# Supplementary Information: Quinone-functionalised carbons as new materials for electrochemical carbon dioxide capture

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# S1. Custom-made gas cell for electrochemical measurements

Figure S 1.1. Schematic diagram of gas manifold adapted from Binford et al.<sup>1</sup>

# S2. Gas sorption of u-CMK-3 and f-CMK-3



**Figure S 2.1.** DFT plots of the pore size distribution for f-CMK-3 (red) and u-CMK-3 (black), obtained from  $N_2$  sorption isotherms at 77 K. Method used was slit pore, NLDFT equilibrium model.



Figure S 2.2. Multi-point BET plot for f-CMK-3 (red) and u-CMK-3 (black).

# S3. FT-IR of 2-AAQ and AQ



Figure S 3.1. FT-IR of 2-aminoanthraquinone (red line) and anthraquinone (black line).





FT-IR (AQ)  $\nu$  cm<sup>-1</sup>: 1673 (C = O); 1571, 1475, 1452 (C - C); 1278, 1166, 1093 (C - H).

(2-AAQ) <sup>*v*</sup> cm<sup>-1</sup>: 3355, 3441, 3216 (N <sup>-</sup> H); 1329 (C <sup>-</sup> N).

#### S4. SEM-EDX of u-CMK-3 and f-CMK-3



**Figure S 4.1.** SEM image of u-CMK-3 (left) and f-CMK-3 (right), with boxes showing the regions studies by SEM-EDX.



**Figure S 4.2.** SEM-EDX spectrum of u-CMK-3 (black) and f-CMK-3 (red). Carbon is seen at 0.27 keV and oxygen at 0.53 keV. Notably, no nitrogen is measured, and no 2-amino anthraquinone is present within the material.

**Table S 4.1.** Chemical composition from EDX for u-CMK-3 and f-CMK-3 in at.%. Anthraquinone loadings could not be calculated from this data due to limitations when comparing f-CMK-3 and u-CMK-3.

Sample	C (at.%)	O (at.%)	S (at.%)
u-CMK-3	u-CMK-3 97.0		0.5
f-CMK-3	F-CMK-3 89.9		0.4

#### S5. XPS of u and f-CMK-3



**Figure S5.1.** XPS spectrum of u-CMK-3 (black) and f-CMK-3 (red). Carbon 1s is seen at 285 eV and oxygen 1s at 532 eV. A trace amount of nitrogen is seen at 400 eV which has been linked to trace amounts of the radical initiator TBN. No nitrogen is seen in any other characterization of f-CMK-3.



Sample	(at.%)	(at.%)	(at.%)
u-CMK-3	2.5	72.3	27.3
f-CMK-3	11.0	58.0	42.0

**Figure S5.2.** XPS fitted O 1s core-level spectrum of u-CMK-3 (left) and f-CMK-3 (right). Fitting shows peaks indicating carbonyl group (red) and C-OH hydroxyl or C-O-C ether group (blue). Atomic percentages of these bonds are included for comparison. Anthraquinone loadings could not be calculated from this data due to limitations when comparing f-CMK-3 and u-CMK-3.

# S6. Determination of quinone loading from electrochemical measurements

$$\Delta C = C_f - C_u$$
$$N_e = \frac{\Delta C}{F}$$

For 
$$AQ^-: n(AQ^-) = N_{e'}$$
 for  $n(AQ^{2-}) = \frac{1}{2}N_e$ 

Assumed AQ<sup>2-</sup> state

 $\frac{1}{2}N_e \times m_{active} = n_{AQ}$ 

 $n_{AQ}$  converted to  $m_{AQ}$ 

$$AQ \ loading \ \% = \frac{m_{AQ}}{m_{active}} \times 100$$

 $C_f$  – capacity of f-CMK-3 (mAh g<sup>-1</sup>),  $C_u$  – capacity of u-CMK-3 (mAh g<sup>-1</sup>),  $\Delta C$  – difference in capacity (mAh g<sup>-1</sup>),  $N_e$  – number of electrons (moles), F – Faraday constant (C mol<sup>-1</sup>),  $m_{active}$  – active mass of electrode (g),  $n_{AQ}$  – number of AQ (moles),  $m_{AQ}$  – mass of AQ (g).

#### S7. TGA of CMK-3 and f-CMK-3



**Figure S7.1.** TGA of u-CMK-3 (black line) and f-CMK-3 (red line) and the percentage difference between the two samples (grey dashed line). Samples were stored at 100 °C before TGA was run. Weight loss below 100 °C is due to water loss.<sup>2</sup> Comte *et al.* linked the significant decrease in mass loss above 375 °C to the loss of the grafted species.<sup>3</sup> Therefore, thermal stability for f-CMK-3 is limited to below 375 °C.

#### **S8. CV experiments for control samples**



**Figure S 8.1.** CV scans of two-electrode cells with u-CMK-3 (black line), and two control experiments where (i) anthraquinone was dissolved within the u-CMK-3 network during the electrode film making process (red dashed line, see methods in main text) and (ii) where the synthesis was carried out without the addition of tert-butyl nitrite (red solid line, see methods in main text). CV scans were ran at 1 mV s<sup>-1</sup> with [bmim][TFSI] ionic liquid electrolyte, oversized YP80F used as positive electrode. Overall, the two CVs of the two controls show similarities with that of u-CMK-3, and do not show the clear two redox peaks observed for f-CMK-3 (see Figure 1c in the main text).

