SUPPORTING INFORMATION

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Unraveling the Dynamic Structural Evolution of Phthalocyanine Catalysts during CO_2 Electroreduction

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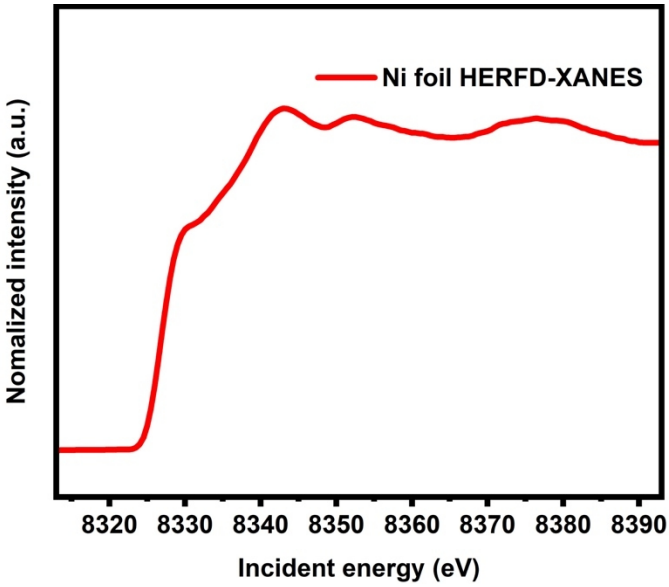

Figure S1. The Ni HERFD-XANES spectrum obtained by integrating the RIXS spectra.

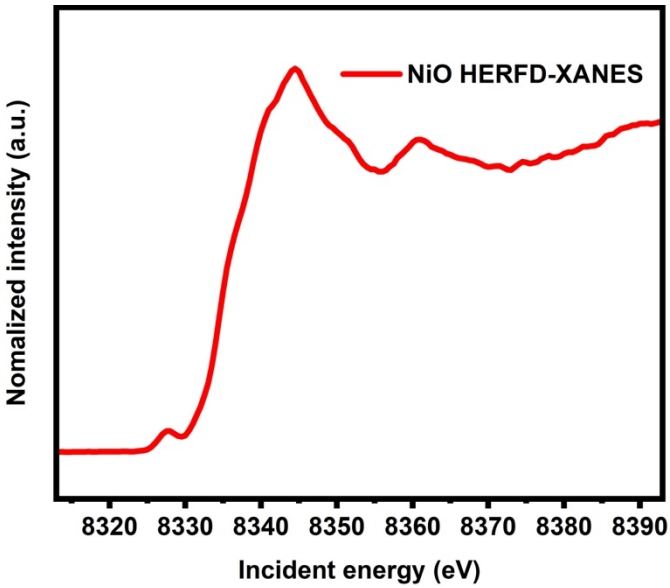

Figure S2. The NiO HERFD-XANES spectrum obtained by integrating the RIXS spectra.

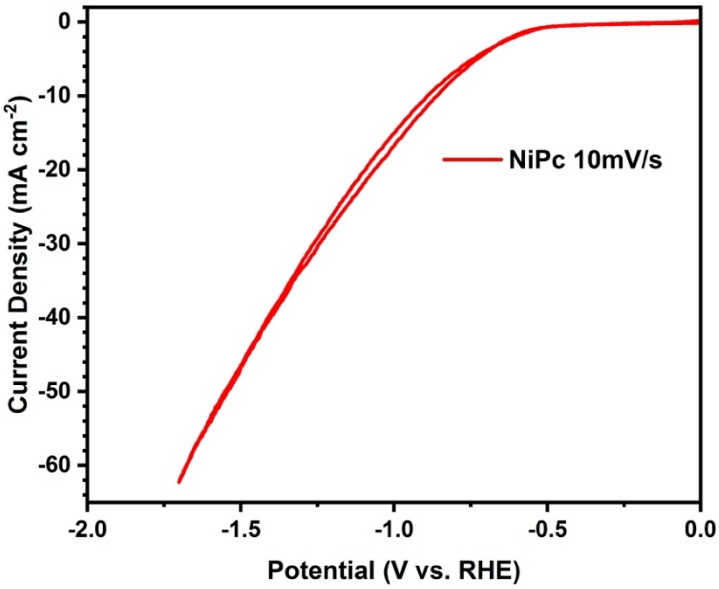

Figure S3. Cyclic voltammetry curves of NiPc at a scan rate of 10 mV s^{-1} in CO_2 saturated 0.1 M $KHCO_3$ aqueous solution.

