Computational Study of Site-dependent Activity of Carbon Dioxide Reduction Reaction on Silver Nanostructures

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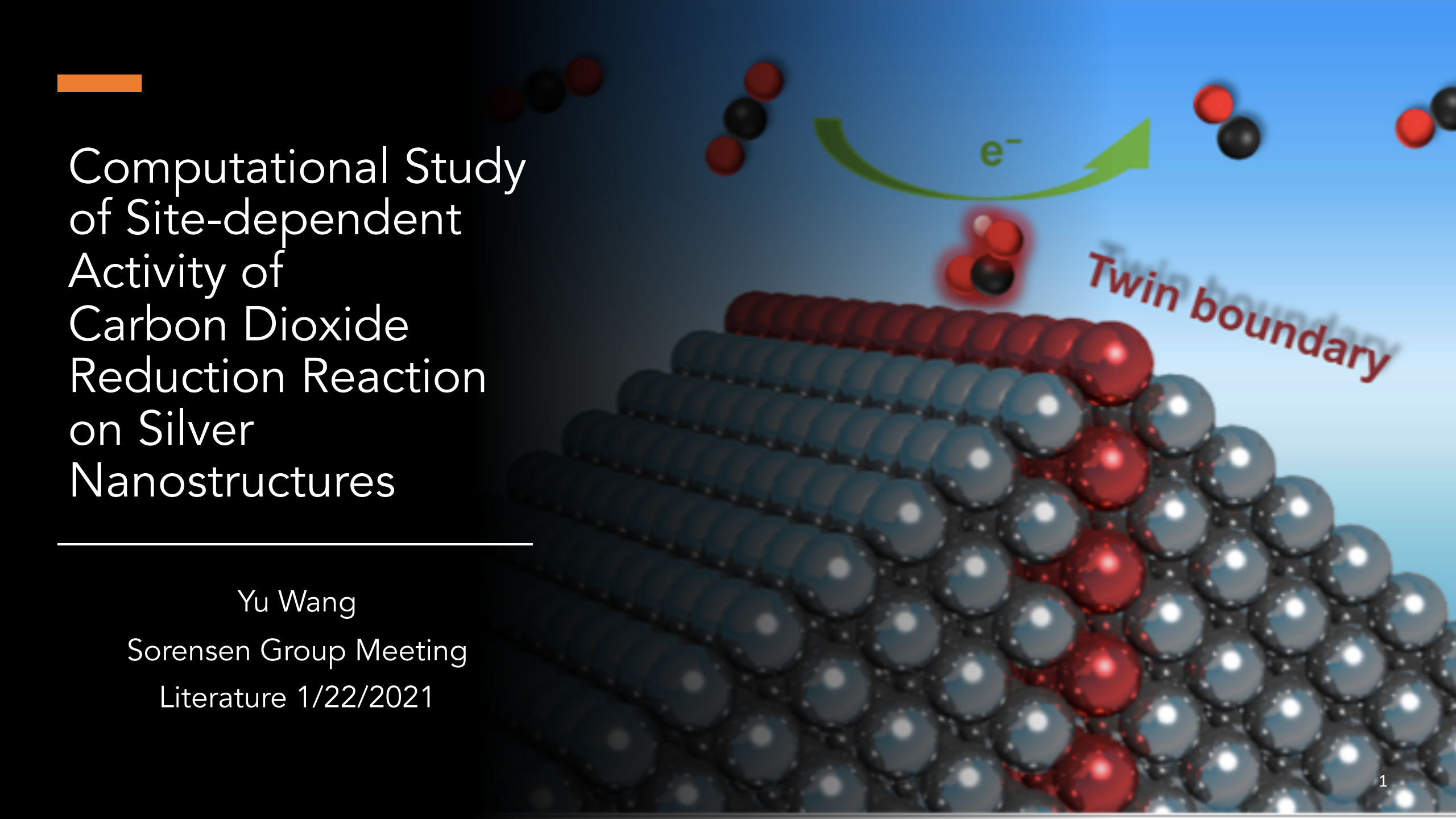
Sorensen Group Meeting

Literature 1/22/2021



Computational Chemistry: The Big Picture

- Computational chemistry is about the use of computer modelling and simulation, including ab initio methods and semi-empirical methods to study the structures and properties of molecules and materials.

