



Grand Canonical Approach to Modeling Dynamic Catalysts

*Electrochemical Restructuring Surfaces
... where Thermodynamics and Kinetics Fight*

Zisheng Zhang

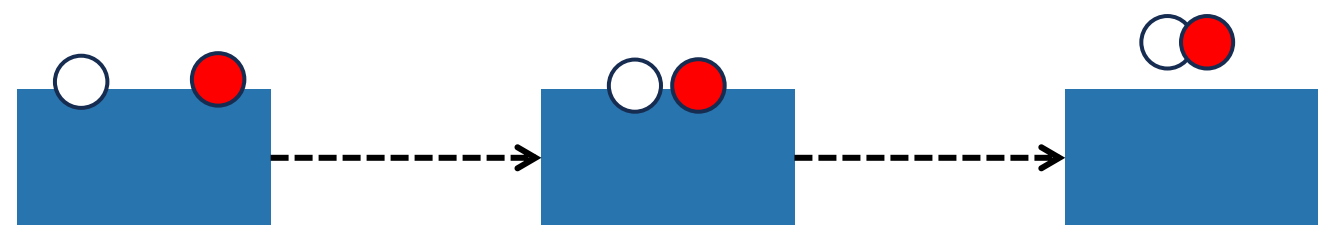
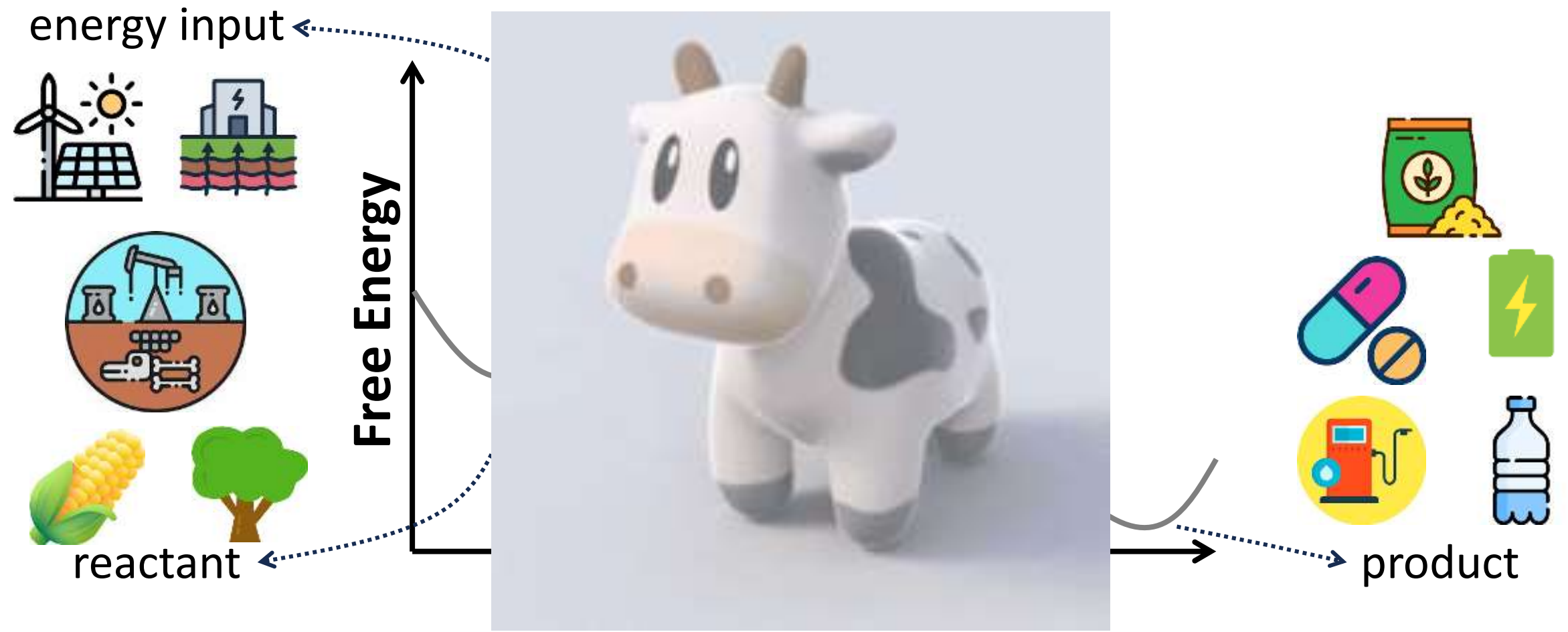
Alexandrova Lab