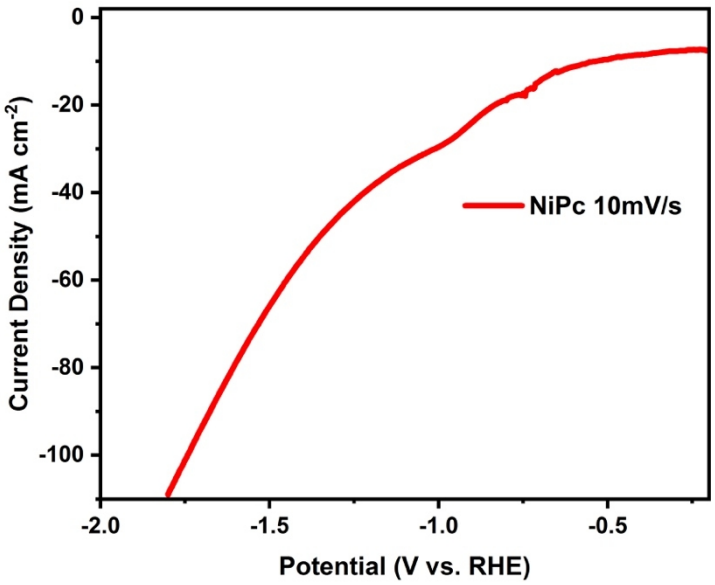

Figure S4. Linear sweep voltammetry curves of NiPc at a scan rate of 10 mV s^{-1} in CO_2 saturated 0.1 M $KHCO_3$ aqueous solution.

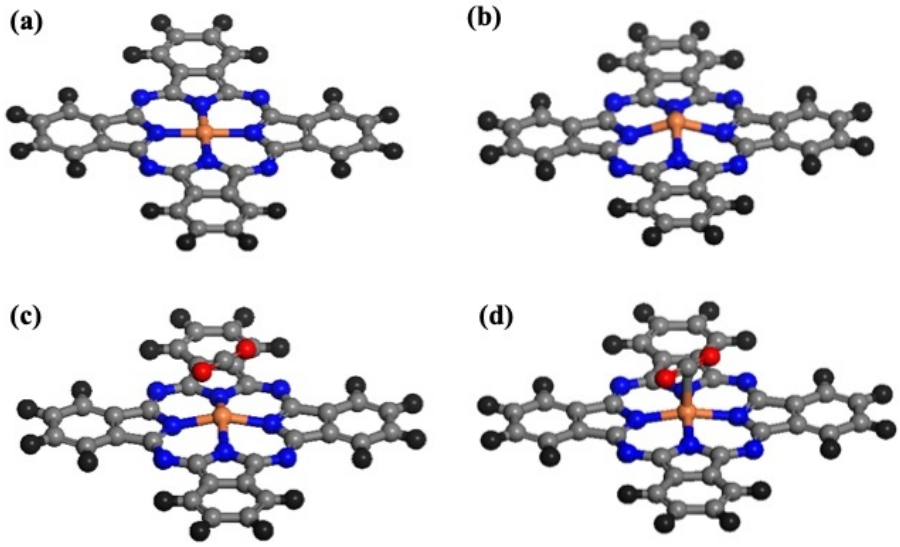

Figure S5. The schemes show the corresponding calculation model for the XANES simulation (Ni (orange), N (blue), C (gray), O (red) and H (black)).

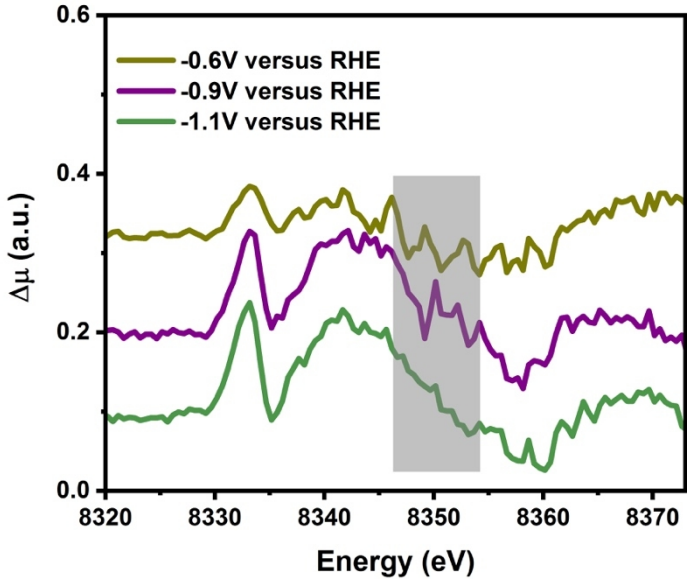

Figure S6. *Operando* Ni K-edge Δμ spectra of NiPc at various potentials vs. RHE by subtracting the wet HERFD-XANES spectrum.

