

Electronic Supplementary Information

Second-Sphere Hydrogen-Bonding Enhances Heterogenous Electrocatalytic CO₂ to CO Reduction by Iron Porphyrin in water

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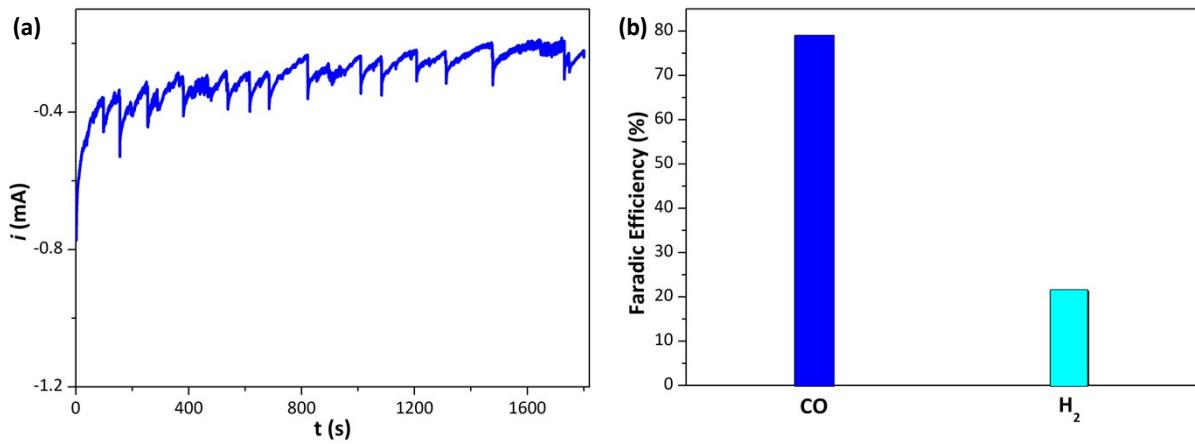


Figure S1. Controlled potential electrolysis using **CNT-UrFe** on GCEs (diameter 3 mm) at -0.88 V vs. RHE in CO₂-saturated 0.1 M NaHCO₃ aqueous solution. a) i vs. t , b) FE of CO (purple column) and FE of H₂ (green column) after 30 minutes electrolysis.

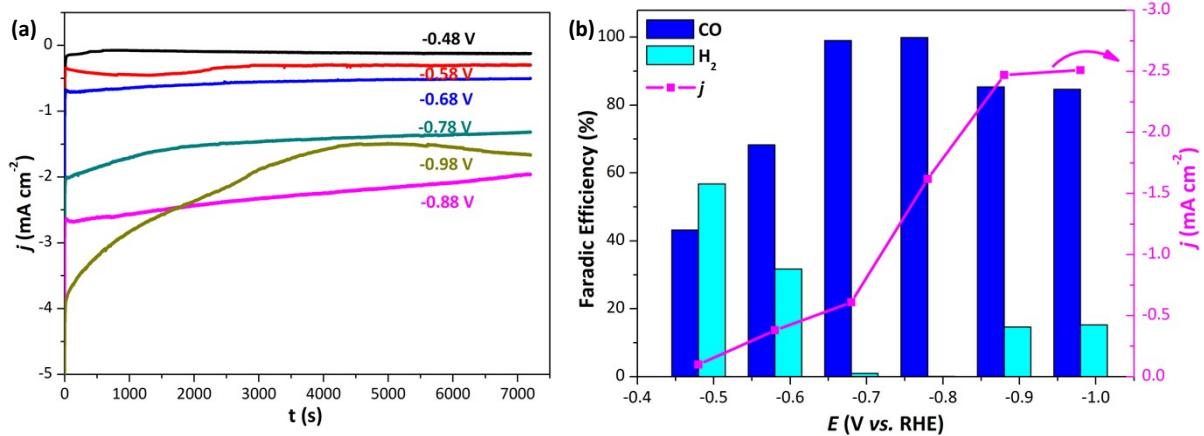


Figure S2. Controlled potential electrolysis using **CNT-UrFe** on carbon paper in CO₂-saturated 0.1 M NaHCO₃ aqueous solutions at various potentials (-0.48 V to -0.98 V vs. RHE).

