

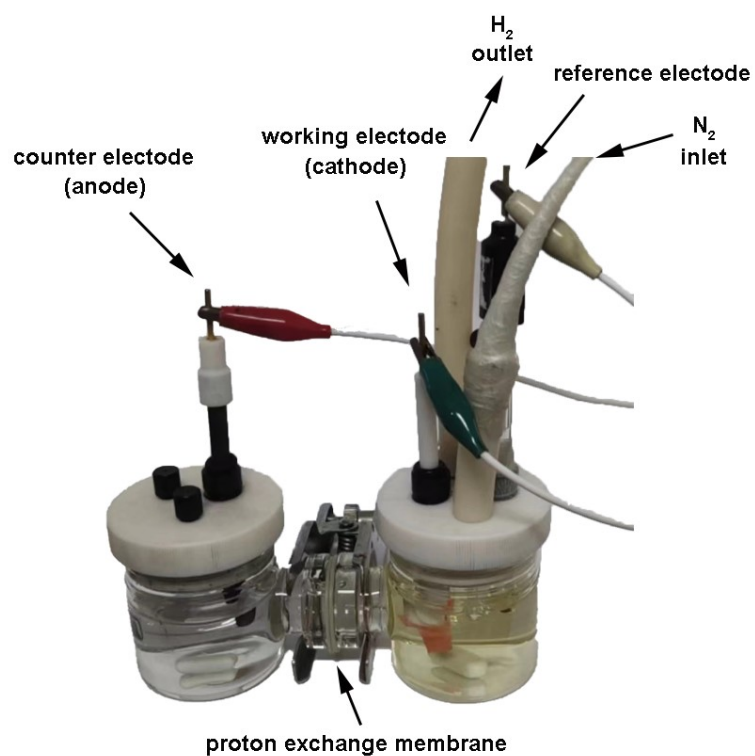
**Electronic supplementary information (ESI) for Catalysis Science & Technology**

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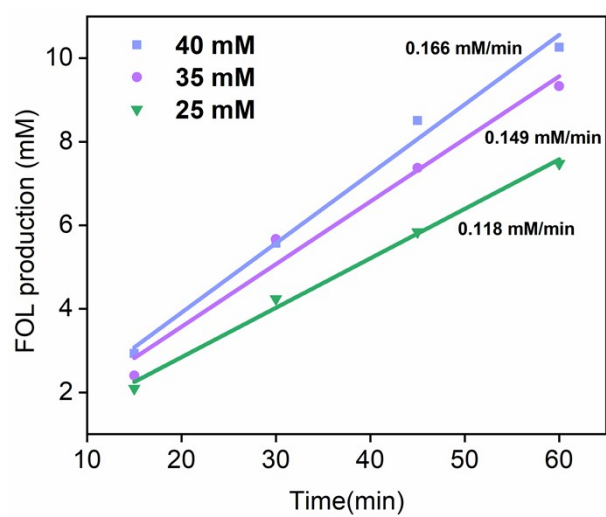
***In-situ* reconfiguration of plasma-engineered copper electrodes  
towards efficient electrocatalytic hydrogenation**

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and Qingsheng Gao<sup>\*a,c</sup>

