

Cobalt Single Atom Anchored Tubular Graphyne for Efficient Electrocatalytic CO₂ Reduction Reaction

Shannan Xu¹, Xiao Tang², Chen Long¹, Dongqiu Zhao^{1,*}, and Lin Ju^{1,*}

¹School of Physics and Electric Engineering, Anyang Normal University, Anyang, 455000, China

²College of Science, Nanjing Forestry University, Nanjing 210037, China

* Corresponding authors.

E-mail address: dqzhao@aynu.edu.cn (D. Zhao); julin@aynu.edu.cn (L. Ju)

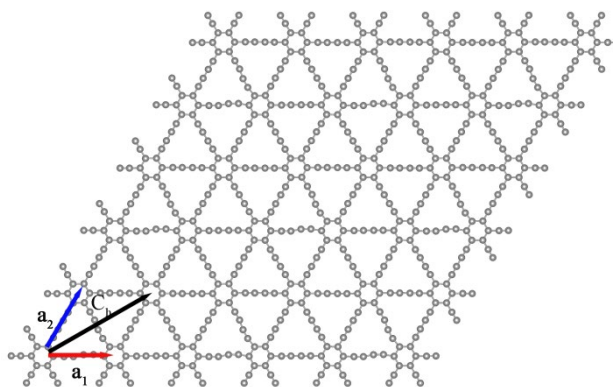


Figure S1. The triangular macroporous structure of a graphyne monolayer and its nanotubes. Top view of the graphyne monolayer, showing its anisotropic lattice with the basis vectors a_1 and a_2 . The chiral vector is defined as $C_h = ma_1 + na_2$ for constructing the nanotubes. The (n, m) nomenclature is applied here, where Armchair-type nanotubes are represented by (n, 0) and Zigzag-type by (n, n).

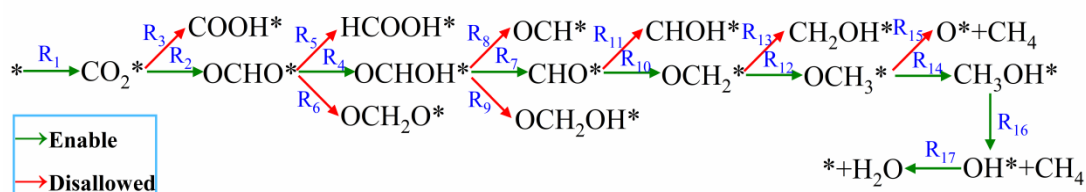


Figure S2. The search process for the minimum energy reaction pathways of the CO₂ reduction reactions on Co@GDY-NT. The red arrows denote disallowed reaction paths, while the green arrows stand for the enabled ones.

Elementary steps in CO₂RR and HER. All the hydrogenation reactions (R1~R17) considered in the search process for the minimum energy reaction pathways of the CO₂ reduction reactions can be written as:

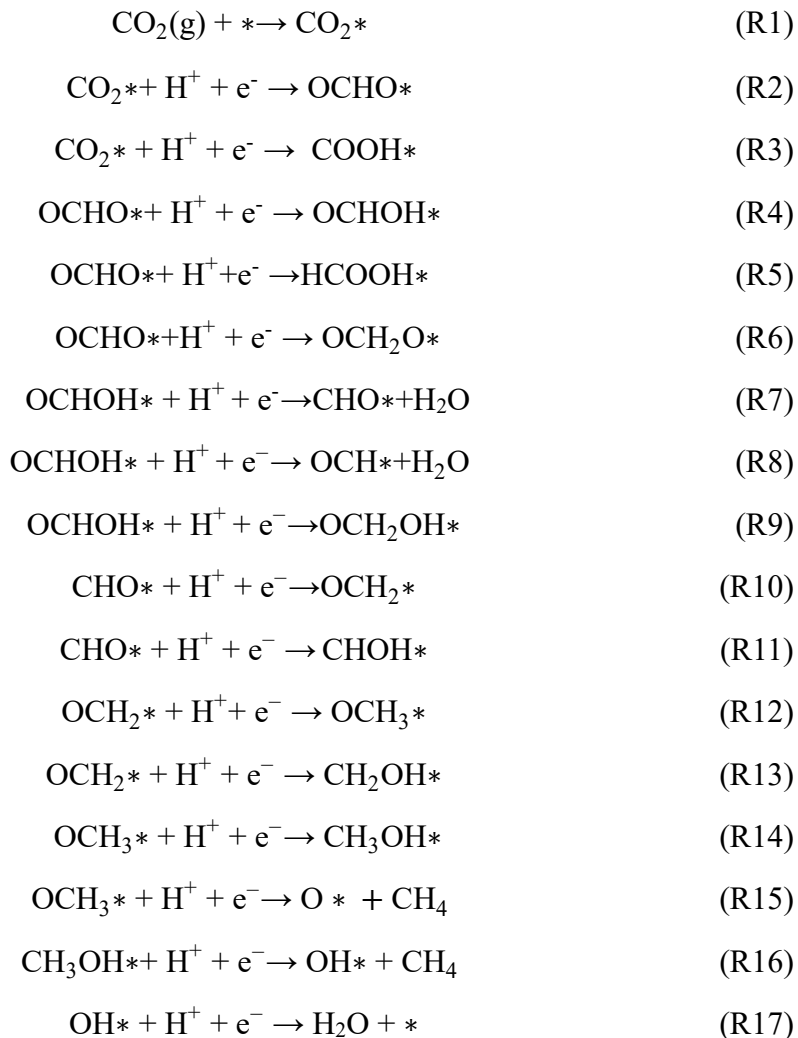


Table S1 Zero-point energy correction (E_{ZPE}), entropy contribution (TS , $T=298.15$ K), total energy (E), and the Gibbs free energy (G) of small molecules.

Species	E (eV)	TS (eV)	E_{ZPE} (eV)	G (eV)
H ₂ O	-471.54	0.11	0.59	-471.06
CO ₂	-1034.64	0.09	0.33	-1034.40
CH ₃ OH	-659.57	0.21	1.37	-658.41
CH ₄	-221.08	0.00	1.18	-219.90

Table S2 Zero-point energy correction (E_{ZPE}), entropy contribution (TS , $T=298.15$ K), total energy (E), and the Gibbs free energy (G) of adsorbates along the reaction pathway on Co@GDY-NT, where * represents the adsorption site.

Species	E (eV)	TS (eV)	E_{ZPE} (eV)	G (eV)
CO ₂ *	-13057.03	0.14	0.32	-13056.85
OCHO*	-13073.37	0.15	0.62	-13072.90
OCHOH*	-13089.33	0.24	0.94	-13088.63
CHO*	-12633.48	0.19	0.47	-12633.20
CH ₂ O*	-12649.63	0.13	0.78	-12648.98
CH ₃ O*	-12666.03	0.18	1.07	-12665.14
CH ₃ OH*	-12682.58	0.19	1.43	-12681.34
OH*	-12477.83	0.10	0.35	-12477.58

Therefore, when $U = 0$ V and $pH = 0$, ΔG for each elementary step (R1-R17) can be rewritten as:

$$\Delta G_{R1} = G_{CO_2^*} - G_{CO_2} - G_* \quad (ES1)$$

$$\Delta G_{R2} = G_{OCHO^*} - G_{CO_2^*} - \frac{1}{2} G_{H_2} \quad (ES2)$$

$$\Delta G_{R3} = G_{COOH^*} - G_{CO_2^*} - \frac{1}{2} G_{H_2} \quad (ES3)$$

$$\Delta G_{R4} = G_{OCHOH^*} - G_{OCHO^*} - \frac{1}{2} G_{H_2} \quad (ES4)$$

$$\Delta G_{R5} = G_{HCOOH^*} - G_{OCHO^*} - \frac{1}{2} G_{H_2} \quad (ES5)$$

$$\Delta G_{R6} = G_{OCH_2O^*} - G_{OCHO^*} - \frac{1}{2} G_{H_2} \quad (ES6)$$

$$\Delta G_{R7} = G_{CHO^*} + G_{H_2O} - G_{OCHOH^*} - \frac{1}{2} G_{H_2} \quad (ES7)$$

$$\Delta G_{R8} = G_{OCH^*} + G_{H_2O} - G_{OCHOH^*} - \frac{1}{2} G_{H_2} \quad (ES8)$$

$$\Delta G_{R9} = G_{OCH_2OH^*} - G_{OCHOH^*} - \frac{1}{2} G_{H_2} \quad (ES9)$$

$$\Delta G_{R10} = G_{OCH_2^*} - G_{CHO^*} - \frac{1}{2} G_{H_2} \quad (ES10)$$

$$\Delta G_{R11} = G_{CHOH^*} - G_{CHO^*} - \frac{1}{2} G_{H_2} \quad (ES11)$$

$$\Delta G_{R12} = G_{OCH_3^*} - G_{OCH_2^*} - \frac{1}{2} G_{H_2} \quad (ES12)$$

$$\Delta G_{R13} = G_{CH_2OH^*} - G_{OCH_2^*} - \frac{1}{2} G_{H_2} \quad (ES13)$$

$$\Delta G_{R14} = G_{O*} + G_{CH_4*} - G_{OCH_3*} - \frac{1}{2}G_{H_2} \quad (ES14)$$

$$\Delta G_{R15} = G_{CH_3OH*} - G_{OCH_3*} - \frac{1}{2}G_{H_2} \quad (ES15)$$

$$\Delta G_{R16} = G_{OH*} - G_{O*} - \frac{1}{2}G_{H_2} \quad (ES16)$$

$$\Delta G_{R17} = G_* + G_{H_2O} - G_{OH*} - \frac{1}{2}G_{H_2} \quad (ES17)$$

The Gibbs free energy of small molecules and the adsorbates on the Co@GDY-NT catalysts along the minimum ΔG reaction pathway for CO₂RR is listed in Table S1 and Table S2.