Electronic Supplementary Information (ESI) for

Why Heterogeneous Single-Atom Catalysts Preferentially Produce CO in the Electrochemical CO_2 Reduction Reaction

Yu Wang,‡ Tianyang Liu‡ and Yafei Li*

Jiangsu Collaborative Innovation Centre of Biomedical Functional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China.

To whom correspondence should be addressed. Email: liyafei@njnu.edu.cn(YL)

‡Y.W. and T.L. contributed equally.

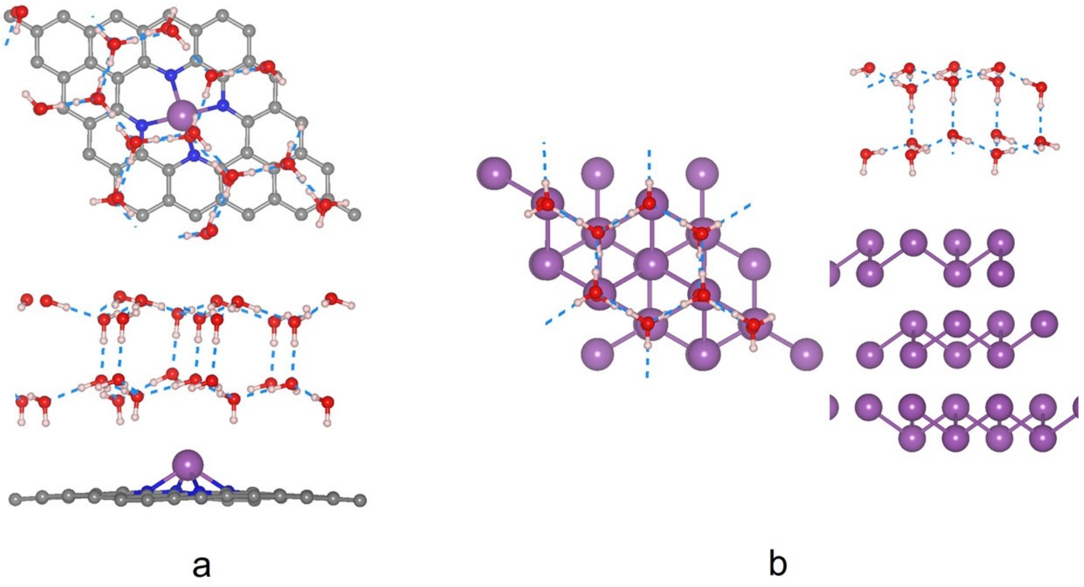


Fig. S1 Top and side views of the geometric structures of the (a) Bi−N−C SAC and (b) Bi nanosheet. The grey, blue, violet, and white spheres represent C, N, Bi, and H atoms, respectively.

