Electronic Supplementary Material (ESI) for Green Chemistry.

Selective electrochemical hydrogenation of furfural to 2-methylfuran over a single atom Cu catalyst under mild pH conditions

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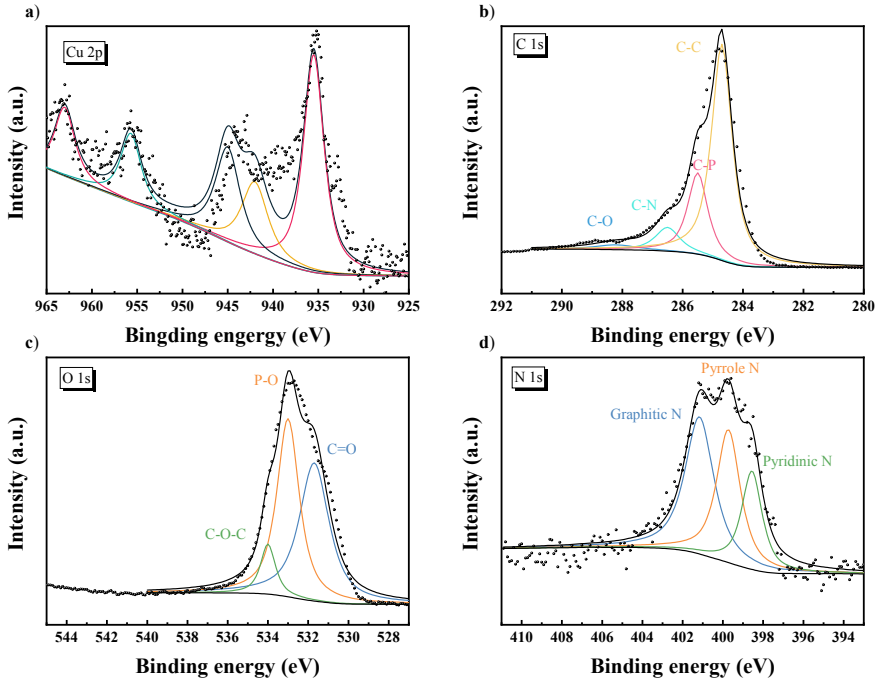

Figure S1. High resolution XPS spectra of Cu_1/PC. a) Cu 2p orbital; b) C 1s orbital; c) O 1s orbital; d) N 1s orbital.

