

## Motivation

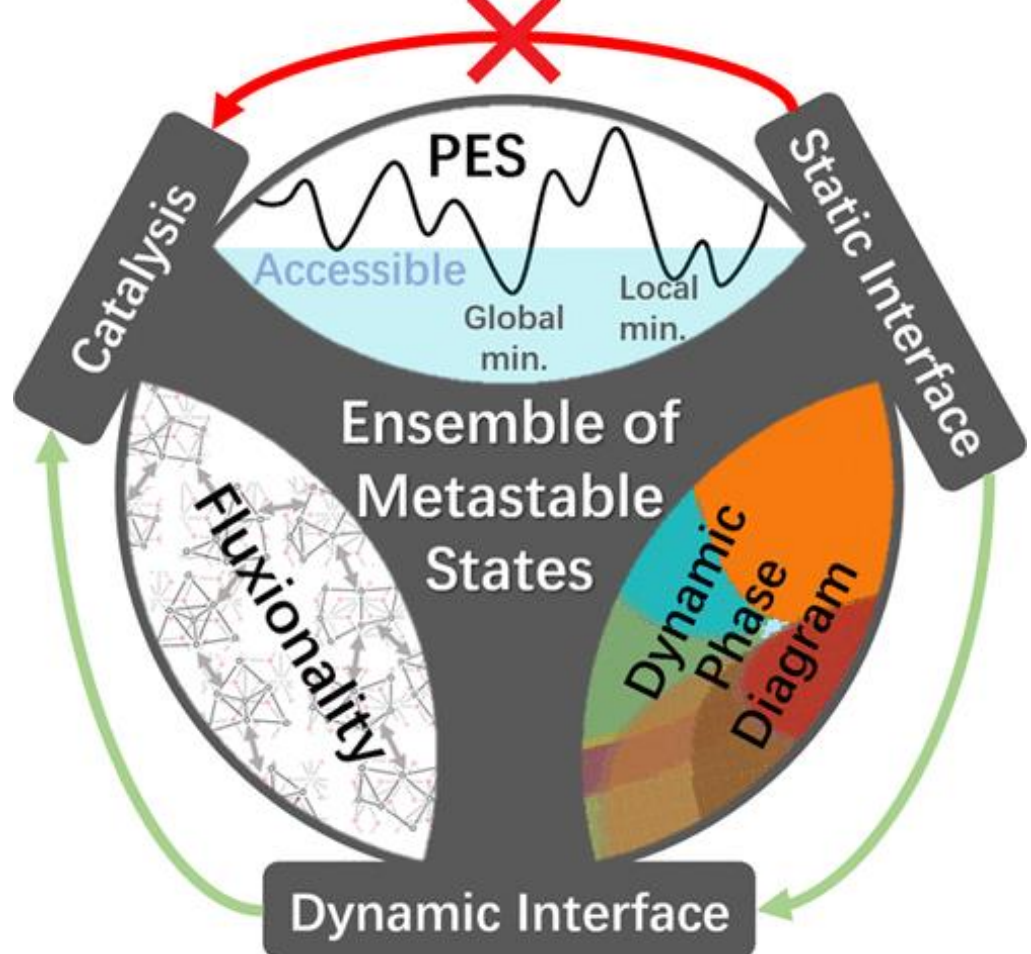
Many heterogeneous catalysts have been shown to become exceptionally fluxional and dynamic under various reaction conditions.<sup>1</sup>

To model them correctly, we need to consider:

- Isomeric configurations
- Off-stoichiometric restructurings
- Varying coverage of adsorbates
- Different adsorbate configurations

Electrocatalysts operating at room  $T$  have extra factors to consider:

- Narrower distribution of states
- Effect of potential and electric double layer



## Methods

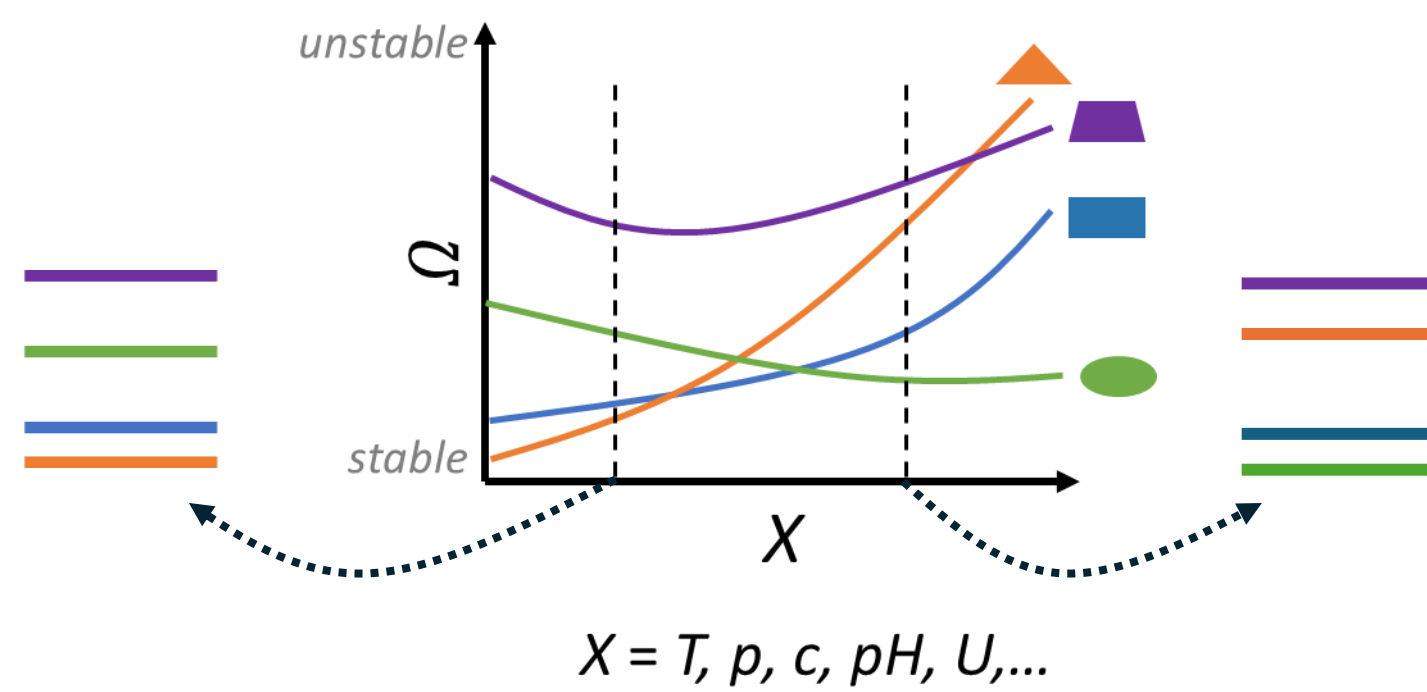
In this collection of our recent works, we applied a combination of state-of-the-art computational methods to address the complexities mentioned in “Motivation”:

- Global optimization search for global and local minima relevant to the reaction
- Grand canonical treatment for varying composition and adsorbate coverages  
Grand Canonical Genetic Algorithm (**GCGA**) as implemented in our open-source package, GOCIA (Global Optimizer for Clusters & Interfaces & Adsorbates).  
The optimization objective is the grand canonical free energy:

$$\Omega_{\text{stoi}} = G_{\text{slab non-stoi}} - G_{\text{slab ref}} - \sum_i \mu_i$$

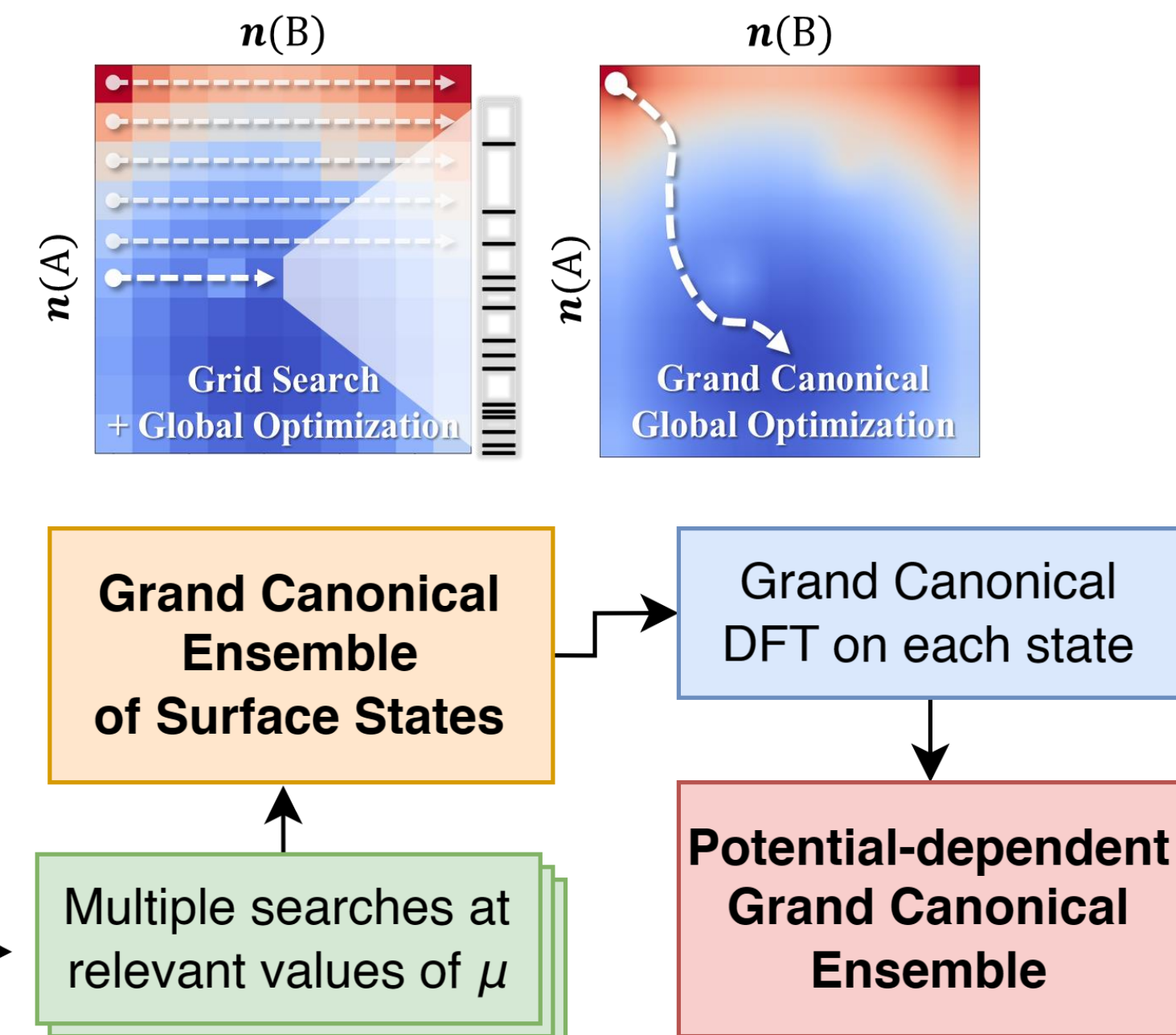
- Grand canonical treatment for electrons  
DFT and linearized Poisson-Boltzmann model for electrolytes  
Electronic free energy under the constant capacity approximation:

$$\Omega_{\text{el}}(U) = E(U) - q(U) \cdot U \approx E(U_0) - \frac{1}{2} C \cdot (U - U_0)^2$$