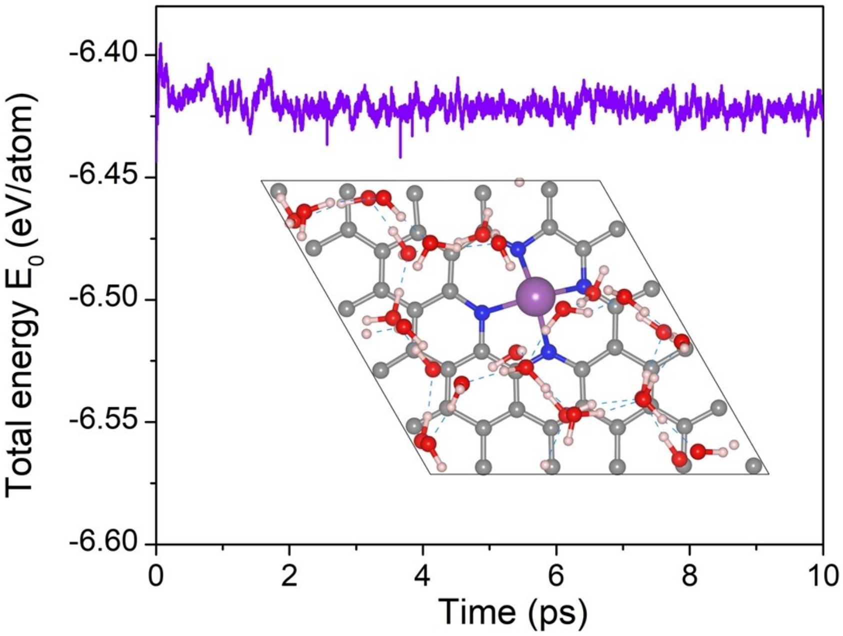


Fig. S2 Evolution of the total energy of first-principles molecular dynamics simulation for the Bi−N−C SAC at 300K. The inset is snapshot of structure at 10 ps. The NVT ensemble was employed in the first-principles molecular dynamics simulation, and the temperature was controlled by using the Nosé-Hoover method.

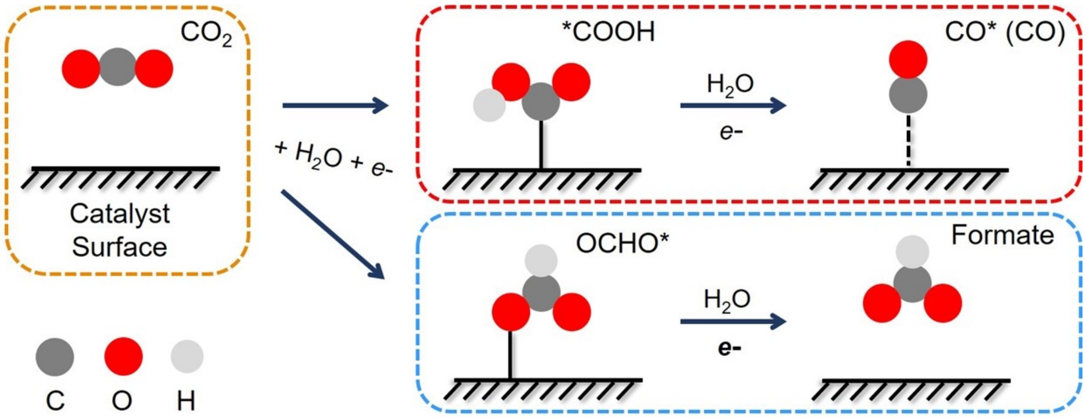


Fig. S3 Mechanistic scheme commonly employed in thermodynamic calculations in literature for the electroreduction of CO_2 to form CO and formate.

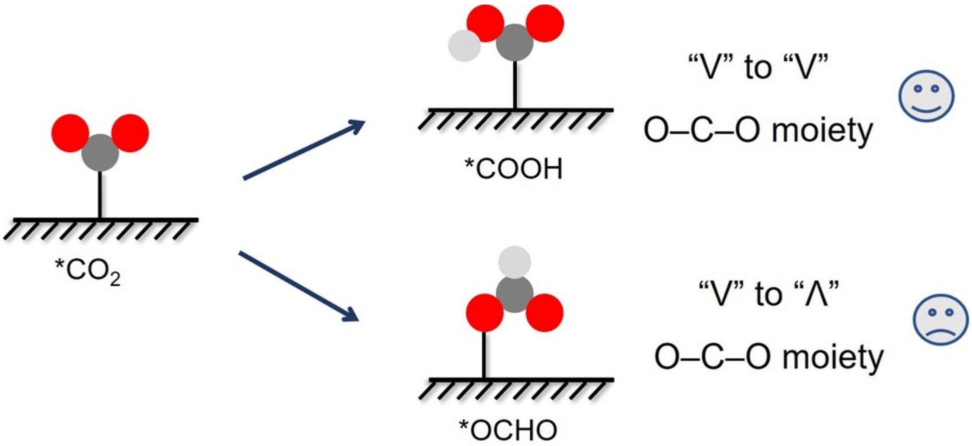


Fig. S4 Scheme for the structural transformation from chemisorbed CO_2 (*CO_2) to *COOH and *OCHO.

