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Supplementary Materials for

Anion exchange-induced single-molecule dispersion of cobalt porphyrins in a cationic porous organic polymer for enhanced electrochemical CO_2 reduction via secondary-coordination sphere interactions

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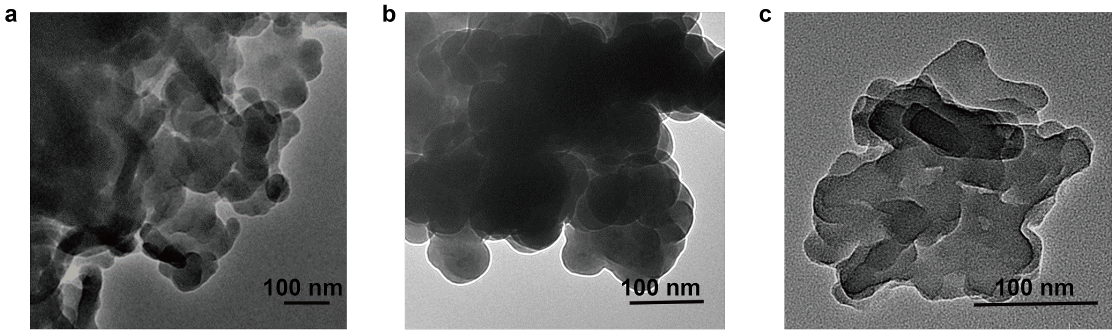

Figure S1 TEM images of POP-Py(0) (a), POP-Py(1) (b) and POP-Py(2) (c). The relatively small size of POP-Py(2) is possibly due to the low degree of polymeration caused by the low solubility of Di(4-pyridyl)biphenyl in NMP solution.

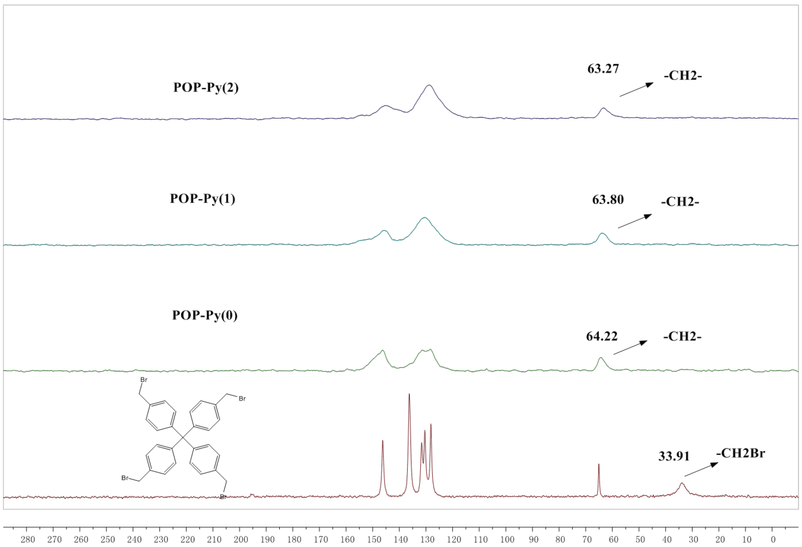

Figure S2 CP/MAS ^{13}C NMR spectrum of TBM, POP-Py(0), POP-Py(1) and POP-Py(2).

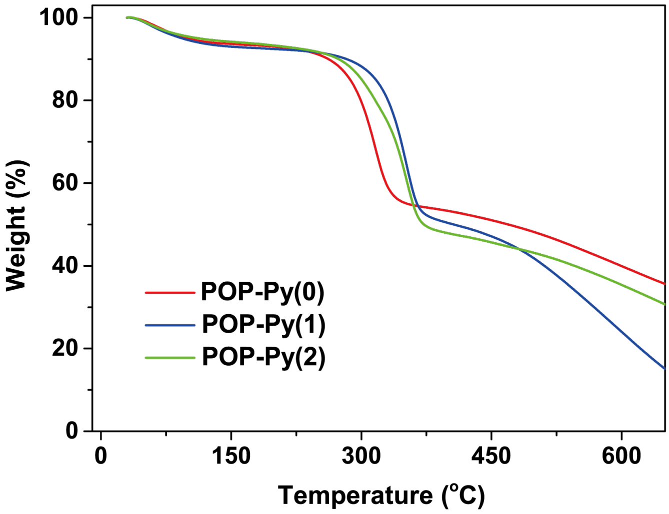

Figure S3 TGA profile of POP-Py(0) , POP-Py(1) and POP-Py(2) under N_2 atmosphere.