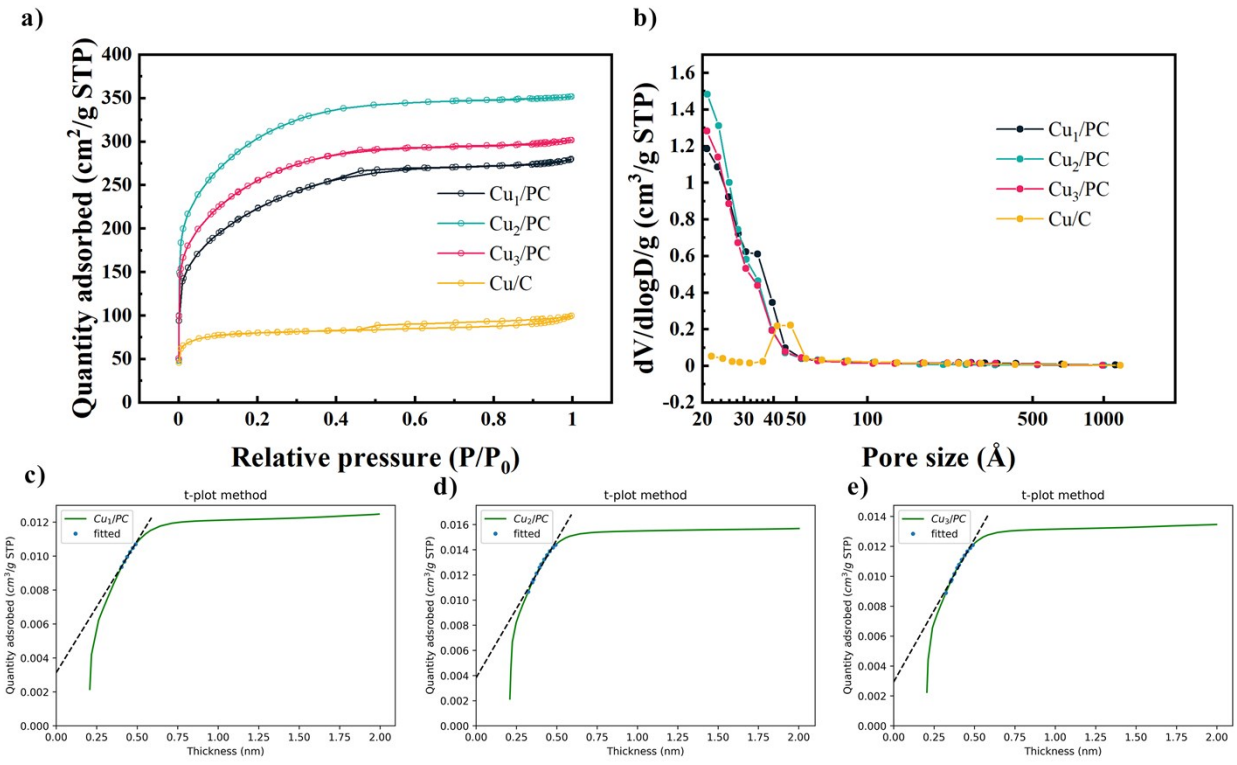

Figure S2. a) N_2 adsorption-desorption isotherms, b) pore size distributions of the Cu_x/PC and Cu/C samples, and t-plot analysis for Cu_1PC (c), Cu_2PC (d), Cu_3PC using the Harkins and Jura thickness model.