- In early 1970s, ab initio programs, such as Gaussian, began to be used.

- The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn and John A. Pople.

Dykstra, C. E. Theory and applications of computational chemistry: the first forty years; Elsevier: Amsterdam, 2005.
The Nobel Prize in Chemistry 1998. NobelPrize.org. Nobel Media AB 2021.

CO2RR: Introduction

- Carbon dioxide (CO_2) reduction reaction (CO2RR) is significant for energy conversion as well as environment protection.
- Carbon dioxide can be reduced on a metal surface using electrochemical approach in a controllable and clean fashion.
- However, no transition metal surface can catalyze carbon dioxide to fuels both efficiently and selectively.
- The aim was to understand the higher catalytic activity of twin boundary edge for CO2RR mechanistically.

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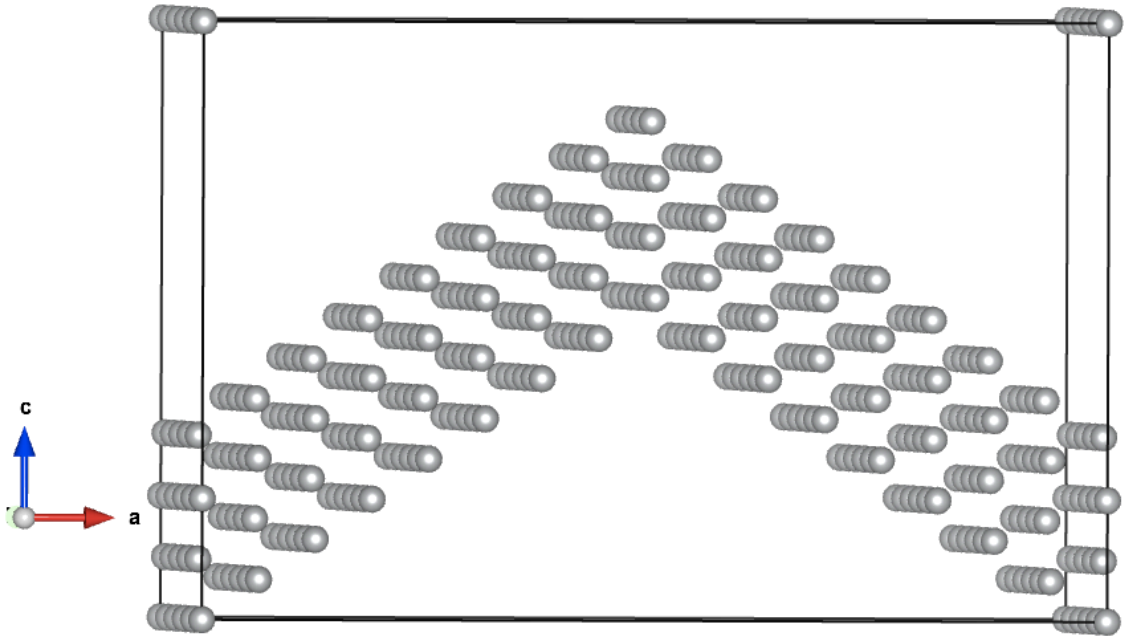
Twin Boundary Edge (TBE)



- A special case of grain boundary with a large angle
- No atomic misfit
- Crystals on either side of the plane are the mirror image of each other

van Vlack, Elements of Materials Science and Engineering, Addison Wesley, 1989

Reaction Model

$CO_2 + * \rightarrow CO_2*$ (* = adsorption site) (Equation 1)

$CO_2* + H^+ + e^- \rightarrow COOH*$ (Equation 2)