Department of Chemistry and Biochemistry

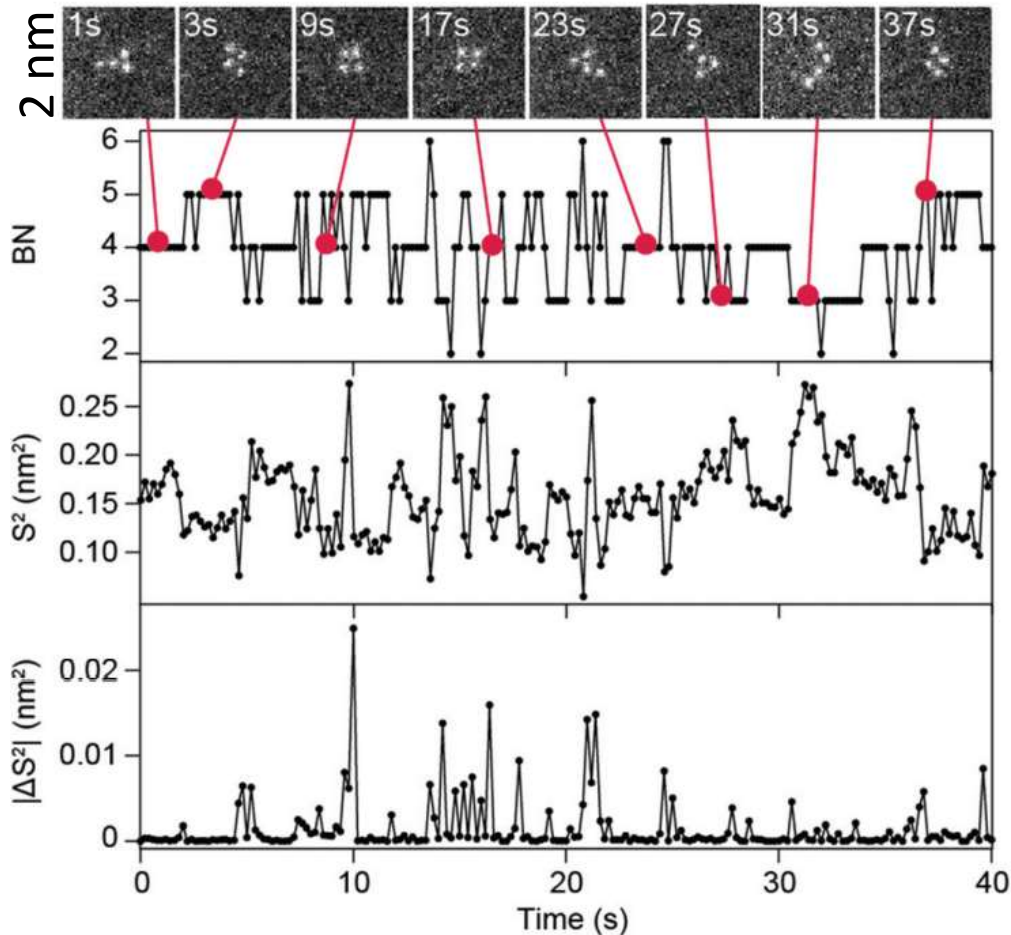
University of California, Los Angeles

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Website: zishengz.github.io

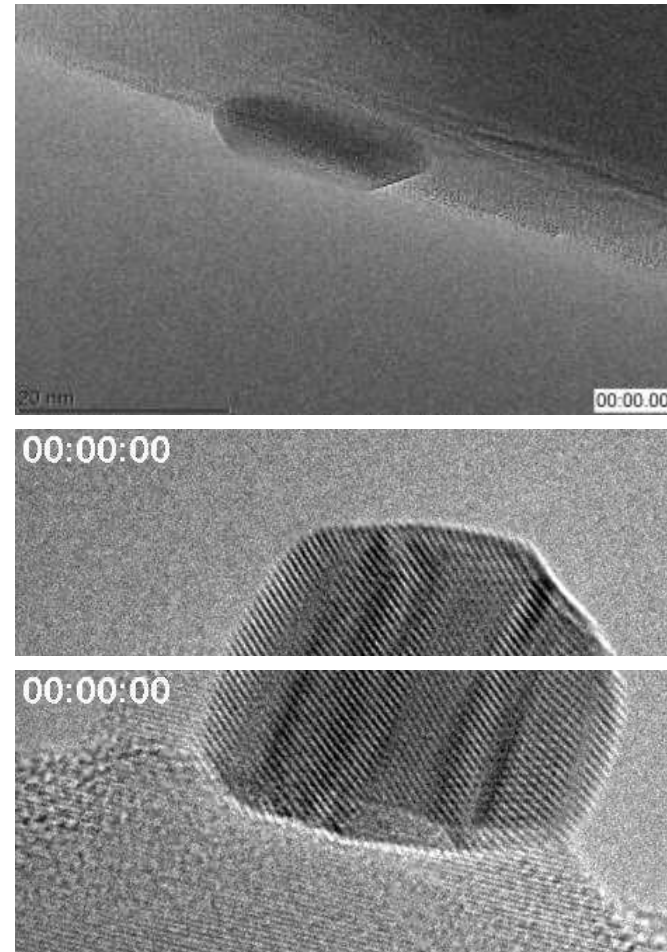


Sub-nanometer Clusters



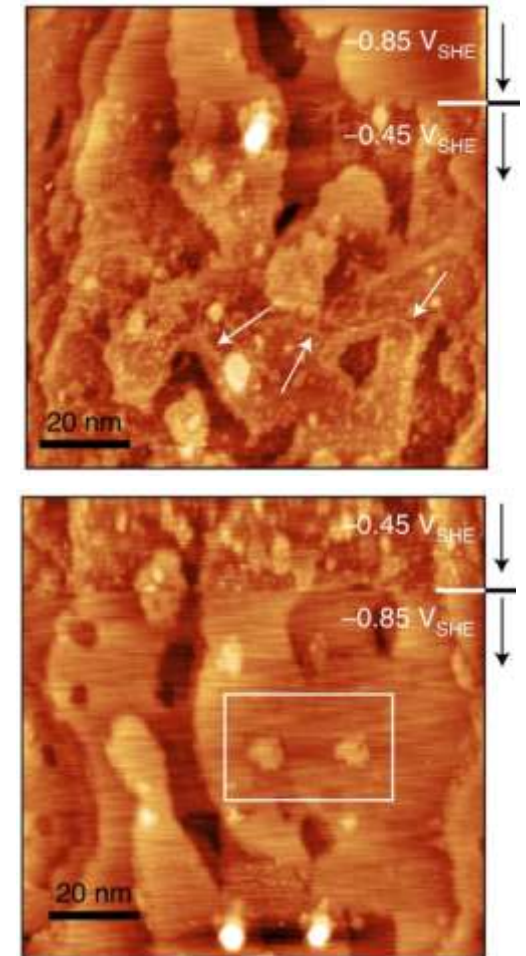
Chem. Comm., 2019, 55, 4753-4756

Nanoparticles

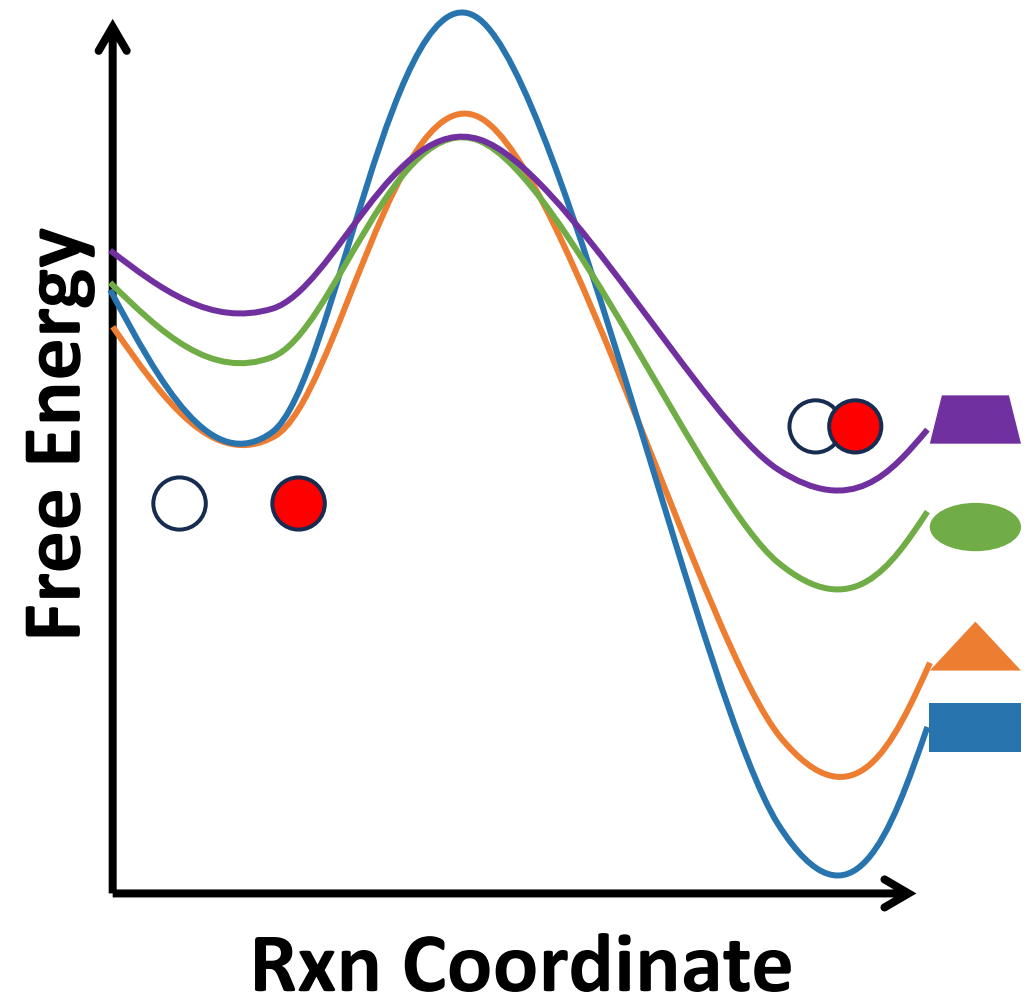
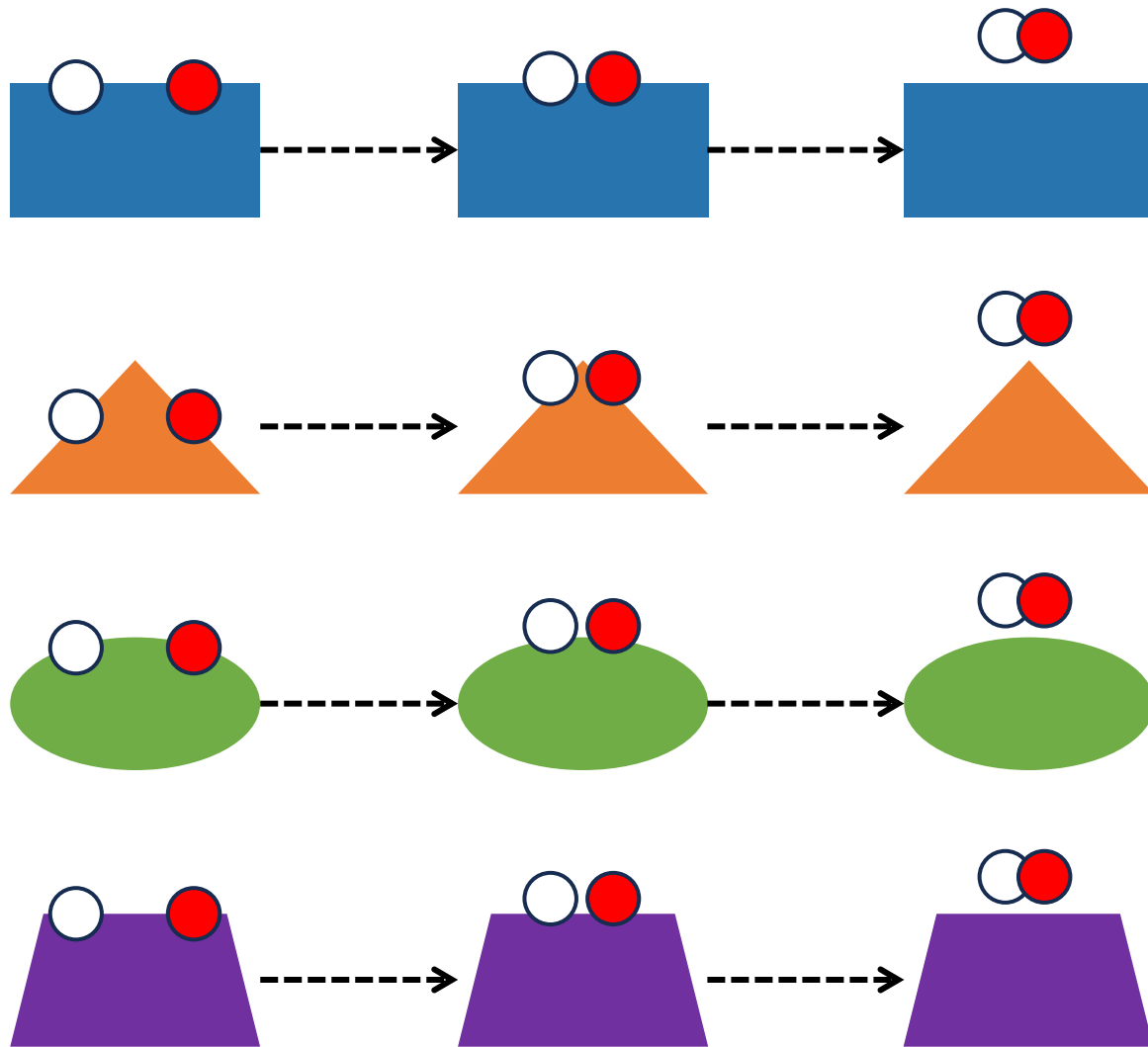


Angew. Chem. Int. Ed., 2018, 57, 1261

Polycrystalline Electrodes



Nat. Catal., 2020, 3, 797-803

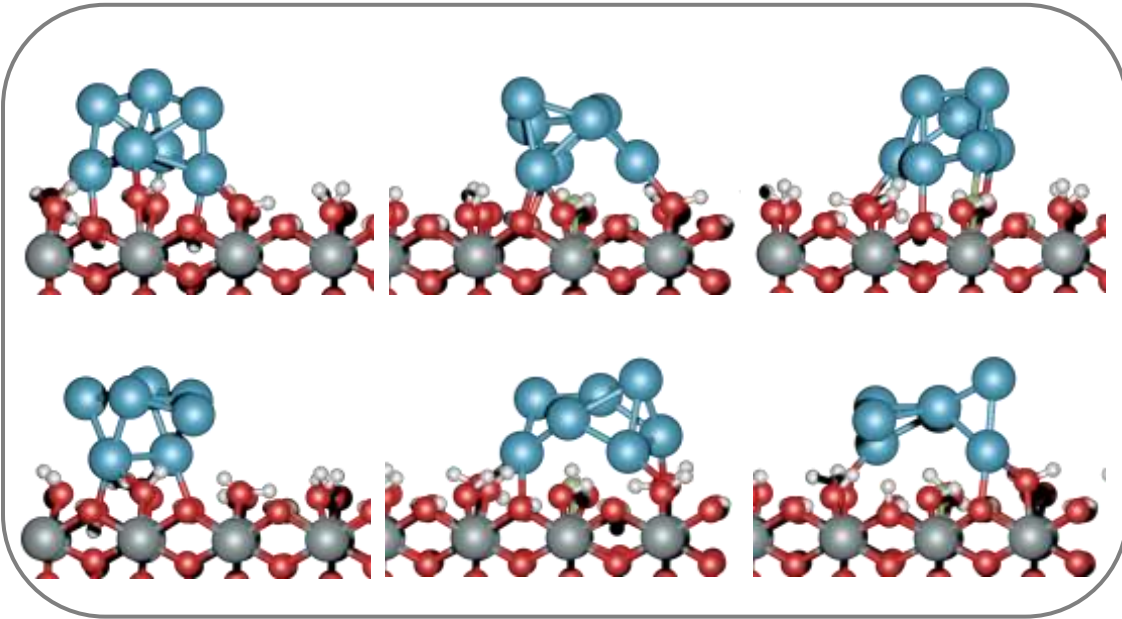


Ensemble of catalyst states

Canonical Ensemble

(NVT)

States: same composition



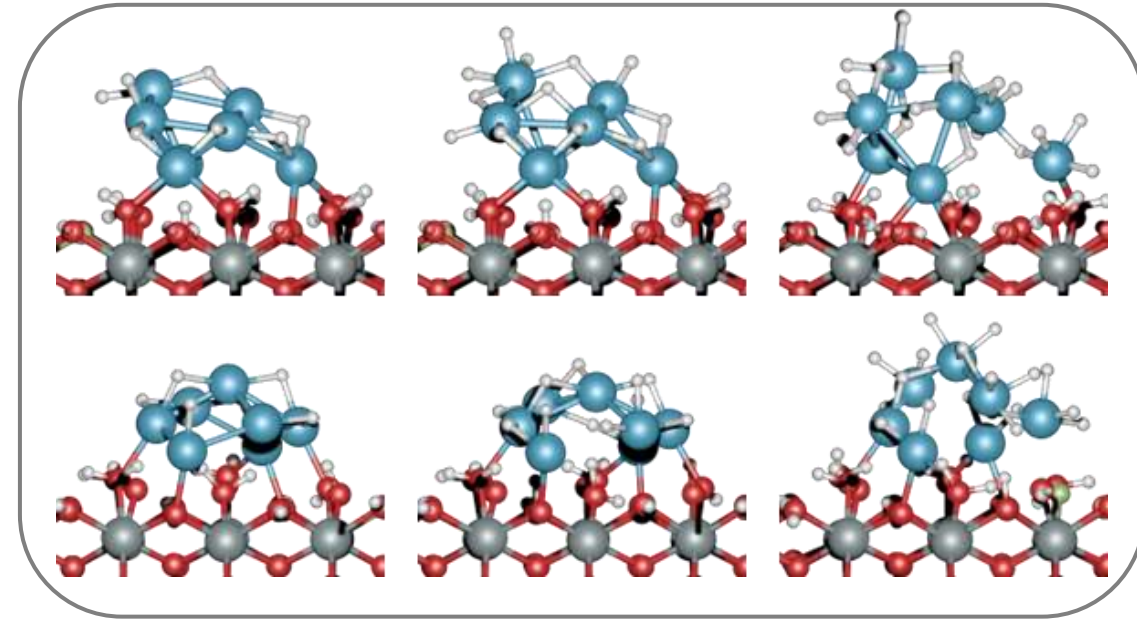
Pt₇/FTO

Grand Canonical Ensemble

(μVT)

States: different composition

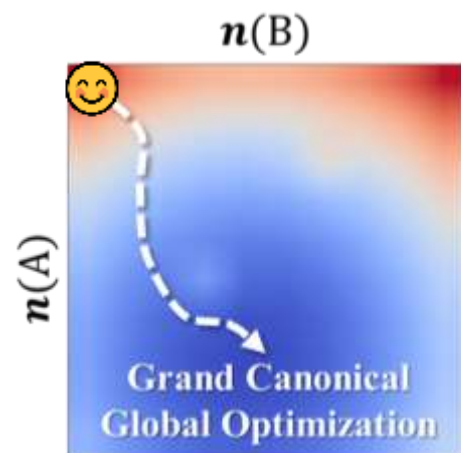
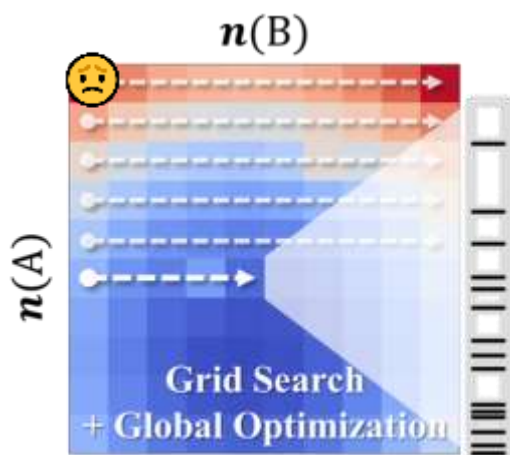
H-rich
condition