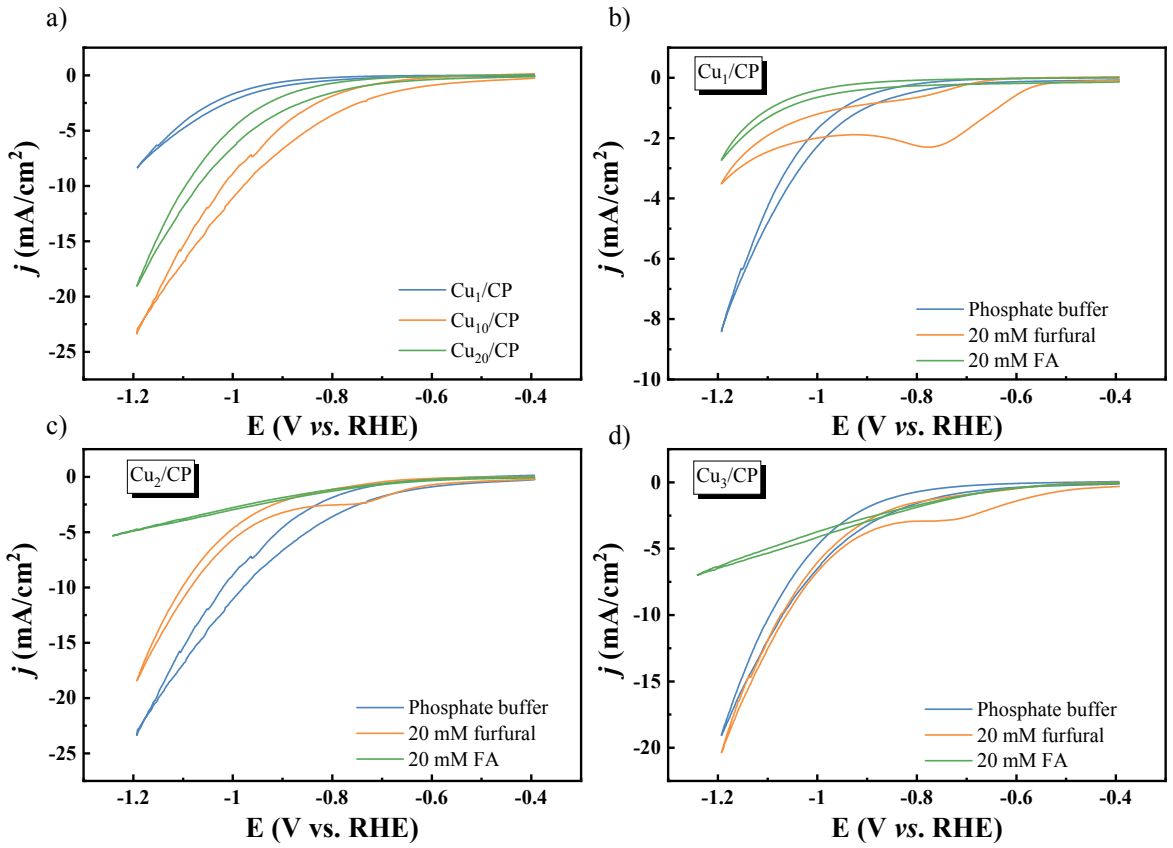

Figure S3. Voltammetric data for the Cu_x/PC catalysts in a) phosphate buffer (pH = 8), and b-d) phosphate buffer (pH = 8) in the presence and absence of furfural or FA. Scan rate = 50 mV s^{-1}.

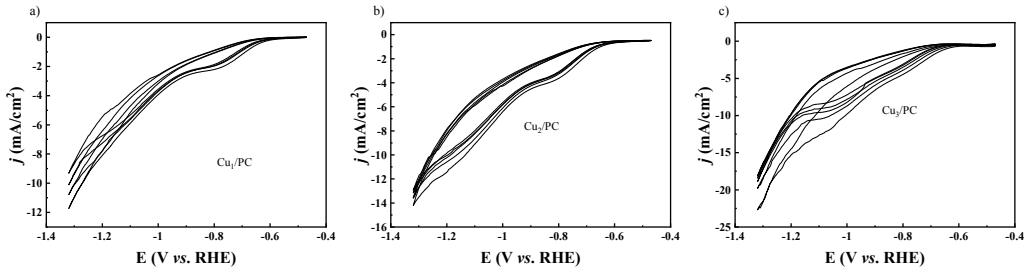

Figure S4 Multi-cycle cyclic voltammograms recorded in a N_2-saturated acetate buffer solution (pH 5) containing 20 mM furfural using a) Cu_1/PC b) Cu_2/PC c) Cu_3/PC modified GC electrodes. Scan rate = 50 mV s^{-1}.

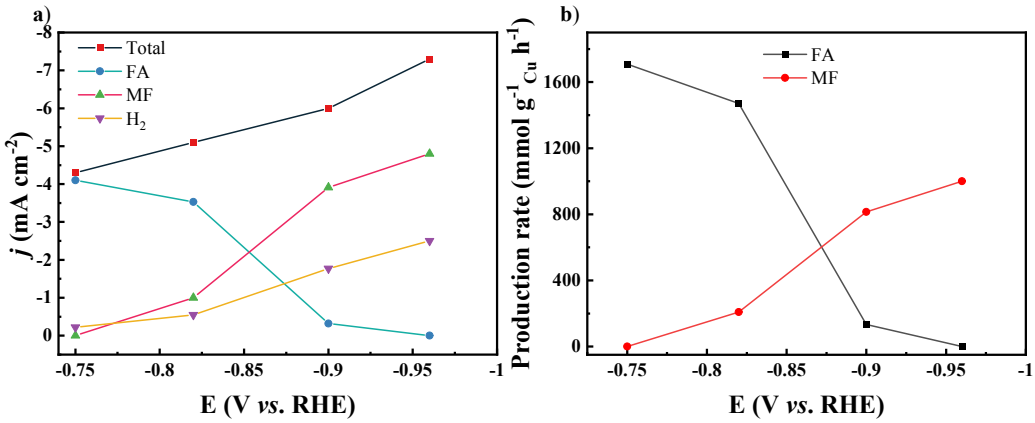

Figure S5. a) Total current density and partial current density for H_2, FA and MF and b) Production rate of FA and MF at Cu_1/PC in electrolysis experiment with Cu_1/PC at various applied potentials in acetate buffer (pH = 5).

