

Supporting Information

New insights into the Enhanced CO₂RR Durability caused by Electron-donating Substitution of Heterogeneous CoPc

Qi Zhang ^{a,b,*}, Pingao Hu ^b, Chao Ma ^{a,b}, Zhiyuan Xu ^{a,b}, Beibei Tang ^b

^a *School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei 230009, China*

^b *Institute of Industry & Equipment Technology, Anhui Province Key Lab of Aerospace Structural Parts Forming Technology and Equipment, Hefei University of Technology, Hefei 230009, China*

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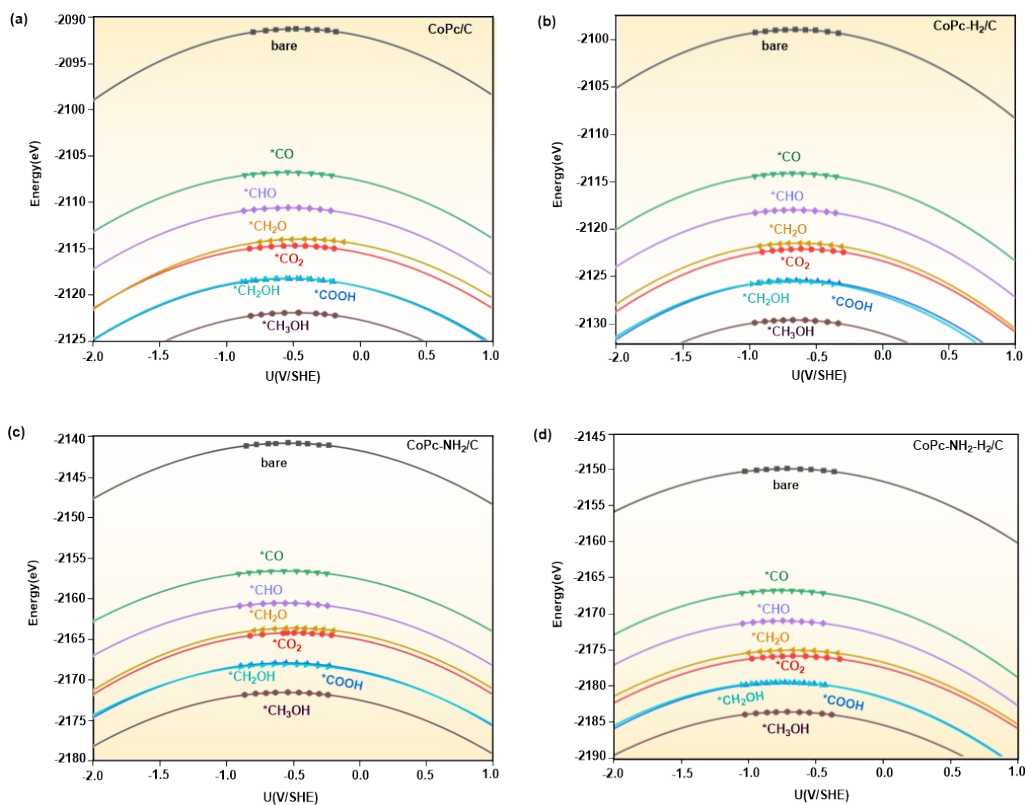


Figure S1 The calculated energies of bare and CO₂RR reaction intermediates as a function of applied electrode potential for (a) CoPc/C; (b) CoPc-H₂/C; (c) CoPc-NH₂/C and (d) CoPc-NH₂-H₂/C, respectively.

Table S1 The formation energies and dissolution potentials of CoPc/C, CoPc-H₂/C, CoPc-NH₂/C, and CoPc-NH₂-H₂/C, respectively.

Systems	Formation energies (eV)	Dissolution potentials (V)
CoPc@CNT	-4.20	1.82
CoPc-H ₂ @CNT	-2.98	1.04
CoPc-NH ₂ @CNT	-3.82	1.63
CoPc-NH ₂ -H ₂ @CNT	-2.63	1.21

Tabel S2 Fitting quadratic function between the energy(E) of the reaction intermediates and applied electrochemical potential(U) for CoPc/C. The C (e/V), U_0 (V/SHE) and E_0 (eV) are the capacitance of the corresponding system, potential of zero charge (PZC) , and the energy of the system at the PZC, respectively.