$COOH* + H^+ + e^- \rightarrow CO* + H_2O$ (Equation 3)

$CO* \rightarrow CO + *$ (Equation 4)

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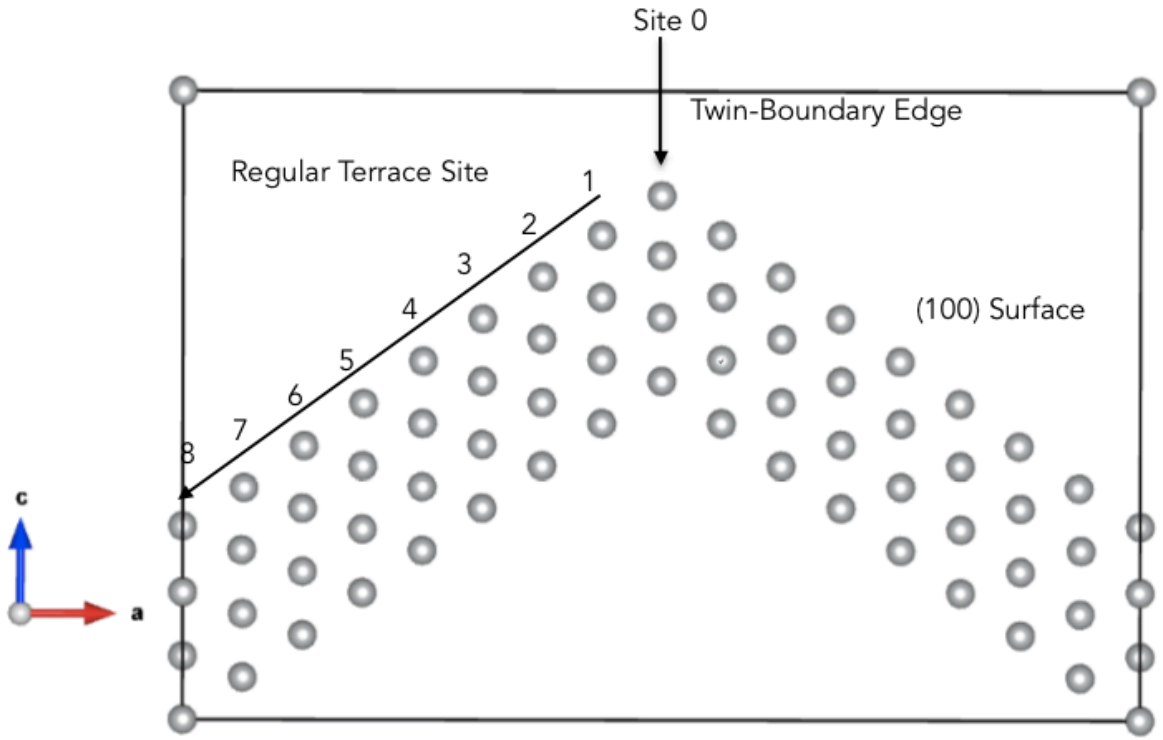
Computational Details

- Total energy of the silver adsorption system was calculated.

- First-principles calculations based on density functional theory as implemented in the Vienna Ab initio Simulation Package (VASP).

VASP Group, Theoretical Physics Departments, Vienna. Retrieved January 11, 2021

Computational Details



- Slab model is used for nanostructure surfaces.
- Other than compared to the terrace surface on nano cubes, TBE is also compared to the side terrace surfaces.