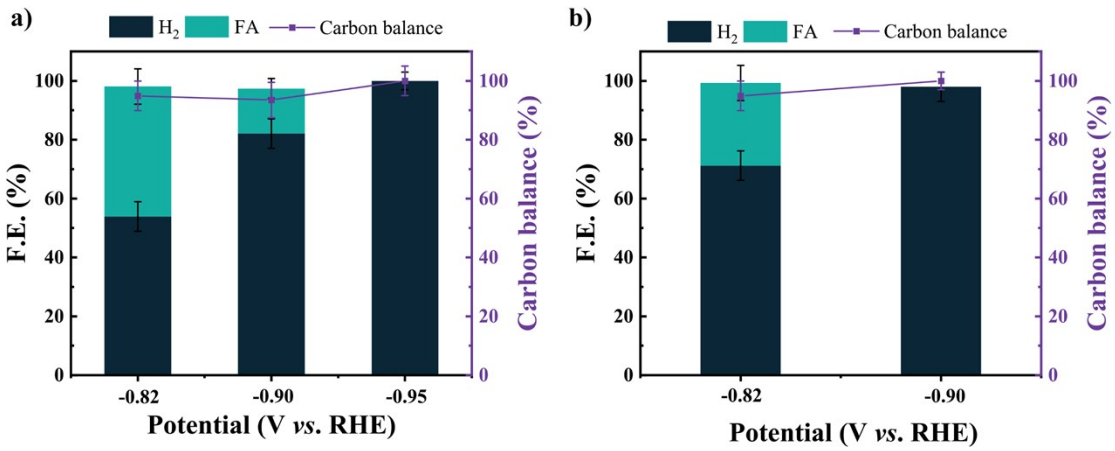

Figure S6. The faraday efficiency and carbon balance data for the bulk electrolysis of 40 mM furfural in an acetate buffer solution (pH = 5) on a) Cu_2/PC, and b) Cu_3/PC at various applied potentials after consuming 10 C of charge.

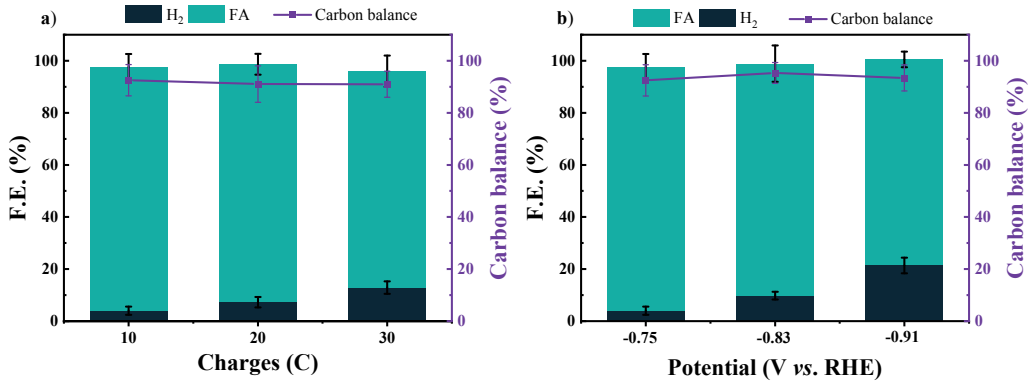

Figure S7. The faraday efficiency and carbon balance data for the bulk electrolysis of 40 mM furfural in a phosphate buffer solution (pH = 8) with Cu_1/PC a) after consuming various amounts of charge at an applied potential of -0.75 V *vs*. RHE, and b) at various applied potential potentials after consuming 10 C of charge.