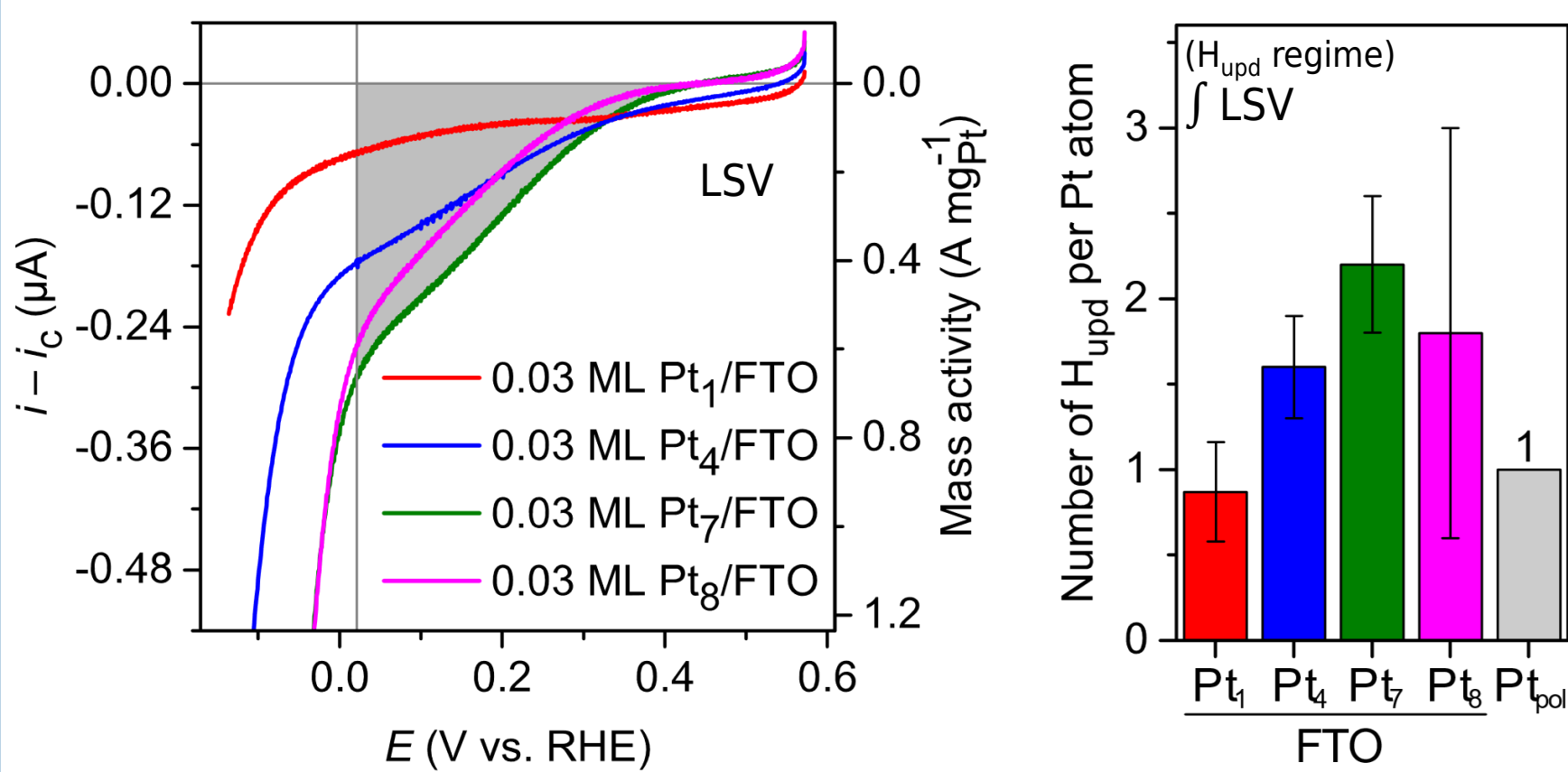


A **statistical ensemble representation** of the interface can be then constructed, including all chemically relevant metastable surface states (of diverse geometry and stoichiometry) and their dependence on the electrode potential.<sup>1,2</sup>

The ensemble encodes the condition-dependent thermodynamics of all relevant catalyst states, and it can serve as the basis of structure identification, reactivity trend study, and the investigation of more complex off-equilibrium or kinetically controlled phenomena.

