Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

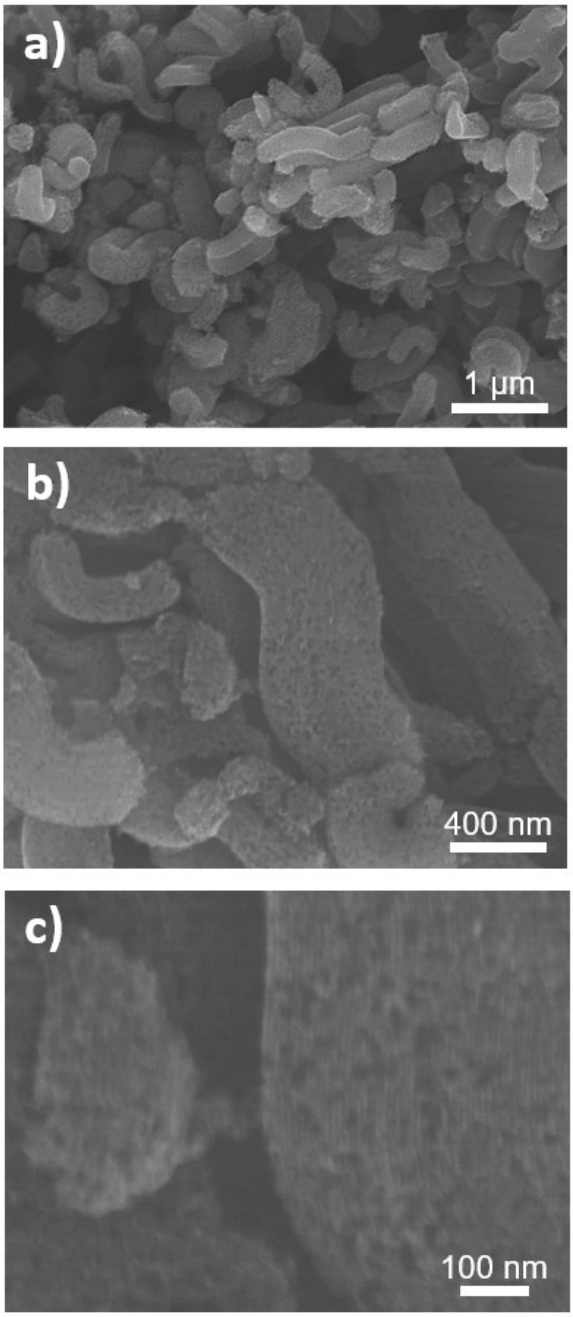

Fig. S1. SEM images of CMK-3 at different scales. (a) ×20,000 (b) ×50,000, and (c) ×150,000.

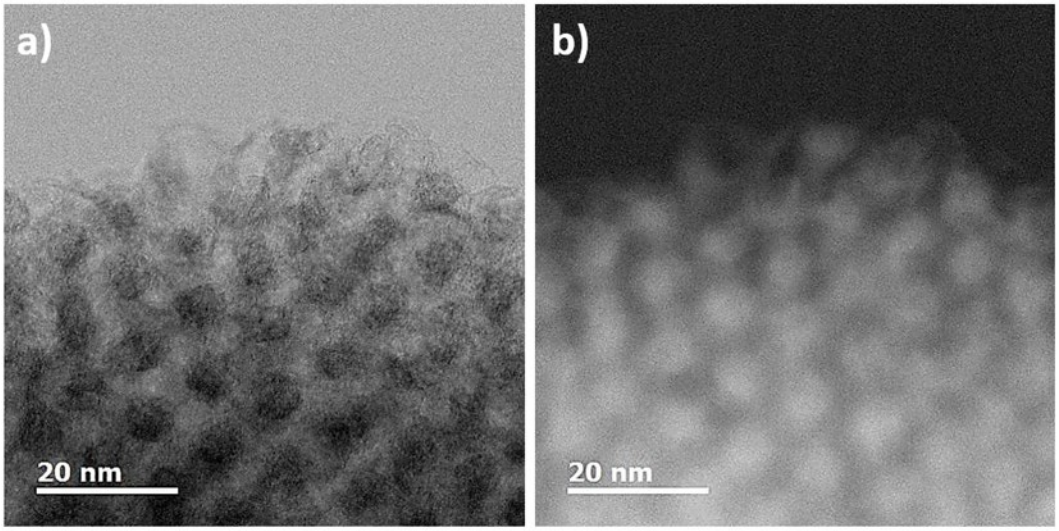

Fig. S2. (a) Bright field TEM image and (b) dark-field STEM image of CMK-3.