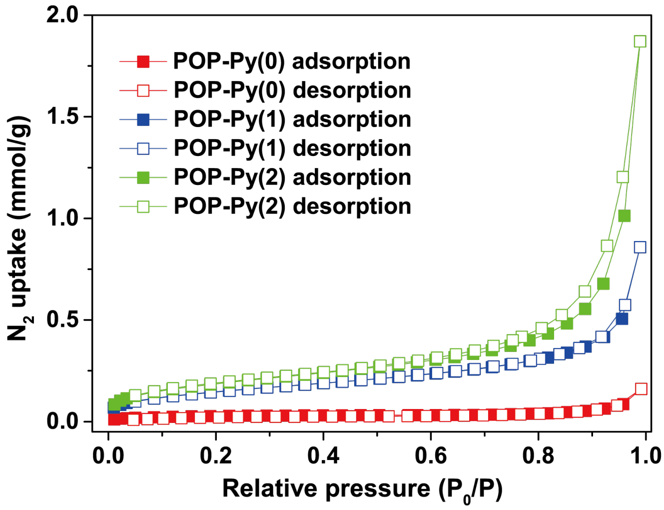

Figure S4 Nitrogen adsorption/desorption isotherms of POP-Py(0), POP-Py(1) and POP-Py(2) at 77 K.

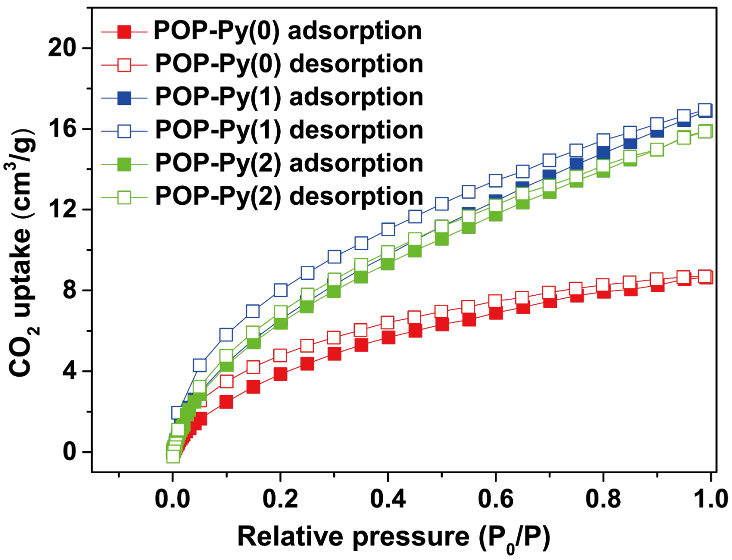

Figure S5 CO_2 adsorption/desorption isotherms of POP-Py(0), POP-Py(1) and POP-Py(2) at 298 K.

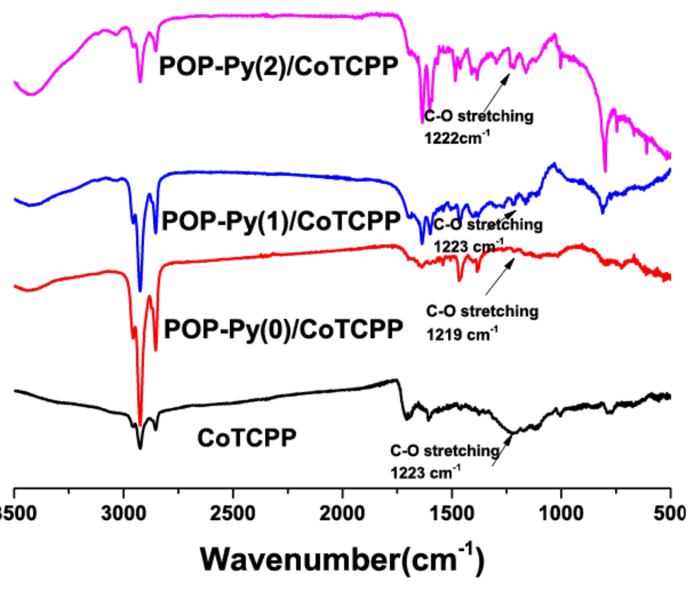

Figure S6 FT-IR spectra of CoTCPP, POP-Py(0)/CoTCPP, POP-Py(1)/CoTCPP and POP-Py(2)/CoTCPP.