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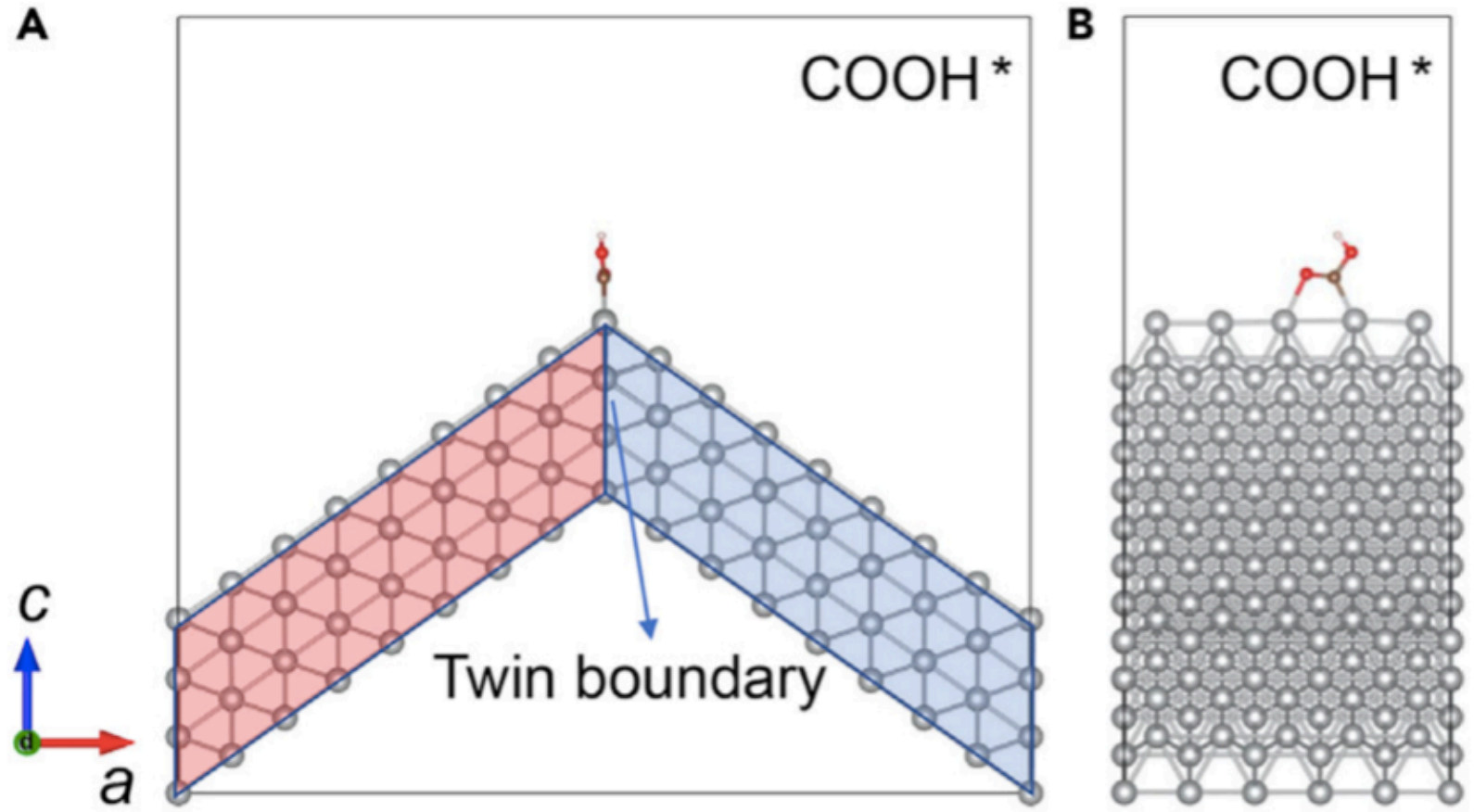
Results: COOH Intermediate*