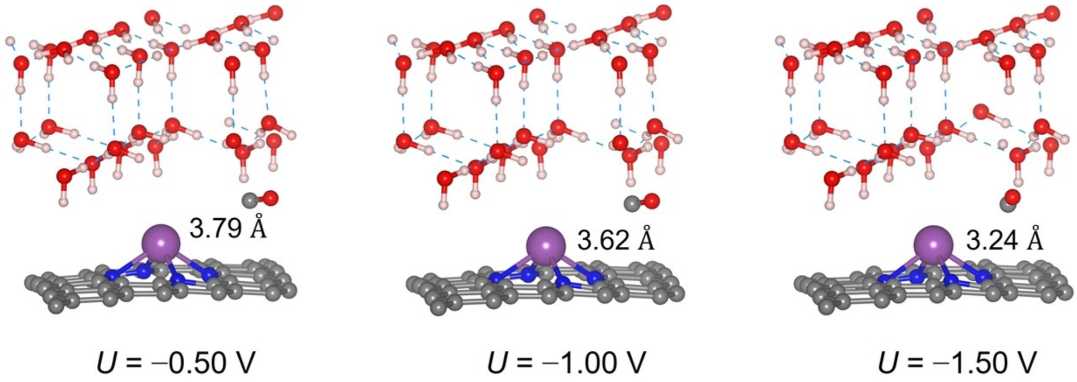


Fig. S5 Views of CO adsorbed on the Bi−N−C SAC at *U* = −0.50, −1.00, and −1.50 V after structure optimization. The numbers represent the distance between Bi and C atoms.

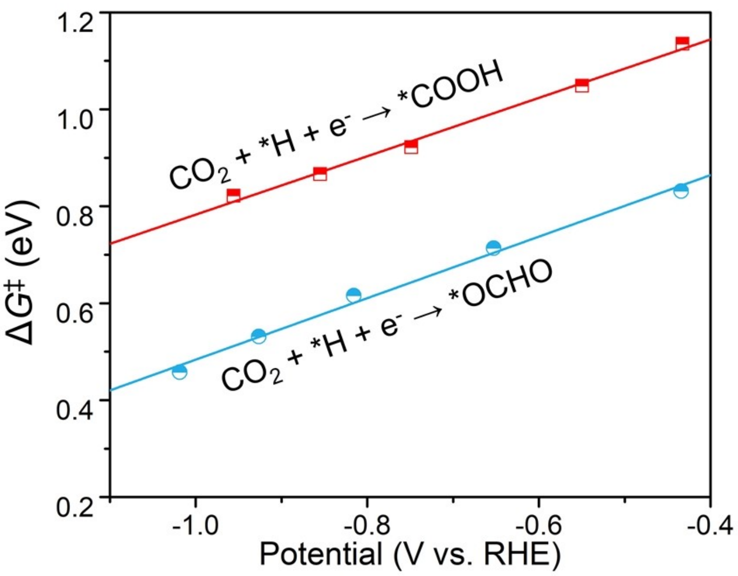


Fig. S6 Kinetic barriers $\Delta G^{\ddagger}$ of the protonation of physisorbed CO_2 to form *COOH and *OCHO on the Bi nanosheet (i.e., surface hydrogenation mechanism) as a function of electrode potential U.

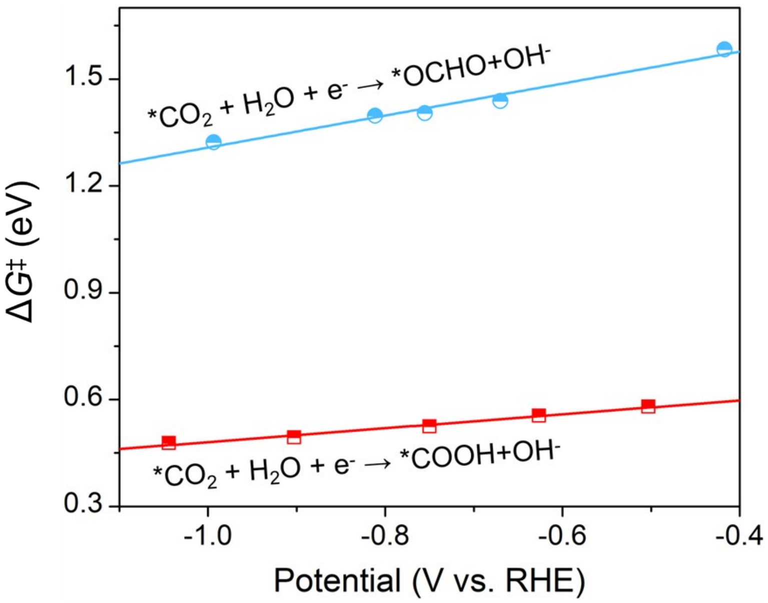


Fig. S7 Kinetic barriers $\Delta G^{\ddagger}$ of the protonation of $*CO_2$ to form *COOH and *OCHO on the Co−N−C SAC as a function of electrode potential *U*.