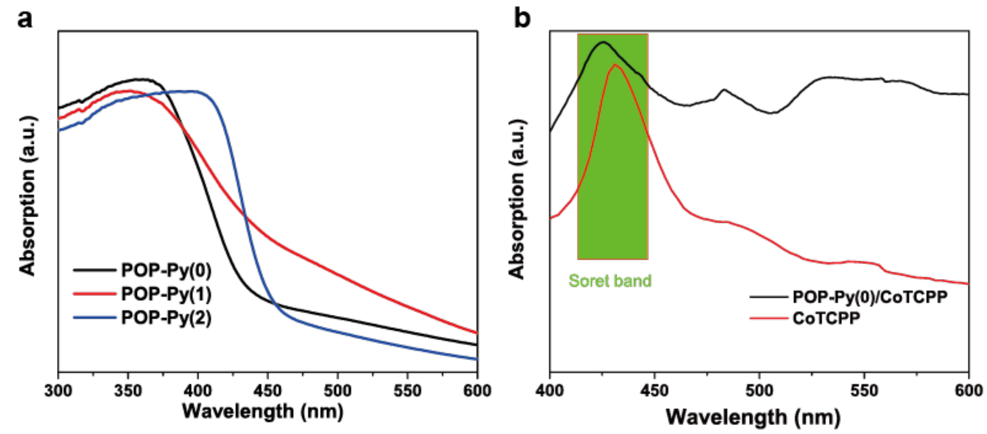

Figure S7 UV-vis spectra of (a) POP-Py(n); (b) CoTCPP and POP-Py(0)/CoTCPP.

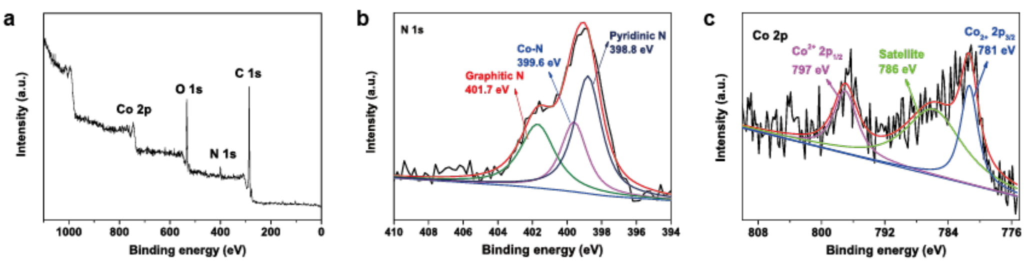

Figure S8 XPS survey (a), high-resolution N 1s (b) and Co 2p (c) spectra of POP-Py(0)/CoTCPP.

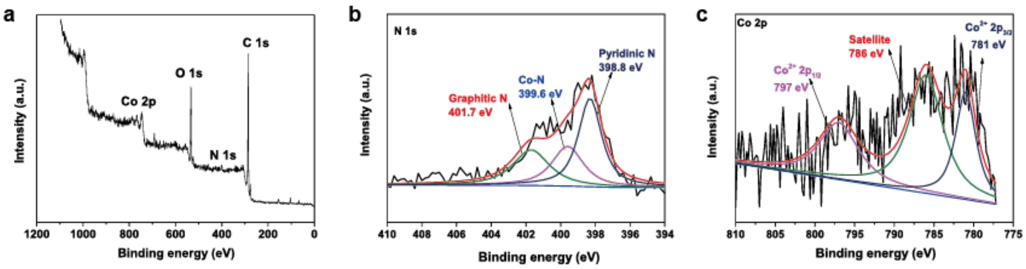

Figure S9 XPS survey (a), high-resolution N 1s (b) and Co 2p (c) spectra of POP-Py(1)/CoTCPP.