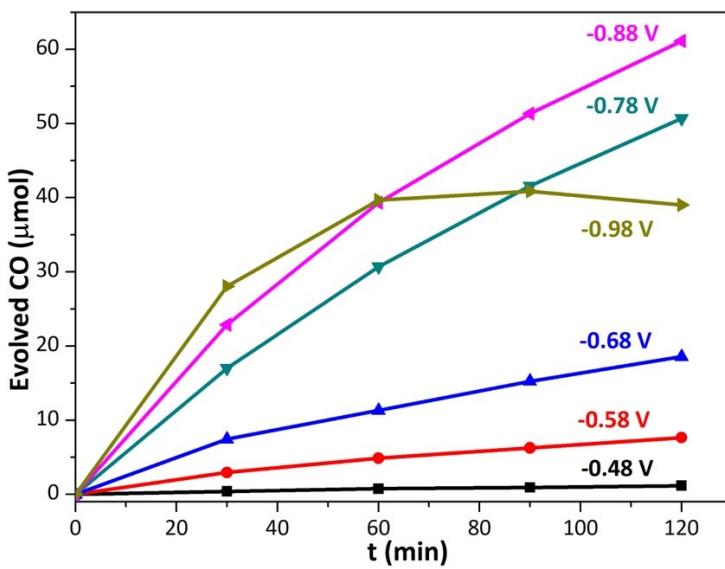


Figure S3. The evolved CO during the controlled potential electrolysis of **CNT-UrFe** on carbon paper in CO₂-saturated 0.1 M NaHCO₃ aqueous solutions at various potentials (-0.48 V to -0.98 V vs. RHE).

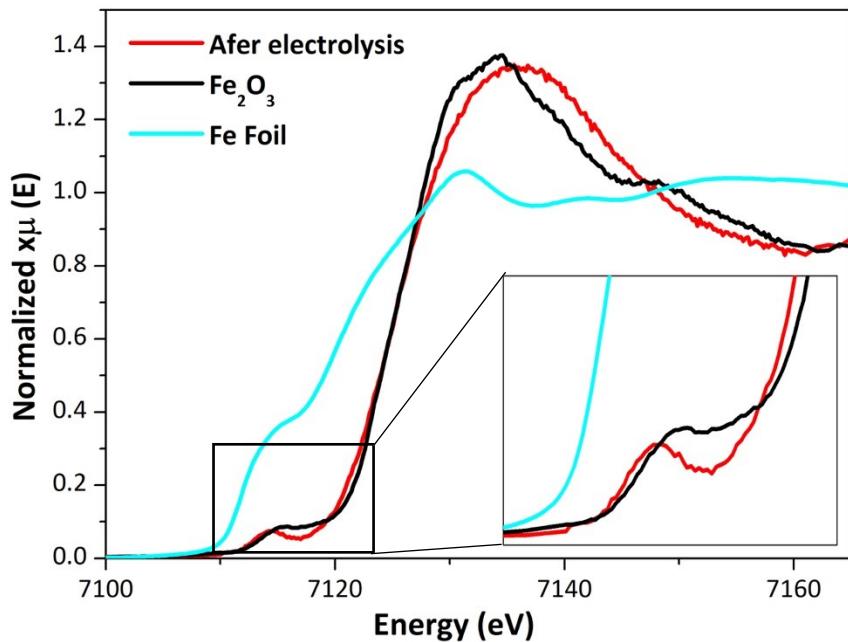


Figure S4. Fe K-edge XANES spectra of CNT-UrFe/CP after electrolysis (red) and the reference compounds: Fe₂O₃(black) and metallic Fe (cyan).