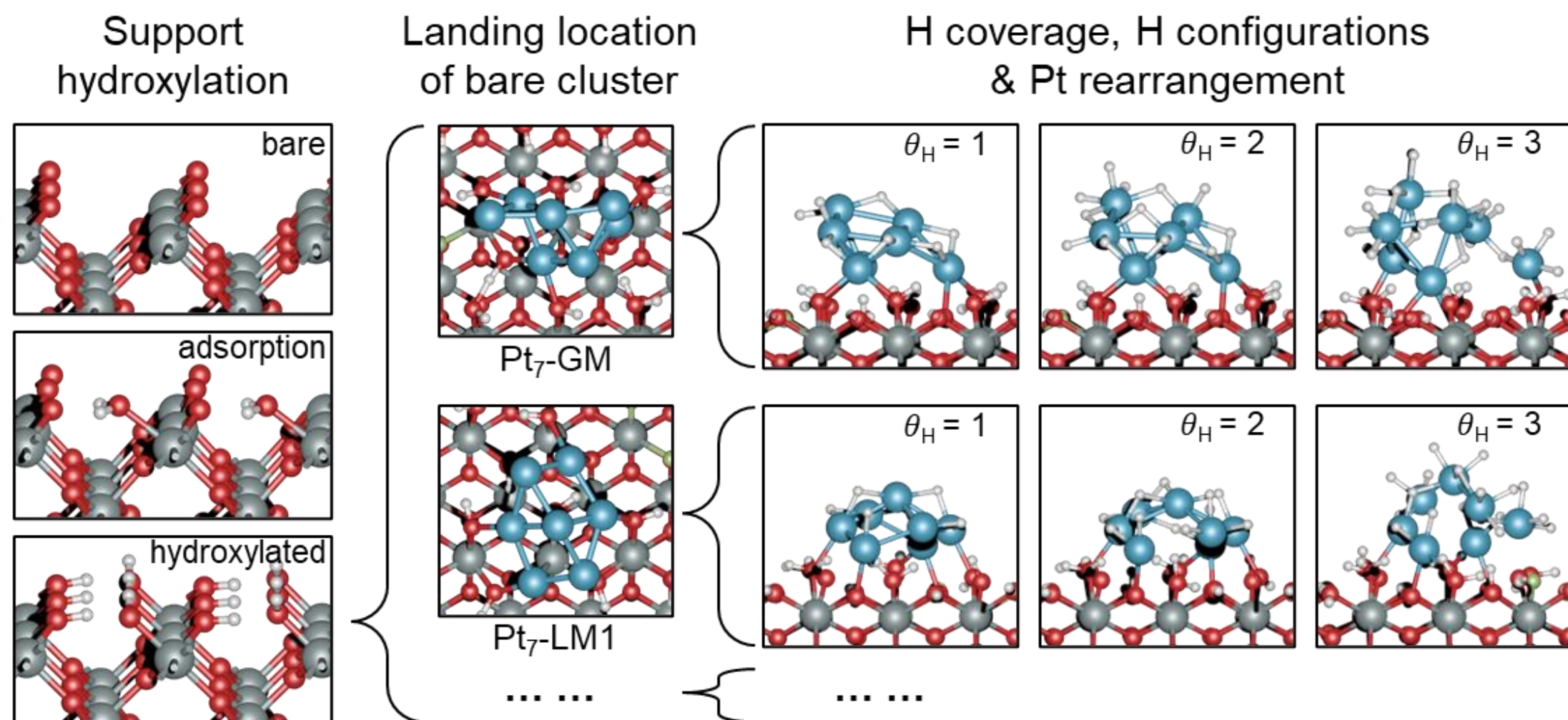


## Hydride states govern HER on Pt clusters<sup>3</sup>

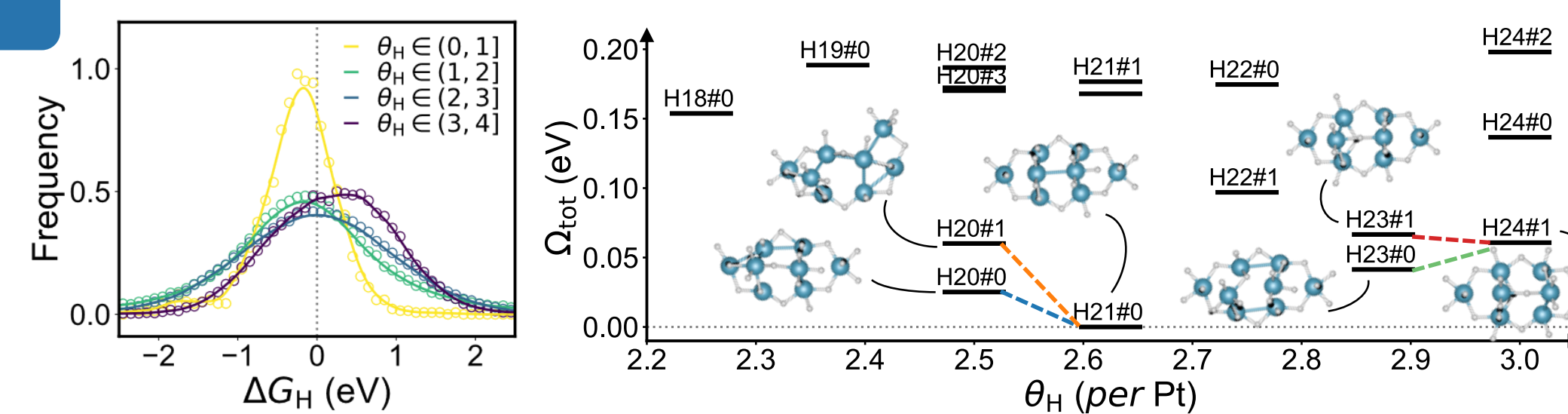


Size-selected cluster synthesis and electrochemical experiments by Anderson group at U of Utah.

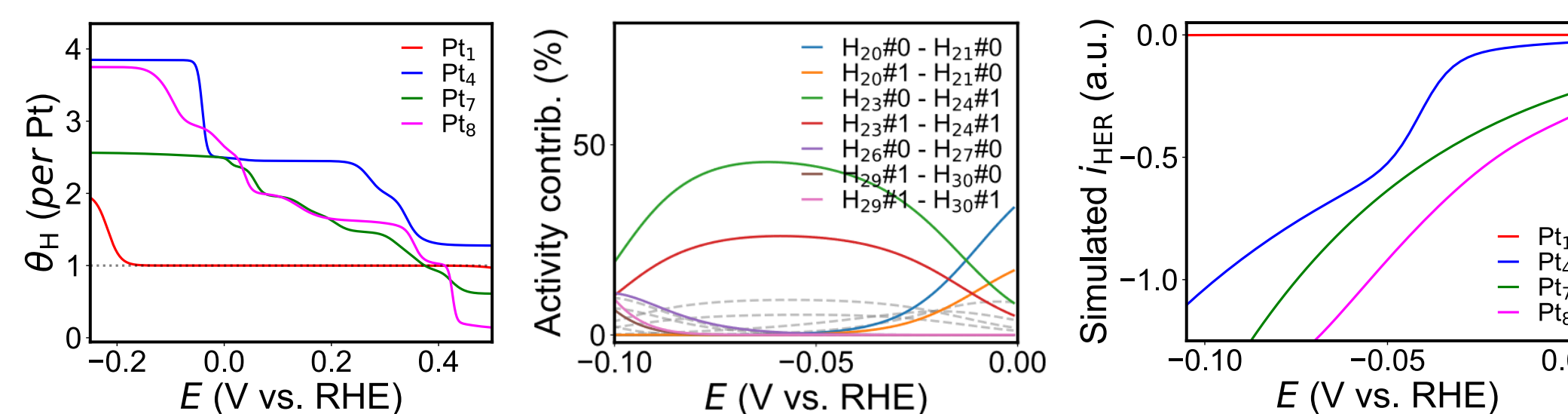
- HER activity:  $\text{Pt}_8 > \text{Pt}_7 > \text{Pt}_4 > \text{Pt}_1$
- HER stability:  $\text{Pt}_4 > \text{Pt}_8 > \text{Pt}_7 > \text{Pt}_1$



