Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Theoretical investigations of electrochemical CO_2 reduction by transition metals anchored on CNTs

Chengcheng Ao,[a] Wei Zhao,[a] Shanshan Ruan,[a] Siyu Qian,[a] Yi Liu,[a] Lei Wang,[a]

Lidong Zhang*[ab]

*Corresponding authors

a National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui, P. R. China

E-mail: zld@ustc.edu.cn

b State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui, P. R. China

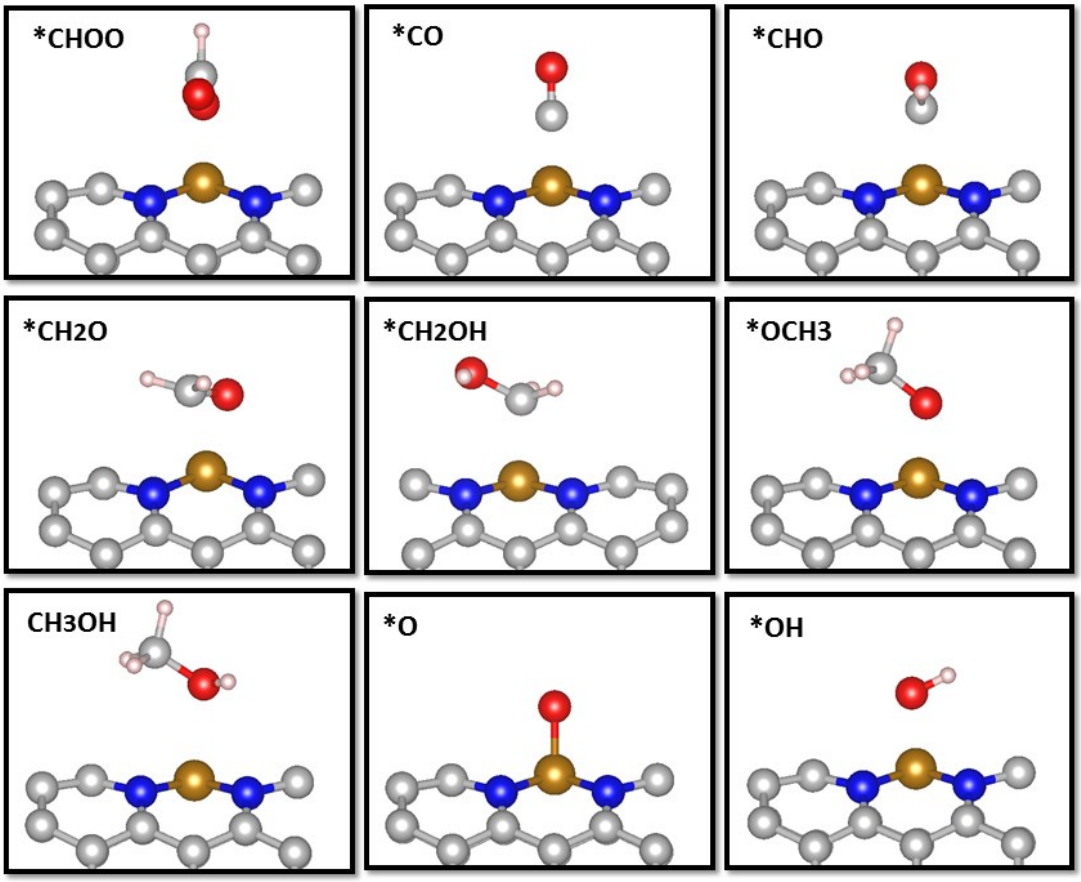

Fig 1. Optimized structures of intermediates adsorbed on Fe-N_4/CNT. C atoms in silver, N atoms in blue, O atoms in red, H atoms in white and Fe atoms in orange.