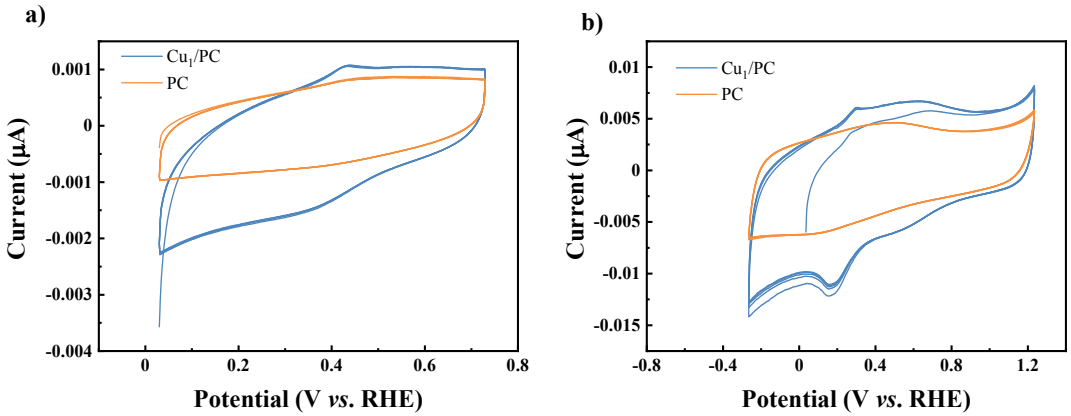

Figure S8. Cyclic voltammograms obtained on the Cu_1/PC and PC modified electrodes in a) acetate buffer (pH = 5), and b) 0.01 M H_2SO_4 aqueous solutions. Scan rate = 50 mV s^{-1}.

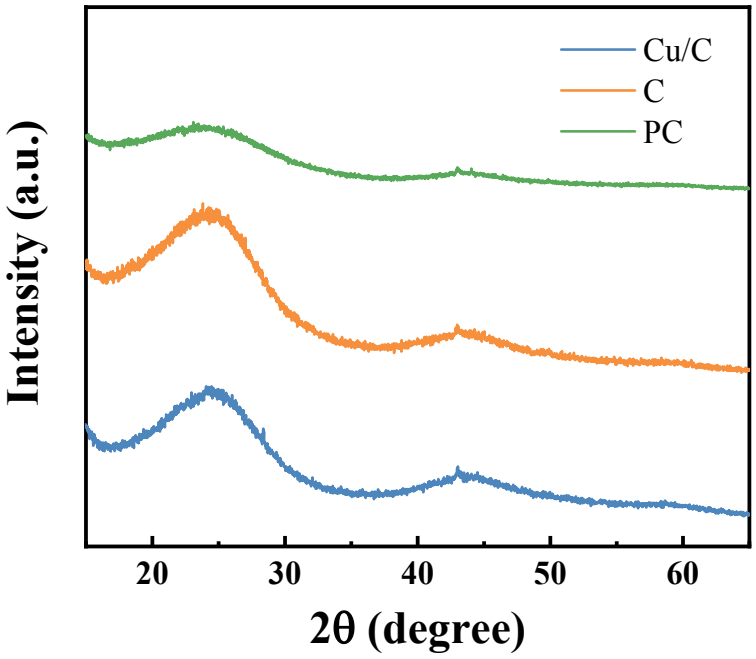

Figure S9. PXRD patterns for Cu/C, C and PC.