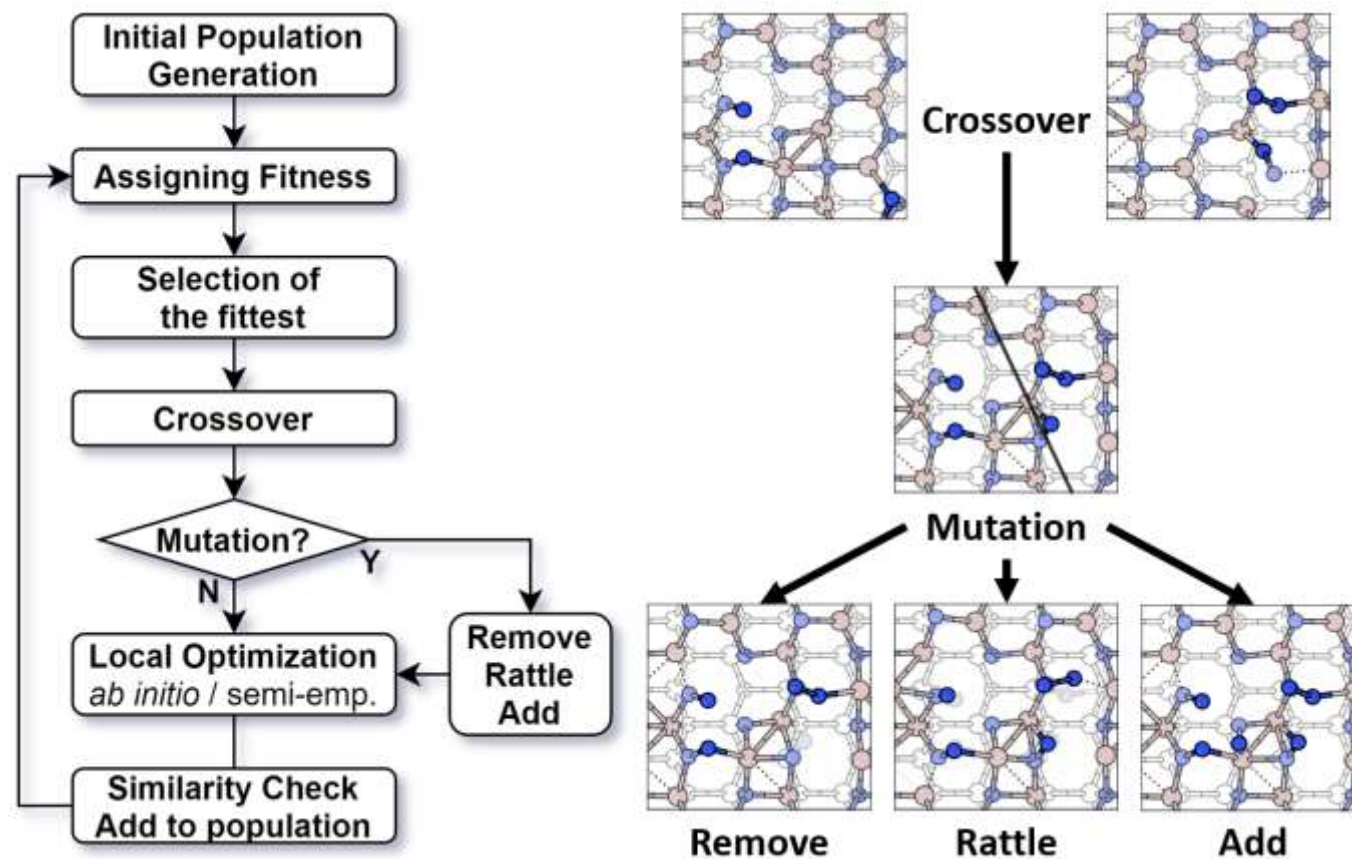
Pt₇H_x/FTO

Angew. Chem. Int. Ed., 2023, 135, e202218575

Exploring the off-stoichiometric chemical space

Composition: A, B 

Grand Canonical Genetic Algorithm



$$\text{GC Free Energy: } \Omega = U - TS - \sum_i^{\text{elem.}} \mu_i N_i$$

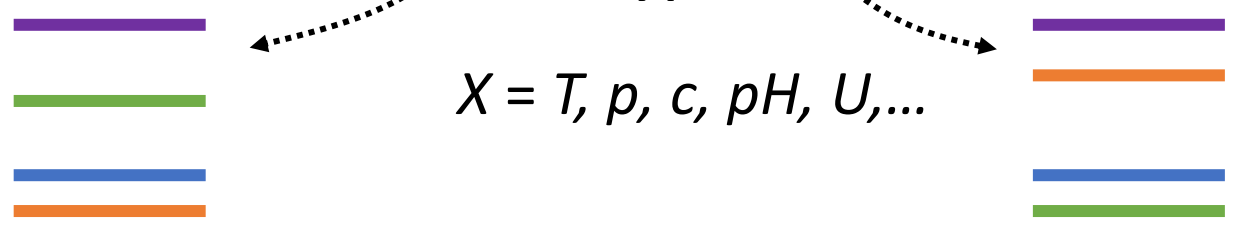
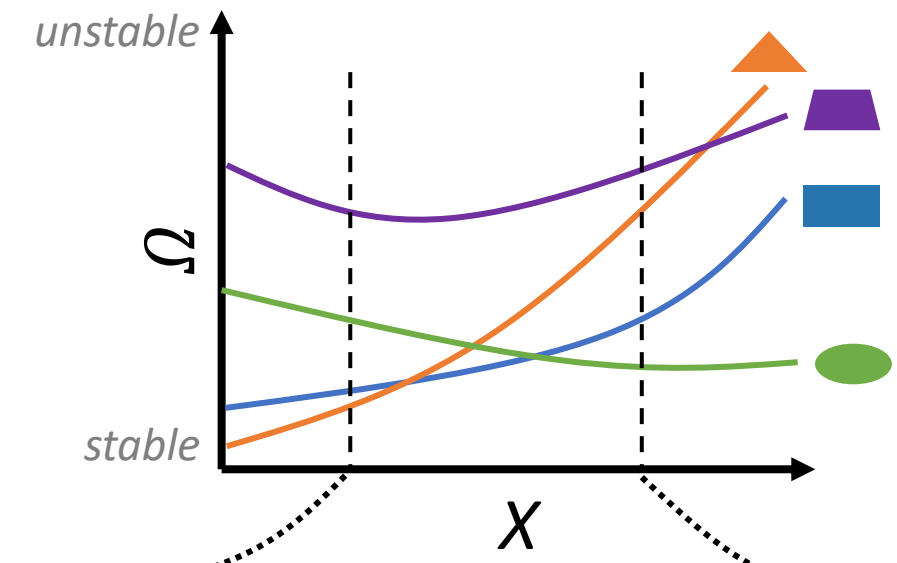

<https://github.com/zishengz/gocia>

JACS, 2022, 144, 19284–19293

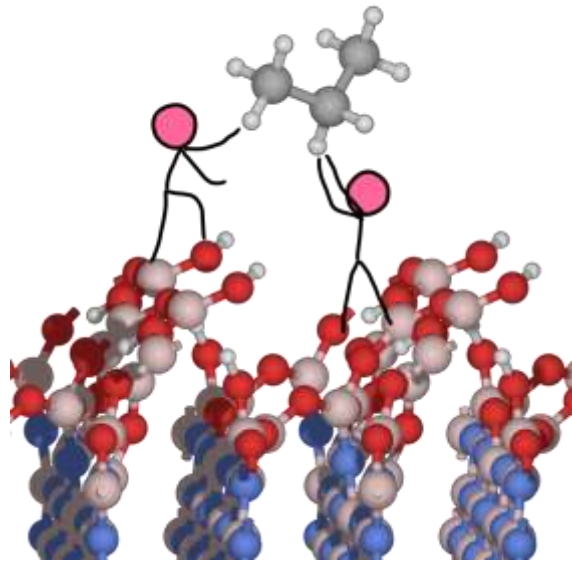
GC Free Energy

$$\Omega = U - TS - \sum_i^{\text{elem.}} \mu_i N_i$$

$$\mu_H(T, p_{H_2}, U, \text{pH}) = \frac{1}{2} G_{H_2}^{\text{gas}} - \ln(10) k_B T \text{pH} + k_B T \ln \frac{p_{H_2}}{p^\circ} - |e| U_{\text{SHE}}$$



X-dependent GC ensemble



h-BN for oxidative dehydrogenation

Dynamic phase diagram:

JPCL, 2018 , 10, 20–25

Rxn mechanism:

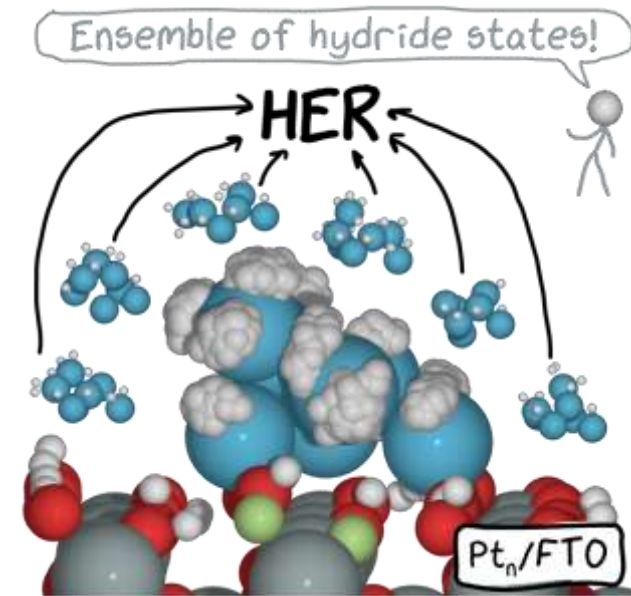
ACIE, 2020, 59, 16527-16535

NMR simulation:

JACS, 2023, 145, 17265-17273

R-ray Raman simulation:

JACS, 2023, 145, 25686–25694 (Cover)



Electrochemistry on supported clusters

B cluster for HER:

ACS Catal., 2020 , 10, 13867–13877

Fluxionality breaks activity volcano:

ChemCatChem, 2022 , 14, e202200345

Potential dependent active site:

ACS Catal., 2022 , 12, 14517–14526

Ensemble-based kinetics model:

ACIE, 2023 , 135, e202218575

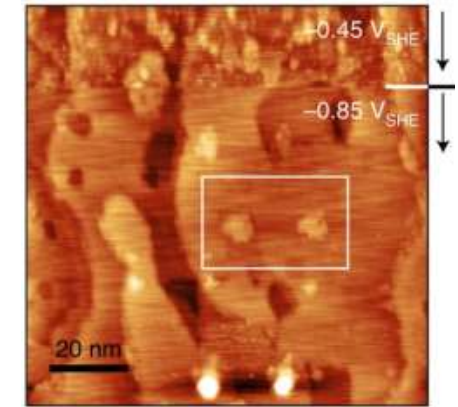
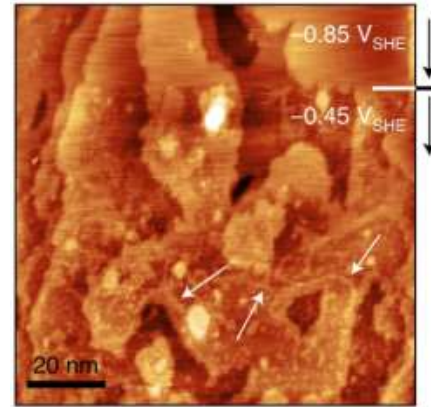
Beyond CO

8		9 VIII 8		10		11 IB 1B		12 IIB 2B	
26 Fe Iron 55.833	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411
76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59					