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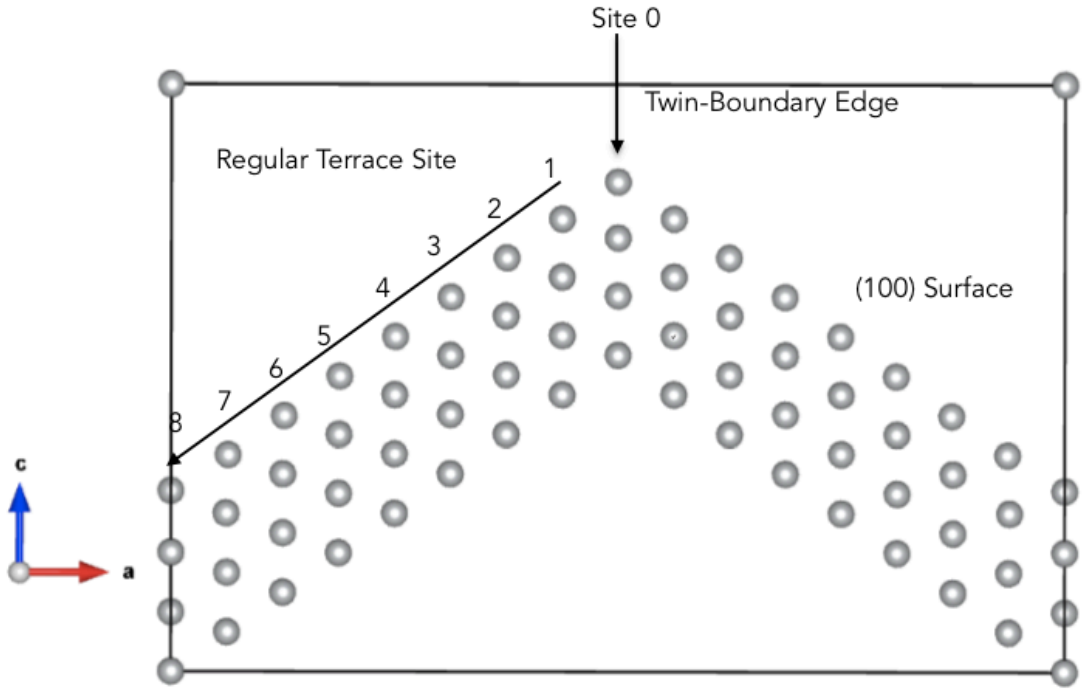