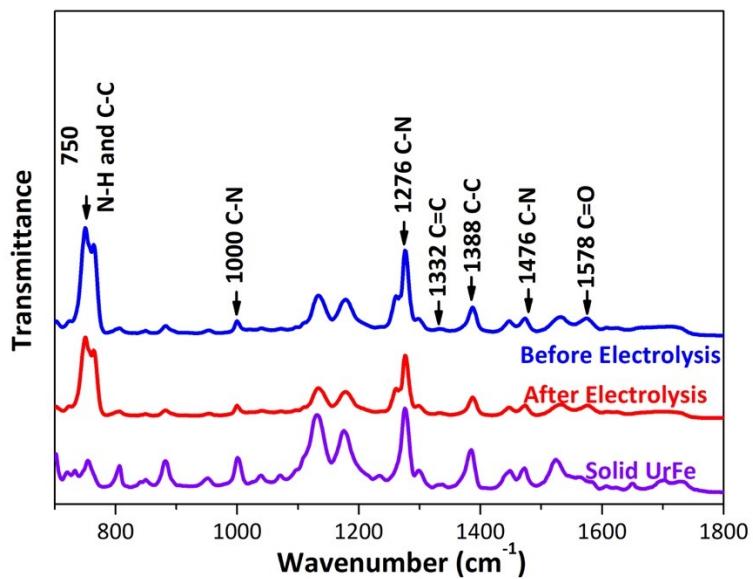


Figure S5. ATR-FTIR spectra of **CNT-UrFe** before (bleu), after (red) 2 hours electrolysis and **UrFe** film (purple).