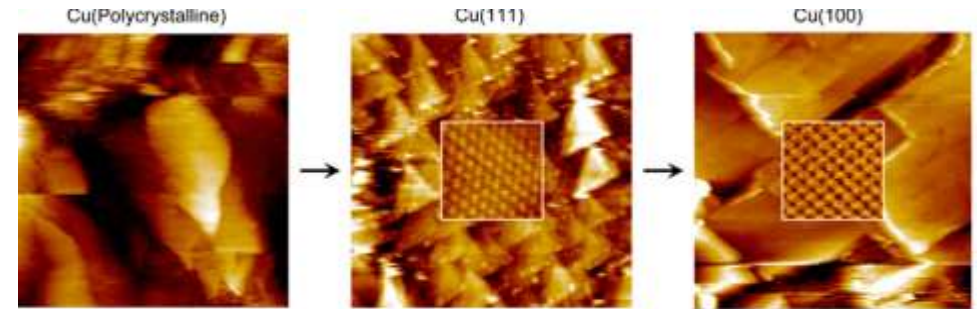
No activity

CO

Formate

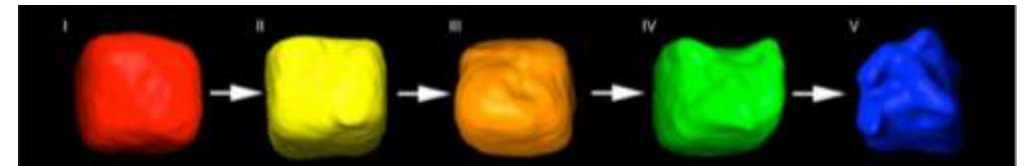


Nat. Catal., 2020, 3, 797–803

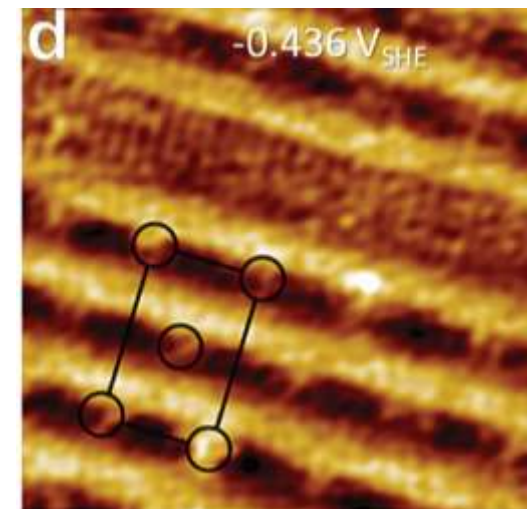
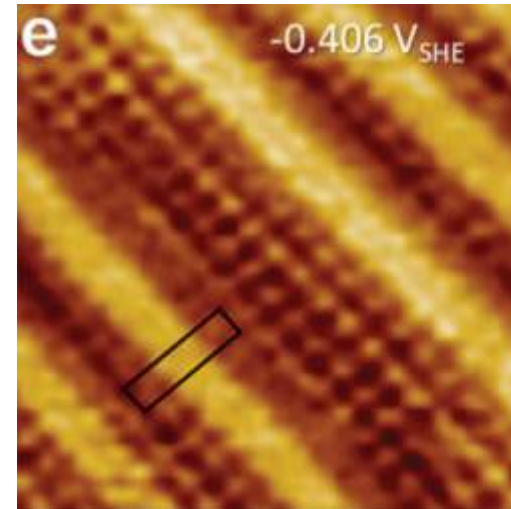
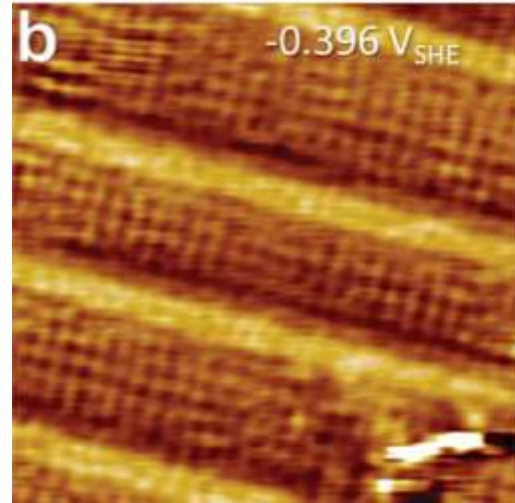
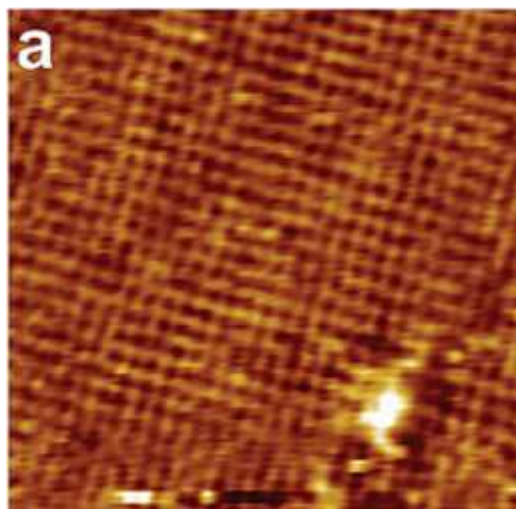


Fixed CO₂RR Potential (-0.90 V vs. SHE) in 0.1 M KOH

Langmuir, 2014, 30, 15053–15056

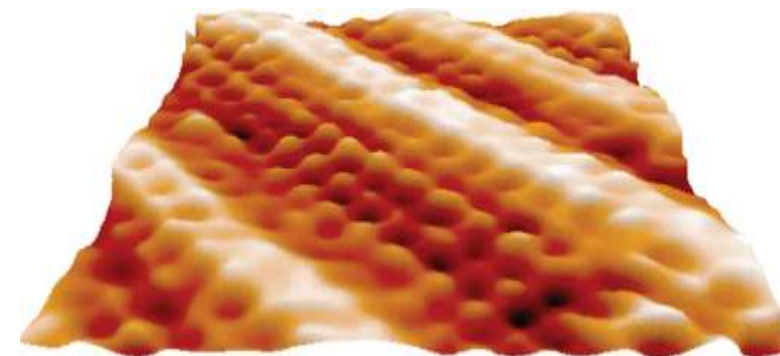


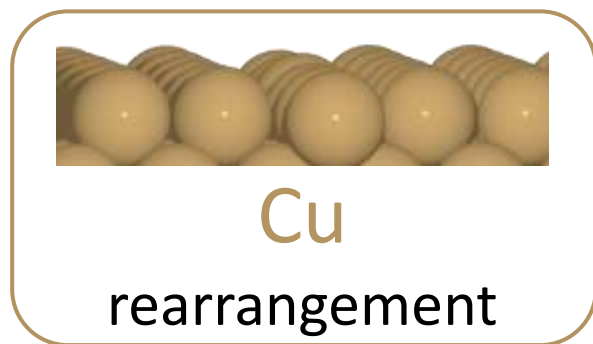
Nat. Commun., 2018, 9, 3117



J. Am. Chem. Soc., 2009, 131, 10362–10363

Electrochemical STM

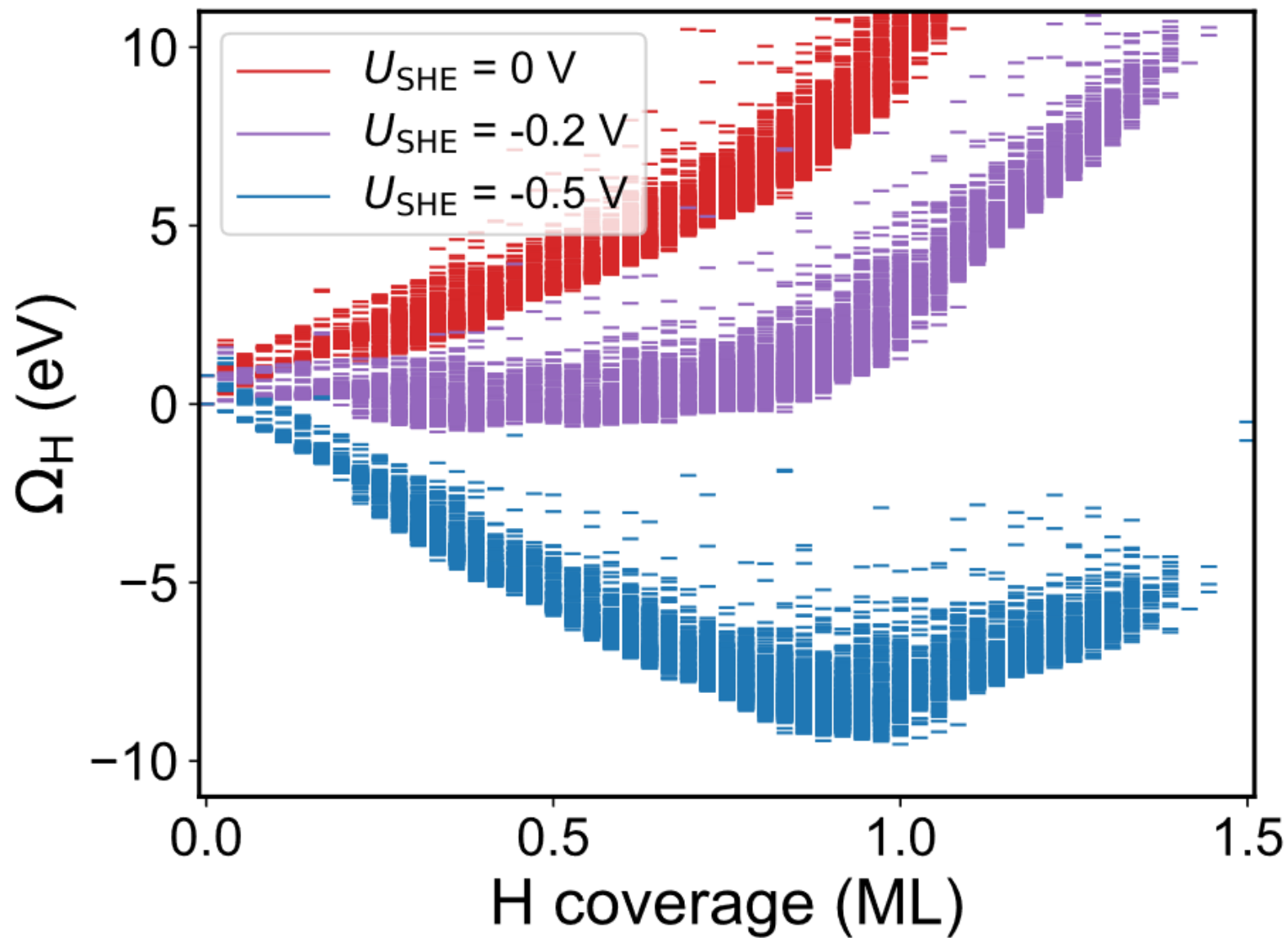
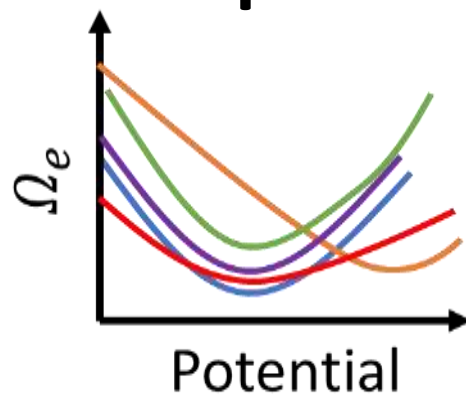




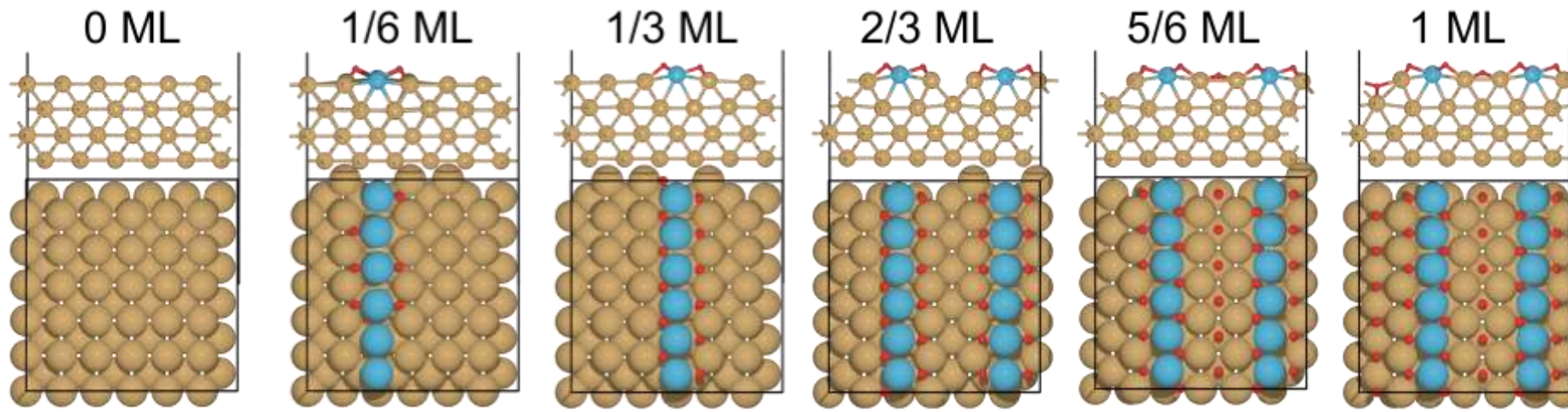
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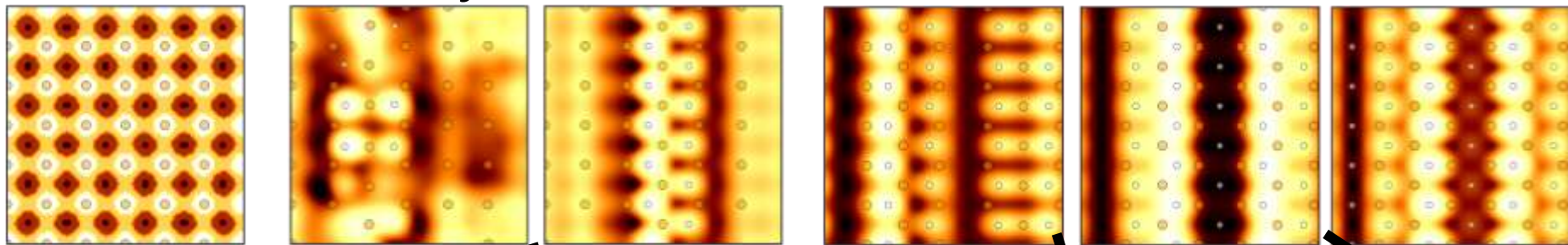
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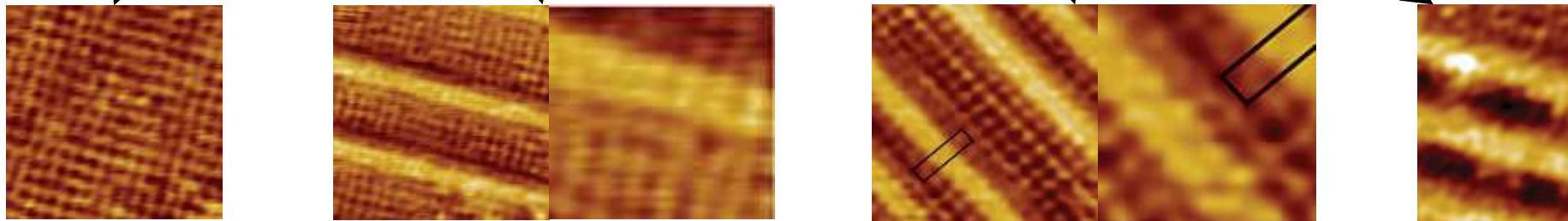
JACS, 2022 , 144, 19284–19293