Reaction intermediates	Energy(eV)	C(e/V)	U_0 (V/SHE)	E_0 (eV)	R^2
bare	$E=-3.29U^2-3.03U-2092.15$	6.58	-0.46	-2091.45	0.985
*CO ₂	$E=-3.00U^2-2.92U-2115.46$	6.00	-0.49	-2114.75	0.995
*COOH	$E=-3.03U^2-3.09U-2119.07$	6.06	-0.51	-2118.28	0.995
*CO	$E=-3.00U^2-3.17U-2107.71$	6.00	-0.53	-2106.87	0.994
*CHO	$E=-3.09U^2-3.21U-2111.50$	6.18	-0.52	-2110.66	0.995
*CH ₂ O	$E=-3.08U^2-2.60U-2114.58$	6.16	-0.42	-2114.03	0.997
*CH ₂ OH	$E=-3.08U^2-3.25U-2119.10$	6.16	-0.53	-2118.24	0.993
*CH ₃ OH	$E=-3.21U^2-3.04U-2122.67$	6.42	-0.47	-2121.95	0.997

Tabel S3 Computed free energy changes (ΔG /eV) for all elementary steps involved in the electrocatalytic CO₂ reduction on the CoPc/C system at 0V/RHE.

Elementary steps	ΔG (eV)
*+CO ₂ →*CO ₂	0.05
*CO ₂ +H ⁺ +e ⁻ →*COOH	0.22
*COOH+H ⁺ +e ⁻ →*CO+H ₂ O	0.00
CO→+CO	0.16
*CO+H ⁺ +e ⁻ →*CHO	-0.15
*CHO+H ⁺ +e ⁻ →*CH ₂ O	0.28
*CH ₂ O+H ⁺ +e ⁻ →*CH ₂ OH	-0.55
*CH ₂ OH+H ⁺ +e ⁻ →*CH ₃ OH	-0.11
CH ₃ OH→+CH ₃ OH	-0.35

Tabel S4 Fitting quadratic function between the energy(E) of the reaction intermediates and applied electrochemical potential(U) for CoPc-H₂/C. The C (e/V), U₀ (V/SHE) and E₀ (eV) are the capacitance of the corresponding system, potential of zero charge (PZC) , and the energy of the system at the PZC, respectively.

Reaction intermediates	Energy(eV)	C(e/V)	U ₀ (V/SHE)	E ₀ (eV)	R ²
bare	E=-3.45U ² -4.43U-2100.33	6.90	-0.64	-2098.91	0.999
*CO ₂	E=-3.40U ² -4.07U-2123.21	6.80	-0.59	-2122.00	0.989
*COOH	E=-3.43U ² -4.26U-2126.63	6.86	-0.63	-2125.30	0.997
*CO	E=-3.36U ² -4.38U-2115.47	6.72	-0.65	-2114.04	0.998
*CHO	E=-3.37U ² -4.37U-2119.29	6.74	-0.65	-2117.87	0.997
*CH ₂ O	E=-3.45U ² -4.22U-2122.67	6.90	-0.61	-2121.38	0.996
*CH ₂ OH	E=-3.41U ² -4.56U-2126.88	6.82	-0.67	-2125.36	0.996
*CH ₃ OH	E=-3.33U ² -4.31U-2130.86	6.66	-0.65	-2129.47	0.996

Tabel S5 Computed free energy changes (ΔG /eV) for all elementary steps involved in the electrocatalytic CO₂ reduction on the CoPc-H₂/C system at 0V/RHE.

Elementary steps	ΔG (eV)
*+CO ₂ →*CO ₂	0.38
*CO ₂ +H ⁺ +e ⁻ →*COOH	0.36
*COOH+H ⁺ +e ⁻ →*CO+H ₂ O	-0.05
CO→+CO	-0.26
*CO+H ⁺ +e ⁻ →*CHO	-0.24
*CHO+H ⁺ +e ⁻ →*CH ₂ O	0.06
*CH ₂ O+H ⁺ +e ⁻ →*CH ₂ OH	-0.29
*CH ₂ OH+H ⁺ +e ⁻ →*CH ₃ OH	-0.56
CH ₃ OH→+CH ₃ OH	-0.27

Tabel S6 Fitting quadratic function between the energy(E) of the reaction intermediates and applied electrochemical potential(U) for CoPc-NH₂/CNT. The C (e/V), U₀ (V/SHE) and E₀ (eV) are the capacitance of the corresponding system, potential of zero charge (PZC) , and the energy of the system at the PZC, respectively.