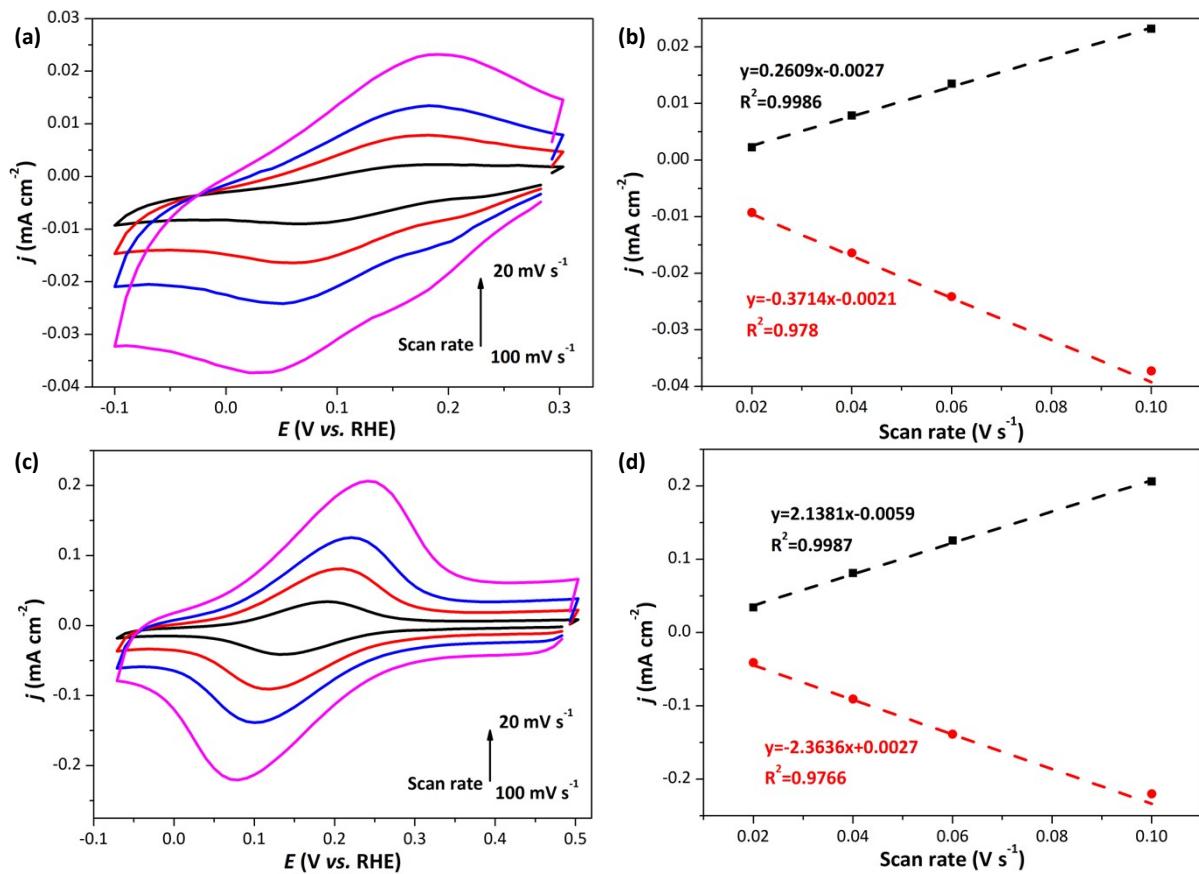


Figure S6. a) CVs of **CNT-UrFe** at various scan rate of $\text{Fe}^{\text{III}}/\text{II}$ wave b) current density vs. scan rate, c) CVs of **CNT-FeTPP** at various scan rate at $\text{Fe}^{\text{III}}/\text{II}$ wave, d) current density vs. scan rate under Ar in acidic electrolyte (pH 1) obtained by adding HClO_4 to an 0.1 M KCl aqueous solution, $i_p = n^2 F^2 \nu S \Gamma / 4RT$.

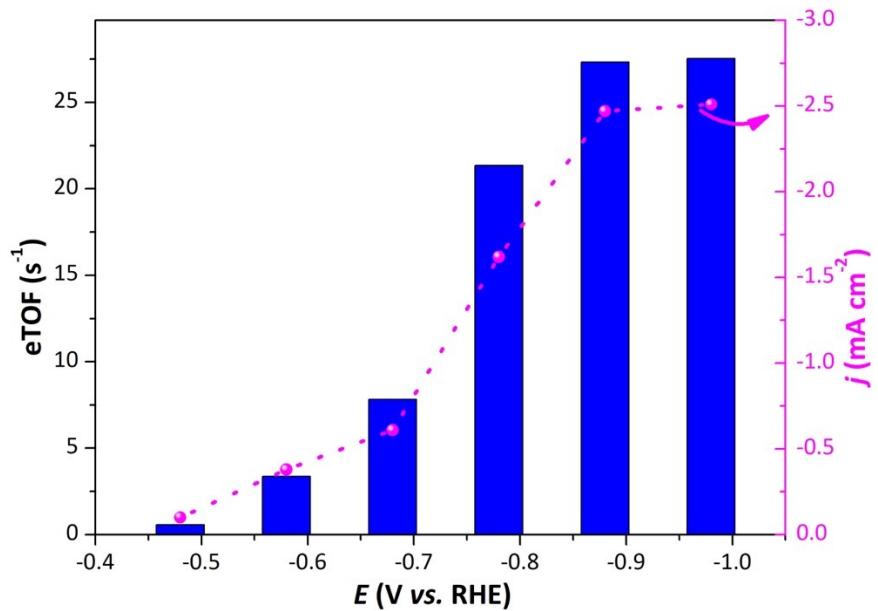


Figure S7. eTOF and the average current densities displayed by CNT-UrFe vs. potential, calculated after 1 hour electrolysis at different applied potentials.

