CO_2 Reduction by Single Copper Atom Supported on g-C_3N_4 with Asymmetrical Active Sites

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1. Background

- Electrochemical reduction of carbon dioxide (CO_2) is a promising approach to reduced anthropogenic CO_2 emission.[1]
- C_2 products are generally regarded as more economically valuable than C_1 products but the whole reaction is suffering from low selectivity and high over potential.[2]
- Cu supported on carbon nitride (Cu-C_3N_4) has shown a unique capability to generate C_2 products by providing asymmetrical active sites.[3]

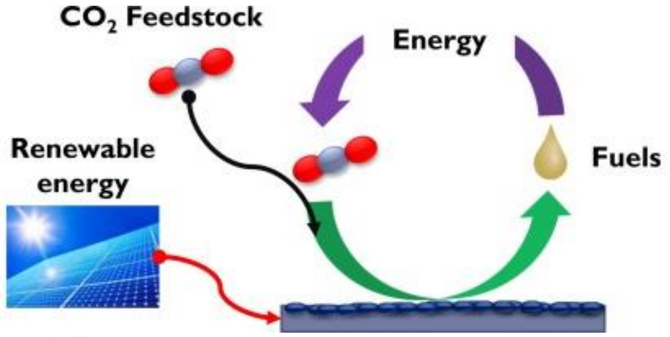

Figure 1. To achieve an anthropogenic and sustainable carbon cycle (Kumar et al., 2016)

2. Methods

The module computations and the electronic structure calculations were based on Density Functional Theory (DFT) in Vienna Ab Initio Simulation Package (VASP).

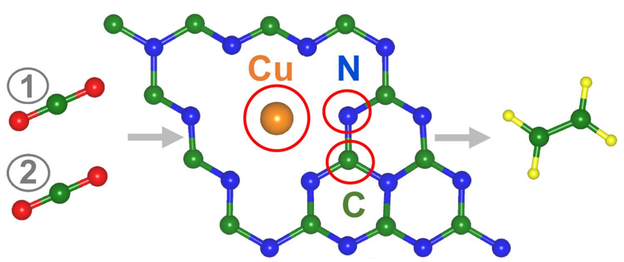

Figure 2. Illustration of the electrocatalyst, reactant, and product for CO_2 reduction to C_2H_4 on Cu-C_3N_4.

3. Results

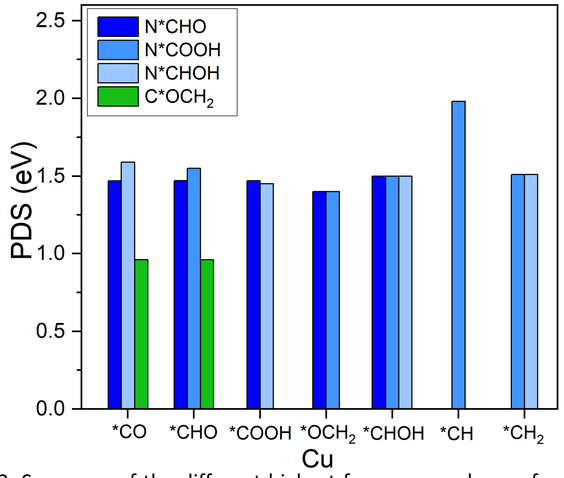

Figure 3. Summary of the different highest free energy change for different ethylene (C_2H_4) production pathways.

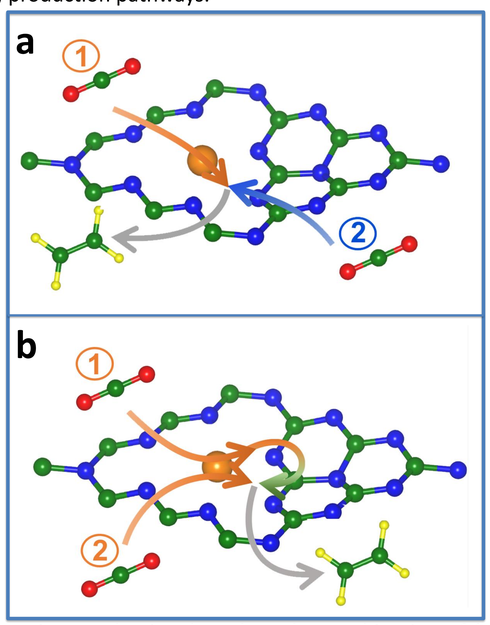

Figure 4. The reaction mechanism based on the combination of (a) copper and nitrogen atoms(Cu/N) or (b) copper and carbon atoms (Cu/C) as active sites.