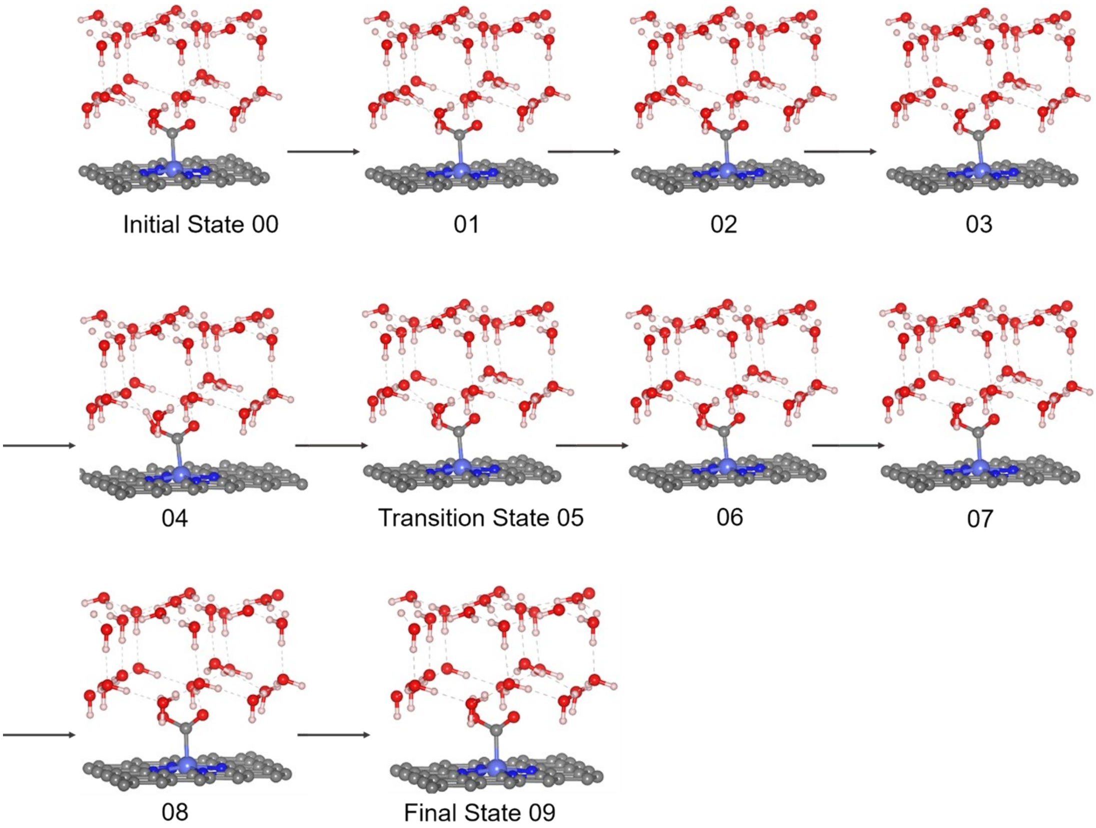