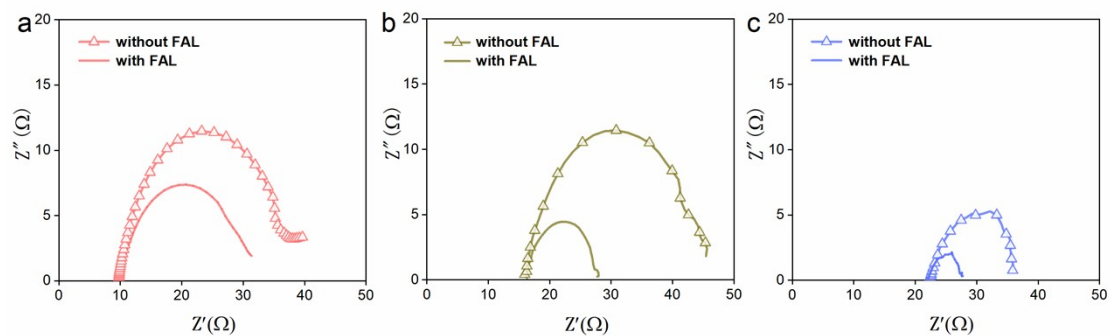
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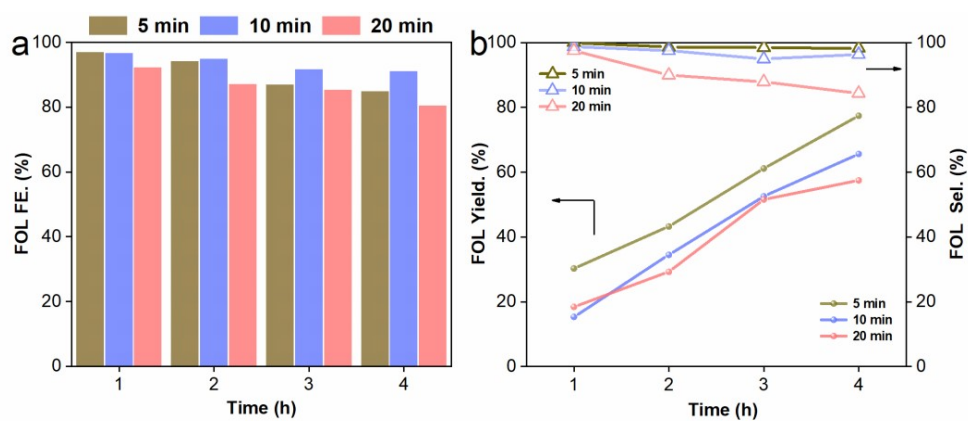
**Fig. S1** Photograph of the setup for ECH experiment.



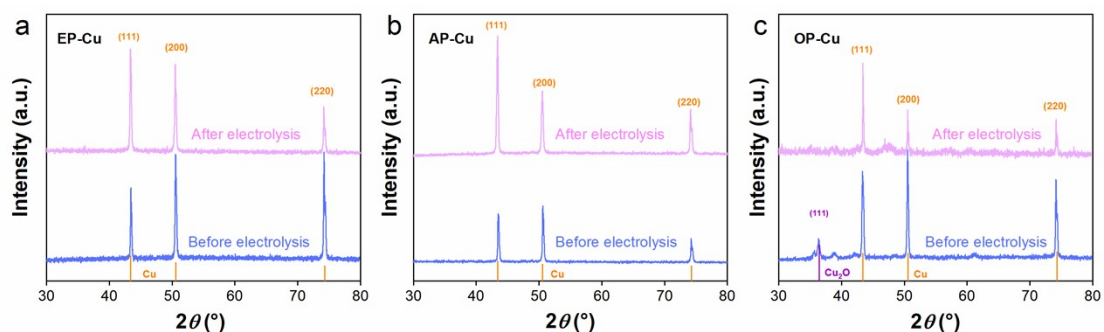
**Fig. S2** FOL production with time under different initial FAL concentration during the initial electrolysis.