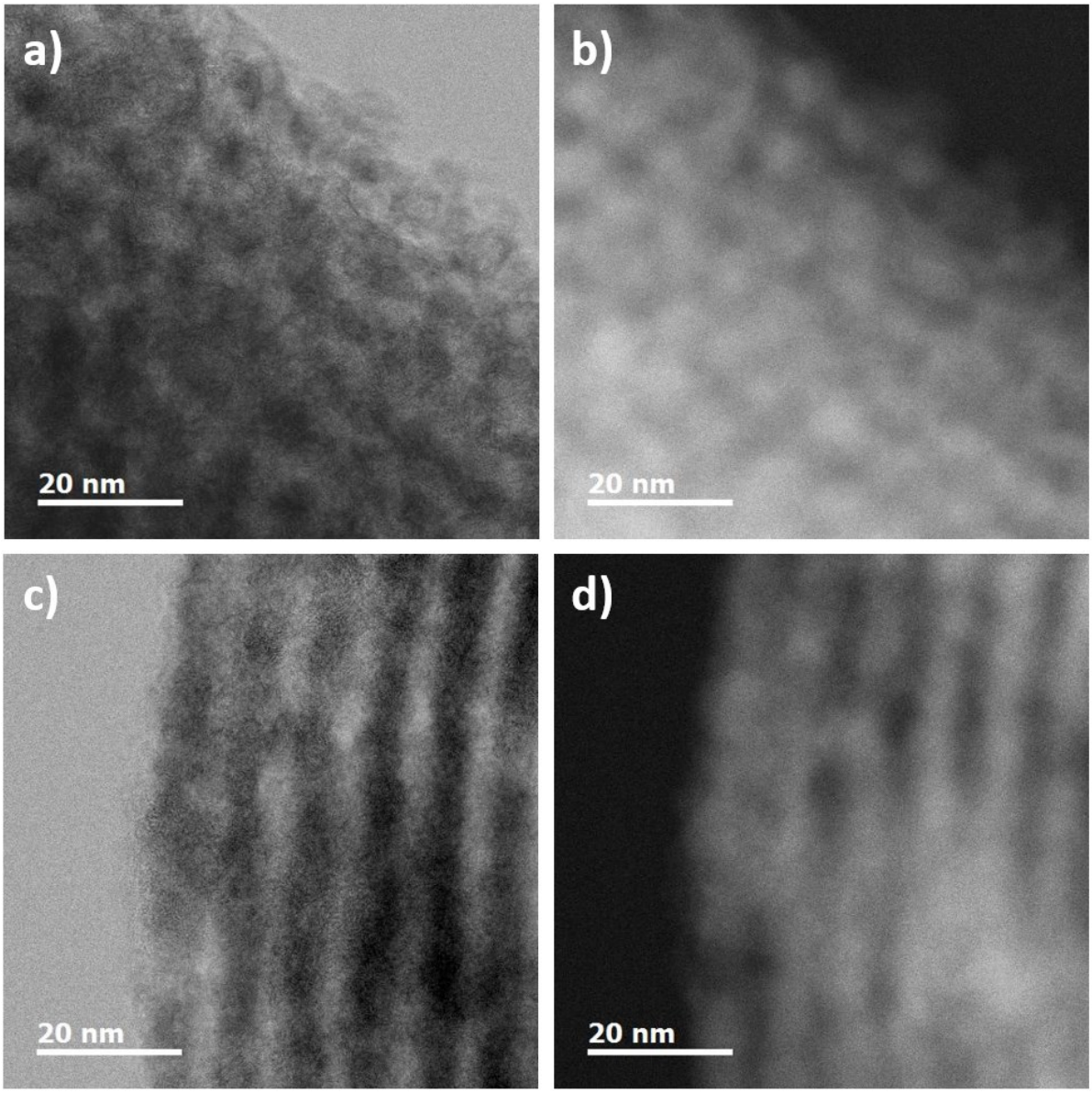

Fig. S3. **(**a and c) Bright field TEM images (b and d) dark field STEM images of CMK-FeTPP obtained in different directions.