Reaction intermediates	Energy(eV)	C(e/V)	U ₀ (V/SHE)	E ₀ (eV)	R ²
bare	$E=-3.20U^2-3.37U-2141.89$	6.40	-0.53	-2141.00	0.932
*CO ₂	$E=-3.38U^2-3.30U-2165.09$	6.76	-0.49	-2164.28	0.992
*COOH	$E=-3.21U^2-3.48U-2168.93$	6.42	-0.54	-2167.99	0.998
*CO	$E=-3.03U^2-3.38U-2157.64$	6.06	-0.56	-2156.70	0.996
*CHO	$E=-3.15U^2-3.49U-2161.58$	6.30	-0.55	-2160.61	0.996
*CH ₂ O	$E=-3.37U^2-3.24U-2164.47$	6.74	-0.48	-2163.69	0.992
*CH ₂ OH	$E=-3.05U^2-3.38U-2169.06$	6.10	-0.55	-2168.12	0.996
*CH ₃ OH	$E=-3.16U^2-3.40U-2172.51$	6.32	-0.54	-2171.60	0.994

Tabel S7 Computed free energy changes ($\Delta G/eV$) for all elementary steps involved in the electrocatalytic CO₂ reduction on the CoPc-NH₂/CNT system at 0V/RHE.

Elementary steps	$\Delta G(eV)$
*+CO ₂ →*CO ₂	0.14
*CO ₂ +H ⁺ +e ⁻ →*COOH	-0.04
*COOH+H ⁺ +e ⁻ →*CO+H ₂ O	0.02
CO→+CO	0.31
*CO+H ⁺ +e ⁻ →*CHO	-0.34
*CHO+H ⁺ +e ⁻ →*CH ₂ O	0.54
*CH ₂ O+H ⁺ +e ⁻ →*CH ₂ OH	-0.76
*CH ₂ OH+H ⁺ +e ⁻ →*CH ₃ OH	-0.06
CH ₃ OH→+CH ₃ OH	-0.23

Tabel S8 Fitting quadratic function between the energy(E) of the reaction intermediates and applied electrochemical potential(U) for CoPc-NH₂-H₂@CNT. The C (e/V), U₀ (V/SHE) and E₀ (eV) are the capacitance of the corresponding system, potential of zero charge (PZC) , and the energy of the system at the PZC, respectively.

Reaction intermediates	Energy(eV)	C(e/V)	U ₀ (V/SHE)	E ₀ (eV)	R ²
bare	E=-3.18U ² -4.42U-2150.74	6.36	-0.69	-2149.20	0.993
*CO ₂	E=-3.26U ² -4.27U-2173.80	6.52	-0.65	-2172.40	0.994
*COOH	E=-3.54U ² -5.09U-2177.51	7.08	-0.72	-2175.68	0.999
*CO	E=-3.53U ² -5.24U-2166.22	7.06	-0.74	-2164.28	0.998
*CHO	E=-3.47U ² -5.10U-2169.93	6.94	-0.73	-2168.06	0.990
*CH ₂ O	E=-3.27U ² -4.38U-2173.15	6.54	-0.67	-2171.68	0.998
*CH ₂ OH	E=-3.48U ² -5.19U-2177.58	6.96	-0.75	-2175.64	0.991
*CH ₃ OH	E=-3.24U ² -4.55U-2180.93	6.48	-0.70	-2179.33	0.997

Tabel S9 Computed free energy changes ($\Delta G/eV$) for all elementary steps involved in the electrocatalytic CO₂ reduction on the CoPc-NH₂-H₂/CNT system at 0V/RHE.

