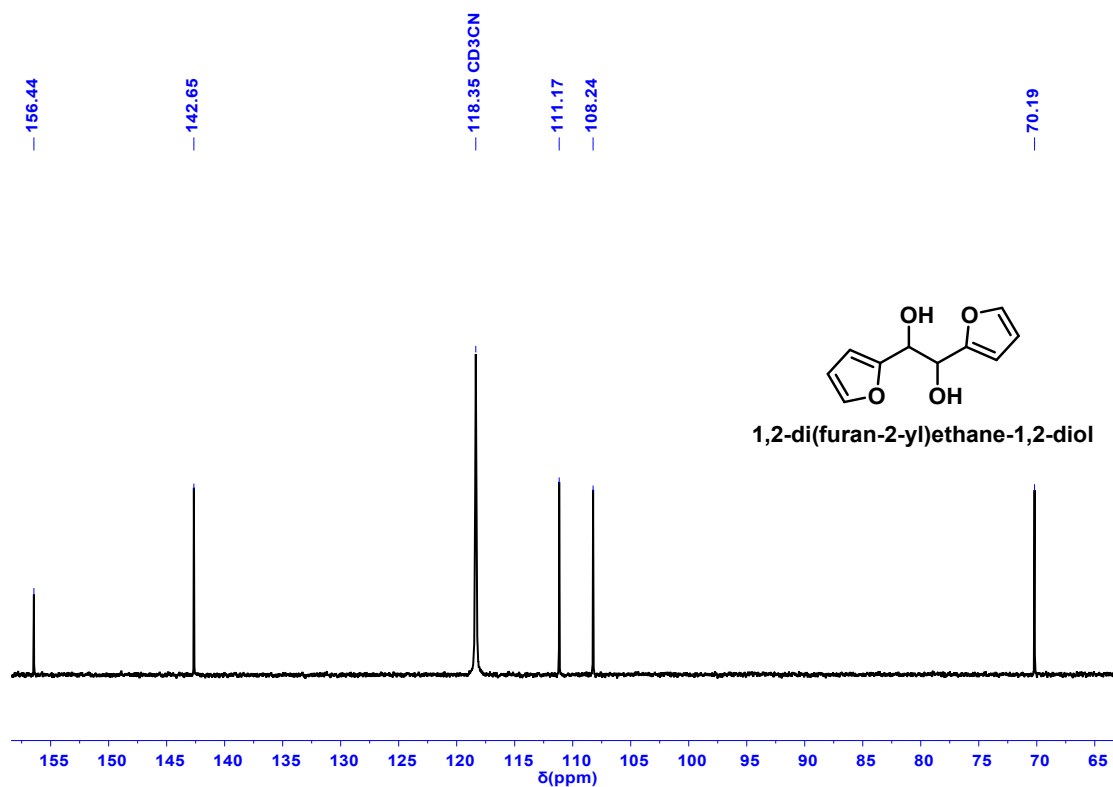
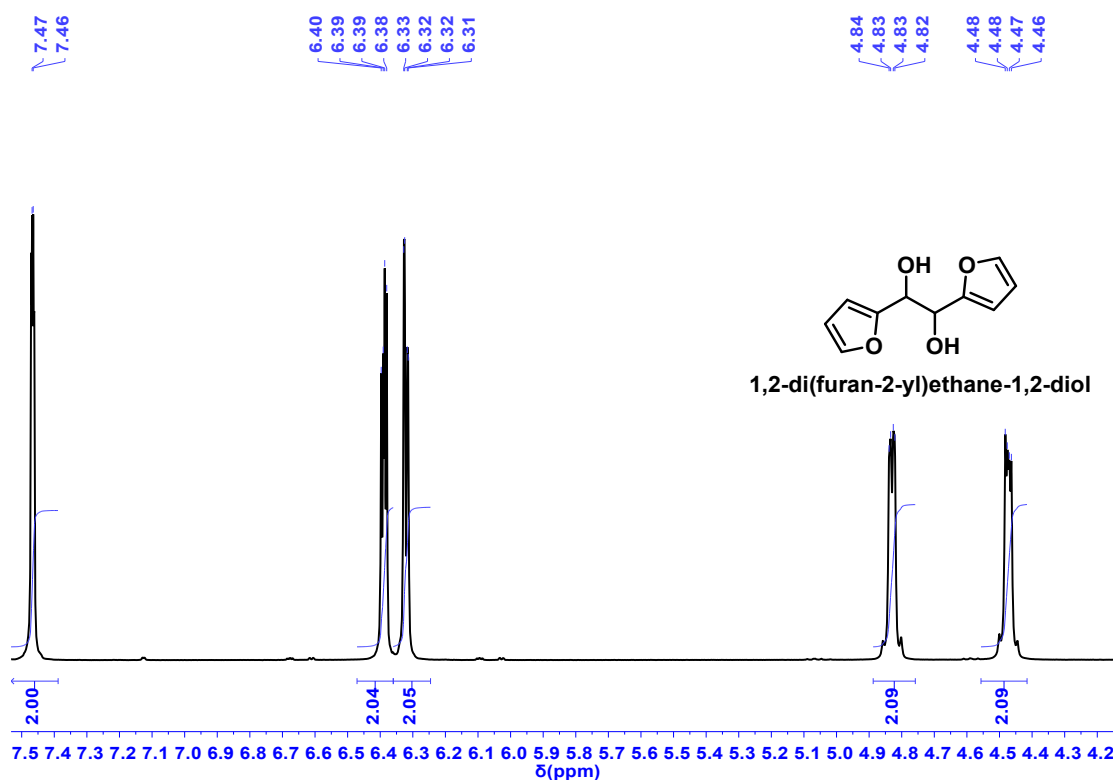
**Fig. S7** Electrocatalytic performance of ER-Cu at different pH level: (a and b) pH 1, (c and d) pH 2 and (e and f) pH 3 for 3 h in the cyclohexane bi-phasic system (at  $-0.73$  V vs. RHE).



**Fig. S8** Comparison of the ECH of FAL in single aqueous and bi-phasic (cyclohexane/water) systems over different electrodes: (a and b) carbon cloth (CC), (c and d) electrodeposited Ag on CC (Ag/CC) and (e and f) electropolished Cu (EP-Cu). Reaction condition: 35 mM FAL in 25 mL of 0.5 M K<sub>2</sub>SO<sub>4</sub> (pH 2) and 20 mL cyclohexane, -0.73 V vs. RHE, 2 h.



**Fig. S9** Determination of the CMC of C<sub>16</sub>TAC by conductometry.



**Fig. S10**  $^1\text{H}$  and  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR of 1,2-di(furan-2-yl)ethane-1,2-diol.  $^1\text{H}$ NMR (300 MHz, Acetonitrile- $d_3$ )  $\delta$  7.47 (d,  $J$  = 1.0 Hz, 2H), 6.39 (dd,  $J$  = 3.2, 1.8 Hz, 2H), 6.32

(dd,  $J = 3.2, 0.8$  Hz, 2H), 4.83 (dd,  $J = 3.9, 1.4$  Hz, 2H), 4.47 (dd,  $J = 3.8, 1.9$  Hz, 2H).

$^{13}\text{C}$  NMR (75 MHz, Acetonitrile- $d_3$ )  $\delta$  156.44 , 142.65 , 111.17 , 108.24 , 70.19.

## References

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