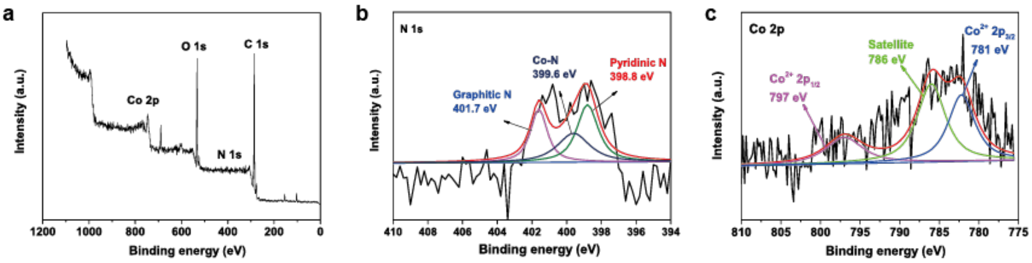

Figure S10 XPS survey (a), high-resolution N 1s (b) and Co 2p (c) spectra of POP-Py(2)/CoTCPP.

Table S1 Anion exchange efficiencies quantified by XPS

	POP-Py(0)/CoTCPP	**POP-Py(1)/CoTCPP**	**POP-Py(2)/CoTCPP**
Bromide/porphyrin ratio after exchange	0.39	0.58	0.40
Exchange efficiency $n_{Br\ exchange}/n_{Br\ total}$	84%	78%	83%

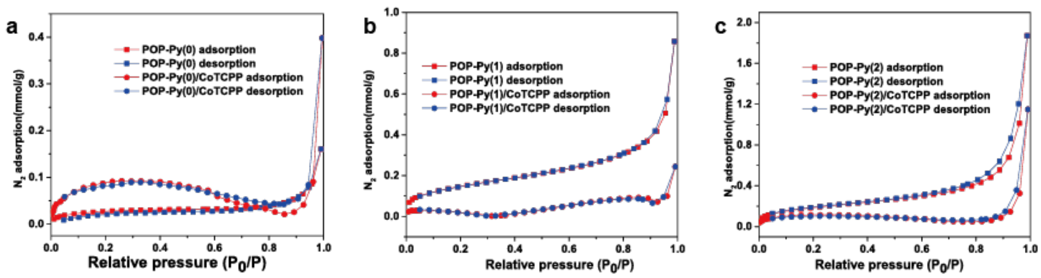

Figure S11 Nitrogen adsorption/desorption isotherms of (a) POP-Py(0) and POP-Py(0)/CoTCPP; (b) POP-Py(1) and POP-Py(1)/CoTCPP; (c)POP-Py(2) and POP-Py(2)/CoTCPP at 77 K.

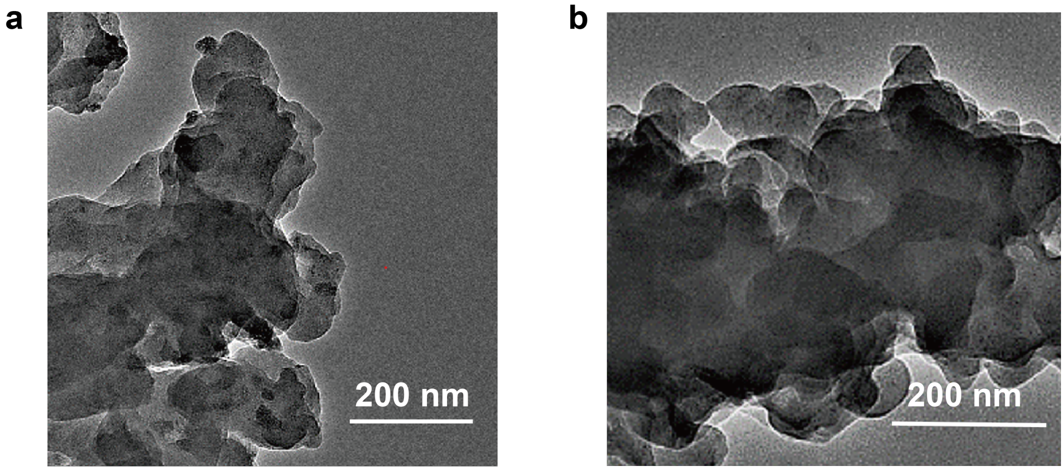

Figure S12 TEM images of POP-Py(1) (a) and POP-Py(2) (b).