- Hydroxylation of the (100) termination in aqueous media
- Assuming clusters to stay at the landing location
- GCGA search: core reshaping and H coverage/configurations



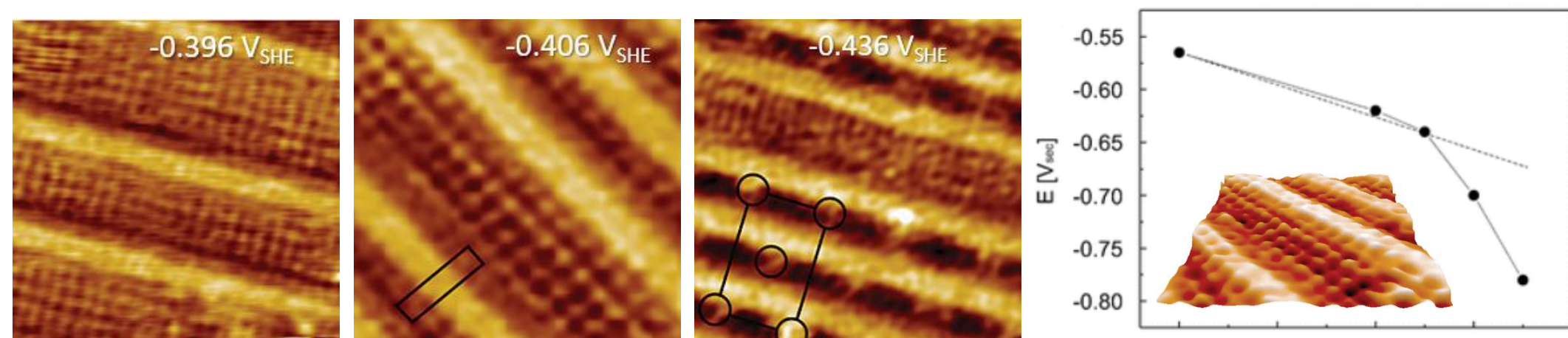
In the potential-dependent GC ensemble, we assume any two states from neighboring H coverage can make a HER pathway.