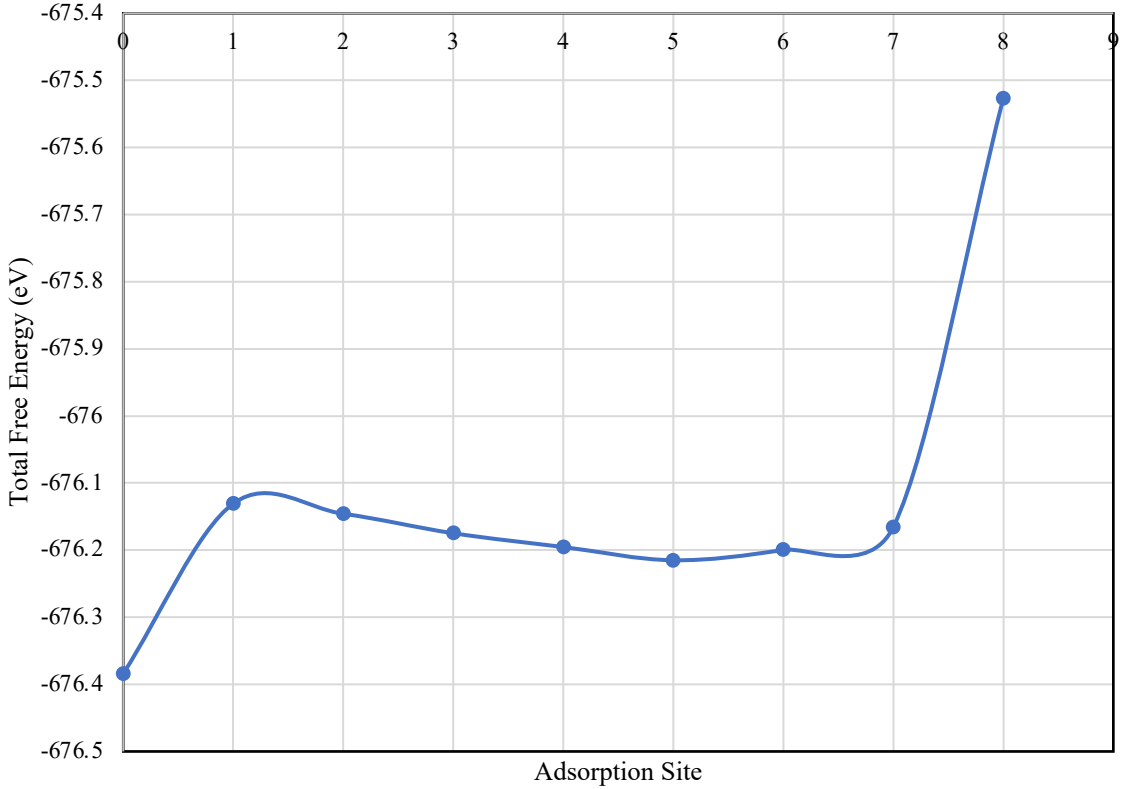
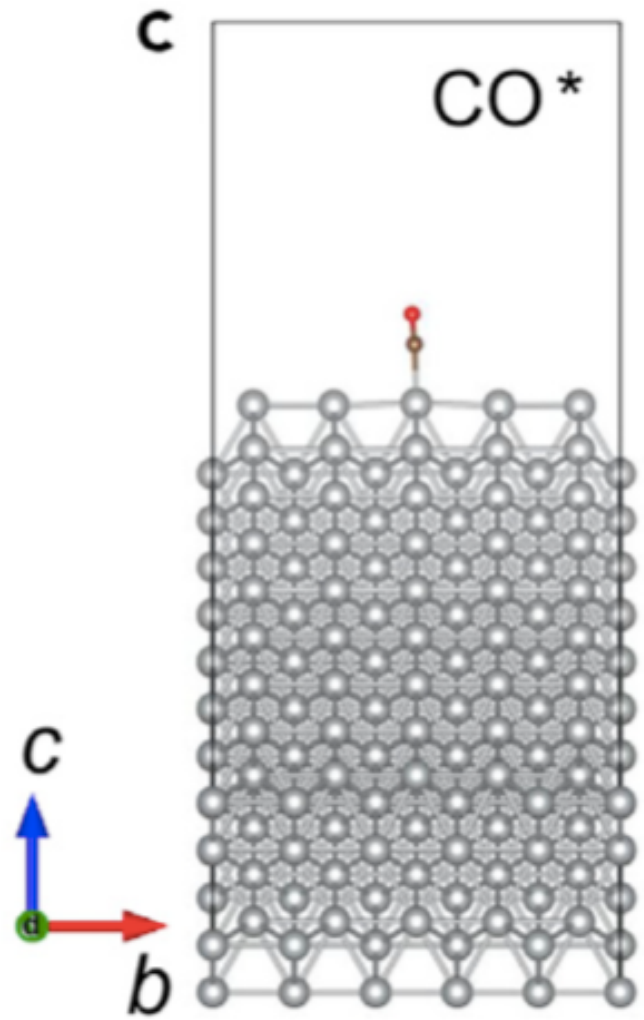