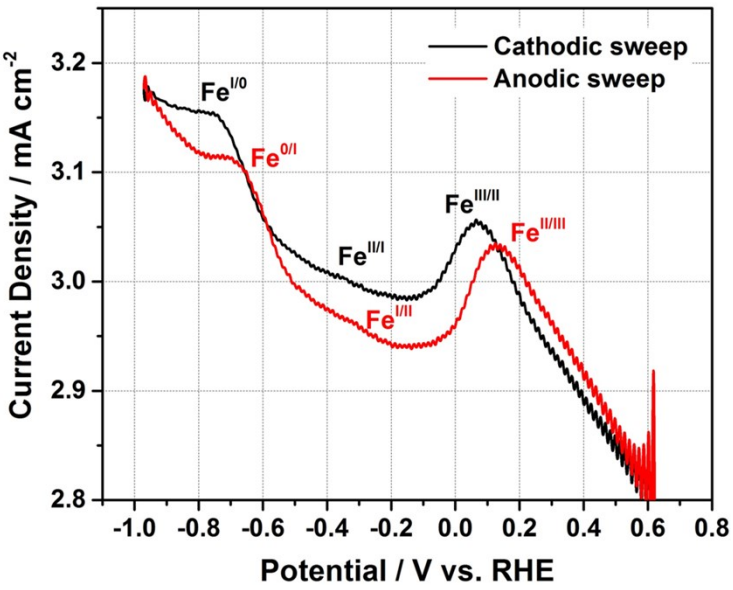

Fig. S4. FTACV to determine the redox potentials of Fe(III) in CMK-FeTPP in argon-saturated 0.1 M KCl.