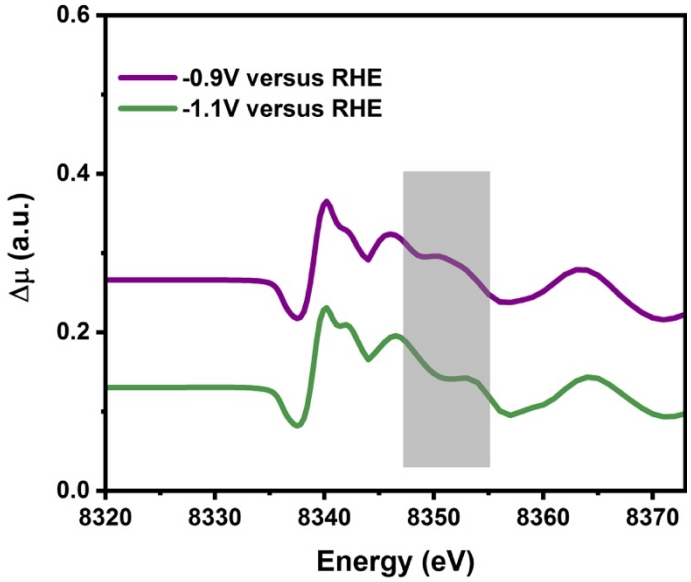

Figure S7. Theoretical Ni K-edge Δμ spectra of NiPc at various potentials vs. RHE by subtracting the wet HERFD-XANES spectrum.

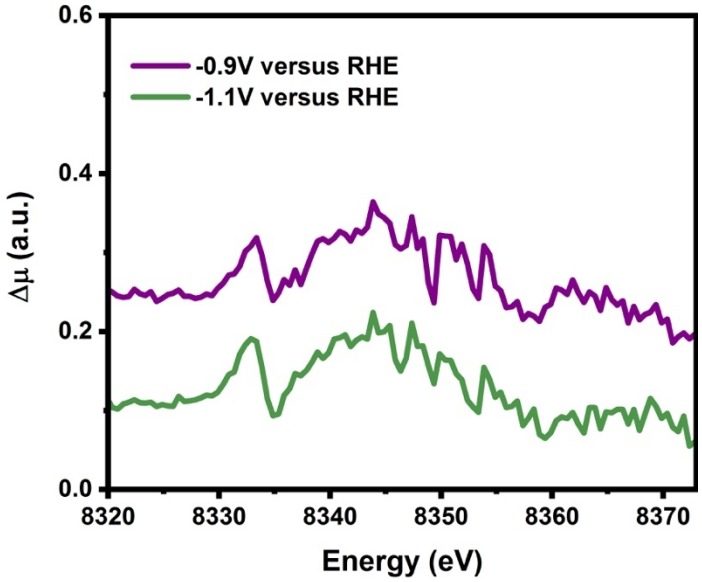

Figure S8. *Operando* Ni K-edge Δμ spectra of NiPc at various potentials vs. RHE by subtracting the HERFD-XANES spectrum at the 0.6V versus RHE.

