Supporting Information

Control of evolution of porous copper-based metal-organic materials for electroreduction of CO₂ to multi-carbon products

Lili Li¹, Lutong Shan¹, Alena M. Sheveleva^{1,2}, Meng He¹, Yujie Ma¹, Yiqi Zhou³, Marek Nikiel^{2,4,5}, Laura Lopez-Odriozola¹, Louise S. Natrajan¹, Eric J. L McInnes^{1,2}, Martin Schröder^{1*}, Sihai Yang^{1*} and Floriana Tuna^{1,2*}

1. Department of Chemistry, University of Manchester, Manchester, M13 9PL (UK)

- M.Schroder@manchester.ac.uk; Sihai.Yang@manchester.ac.uk; Floriana.Tuna@manchester.ac.uk
- 2. Photon Science Institute, University of Manchester, Manchester, M13 9PL (UK)

3. Institute for Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083 (China)

- 4. Department of Materials, University of Manchester, Manchester, M13 9PL (UK)
- 5. National Graphene Institute, University of Manchester, M13 9PL (UK)

Experimental section

Materials. Cu(NO₃)₂·3H₂O (>99%), benzene-1,3,5-tricarboxylic acid (H₃BTC) (>99%), tetracyanoquinodimethane (TCNQ), ethanol (EtOH) (>99%), dimethylformamide (DMF) (>99%), acetone (>99%), dichloromethane (CH₂Cl₂) (>99%), dimethyl sulfoxide (DMSO), 5,5-dimethyl-1pyrroline-N-oxide (DMPO) and deuterium oxide (D₂O) were purchased from Sigma-Aldrich Co., UK. Carbon paper (CP) and polytetrafluoroethylene (PTFE) were purchased from Gaoss Union. KOH (99%), Nafion D521 solution (5% w/w in water and 1-propanol, \geq 0.92 meq/g exchange capacity) and anion exchange membrane were purchased from Alfa Aesar Co., UK. H₃L used for the synthesis of CuMOP was prepared according to our previously reported procedure.¹ All chemicals and reagents used in this study were used as received without further purification.

Synthesis of HKUST-1. A solution of $Cu(NO_3)_2 \cdot 3H_2O(7.8 \text{ g}, 32.1 \text{ mmol})$ in $H_2O(90\text{mL})$ was slowly added to a solution of H_3BTC (2.04 g, 9.6 mmol) in EtOH (90 mL). After continuous stirring for 10 min at room temperature, 6 mL DMF was added to the solution. The vial was sealed and heated at 80 °C for 20 h. The resultant powder was collected and washed several times with DMF and acetone and dried.

Synthesis of CuMOP. CuMOP was synthesised according to our previously reported procedure.¹

Material characterisation. PXRD data were collected from a Philips X'pert X-ray diffractometer (45 kV and 40 mA) using Cu- K α radiation ($\lambda = 1.5406$ Å), and the scan speed was 1°/min. Fourier Transformed Infrared (FTIR) spectra were collected with Nicolet iS5 spectrometer, and Raman spectra were recorded on a Horiba XploRA Plus Raman microscope with a 638 nm laser and 1200 mm⁻¹ grating. Baseline correction was applied to all Raman spectra. Electron paramagnetic resonance (EPR) spectra of solid samples were recorded at different temperature in continuous wave mode on Bruker EMX spectrometers (Q-band, ca. 34 GHz), at mw power of ~0.63mW and modulation amplitude 10 G. EPR spectra of liquid samples was collected at X-band (9.85 GHz) on a Bruker Micro EPR spectrometer at room temperature with a microwave power of 6.325 mW and an modulation amplitude of 1 G. DMPO (200 mmol/L) was dissolved in Ar-degassed de-ionised water and used as a spin trap; a Bruker strong pitch (g = 2.0028) reference was used as a calibrator. Theoretical modelling of the spectra was performed with the EasySpin toolbox within Matlab.² The BET surface areas were obtained from N₂ adsorption/desorption isotherms recorded on a Micromeritics 3-Flex instrument at 77 K. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos Axis Ultra Hybrid spectrometer with monochromatized Al Ka X-ray source, using 20 eV energy pass for core levels spectra. C 1s electron at binding energy of 284.8 eV was used as a standard reference to calibrate the photoelectron energy shift. All the data analysis was performed on the Casa XPS software (version: 2.3.22PR1.0). Peak deconvolution was performed with Tougaard type background and LA peak shape. The morphologies of the materials were measured by scanning electron microscopy (SEM) on a Quanta FEG 650.