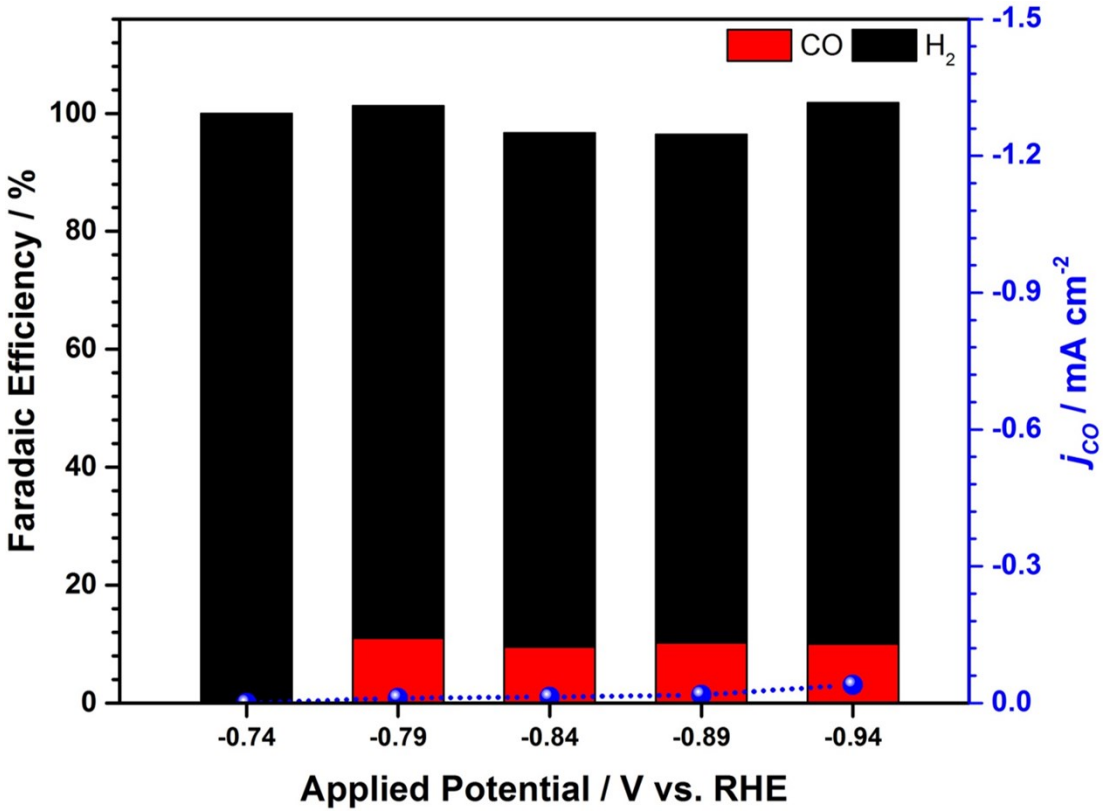

Fig. S5. FEs of an FeTPP-deposited electrode for CO (red) and H_2 (black) and partial current density for CO production (blue).

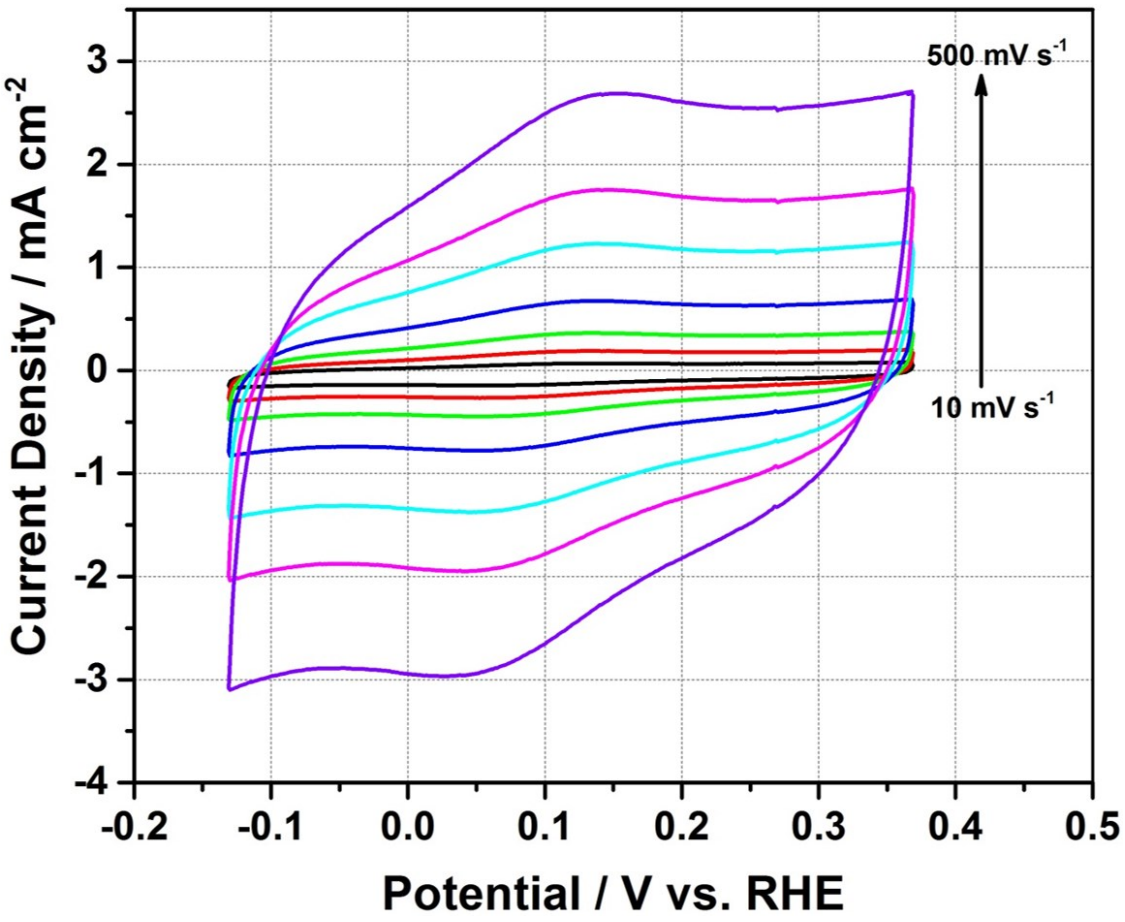

Fig. S6. Fe(III)/Fe(II) cyclic voltammograms at different scan rates in acidic electrolyte (pH 1) obtained by adding $HClO_4$ into 0.1 M KCl electrolyte.