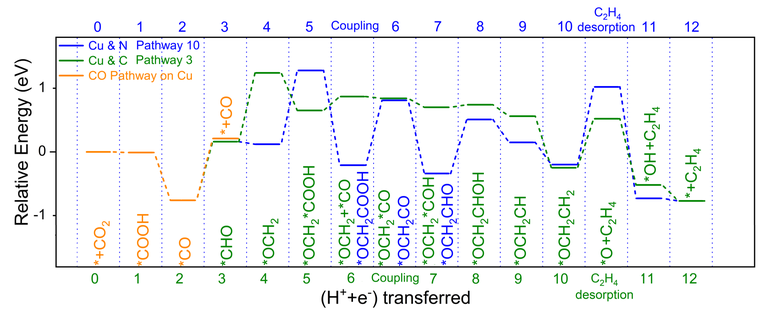

Figure 5. The free energy diagram of pathway 3 (Cu/C), pathway 10 (Cu/N), and that of CO production.

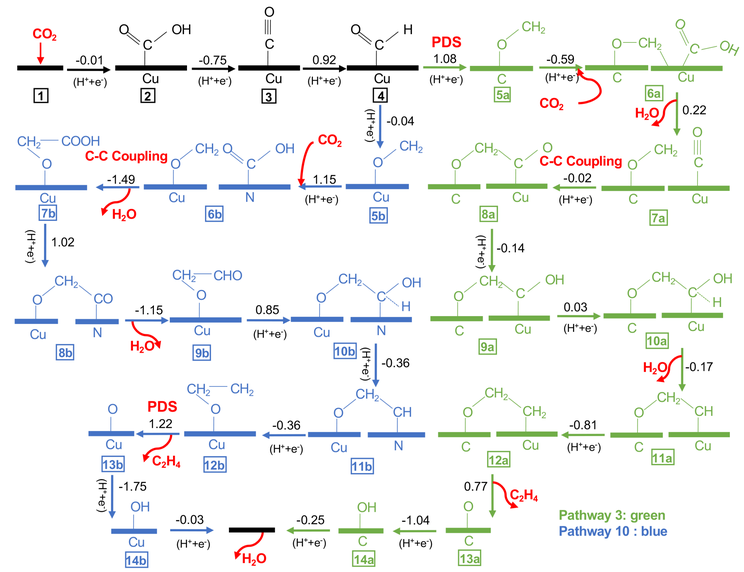

Figure 6. Complete reaction network of pathway 3 (Cu/C), and pathway 10 (Cu/N) for CO_2 electroreduction to C_2H_4 on the surface of Cu-C_3N_4.

4. Conclusions

- The asymmetrical active sites of Cu-C_3N_4 enable C_2 production from CO_2 reduction reaction.
- The combination of Cu /C as active sites present a higher activity than Cu/N from the thermodynamic perspectives

Acknowledge

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Zoom link

https://adelaide.zoom.us/j/81348424923?pwd=OUptZnNsZFRrTU5HbVVGc0xxNkpHdz09

Reference

[1] E.E. Benson, C.P. Kubiak, A.J. Sathrum, J.M. Smieja, Electrocatalytic and homogeneous approaches to conversion of CO_2 to liquid fuels, Chemical Society Reviews, 38 (2009) 89-99.

[2]A.J. Garza, A.T. Bell, M. Head-Gordon, Mechanism of CO_2 reduction at copper surfaces: pathways to C_2 products, ACS Catalysis, 8 (2018) 1490-1499.

[3]Y. Jiao, Y. Zheng, P. Chen, M. Jaroniec, S.Z. Qiao, Molecular Scaffolding Strategy with Synergistic Active Centers To Facilitate Electrocatalytic CO_2 Reduction to Hydrocarbon/Alcohol, Journal of the American Chemical Society, 139 (2017) 18093-18100.

[4] B. Kumar, J.P. Brian, V. Atla, S. Kumari, K.A. Bertram, R.T. White, J.M. Spurgeon, New trends in the development of heterogeneous catalysts for electrochemical CO_2 reduction, Catalysis Today, 270 (2016) 19-30.