Elementary steps	$\Delta G(eV)$
*+CO ₂ →*CO ₂	0.28
*CO ₂ +H ⁺ +e ⁻ →*COOH	0.32
*COOH+H ⁺ +e ⁻ →*CO+H ₂ O	-0.07
CO→+CO	-0.10
*CO+H ⁺ +e ⁻ →*CHO	-0.07
*CHO+H ⁺ +e ⁻ →*CH ₂ O	0.09
*CH ₂ O+H ⁺ +e ⁻ →*CH ₂ OH	-0.44
*CH ₂ OH+H ⁺ +e ⁻ →*CH ₃ OH	0.02
CH ₃ OH→+CH ₃ OH	-0.74

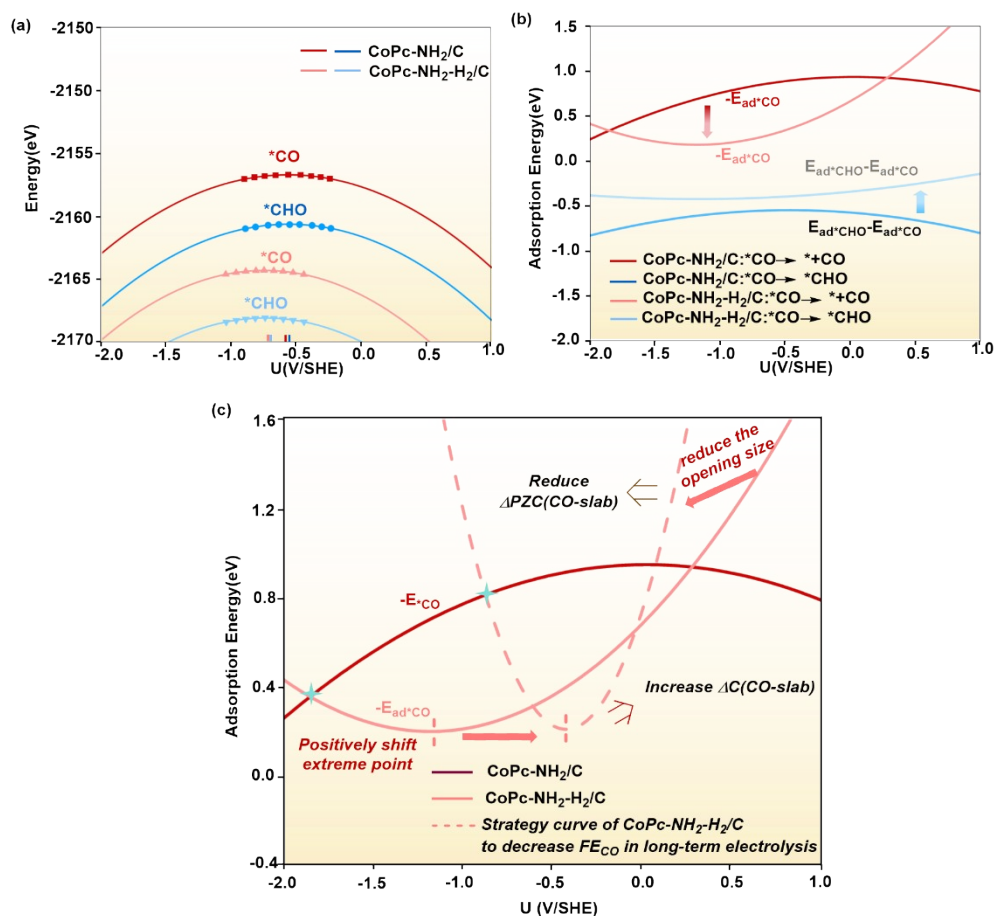


Figure S2. (a) Energies of *CO and *CHO intermediates as a function of applied potentials for CoPc-NH₂/C and CoPc-NH₂-H₂/C; (b) the adsorption energies comparison for the CoPc-NH₂/C and CoPc-NH₂-H₂/C systems; (c) the strategy to decrease the FE_{CO} of CoPc-NH₂/C system in long-term electrolysis.