simulated



experimental

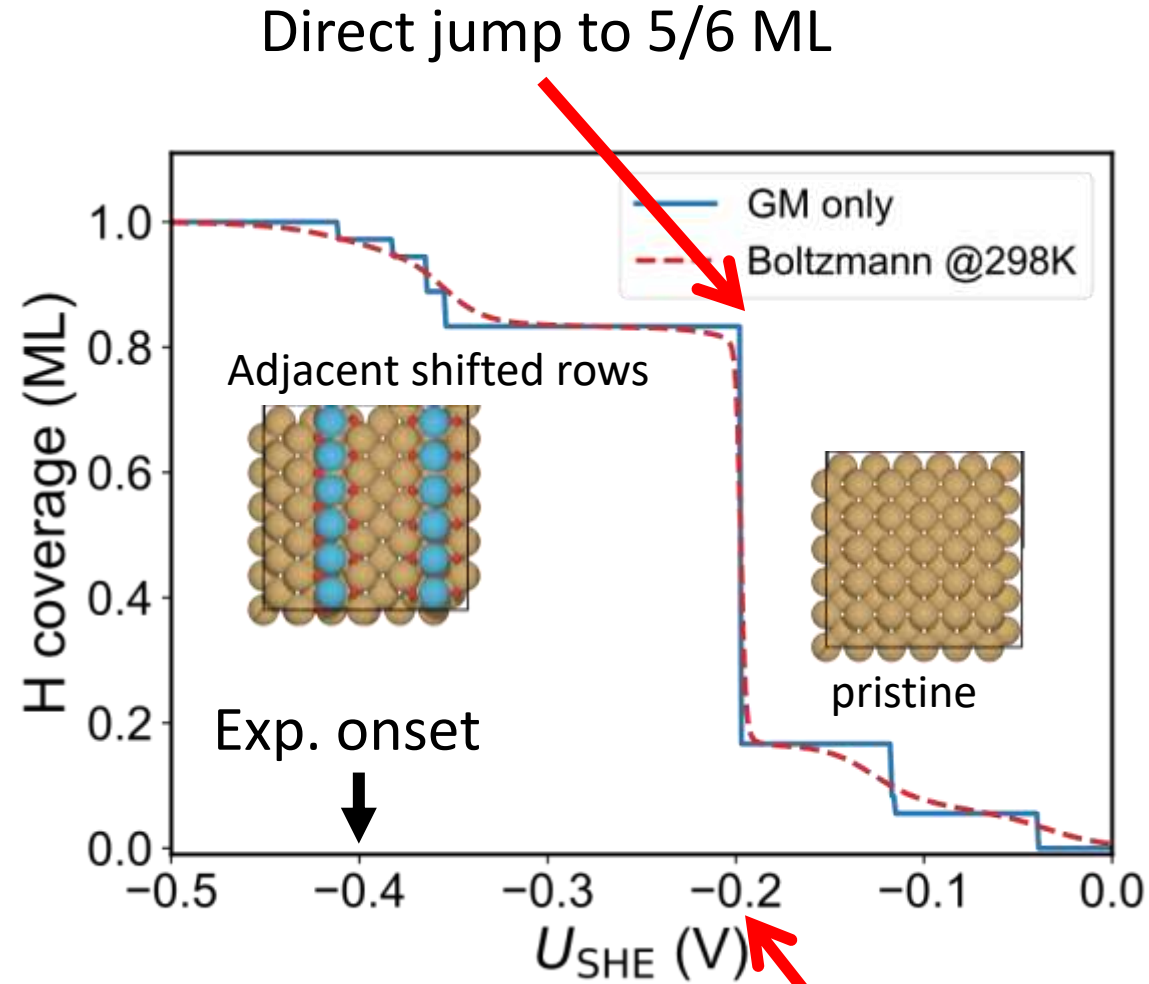


-0.396 V

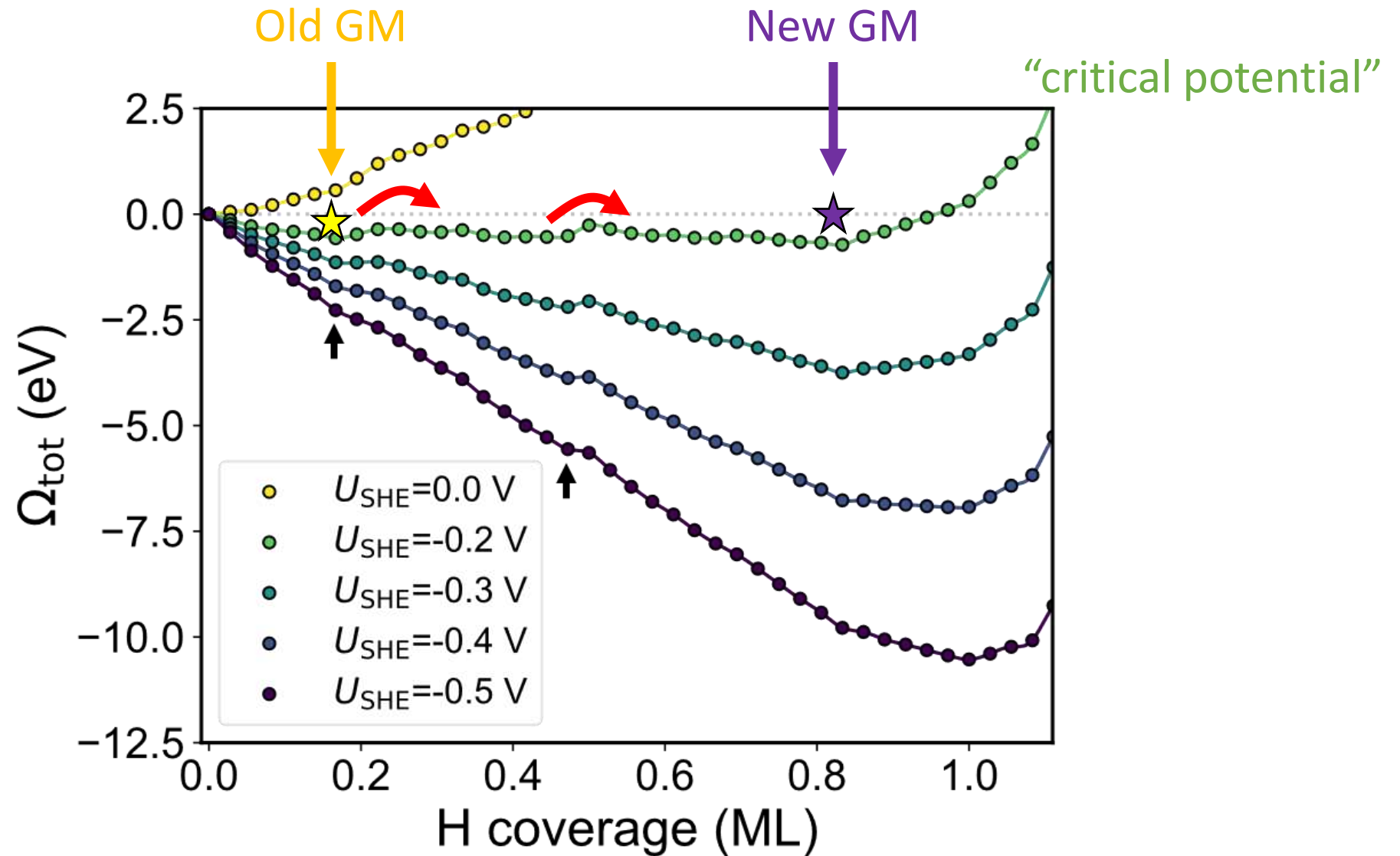
-0.406 V

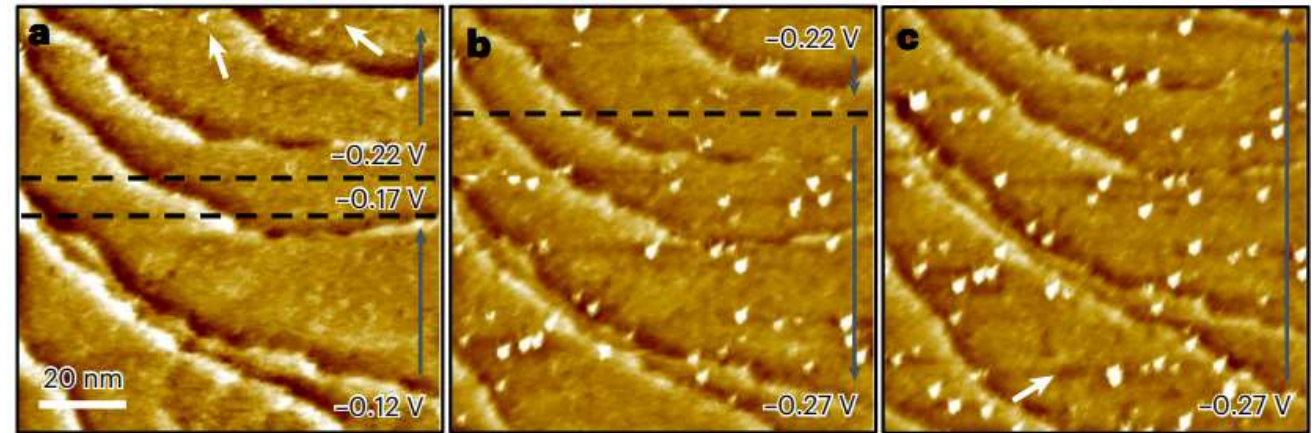
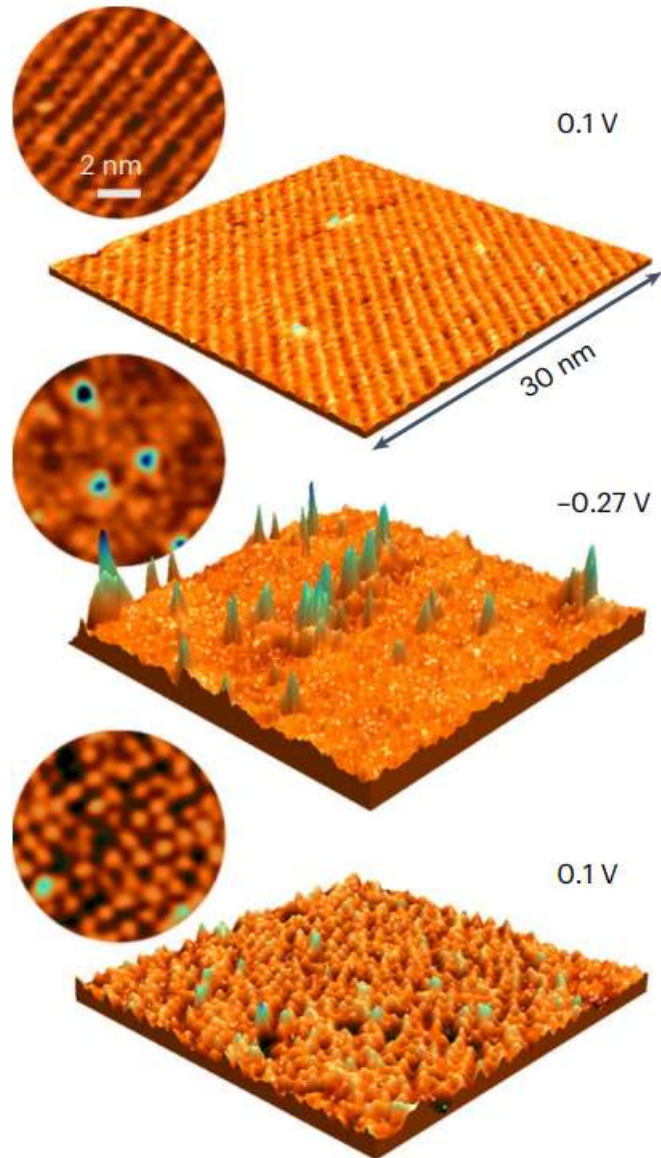
-0.436 V