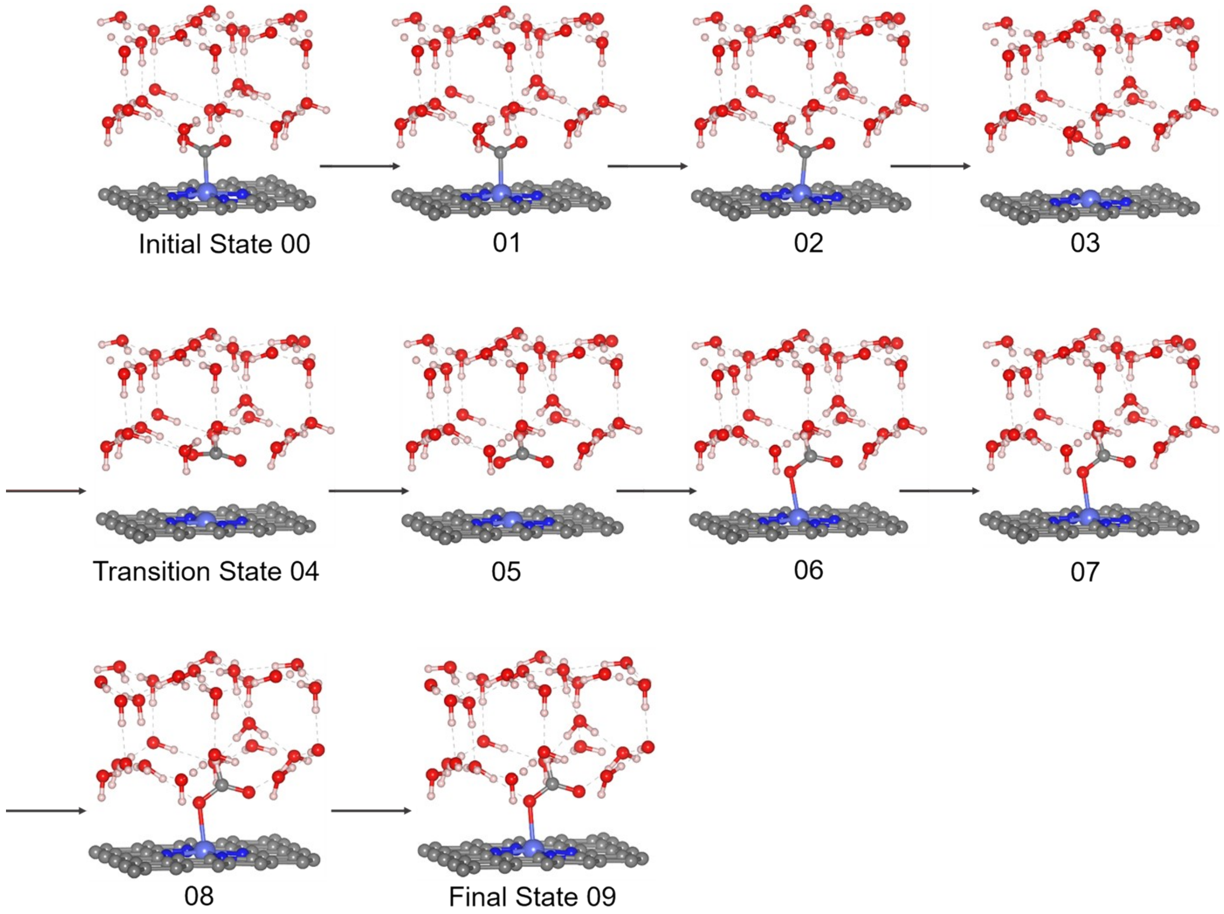