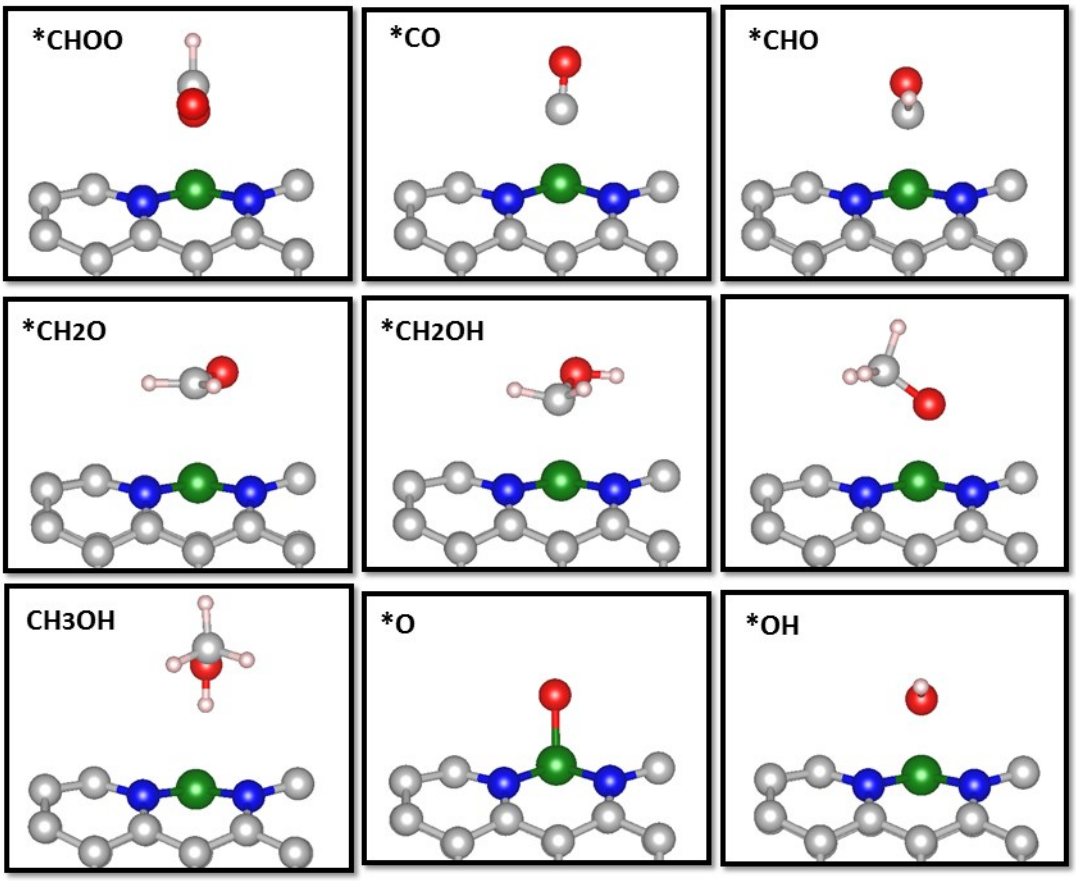

Fig 2. Optimized structures of intermediates adsorbed on Co-N_4/CNT. C atoms in silver, N atoms in blue, O atoms in red, H atoms in white and Co atoms in green.

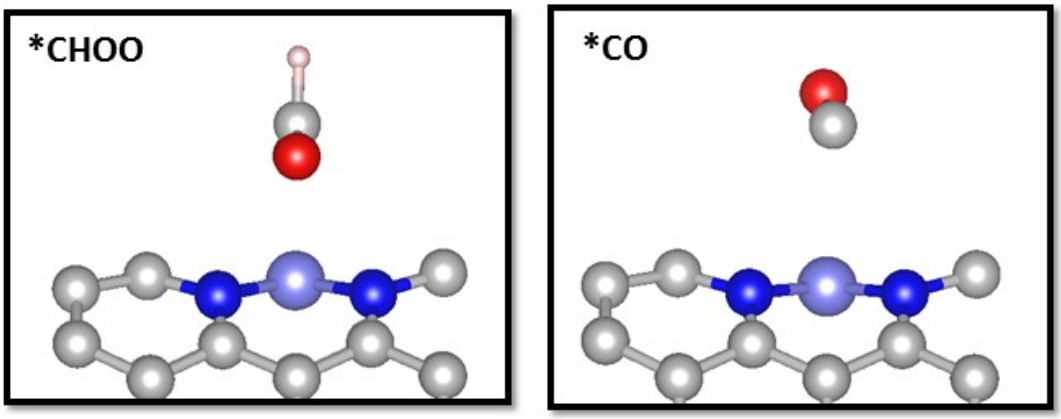

Fig 3. Optimized structures of intermediates adsorbed on Ni-N_4/CNT. C atoms in silver, N atoms in blue, O atoms in red, H atoms in white and Ni atoms in purple.