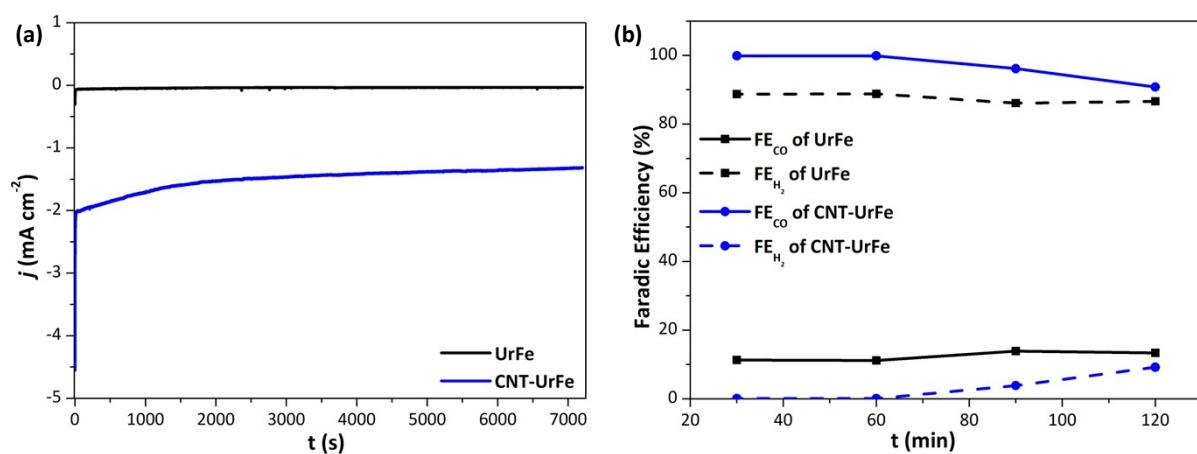


Figure S8. Bulk electrolysis using CNT-UrFe (blue) and the physically absorbed UrFe (black) on carbon paper in 0.1 M NaHCO₃ aqueous solutions at -0.78 V vs. RHE, a) j vs. t , b) FE of CO and H₂ vs. t .

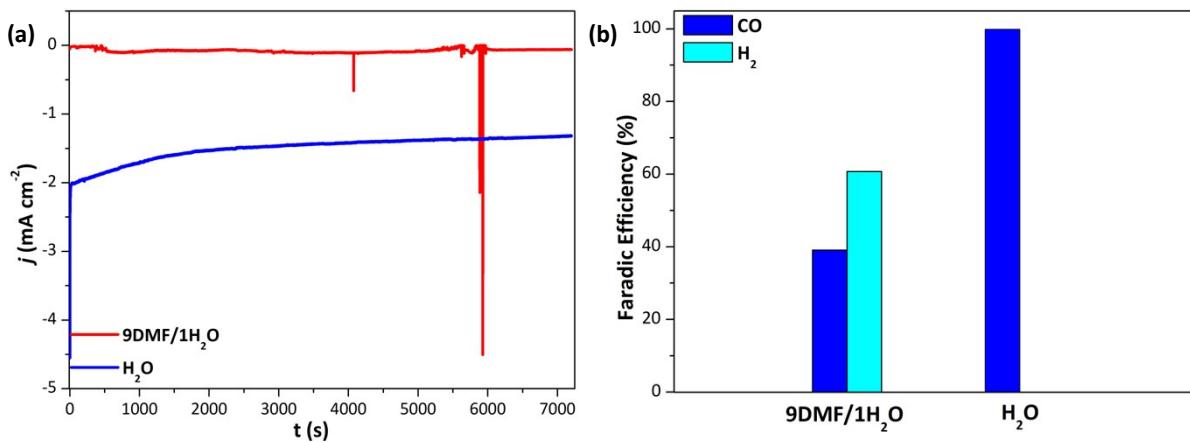


Figure S9. Bulk electrolysis using **CNT-UrFe** in 0.1 M NaHCO₃ aqueous solution (blue) or 0.1 M NBu₄PF₆ (9DMF/1H₂O, red) electrolyte at -0.78 V vs. RHE, a) j vs. t , b) FE of CO and H₂ after 1 hour electrolysis.