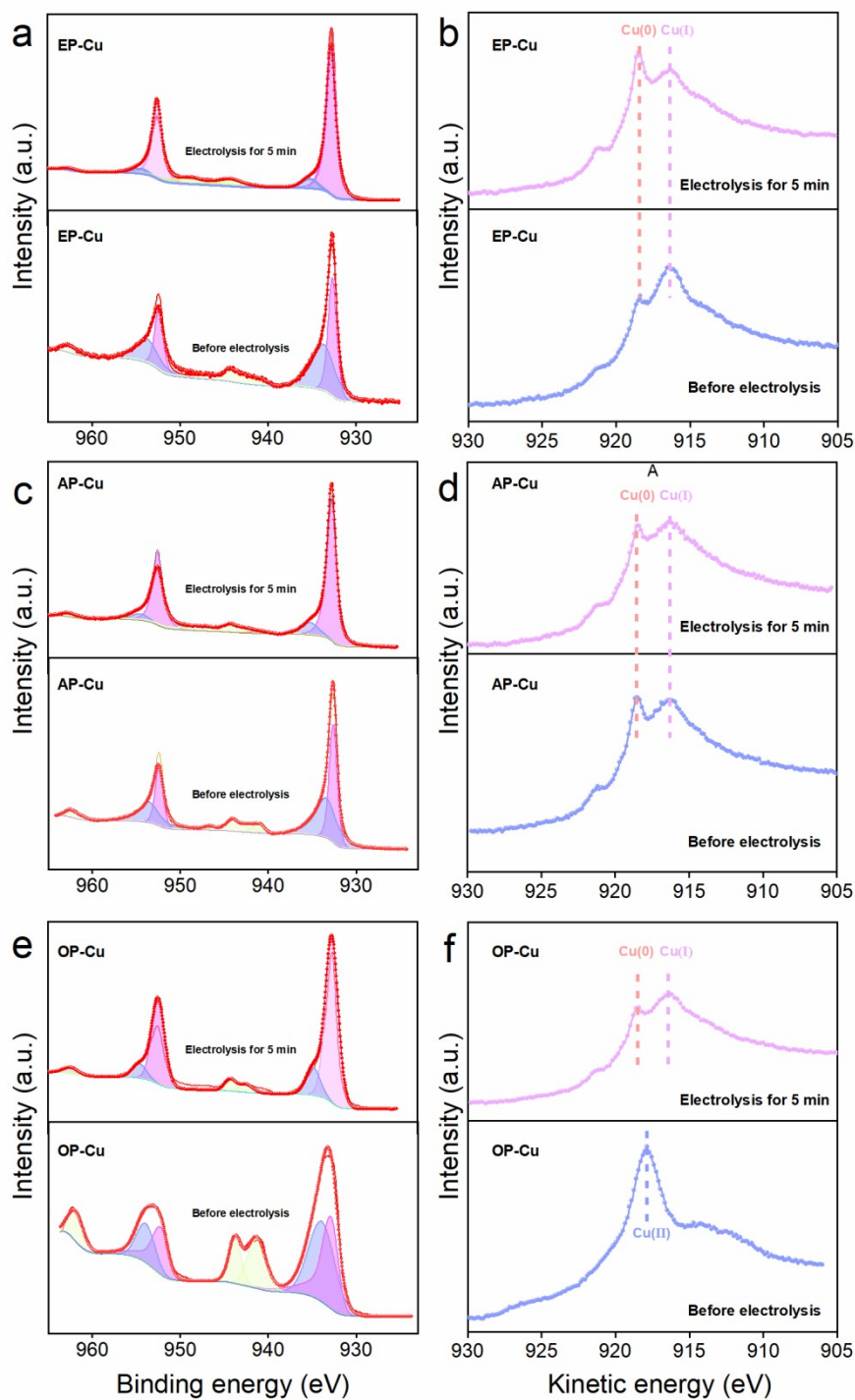
**Fig. S3** Electrochemical impedance spectroscopy of (a) EP-Cu, (b) AP-Cu and (c) OP-Cu electrocatalysts without and with 35 mM FAL.



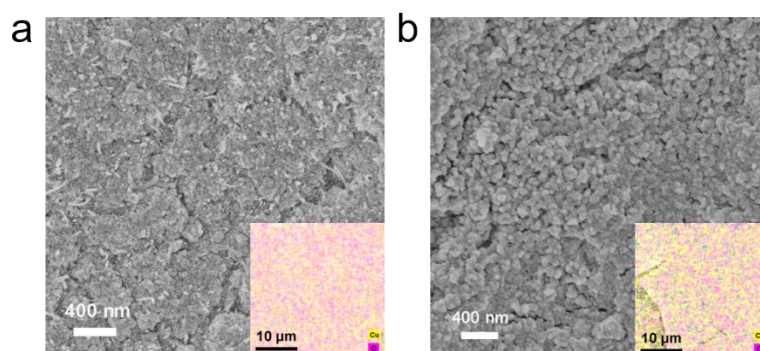
**Fig. S4** (a) FE and (b) yield and selectivity of FOL on OP-Cu received with different O<sub>2</sub>-plasma etching time (5, 10 and 20 min).