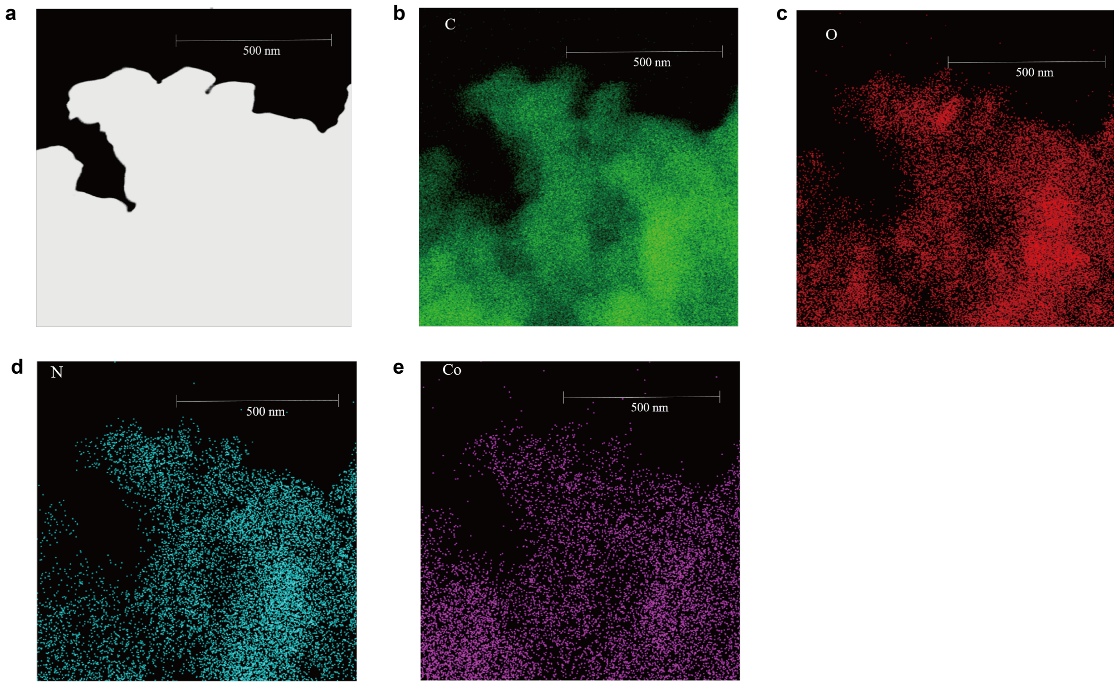

Figure S13 STEM image (a) of POP-Py(1)/CoTCPP and the EDX elemental mapping of C (b), O (c), N (d) and Co (e).