JACS, 2022, 144, 19284–19293



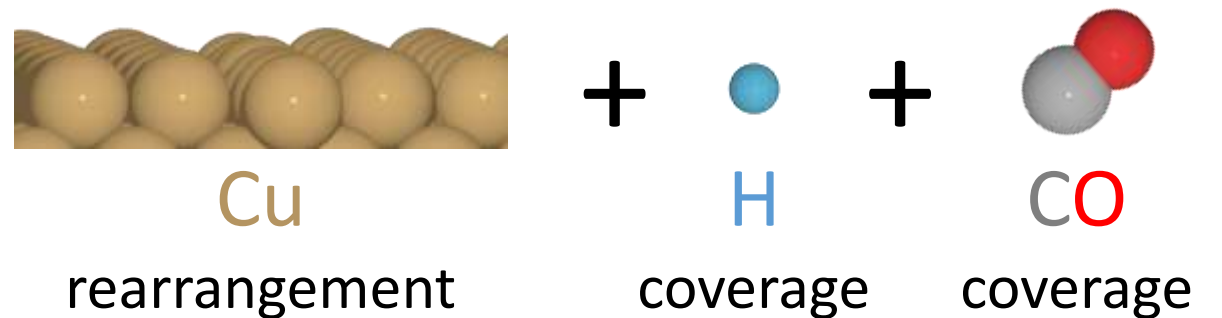
Too early onset (exp: $\sim -0.4V$)



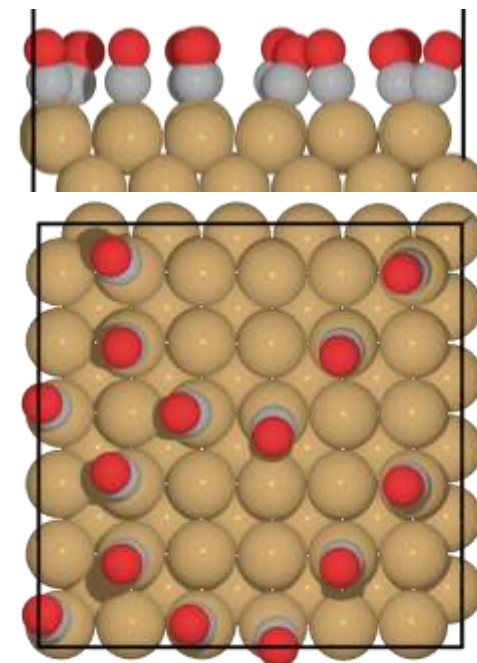
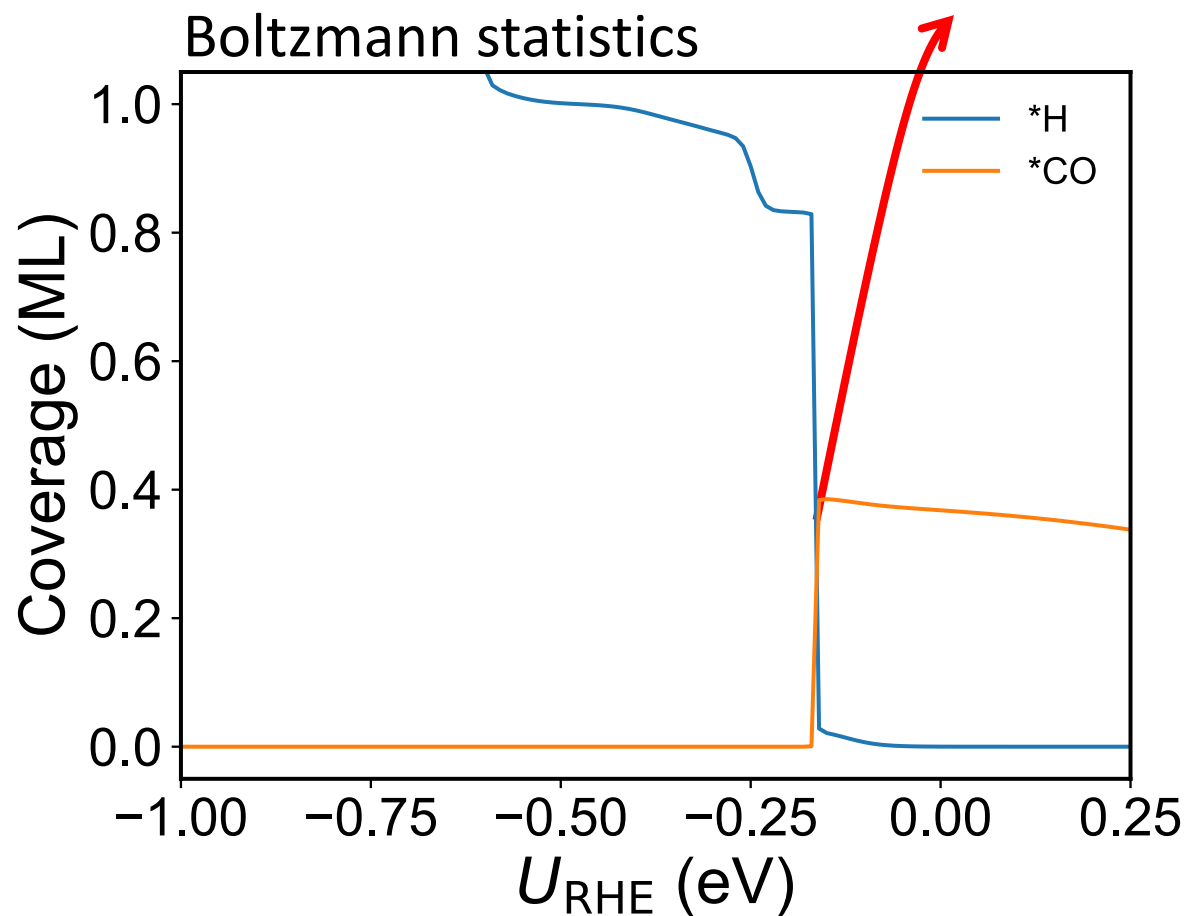
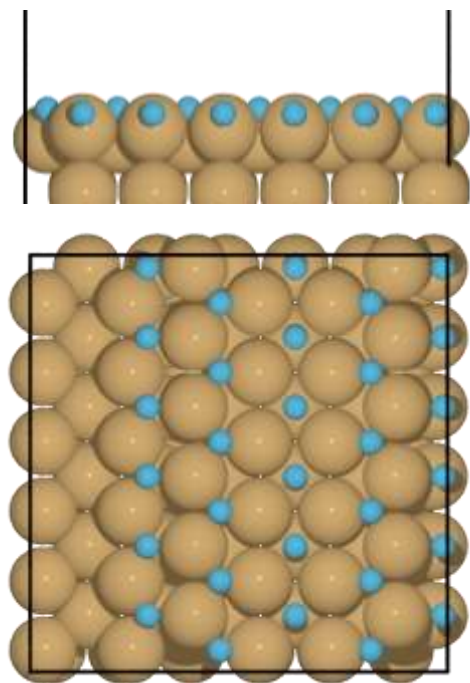


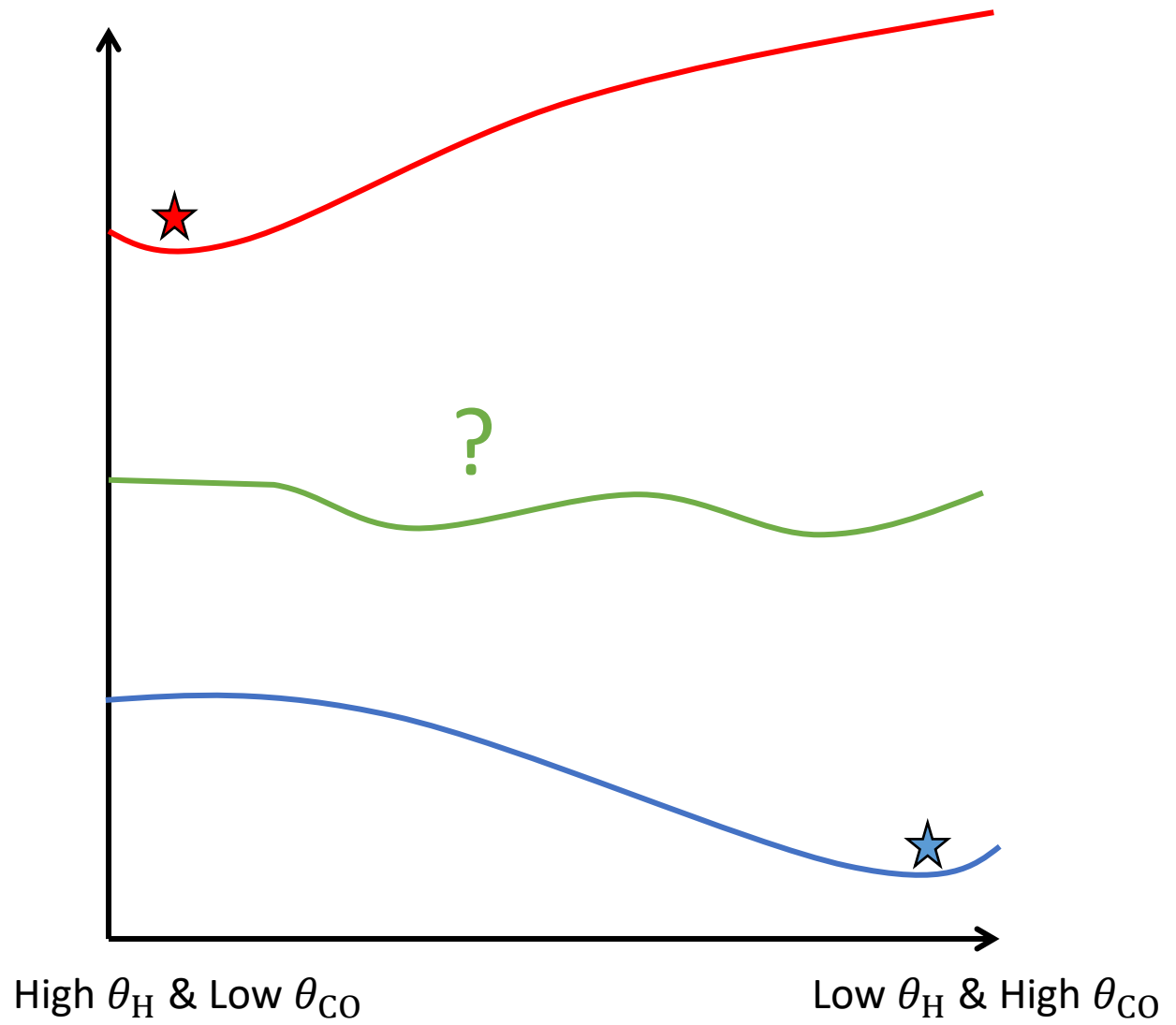
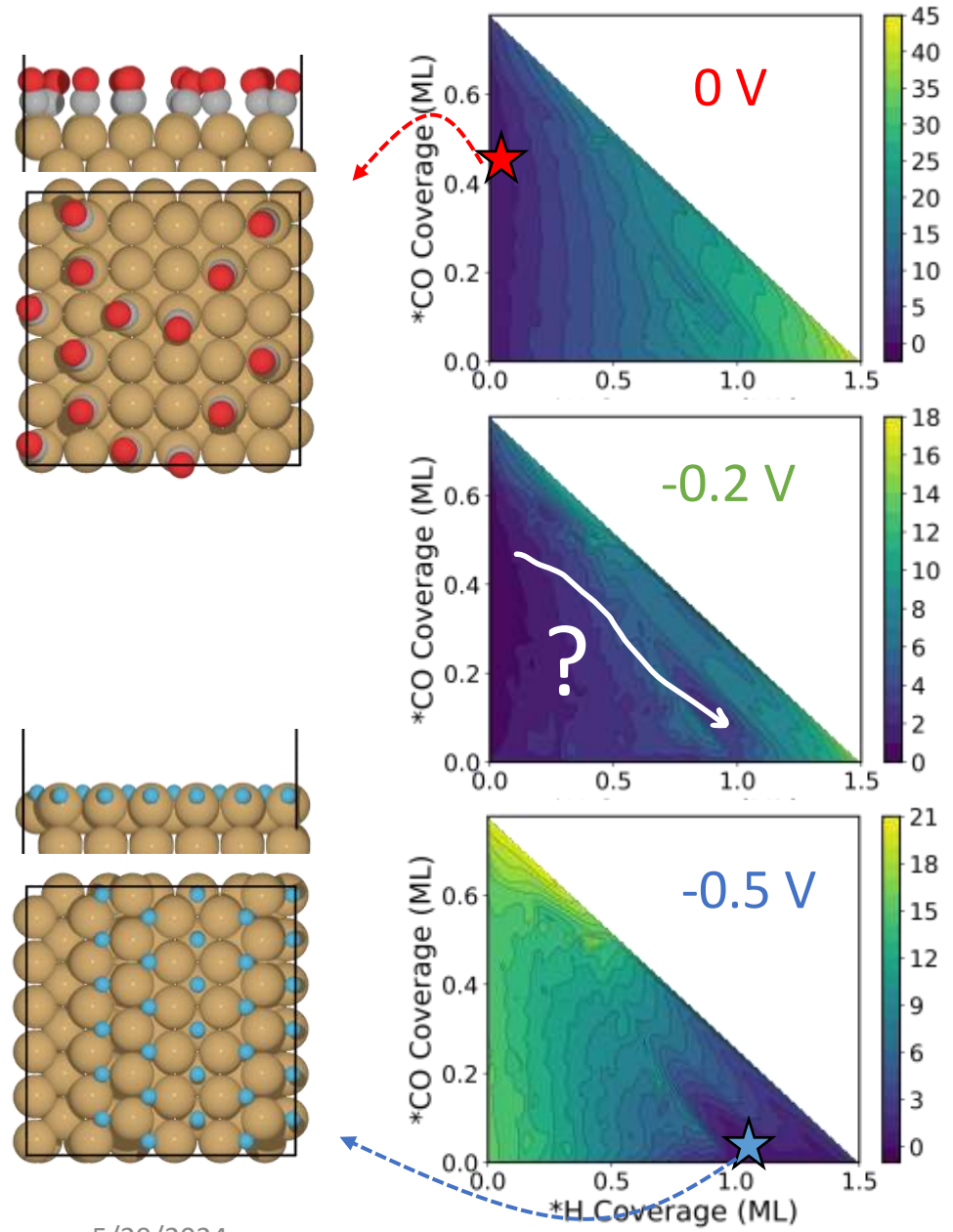
Nat. Catal., 2023, 6, 837–846