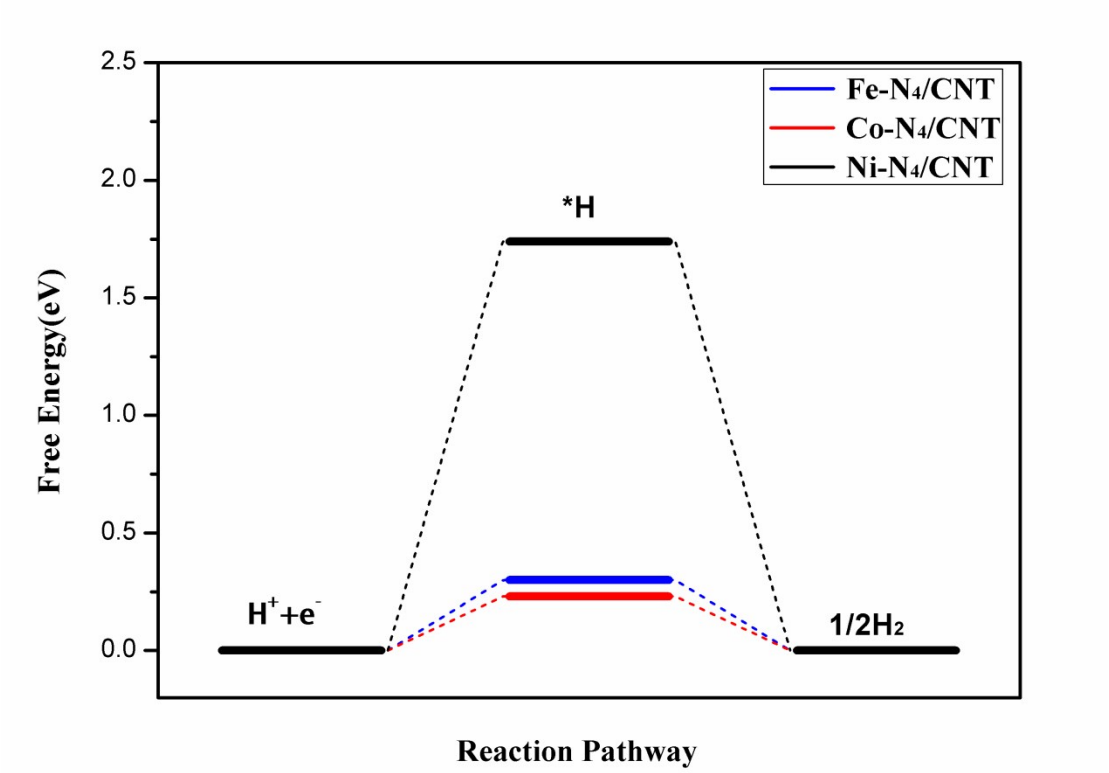

Fig 4. Free energy diagram of HER on three catalysts, Fe-N_4/CNT, Co-N_4/CNT and Ni-N_4/CNT at 0 V vs RHE.

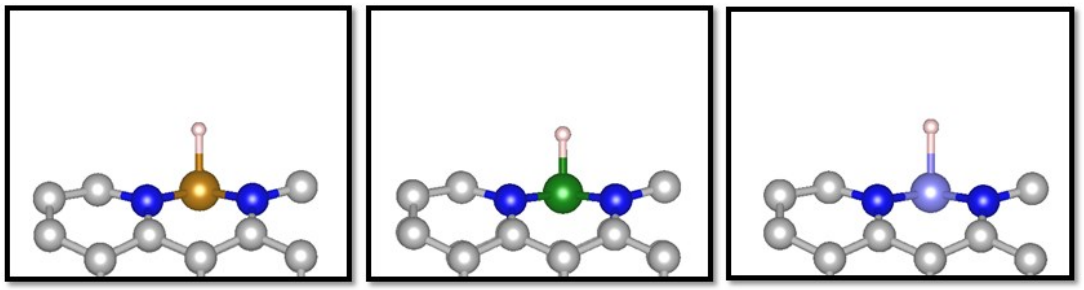

Fig 5. The stable configurations of H atom adsorbed on Fe-N_4/CNT, Co-N_4/CNT and Ni-N_4/CNT. C atoms in silver, N atoms in blue, H atoms in white and Fe, Co, Ni atoms in orange, green, purple, respectively.