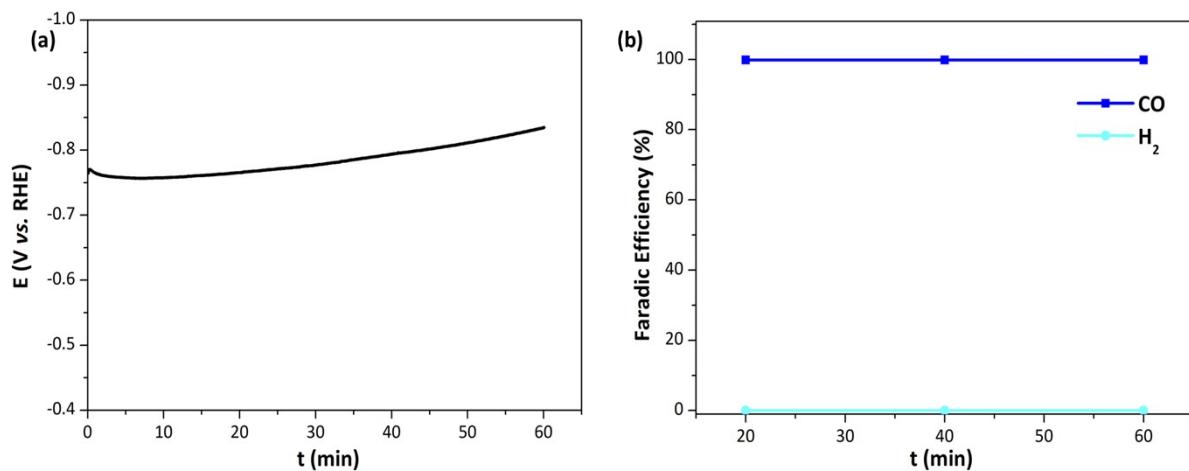


Figure S10. E vs. t (a) and FE vs. t (b) during a controlled current electrolysis at -1.8 mA cm⁻² using a 1 cm² **CNT-UrFe** modified electrode in CO₂-saturated 0.1 M NaHCO₃ aqueous solution for 1 hour.

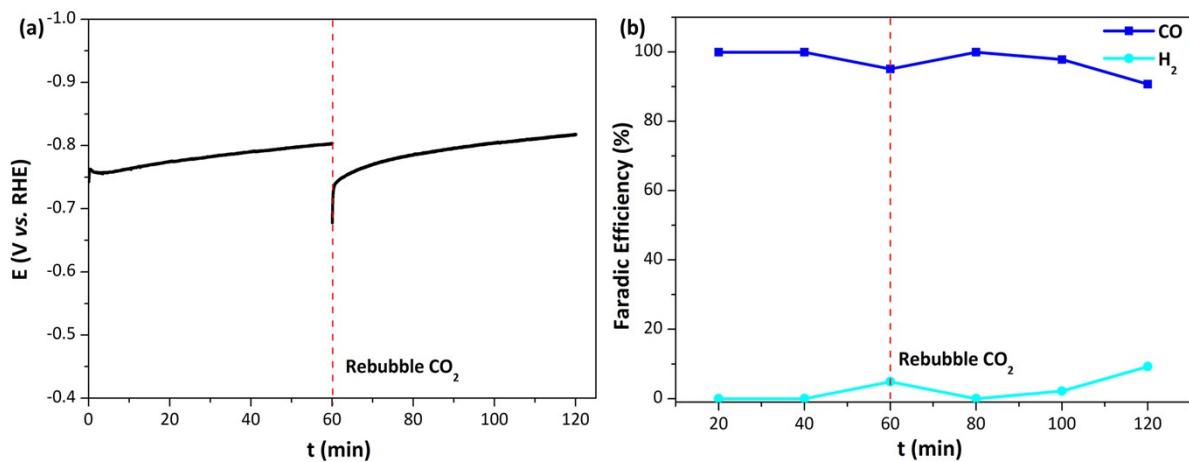


Figure S11. E vs. t (a) and FE vs. t (b) during a controlled current electrolysis at -1.8 mA cm^{-2} using a 2 cm^2 **CNT-UrFe** modified electrode in CO_2 -saturated 0.1 M NaHCO_3 aqueous solution for 2 hours. The red dash line corresponds to CO_2 rebulbing in the electrolyte after 1 hour.

Table S1. Product analysis by GC after 1 hour controlled potential electrolysis using **CNT-UrFe** for CO_2 reduction.

Catalyst	E (V vs. RHE)	j (mA cm ⁻²)	FE CO (%)	FE H ₂ (%)	eTOF (s ⁻¹)
CNT	-0.78 ^a	-0.08	0	100.0	-
CNT-FeTPP	-0.78 ^a	-0.41	67.2	32.8	0.9
	-0.48 ^a	-0.10	43.2	56.8	0.6
	-0.58 ^a	-0.38	68.3	31.7	3.4
	-0.68 ^a	-0.57	99.0	1.0	7.8
CNT-UrFe	-0.78 ^a	-1.50	99.9	0.1	21.3
	-0.88 ^a	-2.30	85.4	14.6	27.3
	-0.98 ^a	-2.04	84.7	15.3	27.5
	-0.78 ^b	-0.08	39.2	60.8	-

^a CO_2 -saturated 0.1 M NaHCO_3 aqueous solution

^b CO_2 -saturated $0.1 \text{ M NBu}_4\text{PF}_6$ (DMF/H₂O, 9:1)