- Bright spots formed in-situ
- universal activation mechanism of Cu?

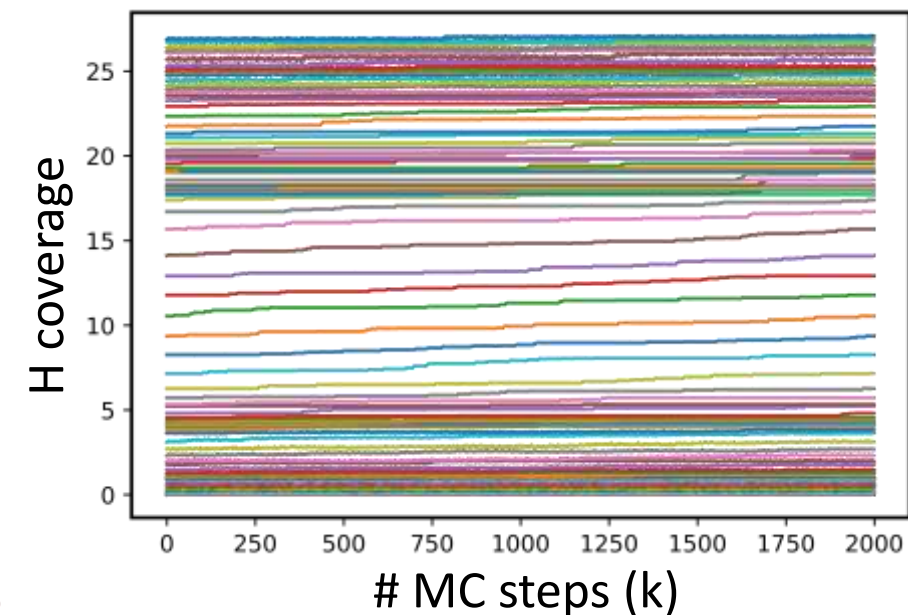
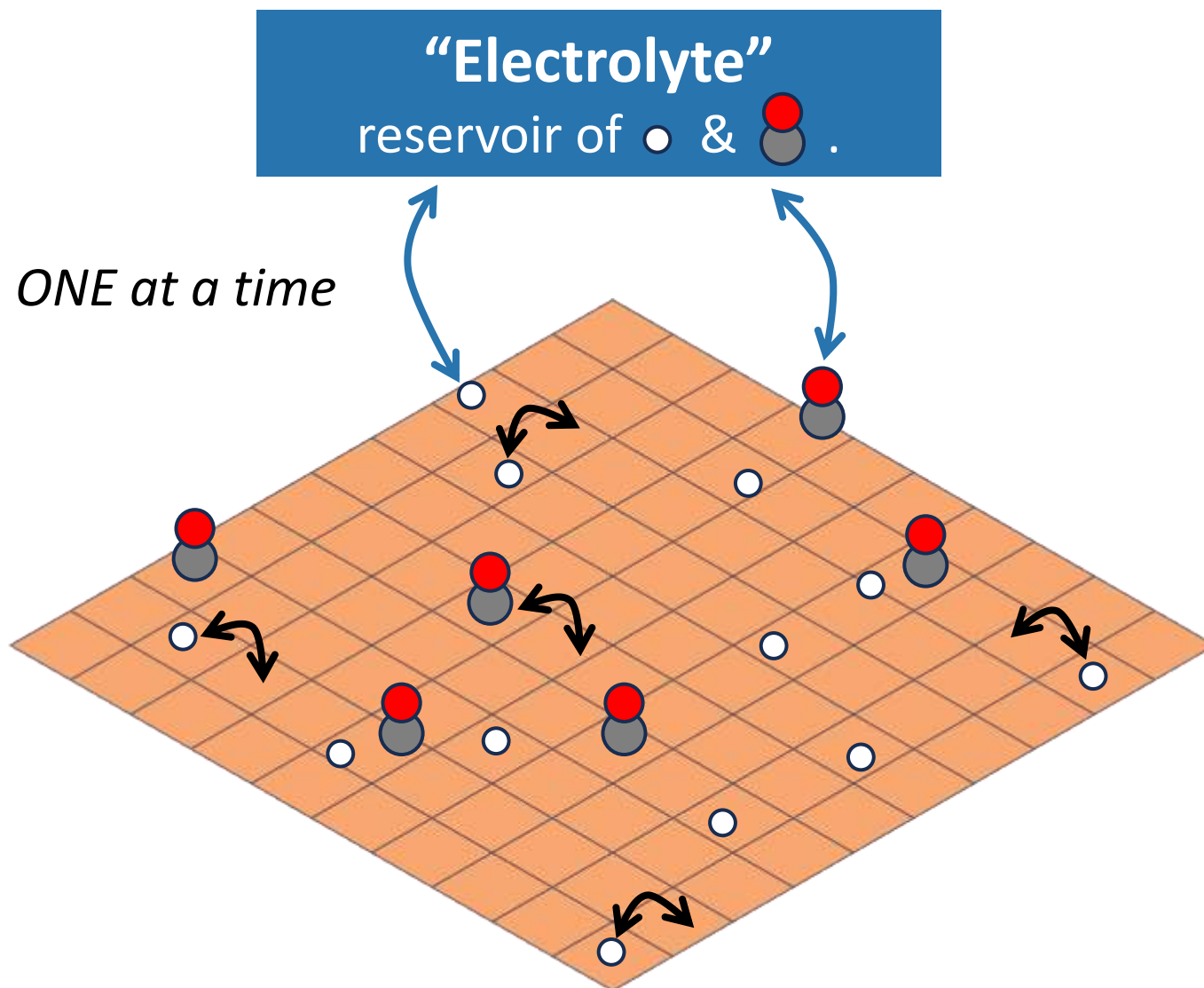


Replacement of ALL *CO by *H???

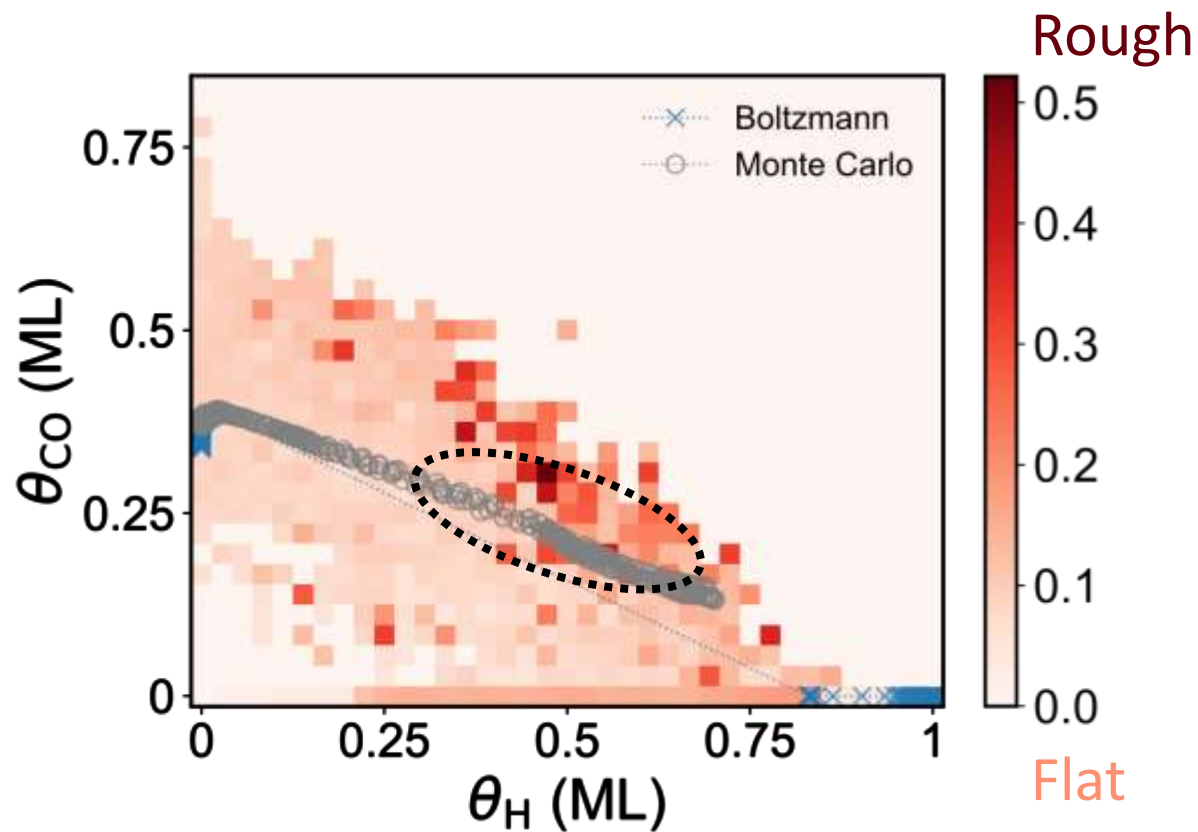
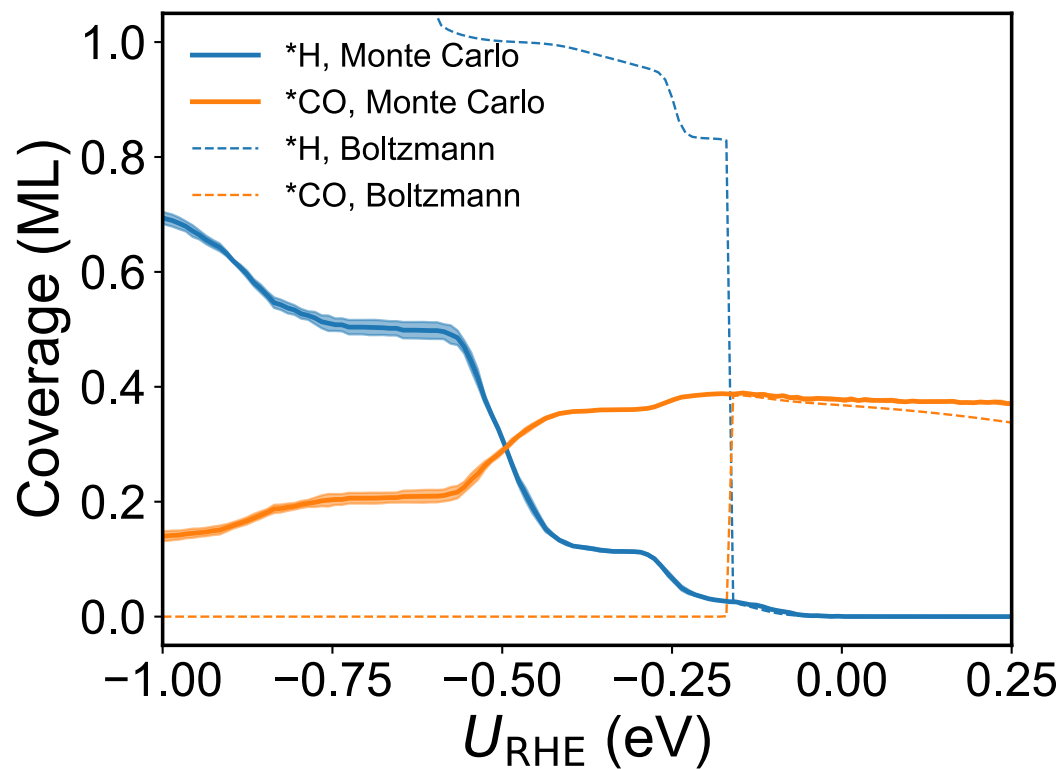