# S9. u-CMK-3 under CO<sub>2</sub> atmosphere



**Figure S 9.1.** OCV of u-CMK-3 under  $CO_2$  before and after constant current cycling. The initial pressure drop is due to the dissolution of  $CO_2$  into the gas cell. This stabilises further through the initial electrochemical experiments leading to a large gap between the OCV pressure data.



**Figure S 9.2.** Constant current (0.1 Ag<sup>-1</sup>) experiments with voltage hold steps (10 mins) of u-CMK-3 under  $CO_2$  atmosphere. Cell voltage window limited at 0 to -1 V.



**Figure S 9.3.** Constant current experiments (0.1 A  $g^{-1}$ ) with voltage hold steps (10 mins) of u-CMK-3 under CO<sub>2</sub> atmosphere. Cell voltage window limited at -1 to -2 V.

# S10. f-CMK-3 under N<sub>2</sub> atmosphere



**Figure S 10.1.** f-CMK-3 under  $N_2$ . Open circuit voltage (OCV) was run before and after charging the cell to check for cell leaks. Pressure data is shown in red.



**Figure S 10.2.** Constant current experiments at  $(0.1 \text{ A g}^{-1})$  with voltage hold steps (10 mins) of f-CMK-3 under N<sub>2</sub> atmosphere. Cell voltage window was 0 to -1 V. Errors shown on pressure data.

# S11. u-CMK-3 under N<sub>2</sub> atmosphere



Figure S 11.1. OCV of u-CMK-3 under N<sub>2</sub> before and after constant current cycling.



**Figure S 11.2.** Constant current experiments (0.1 A  $g^{-1}$ ) with voltage hold steps (10 mins) of u-CMK-3 under N<sub>2</sub> atmosphere. Cell voltage window limited at -1 to -2 V.

#### S12. Adsorption Capacity and efficiency for different voltage windows



**Figure S 12.1.** The capture (filled squares) and release (hollow squares) when f-CMK-3 is cycled between -1 to -2 V (red) and 0 to -2.5 V (blue). The large decrease in adsorption capacity when charged to more negative values was linked to a higher rate of degradation of the material. Gaps in the data are due to inaccurate adsorption capacities when the temperature was not controlled and was therefore omitted.



**Figure S 12.2.** The faradaic efficiency (filled squares) of f-CMK-3 when cycled between -1 to -2 V (red) and 0 to -2.5 V (blue). The charge: capture efficiency (hollow squares) are also shown. The faradaic efficiency for both cycling protocols are increasing as the cell is cycled whereas the charge: capture efficiency when charged between 0 to -2.5 V decreases upon cycling whereas the other cycling protocol is stable. This suggests that for capture experiments, a smaller, less negative voltage window is needed to reduce degradation.

# S13. Optimizing current density of f-CMK-3 under CO<sub>2</sub>



**Figure S 13.1.** A range of current density tested in constant current experiments cycled between 0 to -2.5 V for f-CMK-3 under  $CO_2$  atmosphere. The corresponding capacity (black line), adsorption capacity (red line) and energy consumption (blue line) are given. Adsorption capacity (filled circles) and release (hollow circles) are shown. The measurements were carried out on the same two-electrode cell in the order; 0.1, 0.2 0.05 and 0.5 A g<sup>-1</sup>.

# S14. Determination of energy consumption per CO<sub>2</sub> captured

From constant current experiments

Energy consumption (kJ kg<sup>-1</sup>):

$$E_{consum} = \frac{\int v \, dt \, \times A \times 3.6}{m_{active}}$$

Energy consumed per CO<sub>2</sub> captured (kJ mmol<sup>-1</sup>):

 $\frac{E_{consum}}{C_{ads}}$ 

 $E_{consum}$  – energy consumption per cycle (kJ kg<sup>-1</sup>), v – cell voltage (V), A – current (A),  $C_{ads}$  – adsorption capacity (mol kg<sup>-1</sup>).

# S15. Determination of CO<sub>2</sub> adsorption capacity from gas experiments

Volume of Gas Manifold (Pa) from OCV:

$$V_{res} = \frac{V_{cal}}{\frac{P_{max}}{P_{min}} - 1}$$

Adsorption of CO<sub>2</sub> (mol kg<sup>-1</sup>):

$$\frac{(\Delta P \times V_{res})}{(F \times T)}$$

 $V_{res}$  – volume of gas reservoir (mL),  $V_{cal}$  – calibration volume in gas manifold (mL),  $P_{max}$  – maximum pressure of system (Pa),  $P_{min}$  – minimum pressure of system (Pa),  $\Delta P$  – change in pressure over a single cycle (Pa), T – temperature (K).