For the CoPc-NH₂/C system, during a prolonged electrolysis process of 12 hours at applied voltage of -1.0V/RHE, FE_{CO} suddenly increases after 5 h. Long-term electrolysis is accompanied by hydrogenation. Comparing Figure 3(a) and (b) in text, it can be seen that hydrogenation significantly reduces the energy barrier for the CO dissociation step for CoPc-NH₂/C (from 0.31eV to -0.10eV), making it easier to generate CO. As shown in Figure S2(a) and (b), the influence of voltage on the energy and adsorption energy of key intermediates can provide

further explanation. In Figure 7(b) the deep red and light red curves correspond to the CO dissociation energies of CoPc-NH₂/C and CoPc-NH₂-H₂/C, respectively. The latter is lower, indicating that hydrogenation enhances the tendency of CO dissociation within the applied voltage window. The dark blue and light blue curves correspond to the E_{ad} (*CHO-*CO) of the *CO→*CHO step for CoPc-NH₂/C and CoPc-NH₂-H₂/C, respectively. The latter is located above, indicating that hydrogenation reduces the tendency of this step. Therefore, under prolonged electrolysis, the proportion of CoPc-NH₂-H₂/C system increase, and due to its easier CO dissociation than deep reduction, the FE_{CO} increases.

For the phenomenon of FE_{CO} increases in 12h long-term electrolysis for the CoPc-NH₂/C system, the strategy we give is to reduce the opening size and positively shift the extreme point of the light red curve (potential-dependent CO dissociation energy of CoPc-NH₂-H₂/C, Figure S2 (c), so that its intersection with the deep red curve can be positively shifted. Based on

$G(U_q) = -\frac{1}{2}C(U_q - U_0)^2 + E$, the quadratic term coefficient of the corresponding quadratic function of

the *CO→slab + CO process is $-\frac{1}{2}(C_{*slab} - C_{*CO})$, the abscissa of the extreme point is $U = (C_{*slab}U_{0*slab} - C_{*CO}U_{0*CO} + 1) / (C_{*slab} - C_{*CO})$. Note that in the process *CO→slab + CO, the capacitance decreases (from 7.06 e/V to 6.36 e/V) and the U₀ shifts positively (from -0.74V/SHE to -0.69V/SHE). Increasing the capacitance difference between *slab and *CO can narrow the opening of the curve because the absolute value of the quadratic coefficient increases. At the same time, the denominator of the extreme point decreases, and at this time, it is beneficial to decrease the numerator by reducing the PZC difference, so that the extreme point is shifted to the right.

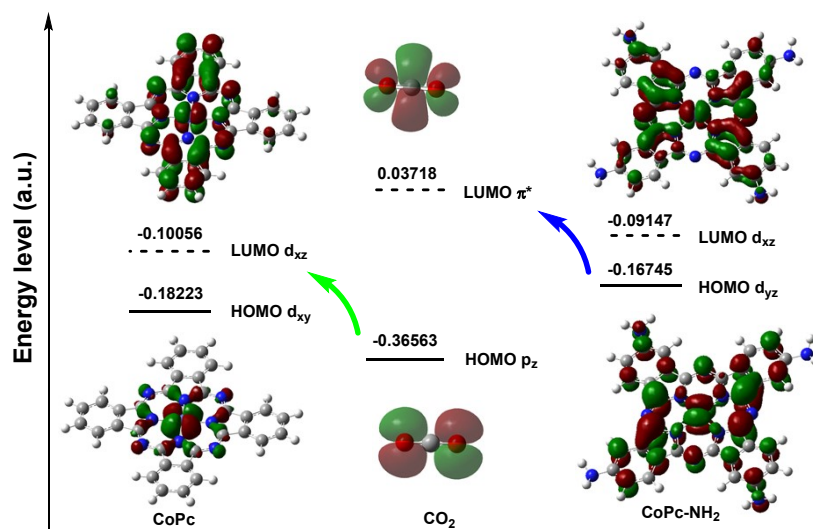


Figure S3. The frontier molecular orbitals of two catalysts with CO₂ species.

Based on the Gaussian calculation, we analyzed the frontier molecular orbitals of two catalysts with CO₂ species. As shown in Figure S3., the HOMO and LUMO energy of CoPc-NH₂ is higher than that of CoPc. Therefore, the high-energy HOMO of CoPc-NH₂ (caused by electron-donating amino substitutions) favors interaction with the LUMO of CO₂ to form Co-C bonds (Blue arrow), while the HOMO electrons of CO₂ have access to the low-energy LUMO of CoPc to form Co-O bonds (Green arrow).