Electrochemical study. All electrochemical experiments were carried out on a CHI 660E, USA electrochemical workstation with a flow cell. Carbon paper (CP) was used as the substrate for preparing working electrodes. The working electrodes HKUST-1/CP, TCNQ@HKUST-1/CP, CuMOP/CP and TCNQ@CuMOP/CP were prepared using the following procedure: 10 mg of HKUST-1, TCNQ@HKUST-1, CuMOP or TCNQ@CuMOP was suspended in 750 μ L isopropanol and 250 μ L H₂O containing 100 μ L Nafion D-521 dispersion (5 wt%). This was treated with ultrasound for 30 mins to form a homogeneous ink. 100 μ L of the ink was spread onto the CP (1×1 cm²) surface and dried at room temperature. To increase the hydrophobicity of the working electrode, PTFE was placed on the gas chamber side, just behind the catalyst/CP working electrode, to prevent the catholyte from entering the gas chamber.

The flow cell (Supplementary Figure 4) contains a hydrophobic and porous cathodic working electrode separating the gas and catholyte chambers. The cathode and anode are separated by an anion exchange membrane, and 1.0 M KOH solution was used as both catholyte and anolyte, and passed through the cathode and anode chambers separately. Ag/AgCl (in saturated KCl) was used as the reference electrode and Pt was the counter electrode. CO_2 (50 sccm) was passed over the porous working electrode, and then reduced over the catalyst into the cathodic section. After electrolysis, the liquid products were studied by ¹H NMR spectroscopy and gas products were collected in a gasbag and analysed by Bruker Matrix MG5 FTIR spectrometer.

Electrochemical impedance spectroscopy (EIS) was recorded at -0.174 V vs RHE with an amplitude of 5.0 mV (10⁻¹ to 10⁶ Hz). The value for the resistance of charge transfer (R_{ct}) was obtained by fitting the EIS spectra using the Zview software (Version 3.5f, Scribner Associates, Inc). Linear sweep voltammetry (LSV) scans were conducted in CO₂ and Ar saturated catholyte.

Quantitative analysis of products in liquid and gas phase. All liquid products were quantified using ¹H NMR spectroscopy. DMSO (1.0g) was dissolved in H₂O (25 mL) and this solution used as the reference. After the CO₂RR, 100 μ L of the as-prepared reference solution of DMSO in H₂O was injected into the catholyte. Then 0.9 mL of catholyte was mixed with 0.1 mL D₂O, and around 0.7 mL of this solution was subsequently transferred into an NMR tube for measurement. Gas products were quantified by Bruker Matrix MG5 FTIR spectrometer The value of FE was calculated using the equation:

$$FE(\%) = \frac{n_{product} \times n_{electrons} \times F}{Q} \times 100\%$$

where n_{product} is the amount of product (mol) from Bruker Matrix MG5 FTIR spectrometer or ¹H NMR spectroscopy (formic acid), $n_{\text{electrons}}$ is electron transfer number (both the production of H₂ and formate are two-electron processes), *F* is the Faraday constant (96485 C mol⁻¹), and *Q* is the total charge passed during the CO₂RR.



Supplementary Figure 1. Synthesis of HKUST-1 and CuMOP.



Supplementary Figure 2. Q-band EPR spectra at different temperatures. (a) HKUST-1, (b) TCNQ@HKUST-1, (c) CuMOP, and (d) TCNQ@CuMOP.



Supplementary Figure 3. Q-band EPR spectra and simulations. (a) HKUST-1, (b) TCNQ-HKUST-1, (c) CuMOP and (d) TCNQ@CuMOP. The experimental EPR spectra for HKUST-1 and TCNQ@HKUST-1 were collected at 100 K; for CuMOP and TCNQ@CuMOP they were collected at 293 K.



Supplementary Figure 4. View of the flow-cell used in this study.



Supplementary Figure 5. Catalytic performance of TCNQ@HKUST-1-p/CP electrode at -2.27 V vs RHE for CO₂RR in different electrolytes.



Supplementary Figure 6. Total current density using TCNQ@HKUST-1-p/CP electrode for CO_2RR in different electrolytes at -2.27 V vs RHE.