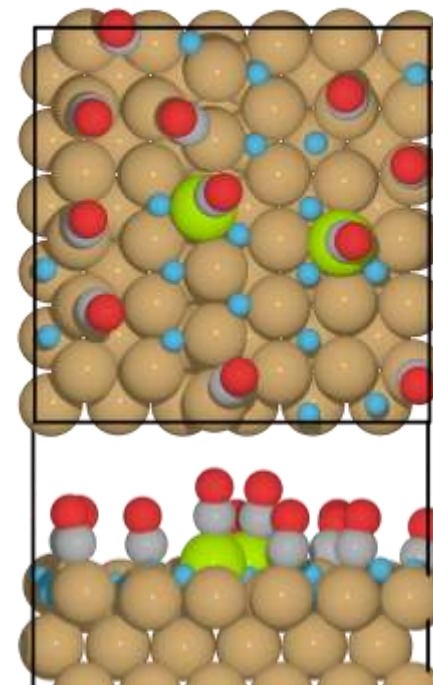
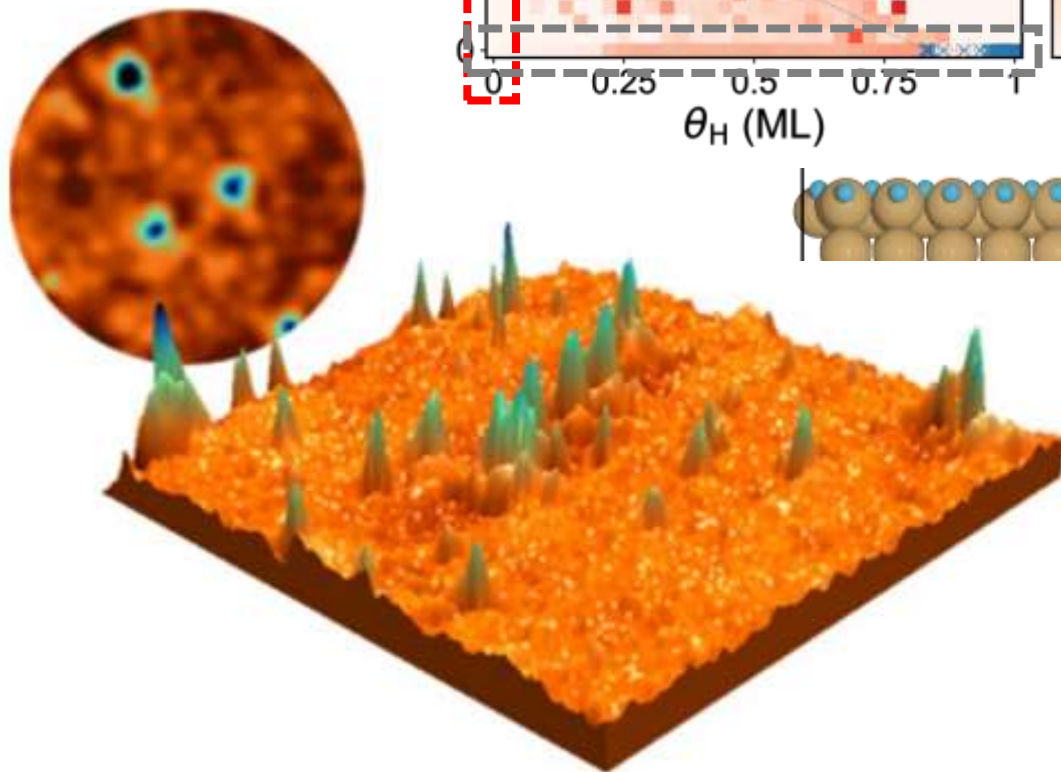
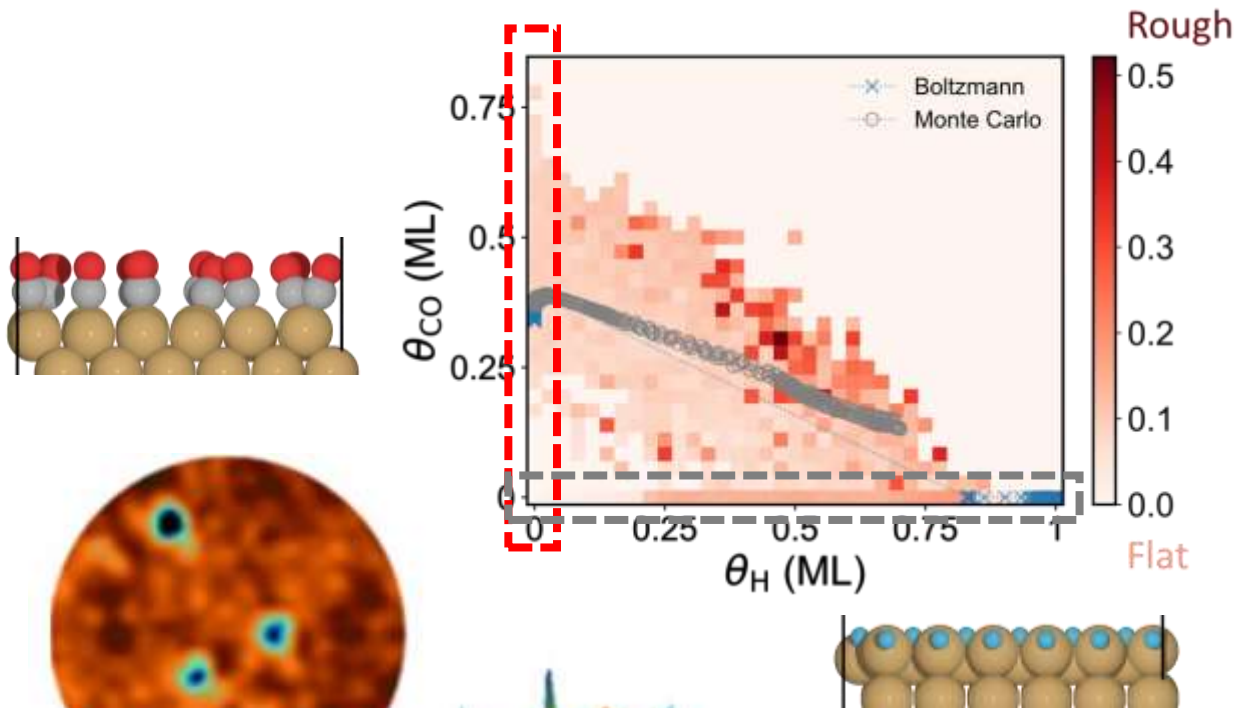


JACS, 2024, accepted, preprint: 10.26434/chemrxiv-2024-j819s



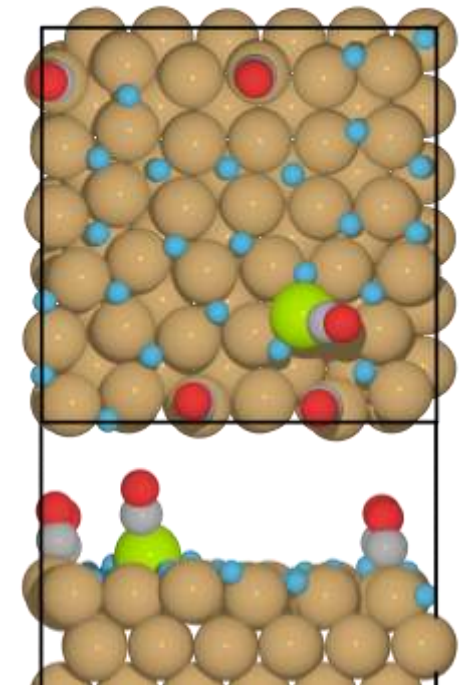
Slow potential scan
change after quasi-equilibrium





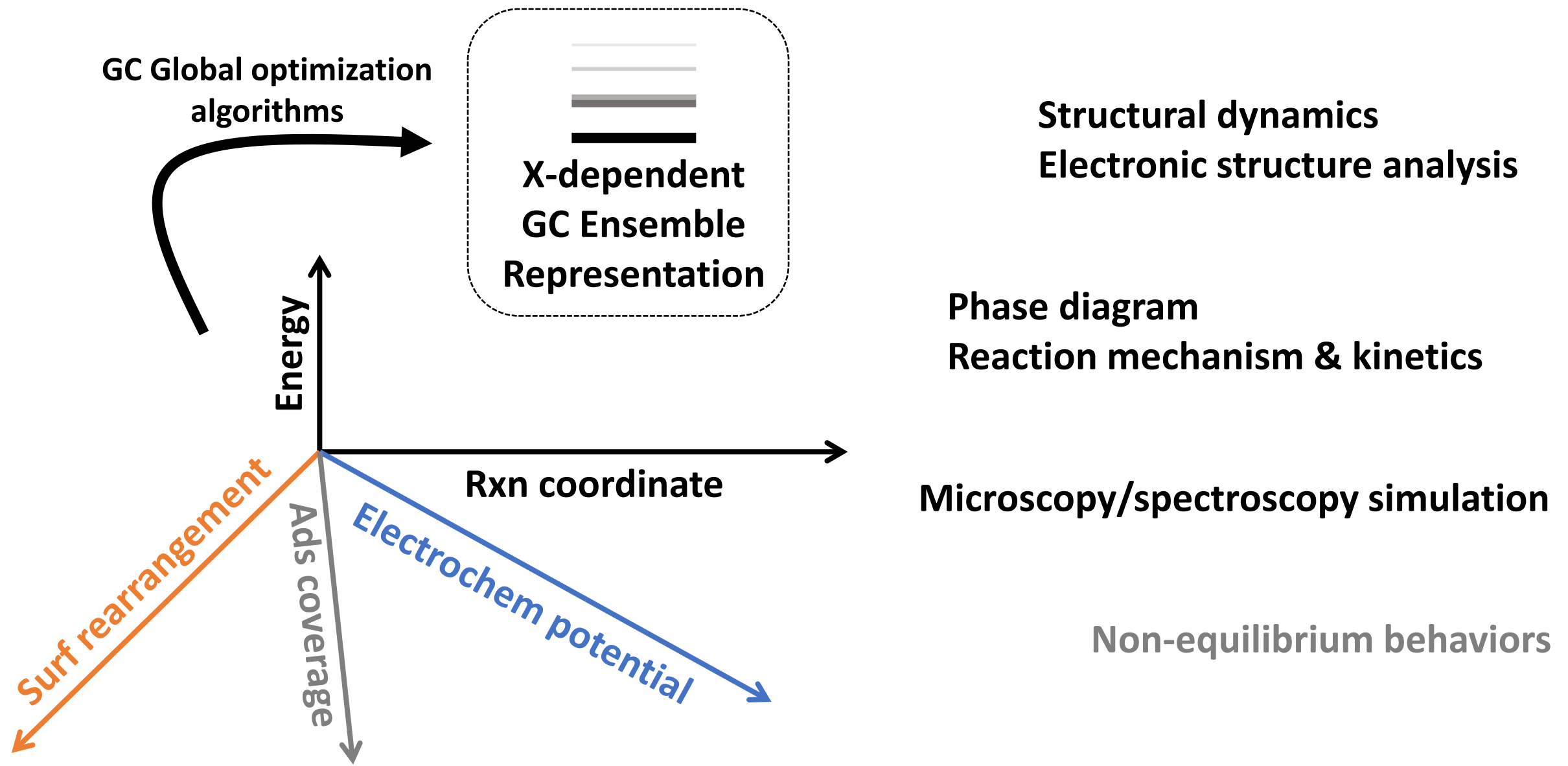
$$\theta_H = 0.50$$

$$\theta_{CO} = 0.31$$



$$\theta_H = 0.67$$

$$\theta_{CO} = 0.14$$





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... ..



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Dr. Simran Kumari
Dongfang Cheng

THANK YOU!
Q & A