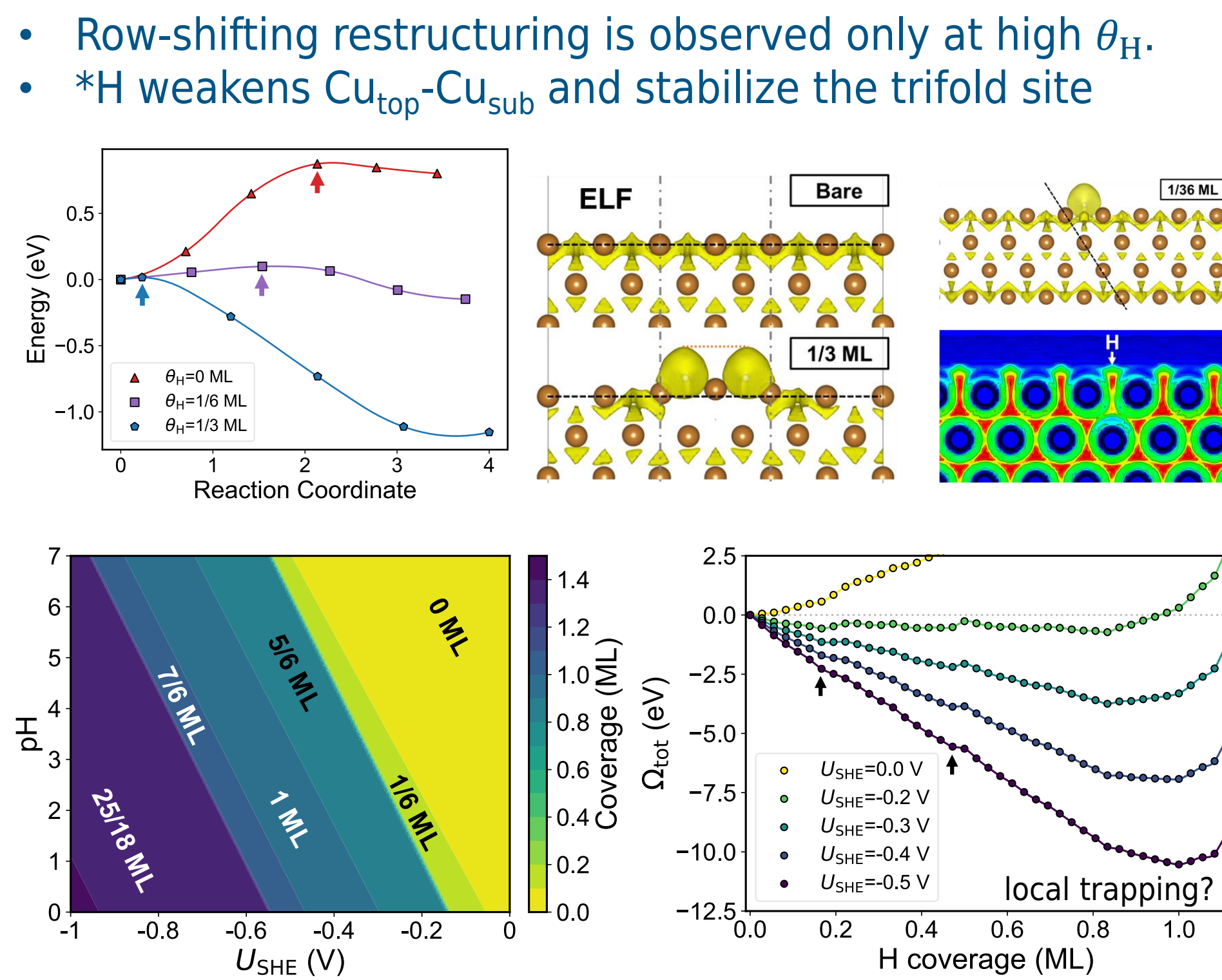
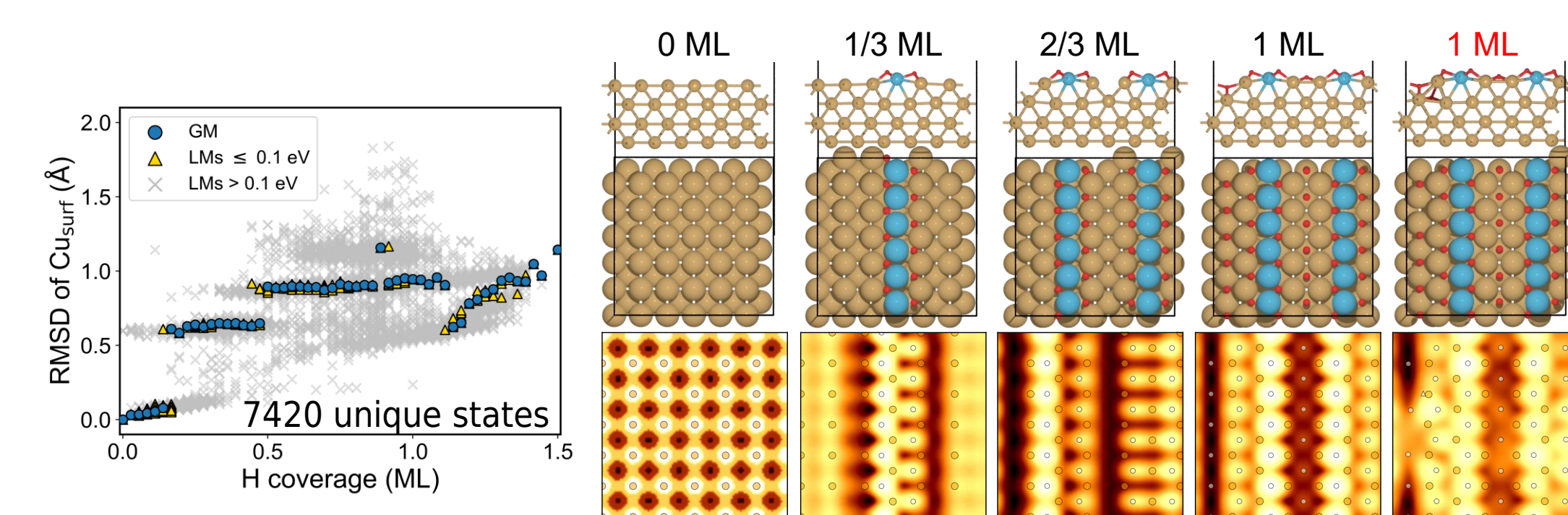
Kinetic model considering both population and pair-wise HER energetics of the states.<sup>2</sup>

Active species are hydride states (formed before HER onset)

## Adsorbate-induced surface restructuring<sup>4</sup>

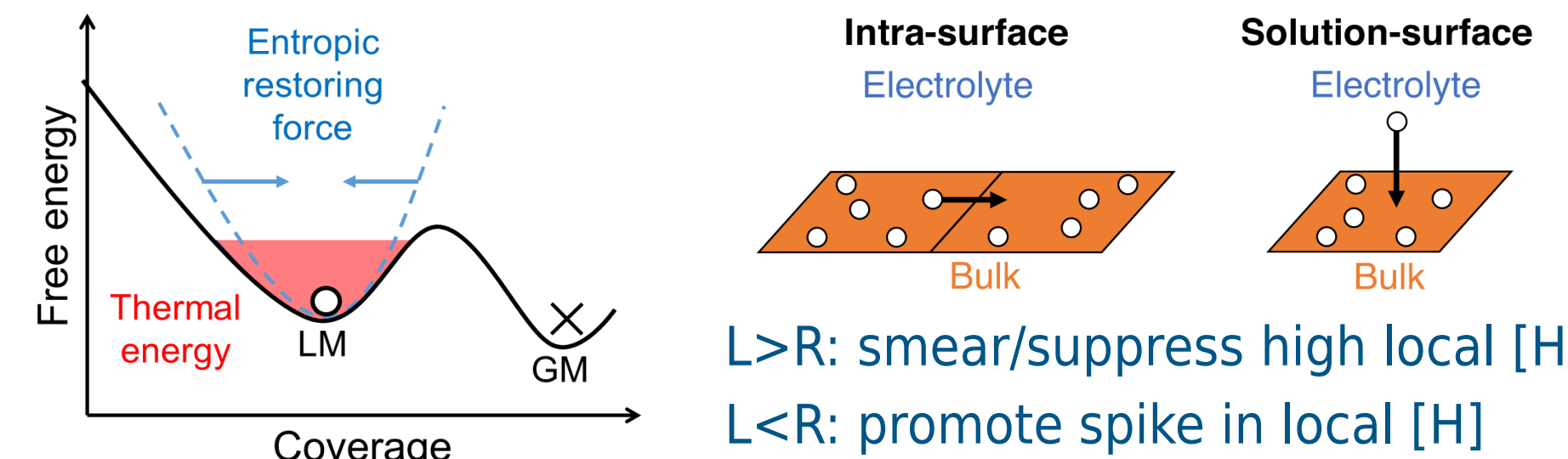


In situ STM showed **stripe formation** on **Cu(100)** in acidic media at c.a.  $-0.4 V_{\text{SHE}}$ , with a non-linear pH-dependence.