Supplementary Figure 7. Catalytic performance of TCNQ@CuMOP-p/CP electrode for CO₂RR in different electrolytes at -2.27 V vs RHE.



Supplementary Figure 8. Total current density using TCNQ@CuMOP-p/CP electrode for CO_2RR in different electrolytes at -2.27 V vs RHE.



Supplementary Figure 9. PXRD patterns of working electrodes before and after 10 mins of electrolysis of CO₂.



Supplementary Figure 10. FTIR spectra of working electrodes before and after 10 mins of



electrolysis of CO₂.

Supplementary Figure 11. Cu 2p XPS spectra of CuMOP and CuMOP-p/CP.



Supplementary Figure 12. Cu 2p XPS spectra of working electrodes before and after 10 mins of electrolysis of CO₂.



Supplementary Figure 13. SEM images. (a) HKUST-1, (b) TCNQ@HKUST-1, (c) CuMOP and (d) TCNQ@CuMOP.



Supplementary Figure 14. SEM images. (a) HKUST-1-p/CP, (b) TCNQ@HKUST-1-p/CP, (c) CuMOP-p/CP and (d) TCNQ@CuMOP-p/CP.



Supplementary Figure 15. Catalytic performance of HKUST-1-p/CP electrode for CO_2RR at different potentials.



Supplementary Figure 16. Catalytic performance of TCNQ@HKUST-1-p/CP electrode for CO₂RR at different potentials.



Supplementary Figure 17. Catalytic performance of CuMOP-p/CP electrode for CO₂RR at different potentials.



Supplementary Figure 18. X-band EPR spectra of electrolyte aliquots taken as a function of time.



Supplementary Figure 19. X-band EPR spectra of spin adducts of free radicals. The complete set of parameters for simulations are given in Supplementary Table 2. Based on the electrochemical CO_2 reduction results, most of the products are multi-carbon products, denoted DMPO-C[•] above. The observed EPR simulated parameters for DMPO carbon-centred radicals are different to those derived from •CO₂ and •COOH radicals. In addition, using DMPO as a spin trap does not differentiate between various carbon-centred radicals.

Supplementary Table 1. Spin-Hamiltonian parameter set extracted from Q-band CW EPR spectra of as-synthesised HKUST-1, TCNQ@HKUST-1, CuMOP, TCNQ@CuMOP.

	feature A: Monomeric Cu(II)	feature B: Intra- nuclear exchange in	feature C: Interdinuclear exchange between
		{Cu(II) ₂ } paddlewheels	neighbouring {Cu(II) ₂ } paddlewheels
HKUST-1	g = [2.069, 2.35]	g = [2.06, 2.35]	g = [2.05, 2.30]
	A = [30 MHz, 450 MHz]	$D = -0.325 \text{ cm}^{-1}$	$J' = 1 \text{ cm}^{-1}$
		$E = 0 \text{ cm}^{-1}$	
TCNQ@HKUST-1	g = [2.090, 2.35]	-	g = [2.15, 2.35]
	A = [30 MHz, 450 MHz]		$J' = 1 \text{ cm}^{-1}$
CuMOP	g = [2.069, 2.35]	g = [2.06, 2.35]	g = [2.07, 2.30]
	A = [30 MHz, 450 MHz]	$D = -0.325 \text{ cm}^{-1}$	$J' = 1 \text{ cm}^{-1}$
		$E = 0 \text{ cm}^{-1}$	
TCNQ@CuMOP	g = [2.069, 2.35]	g = [2.03, 2.2]	g = [2.05, 2.10]
	A = [30 MHz, 450 MHz]	$D = -0.325 \text{ cm}^{-1}$	$J' = 1 \text{ cm}^{-1}$
		$E = 0 \text{ cm}^{-1}$	

g and A are the g-value and Cu hyperfine coupling constants, respectively; D and E are the axial and rhombic zero-field splitting parameters of the S = 1 state, respectively. J' = the exchange coupling constant. The simulation of the inter-binuclear exchange line follows previous research in which only one inter-binuclear exchange pathway with an exchange coupling constant J' was considered.³

Supplementary Table 2. EPR spectra simulation parameters of the radicals produced during CO₂RR.