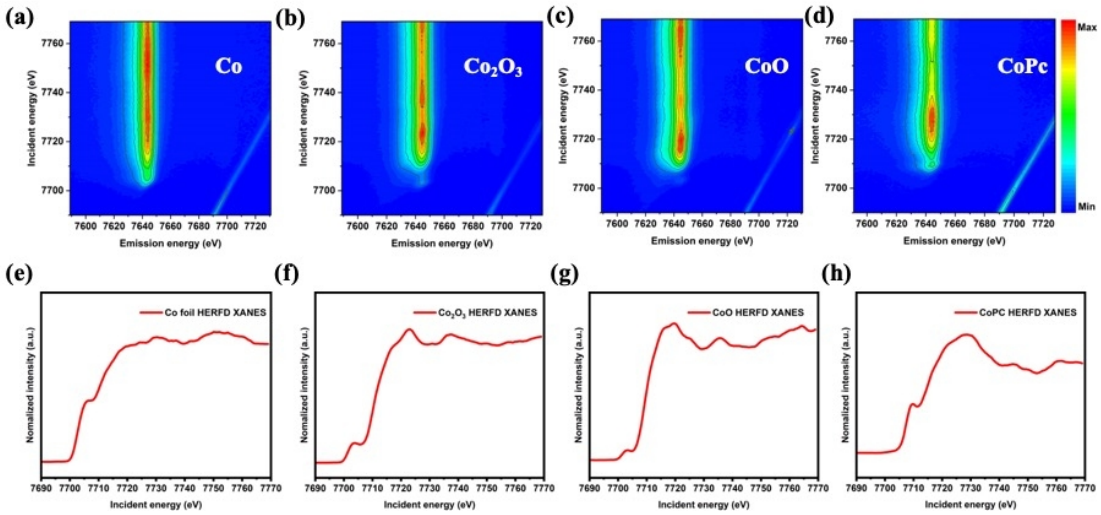

Figure S9. (a) K$\beta_{1,3}$-RIXS plane of Co foil. The contour plane at the emission energy of ~7644 eV is the K$\beta_{1,3}$-RIXS plane. (b) K$\beta_{1,3}$-RIXS plane of Co_2O_3. (c) K$\beta_{1,3}$-RIXS plane of CoO. (d) K$\beta_{1,3}$-RIXS plane of CoO. (e-f) HERFD-XANES spectra of Co foil, Co_2O_3, CoO and CoPc. The HERFD-XANES spectrum was obtained by integrating the RIXS intensity.

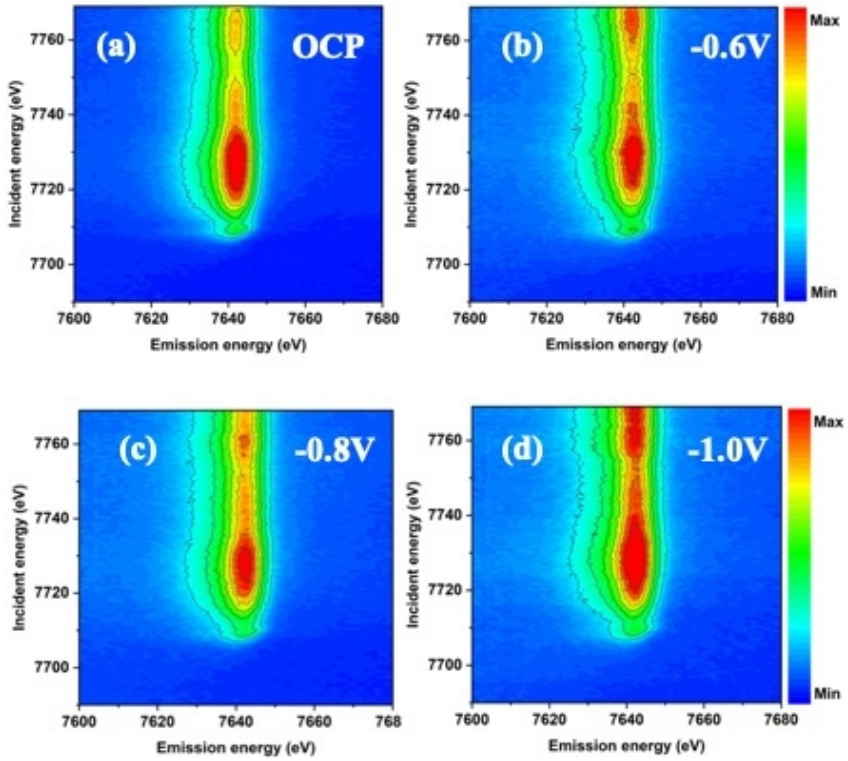

Figure S10. *Operando* $K\beta_{1,3}$-RIXS planes of CoPc without potential applied (a) and NiPc under (b-d) various potentials vs. RHE in a 0.5 M $KHCO_3$ solution during the ECO_2RR.