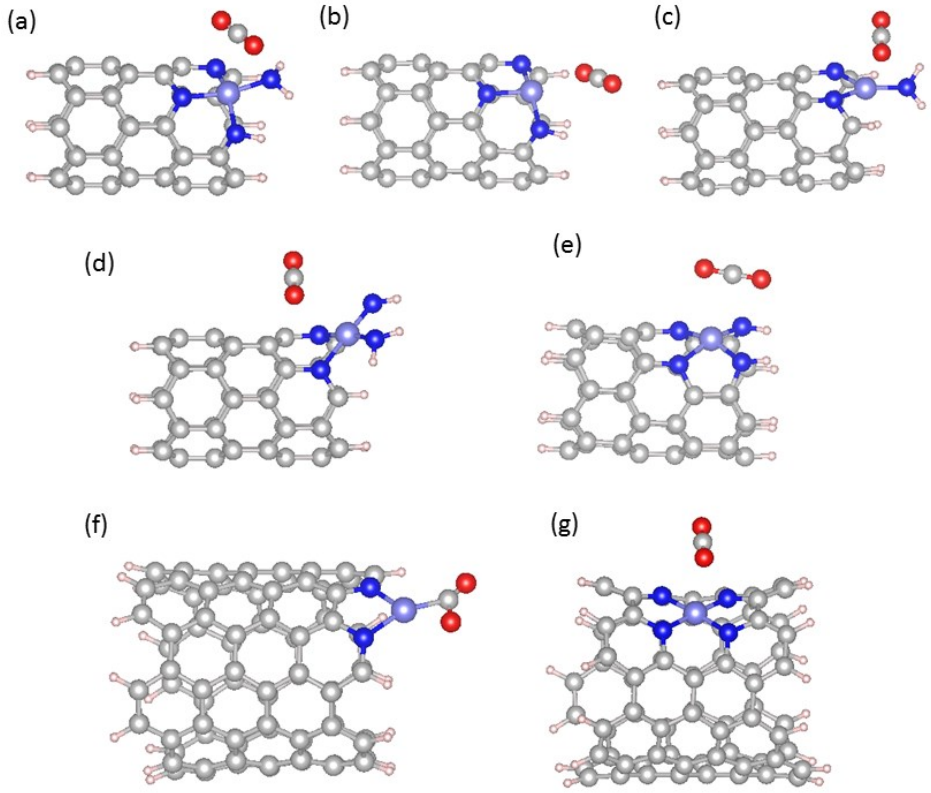

Fig 6. Optimized structures of CO_2 adsorbed on (a) NiN_3NH_2, (b) NiN_3, (c) NiN_2NH_2, (d) $NiN_2(NH_2)_2$, (e) NiN_4, (f) NiN_2 and (g) NiN_4(chirality type). C atoms in silver, N atoms in blue, Ni atom in purple and H atom in white.

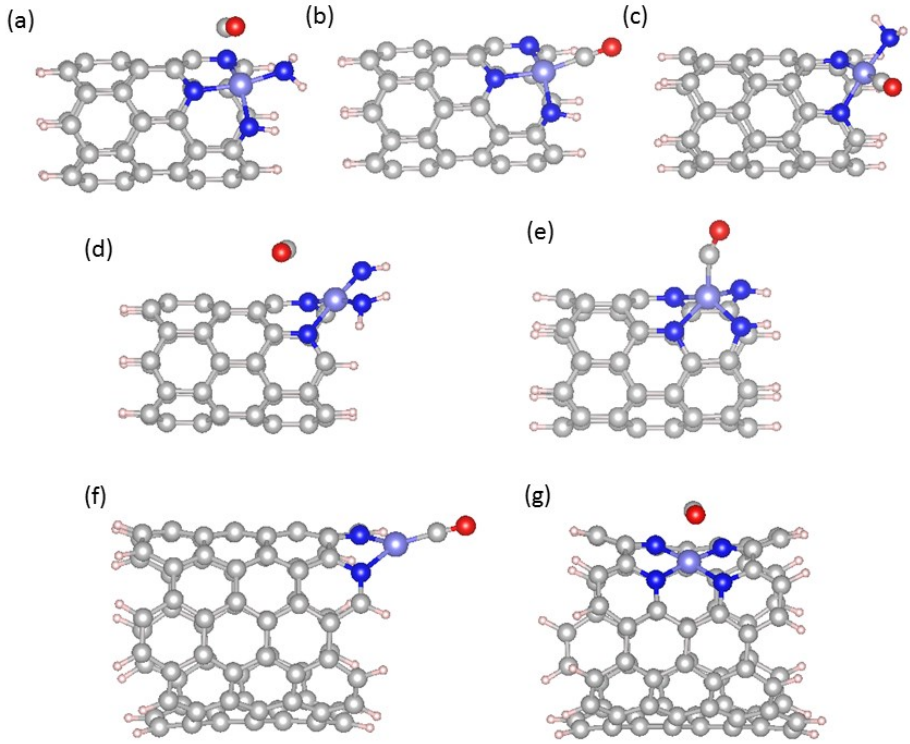

Fig 7. Optimized structures of CO adsorbed on (a) NiN_3NH_2, (b) NiN_3, (c) NiN_2NH_2, (d) $NiN_2(NH_2)_2$, (e) NiN_4, (f) NiN_2 and (g) NiN_4(chirality type). C atoms in silver, N atoms in blue, Ni atom in purple and H atom in white.