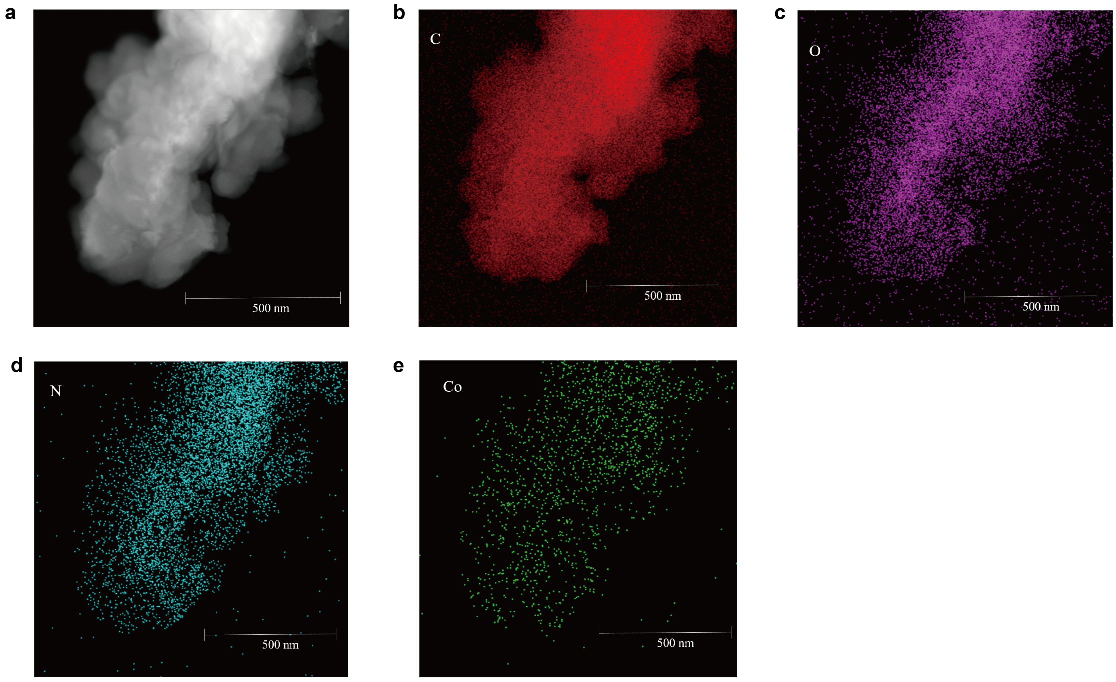

Figure S14 STEM image (a) of POP-Py(2)/CoTCPP and the EDX elemental mapping of C (b), O (c), N (d) and Co (e).

Table S2 Contents of CoTCPP in the hybrid catalysts determined by ICP-AES

Initial CoTCPP/carbon weight ratio before mixing	Mass percentage of Co in the hybrid (%)	Mass percentage of CoTCPP in the hybrid (%)	Co Catalyst loading drop-casted in the paper (mol/cm^2)
CoTCPP/POP-Py(0) =1/1	0.279	4.2	$1.42*10^{-8}$
CoTCPP/POP-Py(1) =1/1	0.101	1.53	$5.14*10^{-9}$
CoTCPP/POP-Py(2) =1/1	0.154	2.33	$7.84*10^{-9}$
CNT/CoTCPP=10/1	0.615	9.30	$3.30*10^{-8}$

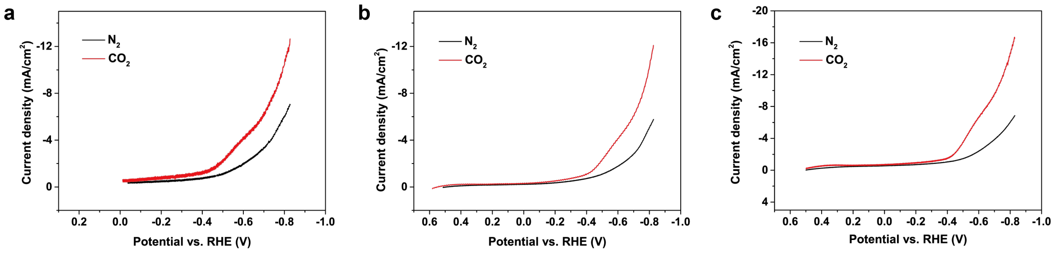

Figure S15 Linear sweep voltammetry of POP-Py(0)/CoTCPP(a), POP-Py(1)/CoTCPP (b) and POP-Py(2)/CoTCPP (c) in a 0.5 M $KHCO_3$ aqueous solution saturated with N_2 or CO_2.