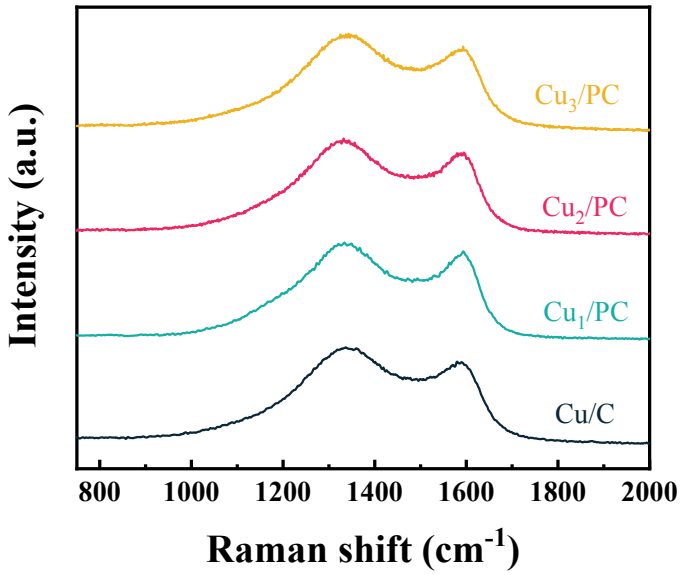

Figure S10. Raman spectra for Cu_x/PC and Cu/C.

Table S1 Elemental composition of Cu_1/PC

Element	Composition (mass %)	
	XPS	Elemental analysis
C	61.3	32.6
O	22.2	37.3
N	4.5	8.1
P	10.4	19.5[a]
H	-	2.0

[a] Estimated by subtracting other element in the sample.

Table S2. Parameters of the best Cu K-edge EXAFS fitting results for Cu_1/PC.

Shell	CN	R	σ^2	e0
Cu-O_1	4.0	1.95	0.00325	-2.371
Cu-O_2	2.0	2.95	0.00273	-2.371

Table S3. Summary of texture parameters for Cu_x/PC.

Sample	Surface area (BET)[a] ($m^2\ g^{-1}$)	Pore diameter (BJH)[b] (nm)	Pore volume (BJH)[c] ($cm^3\ g^{-1}$)	Microporous area ($m^2\ g^{-1}$)[d]
Cu/C	245	5.09	0.05	-
Cu_1/PC	751	2.78	0.25	212
Cu_2/PC	997	2.61	0.25	235
Cu_3/PC	844	2.68	0.23	181

[a] Specific surface area, calculated from multi-point BET analysis.

[b] The pore dimeter calculated from the adsorption part of isotherm using the BJH method.

[c] Total pore volume calculated from the BJH method.

[d] Calculated from t-plot with the equation: $S_{mic} = S_{BET}-S_{mes+ext}$ in which S_{mic} and S_{BET} represent the microporous area and BET surface area, $S_{mes+ext}$ are obtained from t-plot[S1].

Table S4. Effect of the substrate and product concentration on the F.E. of the products.[a]

Entry	Substrates	F.E. (%)		
		H_2	FA	MF
1	40 mM FF	29.1	5.0	62.7
2	40 mM FF + 10 mM FF	18.2	7.9	74.1
3[b]	40 mM FF + 10 mM FA	23.7	6.3	70.2
4	40 mM FF + 10 mM MF	27.9	5.4	60.9

[a] Conducted in acetate buffer (pH = 5) at -0.90 V *vs*. RHE and 10 C of charge were collected.

[b] Assuming MF to be the 4 e- reduction product of FF since the concentration of FF and FE of MF from FF reduction are significantly higher.

Table S5. Comparison of our catalyst with the state-of-the-art furfural electrochemical hydrogenation catalysts.

Catalysts	pH	Potential (V *vs*.RHE)	F.E. (%)	Carbon balance (%)	Reference
Cu_1/PC	5	-0.75	94[a]	100	This work
Cu_1/PC	5	-0.90	62[b]	100	This work
Cu/Cu-400nm	0	-0.5	73[b]	67	S2
Cu	0	NA	56.8[c]	< 70	S3
Ni	1	NA	39[b]	79	S4
Pd/C or Pt/C	7	-1.15- -1.75	24-30[c]	10	S5
Cu	10	-1.4	71[c]	NA	S6
Pb, Ni, Fe, Ti, C, Pt	10	-1.4	< 40[c]	NA	S6
CuP_3/CFC	1.0 M KOH (pH = 13.5)	-1.5	> 95[a]	100	S7
NiP_3/CFC	1.0 M KOH (pH = 13.5)	-1.5	90[a]	100	S7

[a] F.E. for FA

[b] F.E. for MF

[c] Total F.E. for MF and FA

References:

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