Working electrode	Adduct	g-factor	A ¹⁴ N / G	A ¹ H/G	lw/mT
HKUST-1-p/CP	DMPO-C•	2.0054	16.0	24.3	0.2
					0.2
	DMPO-O•	2.0054	16.0	16.0	0.12
					0.09
	Oxidised DMPO	2.0055	15.1	-	0.12
TCNQ@HKUST-1-p/CP	DMPO-C•	2.0054	16.0	24.3	0.2
					0.2
	DMPO-O•	2.0054	16.0	16.0	0.12
					0.09
	Oxidised DMPO	2.0055	15.1	-	0.12
CuMOP-p/CP	DMPO-C•	2.0054	16.0	24.3	0.2
					0.2
	DMPO-O•	2.0054	16.0	16.0	0.12
					0.09
	Oxidised DMPO	2.0055	15.1	-	0.12
TCNQ@CuMOP-p/CP	DMPO-C•	2.0054	16.0	24.3	0.2
					0.2
	DMPO-O•	2.0054	16.0	16.0	0.12
					0.09
	Oxidised DMPO	2.0055	15.1	-	0.12

^{*} lw is the homogeneous Lorentzian linewidth; g and A are the g and hyperfine constant parameters, respectively. The spin trap DMPO can be oxidized by O₂ during the EPR measurement. Therefore, it is normal to detect oxidised DMPO in such experiments.

Catalyst	Pre-	Main	Electrolyte	Faradaic	Potential	Current	Ref
	processing	product		efficiency	V vs	density	
	method			(%)	RHE	mA·cm ⁻²	
Cu ₂ O@Cu-MOF	-	CH ₄	0.1 M KHCO ₃	63	-1.71	8.4	4
Cu-THQ	-	CO	1 M C ₅ H ₁₄ CINO	91	-0.45	173	5
			+ 1 M KOH				
d-Cu-1 derivatives	Electro-	formate	IL/MeCN/H ₂ O	98	-1.85	102.1	6
	reduction				VS		
					Ag/Ag+		
S-HKUST-1	Guest	C ₂ H ₄	1 M KOH	57	NA	400	7
	introducing						
Cu NPs from Cu-	Electro-	CH ₄	0.1 M KHCO3	50	-1.3	10	8
MOF-74	reduction						
Cu-DBC	-	CH ₄	0.1 M KHCO3	56	-1.4	11.4	9
MAF-2E	-	$CH_4 +$	0.1 M KHCO3	77	-1.5	~17	10
		C_2H_4					
Cu-MOF/NP	Calcination	CO	0.5 M KHCO ₃	44	-0.86	230	11
H-	-	acetic acid	0.5 M EMIMBF ₄	26	-1.6 vs.	~7.5	12
CuTCPP@Cu(OH) ₂			$MeCN (1 M H_2O)$		Ag/Ag+		
HATNA-Cu-MOF	-	CH ₄	0.1 M KHCO ₃	78	-1.5	8.2	13
HKUST@800	Calcination	C ₂₊	1 M KOH	54	NA	80	14
		product					
Cu ₄ -MFU-41	-	CH ₄	0.5 M NaHCO ₃	88	-1.3	18.3	15
H-265	Calcination	C ₂ H ₄	1 M KOH	51	-1.58	150	16
CPFs	-	$CH_4 +$	0.1 M KHCO3	74	-1.4	7.5	17
		C_2H_4					
Cu(111)@Cu-THQ	Electro-	C ₂ H ₄	0.1 M KHCO3	42	-1.4	14.3	18
	reduction						
Cu ₂ O/Cu@NC-800	Calcination	formate	0.1 M KHCO ₃	71	-0.68	4.4	19
Cu ₂ O@CuHHTP	Electro-	CH ₄	0.1 M KCl/0.1 M	73	-1.4	10.8	20
	reduction		KHCO3				
OD-Cu-3	Calcination	C ₂₊	1 M KOH	70	-1.3	141	21
		product					
HKUST-1-p	Electro-	C ₂₊	1 M KOH	37	-2.27	100	THIS
	reduction	product					WORK
TCNQ@HKUST-1-p	Electro-	C ₂₊	1 M KOH	33	-2.27	52.2	THIS
	reduction	product					WORK
CuMOP-p	Electro-	C ₂₊	1 M KOH	31	-2.27	40.9	THIS
	reduction	product					WORK
TCNQ@CuMOP-p	Electro-	C ₂₊	1 M KOH	20	-2.27	24.0	THIS
	reduction	product					WORK

Supplementary Table 3. The performance of Cu(II)-based MOFs and their derivatives for CO₂RR.

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