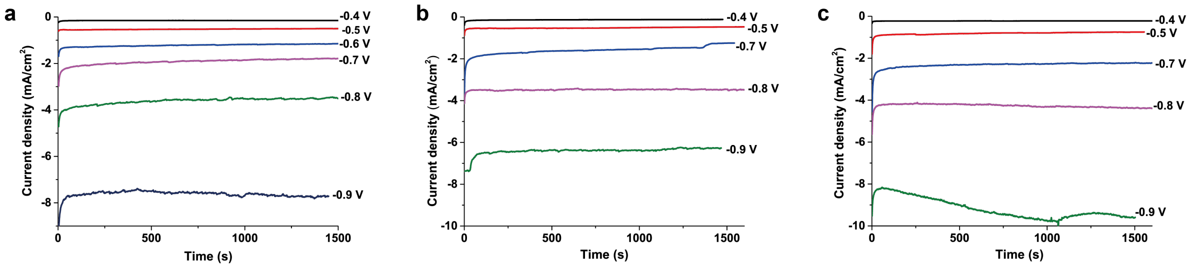

Figure S16 Representative chronoamperograms of CO_2 electroreduction catalyzed by POP-Py(0)/CoTCPP (a), POP-Py(1)/CoTCPP (b) and POP-Py(2)/CoTCPP (c) at various potentials in a 0.5 M $KHCO_3$ aqueous solution.

Table S3 Faradaic efficiencies and Operating durability comparison with different metal porphyrin(MPP) catalysts

Catalyst	Electrolyte	Applied potential (V vs. RHE)	I (mA/cm^2)	F.E. of CO (%)	TOF_{CO} (s^{-1})	Stability (hours)	Ref
POP-Py(0)/CoTCPP	0.5 M $KHCO_3$	-0.6	~1.1	83	1.4	7	This work
$Al_2(OH)_2$TCPP-Co	0.5 M $KHCO_3$	-0.7	~1	76	0.06	7	S1
CoTPP-cov	0.5 M $KHCO_3$	-0.63	1.5	67	8.3	4	S2
CoTPP-noncov	0.5 M $KHCO_3$	-0.63	1	52	4.4	4	S2
CoTPP/CNT	0.5 M $KHCO_3$	-0.70	~3	~70	2.75	4	S3
CoP@NrGO	0.5 M $NaHCO_3$	-0.70	~2.3	80	N.A.	0.5	S4
CoPP@CNT	0.5 M $NaHCO_3$	-0.60	25.1	>90	1.37	12	S5
COF-367-Co	0.5 M $KHCO_3$	-0.67	3.3	91	0.53	24	S6
COF-366-F-Co	0.5 M $KHCO_3$	-0.67	N.A.	87	N.A.	N.A.	S7
CATpyr	0.5 M $KHCO_3$	-0.59	0.24	93	0.04	3	S8

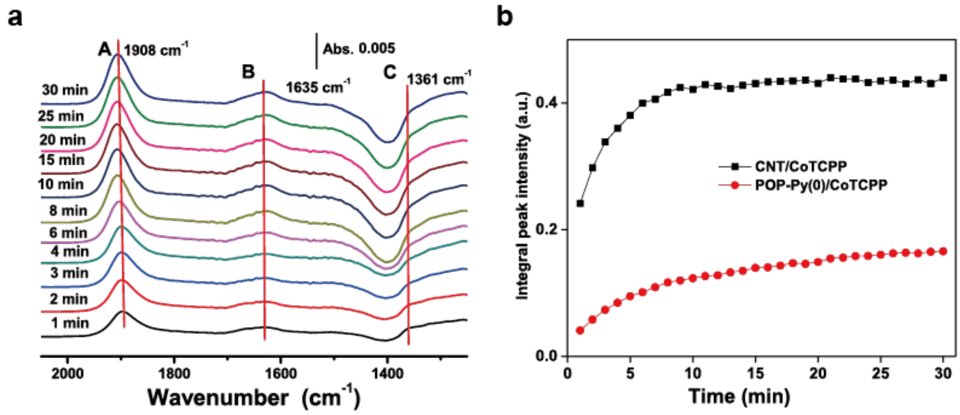

Figure S17 (a) *In-situ* ATR-SEIRAS spectra recorded with time after stepping CNT/CoTCPP to -0.6 V *vs.* RHE in a CO_2-saturated 0.5 M $KHCO_3$ aqueous solution. Reference spectrum was taken at an open circuit potential. (b) Integral intensities of peak A in the *in-situ* ATR-SEIRAS spectra of CNT/CoTCPP and POP-Py(0)/CoTCPP recorded with time at -0.6 V *vs.* RHE in a CO_2-saturated 0.5 M $KHCO_3$ aqueous solution.