Results: CO Intermediate*



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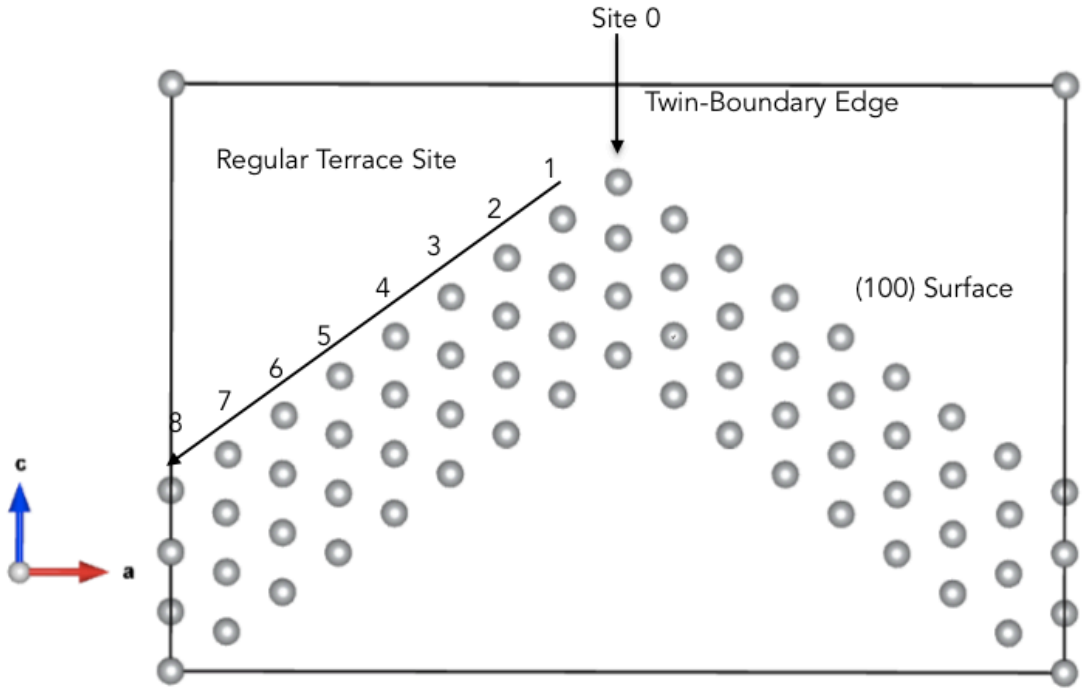
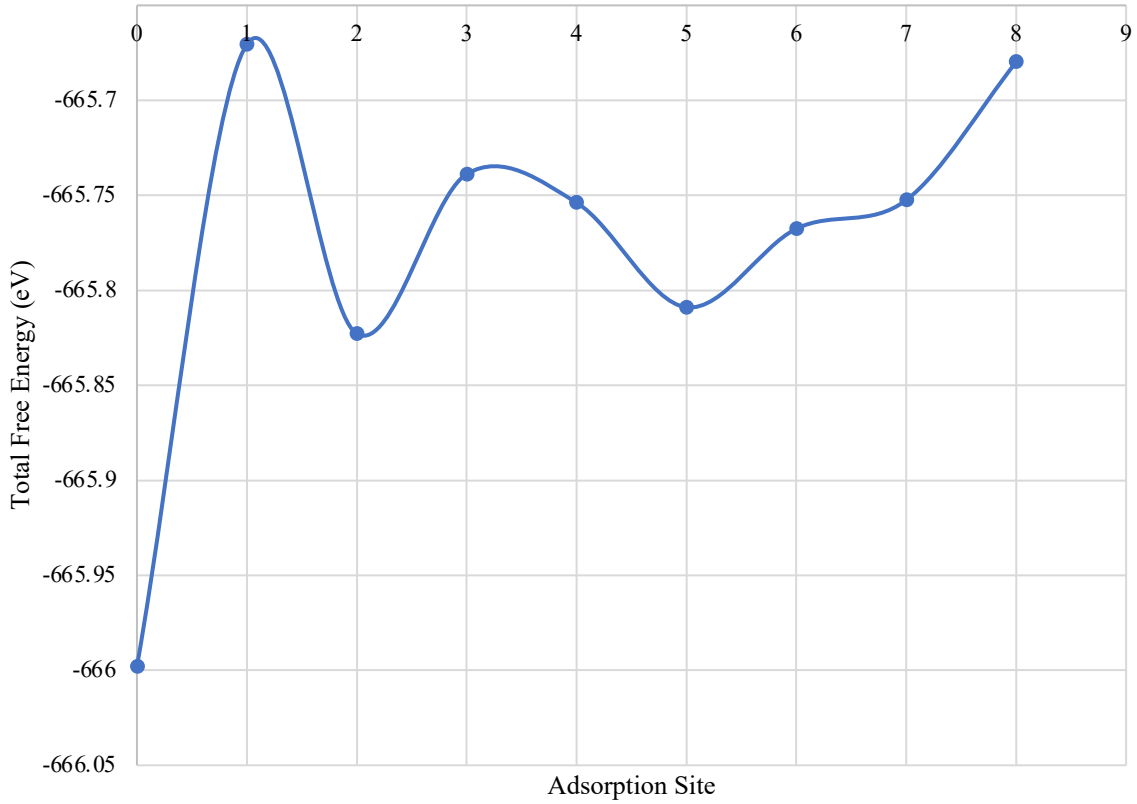
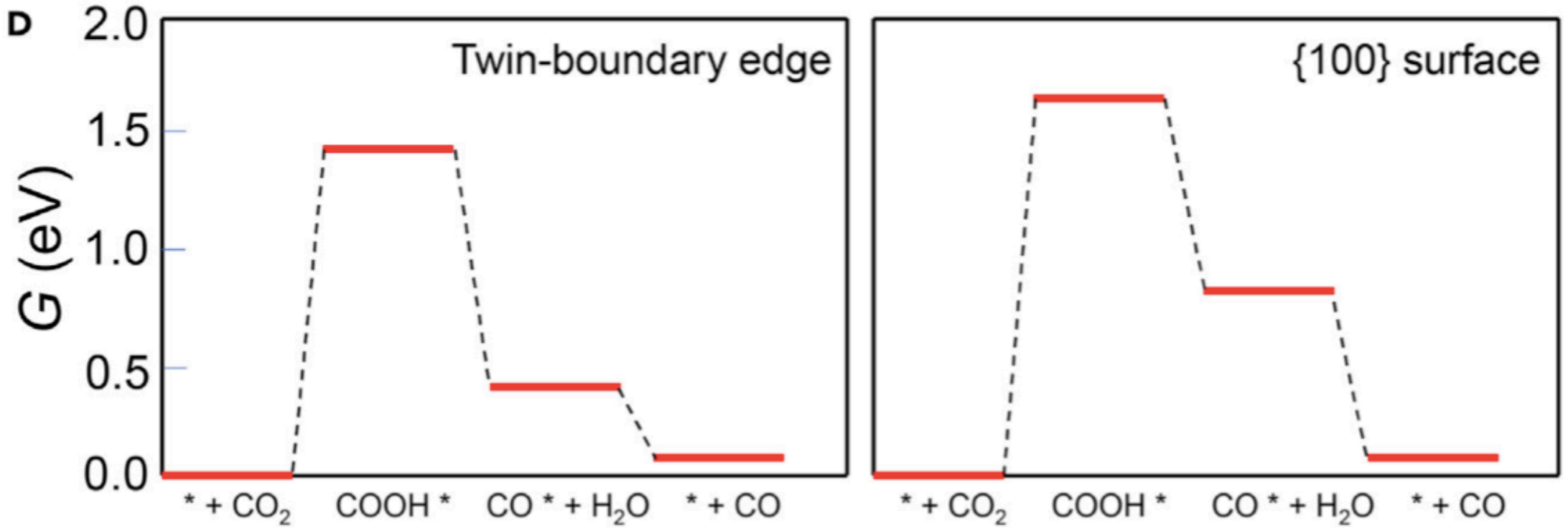
Results: CO Intermediate*





Results: TBE vs. (100) Surface



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Discussion and Conclusion

- Generation of COOH* intermediate is the rate-limiting step.
- Twin-boundary edge has much higher catalytic activity of CO2RR compared to the {100} surface atoms.
- The catalytic activity of TBE atoms was more than two orders higher than that of the {100} surfaces atoms, experimentally.
- The deviation of experimental and theoretical rate ratio might be the geometric roundness of TBEs of nanowires in experiment.

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