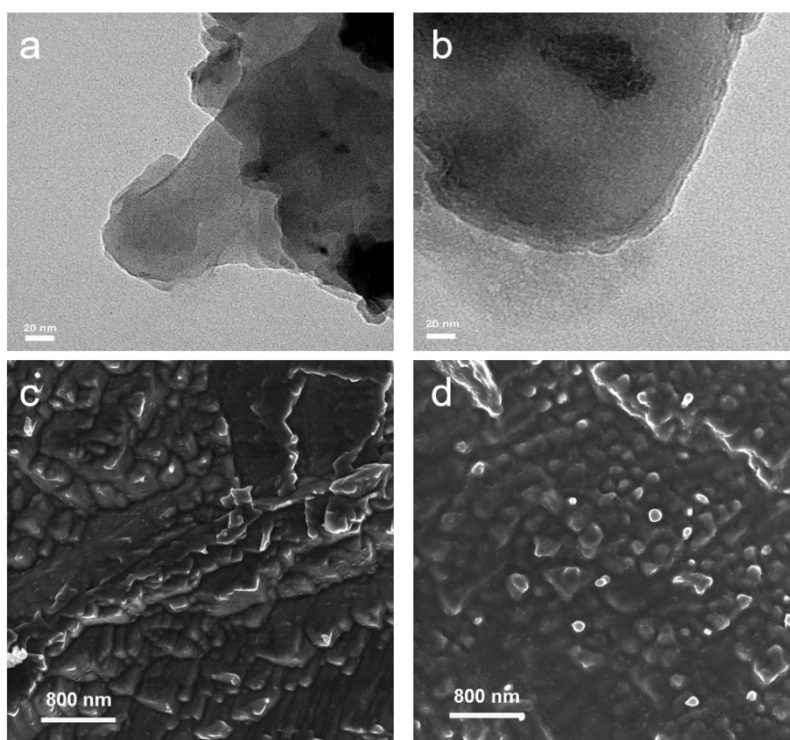
**Fig. S5** XRD patterns of EP-Cu, AP-Cu and OP-Cu before and after the ECH of FAL at  $-0.56$  V vs. RHE for 4 hours.