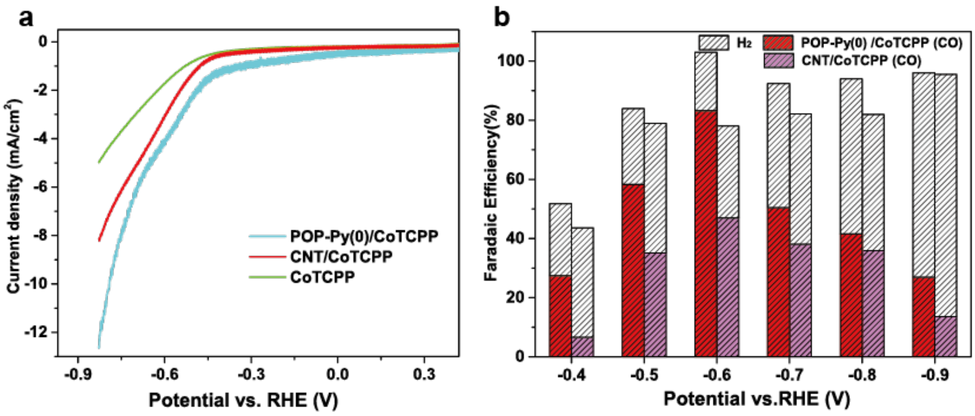

Figure S18 (a) Linear sweep voltammetry of POP-Py(0)/CoTCPP, CNT/CoTCPP and CoTCPP. (b) Faradaic efficiencies for CO and H_2 production on CNT/CoTCPP and POP-Py(0)/CoTCPP across the potential range from -0.4 to -0.9 V *vs.* RHE.

Table S4 Band assignments in Figure 5 and Figure S17a

Wavenumber (cm^{-1})				Assignment
POP-Py(0)/CoTCPP	POP-Py(1)/CoTCPP	POP-Py(2)/CoTCPP	CNT/CoTCPP	
1357	1354	1357	1361	ν(C-O) stretching of *COOH
1643	1654	1653	1635	ν(C=O) stretching of *COOH
1912-1842	1922-1859	1910-1879	1908	ν(C-O) stretching of *CO(ad)

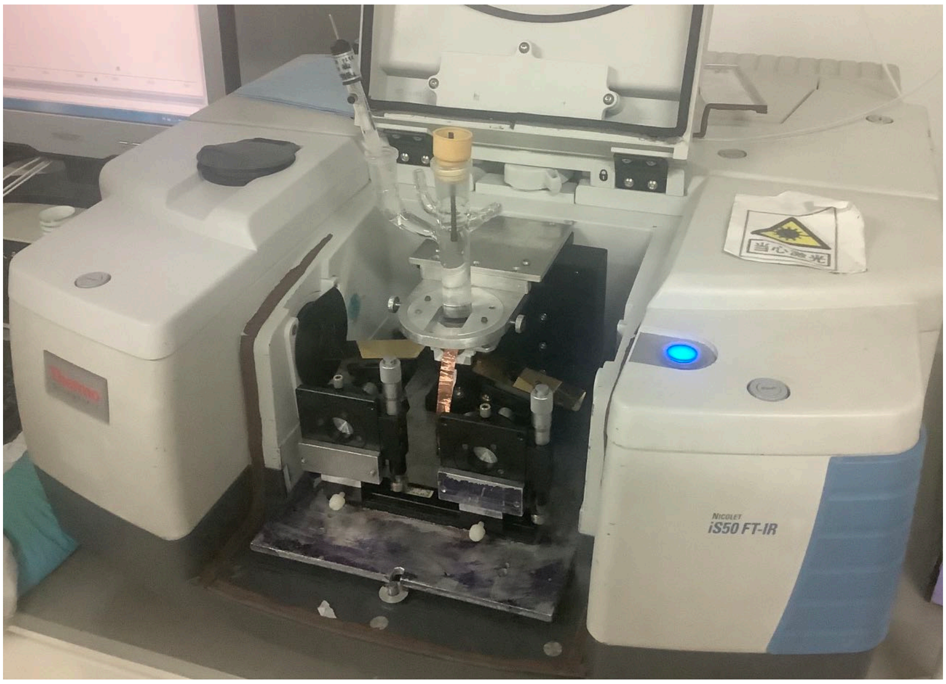

Figure S19 Cell configuration of *in-situ* SEIRAS measurements.

Reference

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