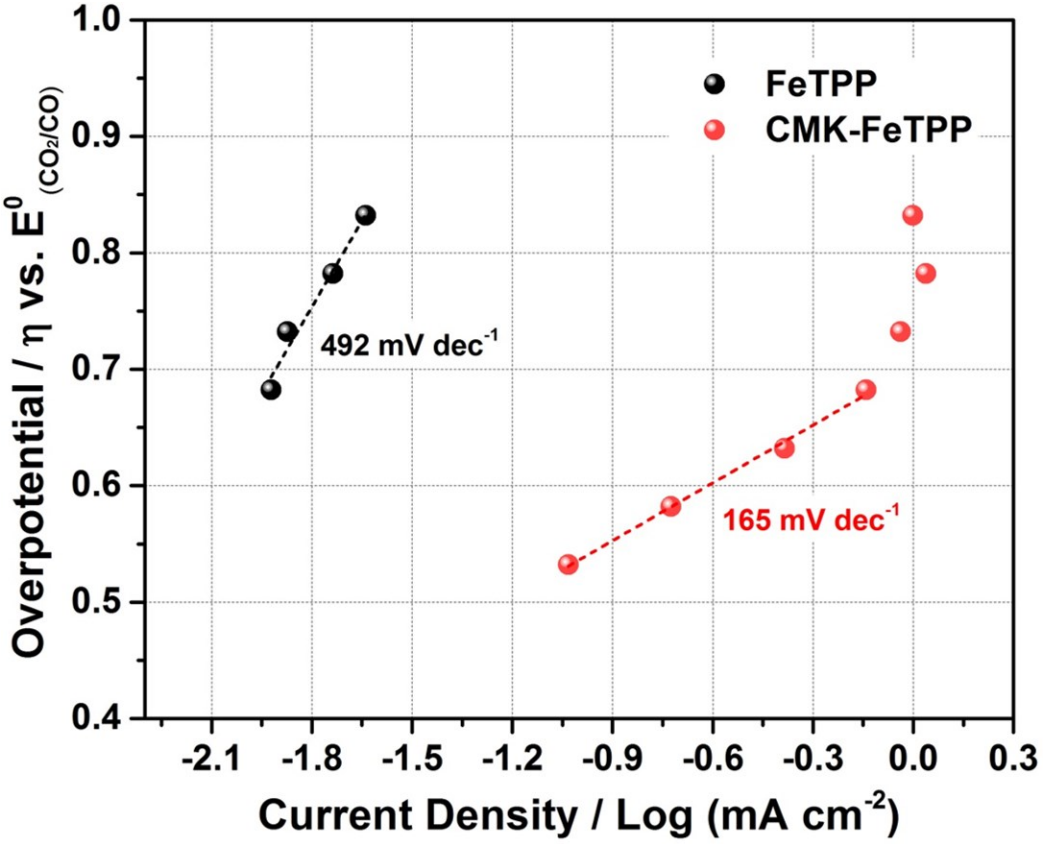

Fig. S7. Tafel analysis for CMK-FeTPP (red) and Fe(III) TPP (black).

Table S1. Comparison of catalytic activities of CMK-FeTPP prepared in this study with the state-of-the-art of immobilised porphyrin complex catalysts onto glassy carbon substrate for electrochemical CO_2 reduction.