# S16. Theoretical $CO_2$ adsorption capacity for anthraquinone capture mechanism

Assume 9.6 wt.% AQ on CMK-3 surface

 $m_{active} \times 9.6\% = m_{AQ}$ 

 $m_{AQ}$  converted to  $n_{AQ}$ 

For AQ<sup>-</sup>, if stoichiometry is 1:1:

 $n_{AQ} = n_{CO_2}$ 

For AQ<sup>-2</sup>, if stoichiometry is 1:2:

 $n_{AQ} \times 2 = n_{CO_2}$ 

Adsorption of CO<sub>2</sub> (mmol kg<sup>-1</sup>):

n<sub>CO2</sub>

 $\overline{m_{active}}$ 

 $n_{CO_2}$  – number of carbon dioxide (moles).

#### S17. f-CMK-3 under CO<sub>2</sub> atmosphere



**Figure S 17.1.** OCV of f-CMK-3 under  $CO_2$  before and after constant current cycling. The initial drop in pressure is due to the dissolution of  $CO_2$  into the gas cell. This stabilises further through the initial electrochemical experiments leading to a large gap between the OCV pressure data.



**Figure S 17.2.** Constant current experiments (0.1 Ag<sup>-1</sup>) with voltage hold steps (10 mins) of f-CMK-3 under CO<sub>2</sub> atmosphere. Cell voltage window limited at -1 to -2 V. This figure is a more complete view of the dataset shown in Figure 2C.



**Figure S 17.3.** The capture (red filled) and release (red hollow) data when cycled between - 1 to -2 V. Charge (black filled) and discharge (black hollow) are also given for u-CMK-3 (squares) and f-CMK-3 (circles).



**Figure S 17.4.** Faradaic and charge: capture efficiency calculated for f-CMK-3 systems cycled between -1 to -2 V under carbon dioxide (red) and nitrogen (black).



**Figure S 17.5.** Constant current experiments (0.1 Ag<sup>-1</sup>) with voltage hold steps (10 mins) of f-CMK-3 under CO<sub>2</sub> atmosphere. Cell voltage window cycled between 0 to -2.5 V.



**Figure S 17.6.** Calculated  $CO_2$  adsorption capacity of f-CMK-3 (blue) and release (black) while cycling between 0 to -2.5 V. The theoretical capture for 1 or 2 equivalence of  $CO_2$  per anthraquinone has also been added (black dashed line).



**Figure S17.7.** Charge (black filled squares) and discharge (black hollow squares) of f-CMK-3 while cycling between 0 to -2.5 V. Faradaic and charge: capture efficiency (solid black lines) have also been added.

# S18. Elemental Analysis

Sample	Weight /mg	C (wt.%)	H (wt.%)	N (wt.%)
f-CMK-3	1.0157	85.97	1.01	0.66
f-CMK-3	1.0966	85.94	0.90	0.61
u-CMK-3	1.1171	87.45	0.51	0.00
u-CMK-3	1.7674	87.22	0.59	0.00

**Table S 18.1.** Elemental Analysis CHN of u-CMK-3 and f-CMK-3, for two independent samples in each case.

# S19. Error calculations for adsorption capacities

Lower quartile =  $\mu_N - \sigma$ 

Upper quartile =  $\mu_N + \sigma$ 

 $\mu_N$  – moving average of adsorption (mmol kg<sup>-1</sup>) averaged every data point in 100 seconds (100 points),  $\sigma$  – standard deviation of pressure recorded in OCV experiment (mmol kg<sup>-1</sup>).

# S20. Capacity of f-CMK-3 under $N_2$ and $CO_2$ for 1000 cycles.



**Figure S 20.1.** Constant current experiments at 2 A g<sup>-1</sup> of f-CMK-3 under N<sub>2</sub> (black line) and CO<sub>2</sub> (red line). The current was held between 0 to -2.5 V. Capacity of the cells are shown over 3000 cycles. Two-electrode cells using oversized YP80F as the positive electrode and [bmim][TFSI] as an ionic liquid electrolyte.

S21. <sup>1</sup>H NMR of electrolyte after f-CMK-3 constant current cycling under CO<sub>2</sub> atmosphere.



**Figure S 21.1.** <sup>1</sup>H NMR (400 MHz, D<sub>6</sub>-DMSO) of [bmim][TFSI] (structure shown of cation and spectrum in dark blue), anthraquinone (structure shown and spectrum in light blue) and electrolyte recovered from the separator (red spectrum) after f-CMK-3 was cycled 200 times. [bmim] peaks present in the electrolyte sample have been assigned and unknown two aromatic peaks at 8.8 and 7.7 ppm are highlighted in the enlarged spectrum. Unassigned peaks at 2.6, 2.9 and 3.8 ppm are from residual acetone, DMSO and water respectively.

S22. Gas measurements of functionalised YP80F under CO<sub>2</sub>



**Figure S 22.1.** Electrochemical gas sorption measurement of anthraquinone functionalised YP80F (i.e. f-YP80F) under CO<sub>2</sub> with oversized YP80F as the positive electrode, and [bmim][TFSI] ionic liquid as the electrolyte. Constant voltage experiments were used with 2 hour voltage holds, alternating between 0 and -2.5 V.

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