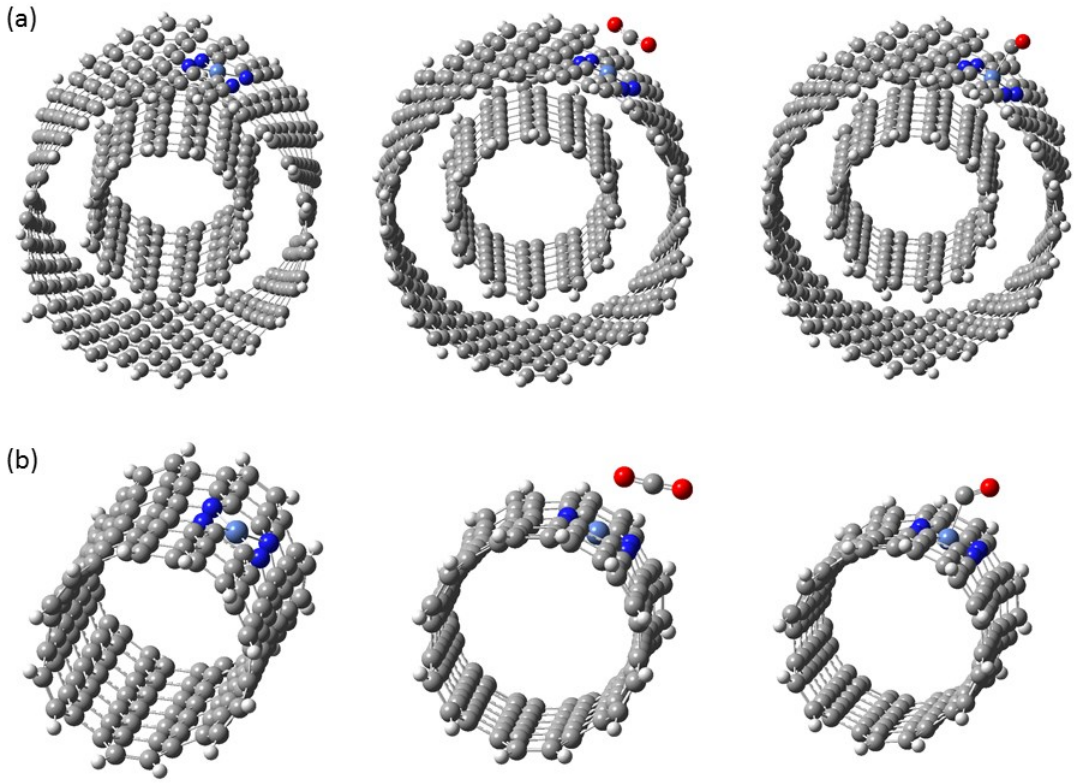

Fig 8. Optimized structures of Ni-N_4 embedded in (a) multi-walled CNTs and (b) single-walled CNTs as well as CO_2 and CO adsorbed on them, respectively. C atoms in silver, N atoms in blue, O atoms in red, H atoms in white and Ni atoms in purple.

Tab 1. Adsorption energies (eV) of CO_2 and CO adsorbed on different Ni-N active site structures on CNTs.

adsorbents	multi-walled CNTs	single-walled CNTs
CO_2	-0.88	-0.05
CO	-1.39	-0.10

In this section, the effect of multi-walled CNTs toward CO_2RR was discussed. However, DFT calculations are heavily depend on atom numbers. Hence, PBEPBE/6-31G(d)//PM6 in Gaussian16 were adopted to optimize the configurations of multi-walled CNTs, CO_2 and CO adsorption.[1] To verify the accuracy of the method, single-walled CNTs were also calculated. The binding energies of CO_2 and CO on multi-

walled CNTs are -0.88 eV and -1.39 eV, high than single-walled CNTs and neither too strong or too weak which indicates that multi-walled CNTs are promising catalysts toward CO_2RR.

Acknowledgements

The numerical calculations in this paper have been done on the supercomputing system in the Supercomputing Center of University of Science and Technology of China.

References

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