#	Catalysts (Electrolysis V vs. RHE, pH)	Substrate	Active amount of molecule $\times 10^{-8}$ mol cm^{-2}	Current Density $mAcm^{-2}$	FE CO/H_2 %	eTOF s^{-1}	Reference
1	CMK-FeTPP (-0.79V, pH 4.2)	Glassy carbon plate	0.088	~ 0.72	92.1% / 9.1%	3.9	This work
2	CMK-FeTPP (-0.89V, pH 4.2)	Glassy carbon plate	0.088	~ 1.16	90.7% / 10.2%	6.2	This work
3	FePGF (-0.59V. pH 4.2)	Glassy carbon plate	0.13	~ 0.20	97.0% / 4.0%	0.8	[1]
4	CAT_{pyr}/MWCNT (-0.59V, pH 7.3)	Glassy carbon plate	2.4	~ 0.20	93% / 4%	0.04	[2]
5	CAT_{CO2H}/MWCNT (-0.62V, pH 7.3)	Glassy carbon plate	0.64	~ 0.16	80% / n.a.	0.1	[3]
6	CoTPP/SWCNT (-0.68V, pH 7.2)	Glassy carbon plate	17	~ 3.2	85% / 9%	0.08	[4]
7	FeTPP/SWCNT (-0.68V, pH 7.2)	Glassy carbon plate	17	~ 0.9	64% / 9%	0.08	[4]
8	Fe-PB/MWCNT (-0.63V, pH 7.3)	Glassy carbon plate	0.37	~ 0.49	100% / 0 %	1.5	[5]
9	Fe-PB/MWCNT (-0.78V, pH 7.3)	Glassy carbon plate	0.37	~ 1.5	95% / 5 %	4.5	[5]
10	FeTPP/MWCNT (-0.63V, pH 7.3)	Glassy carbon plate	0.25	~ 0.22	96% / 6%	1.0	[5]
11	FeTPP/MWCNT (-0.78V, pH 7.3)	Glassy carbon plate	0.25	~ 0.6	78% / 22%	2.5	[5]
12	D-P-CoPc/Ketjen black (-0.61V, pH 7.3)	Glassy carbon plate	11.1	~ 2.5	97 % / n.a.	0.1	[6]

Note S1. Calculation of eTOF for CMK-FeTPP at -0.79 V vs. RHE

The effective turnover frequency (eTOF) was calculated based on the amount of current from the chronoamperometric analysis and the amount of electrochemically active catalyst from the integration of the Fe(III)/Fe(II) redox wave in Fig. S6.

I : The current obtained by electrolysis at -0.79 V (0.00072 A cm^{-2} × 2 cm^2 = 0.00144 A)

FE : The CO faradaic efficiency obtained by electrolysis at -0.79 V (92.1 %)

F: Faraday constant (96485 C mol^{-1})

n: The amount of catalyst utilized for catalysis (8.8×10^{-10} mol cm^{-2} × 2 cm^2 = 1.76×10^{-9} mol)

$$eTOF\ (s^{-1}) = \frac{0.00144A \cdot 0.921}{2 \cdot 96485\ C\ mol^{-1} \cdot 1.76 \times 10^{-9} mol} = 3.9\ s^{-1}$$

References

1. J. Choi, P. Wagner, R. Jalili, J. Kim, D. R. MacFarlane, G. G. Wallace and D. L. Officer, *Adv. Energy Mater.*, 2018, **8**, 1801280.
2. A. Maurin and M. Robert, *J. Am. Chem. Soc.*, 2016, **138**, 2492-2495.
3. A. Maurin and M. Robert, *Chem. Commun.*, 2016, **52**, 12084-12087.
4. X. M. Hu, M. H. Rønne, S. U. Pedersen, T. Skrydstrup and K. Daasbjerg, *Angew. Chem., Int. Ed.*, 2017, **56**, 6468-6472.
5. P. T. Smith, B. P. Benke, Z. Cao, Y. Kim, E. M. Nichols, K. Kim and C. J. Chang, *Angew. Chem., Int. Ed.*, 2018, **57**, 9684-9688.
6. H. Wu, M. Zeng, X. Zhu, C. Tian, B. Mei, Y. Song, X. L. Du, Z. Jiang, L. He and C. Xia, *ChemElectroChem*, 2018, **5**, 2717-2721.