Fig. S8 Snapshoots of the path for the protonation of $^{*}CO_2$ to $^{*}COOH$ on the Co–N–C SAC.



Initial State 00

01

02

03

Transition State 04

05

06

07

08

Final State 09

Fig. S9 Snapshoots of the path for the protonation of $*CO_2$ to *OCHO on the Co–N–C SAC.

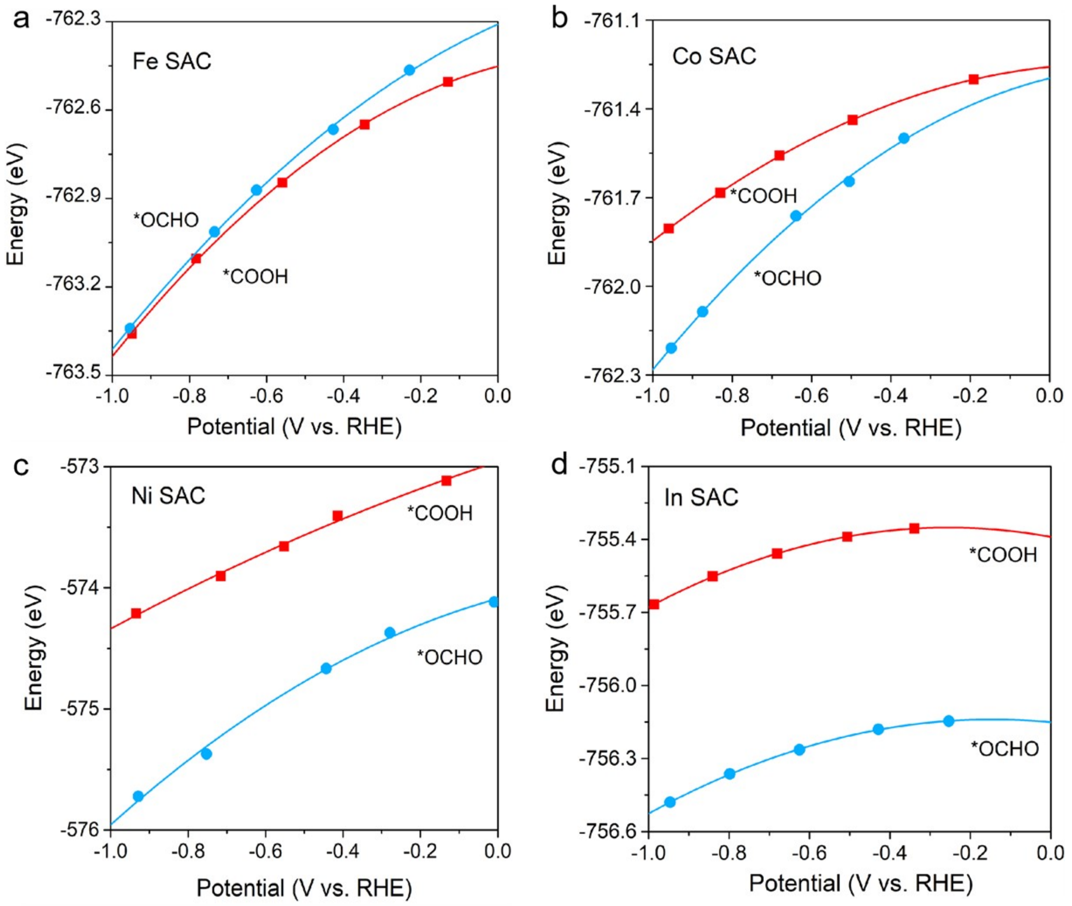


Fig. S10 Calculated total energies of *COOH and *OCHO of the (a) Fe−N−C, (b) Co−N−C, (c) Ni−N−C, (d) In−N−C SACs as a function of electrode potential *U*.

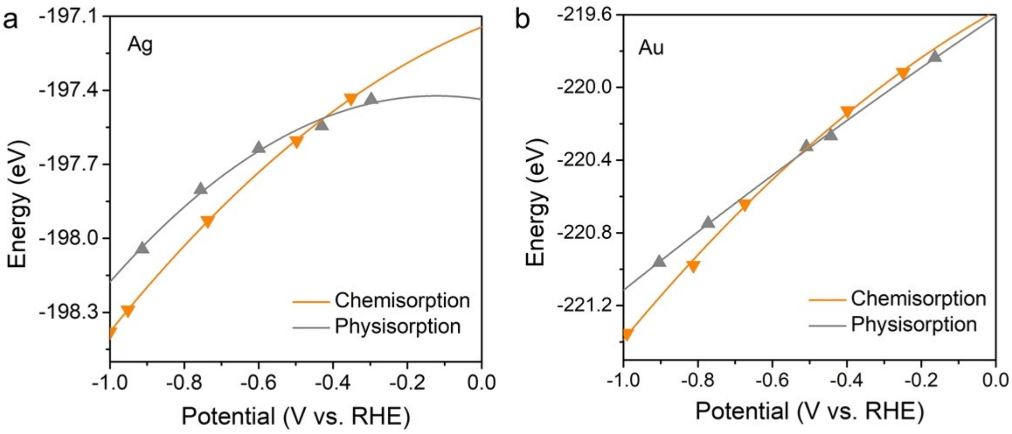


Fig. S11 Calculated total energies of chemisorbed and physisorbed CO_2 on (a) Ag and (b) Au as a function of electrode potential *U*.