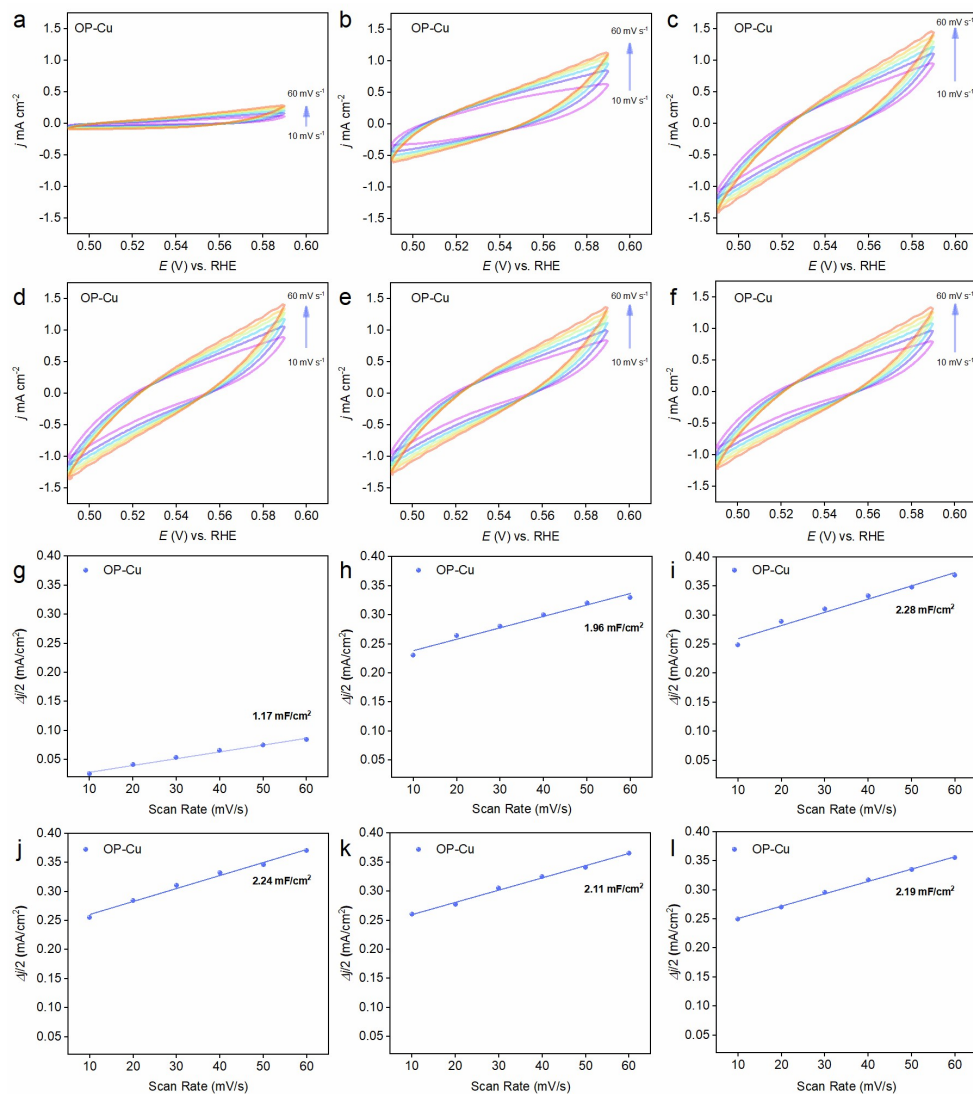
**Fig. S6** XPS and Auger Cu LMM profiles of (a) and (b) EP-Cu, (c) and (d) AP-Cu, (e) and (f) OP-Cu before and after 5 min ECH at  $-0.56$  V vs. RHE, respectively



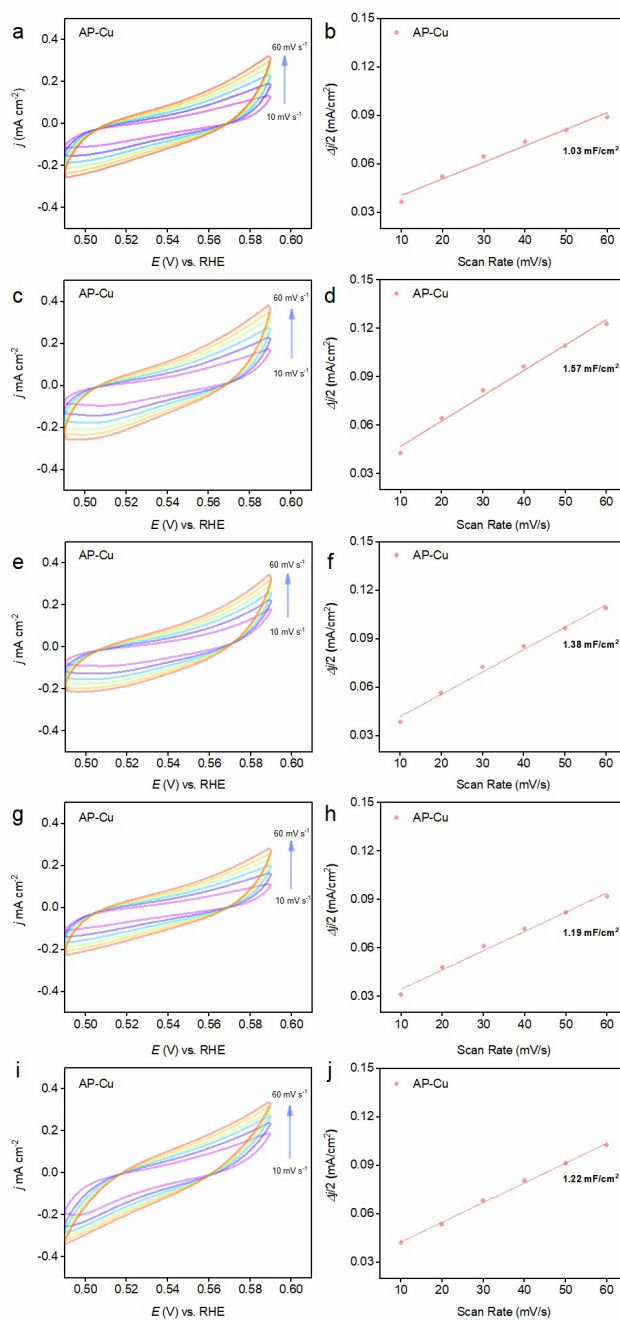
**Fig. S7** SEM images of OP-Cu (a) before and (b) after 5 min ECH at  $-0.56$  V vs. RHE.