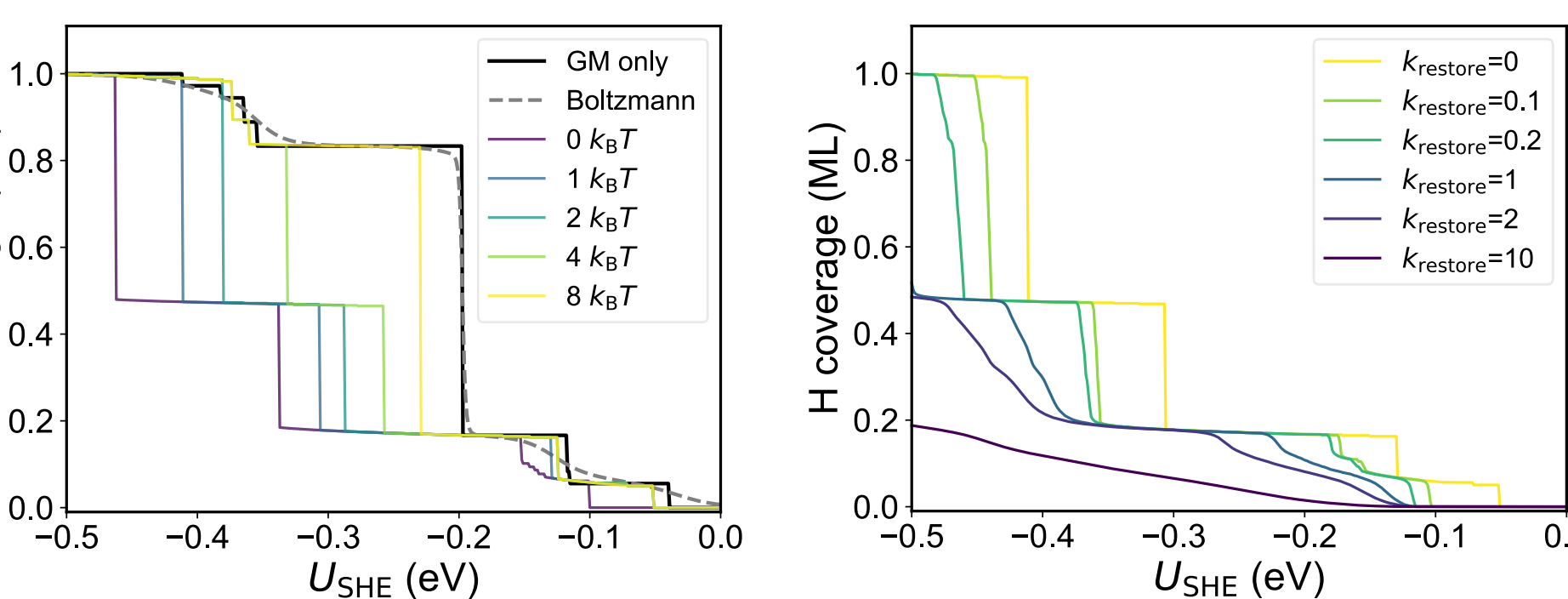


Consider extra factors to recover the physics

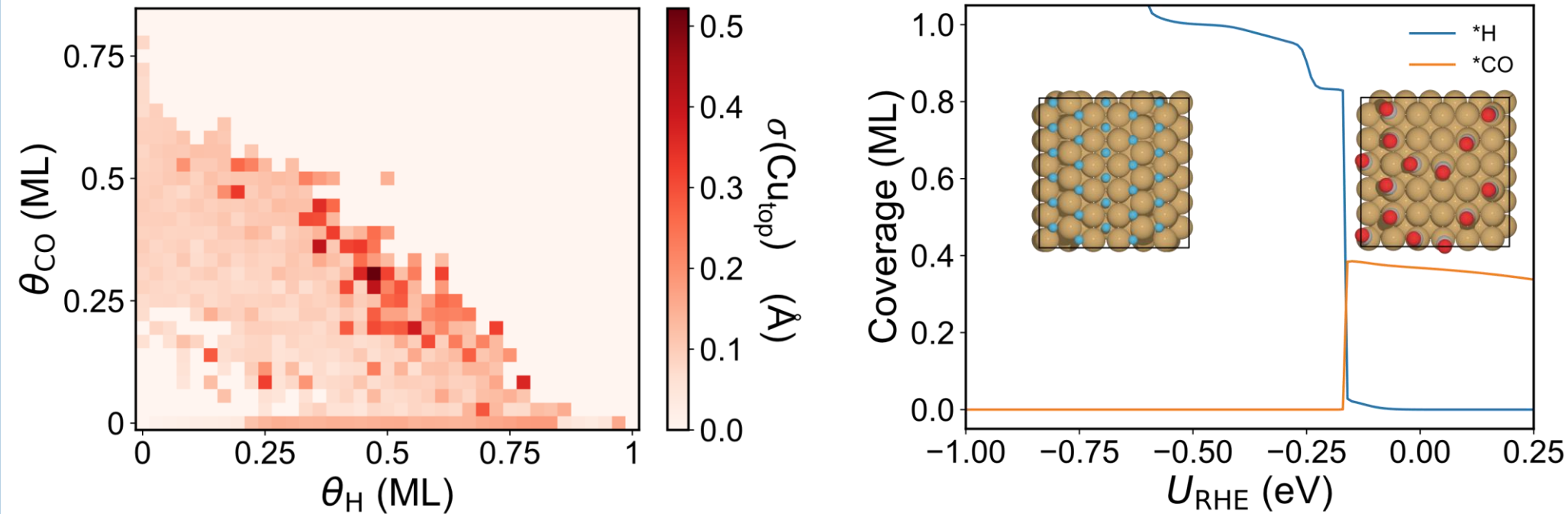
- Finite thermal energy  $\rightarrow$  trapping in metastable  $\theta_H$
- Collective entropic force  $\rightarrow$  non-linear pH-dependence