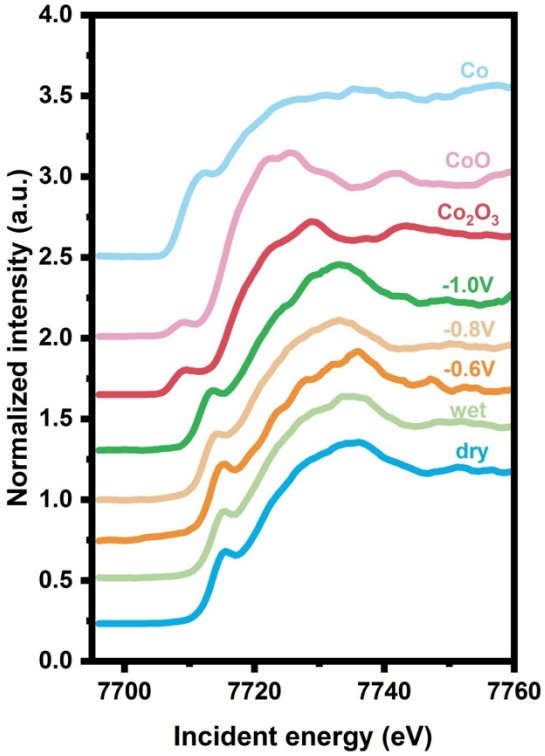

Figure S11. Normalized K-edge HERFD-XANES of CoPc at various applied potentials vs. RHE during the CO_2RR and corresponding standard references of Co, Co_2O_3 and CoO.

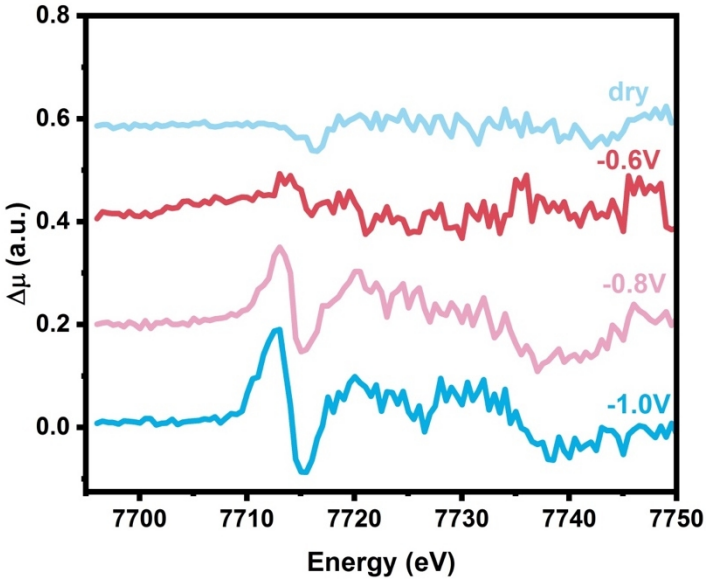

Figure S12. *Operando* Co K-edge Δμ spectra of CoPc at various potentials vs. RHE by subtracting the dry HERFD-XANES spectrum.

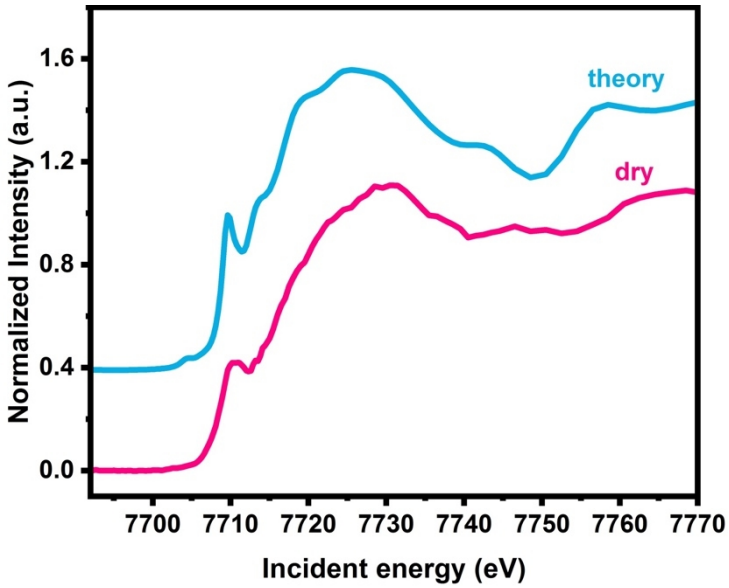

Figure S13. Theoretical HERFD-XANES spectrum of CoPc (blue) and the normalized K-edge HERFD-XANES spectrum of CoPc (pink).