**Fig. S8** (a and b) TEM and (c and d) SEM images of (a and c) EP-Cu and (b and d) AP-Cu after electrolysis (5 min) at  $-0.56$  V vs. RHE.

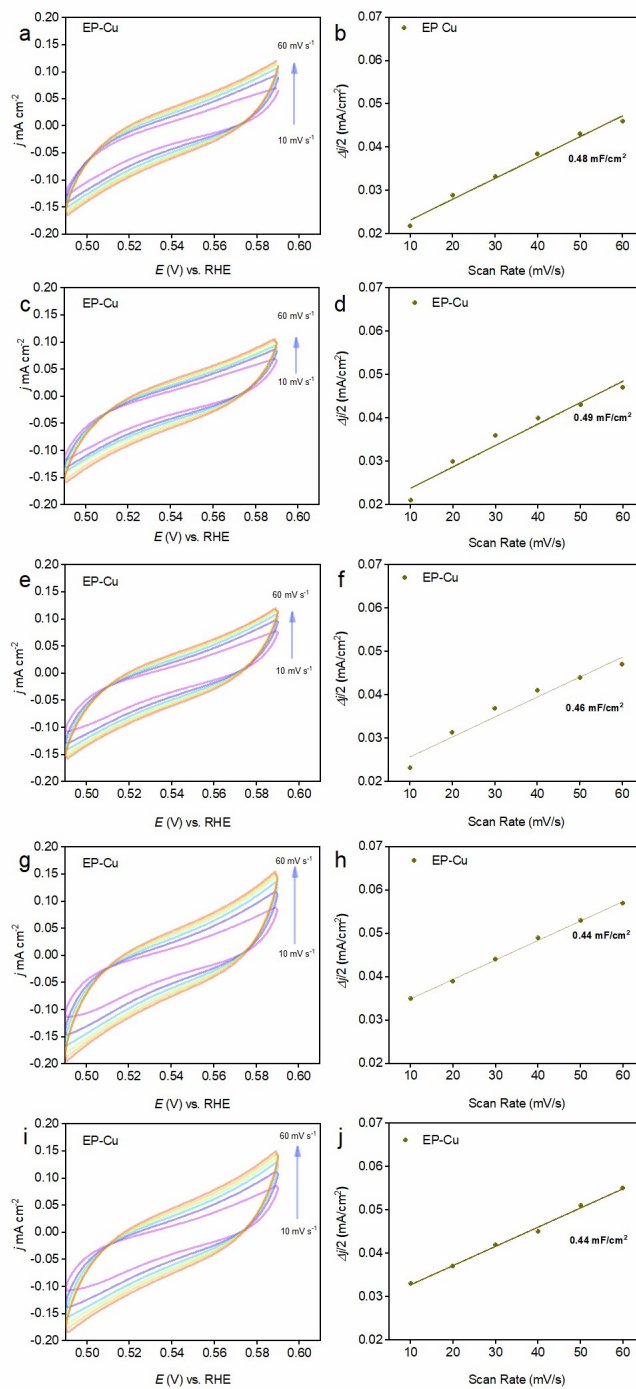


**Fig. S9** (a ~ h) CV curves collected in  $N_2$ -saturated 0.25 M phosphate buffer solution (pH 6.8) with different scan rates and (g ~ l) the corresponding charging current density variation ( $\Delta j = (j_a - j_c)/2$ , at 0.54 V vs RHE; data obtained from the CV in Fig. S9a – S9f) vs. scan rate plots of OP-Cu after the electrolysis for (a, g) 0 min, (b, h) 2 min, (c, i) 5 min, (d, j) 10 min, (e, k) 30 min, (f, l) 1 h.



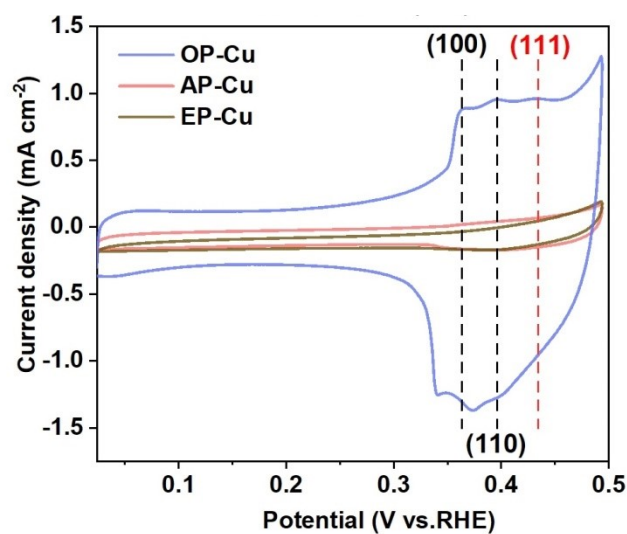
**Fig. S10** CV curves collected in  $\text{N}_2$ -saturated 0.25 M phosphate buffer solution (pH 6.8) with different scan rates and the corresponding charging current density variation ( $\Delta j = (j_a - j_c)/2$ , at 0.54 V vs RHE; data obtained from the CV in Fig. S10a, S10c, S10e, S10g and S10i) vs. scan rate plots of AP-Cu after electrolysis for (a, b) 0 min, (c, d) 5 min, (e, f) 10 min, (g, h) 30 min, (i, j) 1 h.



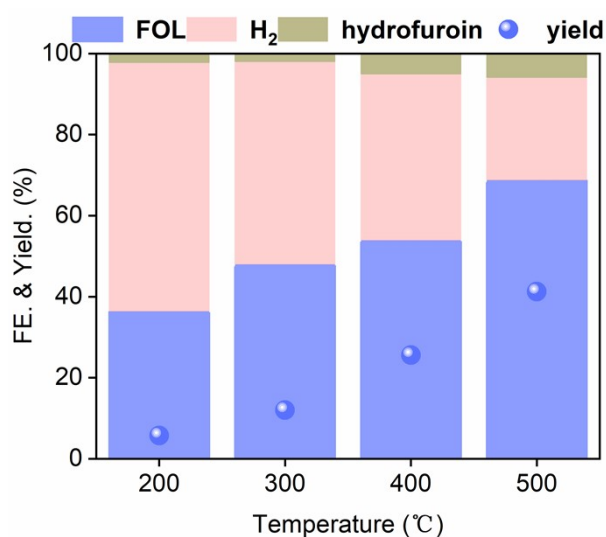


**Fig. S11** CV curves collected in  $\text{N}_2$ -saturated 0.25 M phosphate buffer solution (pH 6.8) with different scan rates and the corresponding charging current density variation ( $\Delta j = (j_a - j_c)/2$ , at 0.54 V vs RHE; data obtained from the CV in Fig. S11a, S11c, S11e, S11g and S11i) vs. scan rate plots of EP-Cu after electrolysis for (a, b) 0 min, (c, d) 5 min, (e, f) 10 min, (g, h) 30 min, (i, j) 1 h.





**Fig. S12** CV curves collected in N<sub>2</sub>-saturated 0.1 M KOH for EP-Cu, AP-Cu and OP-Cu after 5 min electrolysis.



**Fig. S13** FE and yield of FOL over heated Cu foils under a O<sub>2</sub> flow at different temperature. The electrolysis was conducted at -0.56 V vs. RHE for 4 hours in 0.25 M phosphate buffer solution (pH 6.8) containing 35 mM FAL.