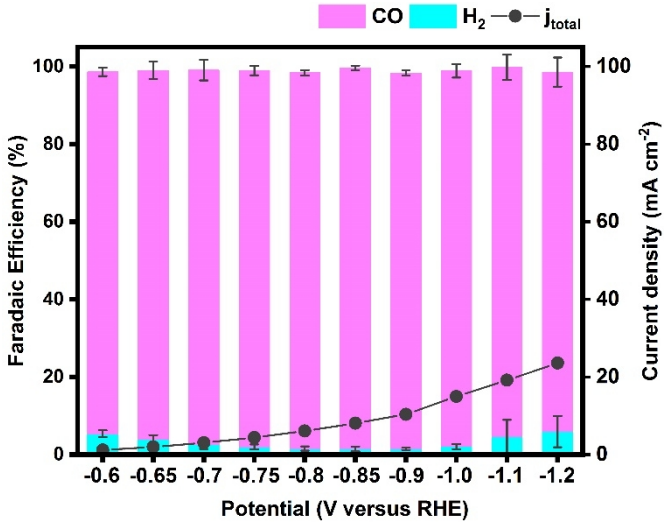

Figure S14. Faradaic efficiency and total current density of CoPc at the applied potentials (0.5 M $KHCO_3$ saturated by CO_2). The faradaic efficiency is stated as an average and calculated at the steady-state current and product concentration.

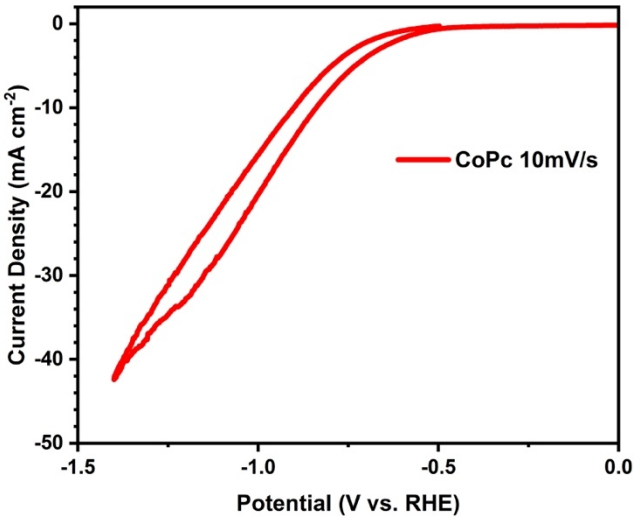

Figure S15. Cyclic voltammetry curves of CoPc at a scan rate of 10 mV s^{-1} in CO_2 saturated 0.1 M $KHCO_3$ aqueous solution.

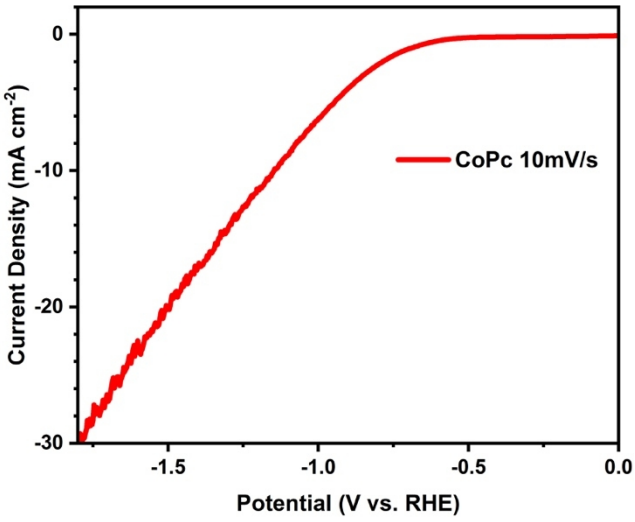

Figure S16. Linear sweep voltammetry curves of CoPc at a scan rate of 10 mV s^{-1} in CO_2 saturated 0.1 M $KHCO_3$ aqueous solution.

Table 1. Electron Number and d-Band Center of NiPc, Distorted NiPc and NiPc-CO_2

Model	Electron number	d-Band center
NiPc	6.39	-0.93
Distorted NiPc	7.28	-1.25
NiPc-CO_2	2.71	-1.05