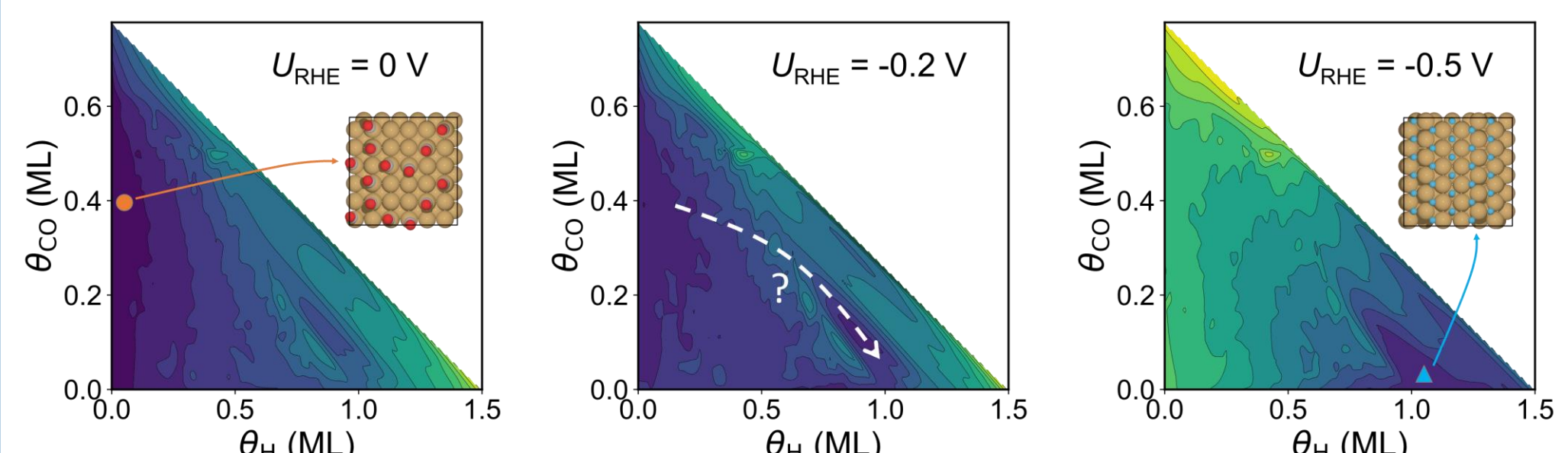
$L > R$ : smear/suppress high local  $[H]$   
 $L < R$ : promote spike in local  $[H]$



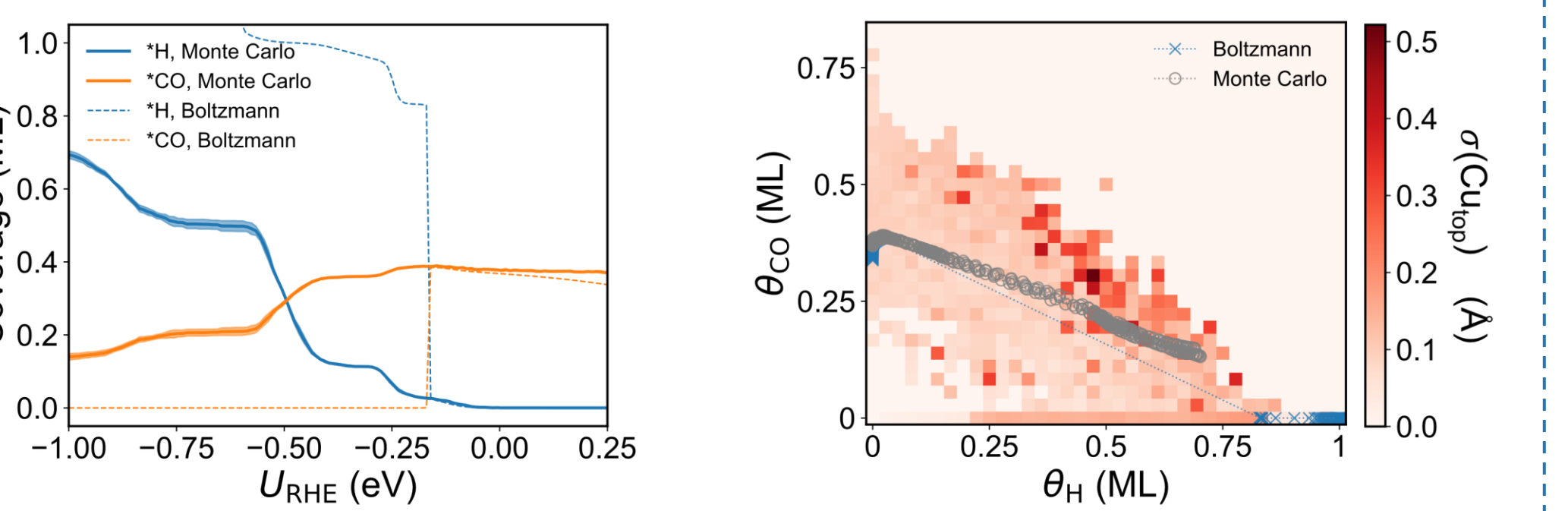
## Addressing off-equilibrium restructuring<sup>5</sup>



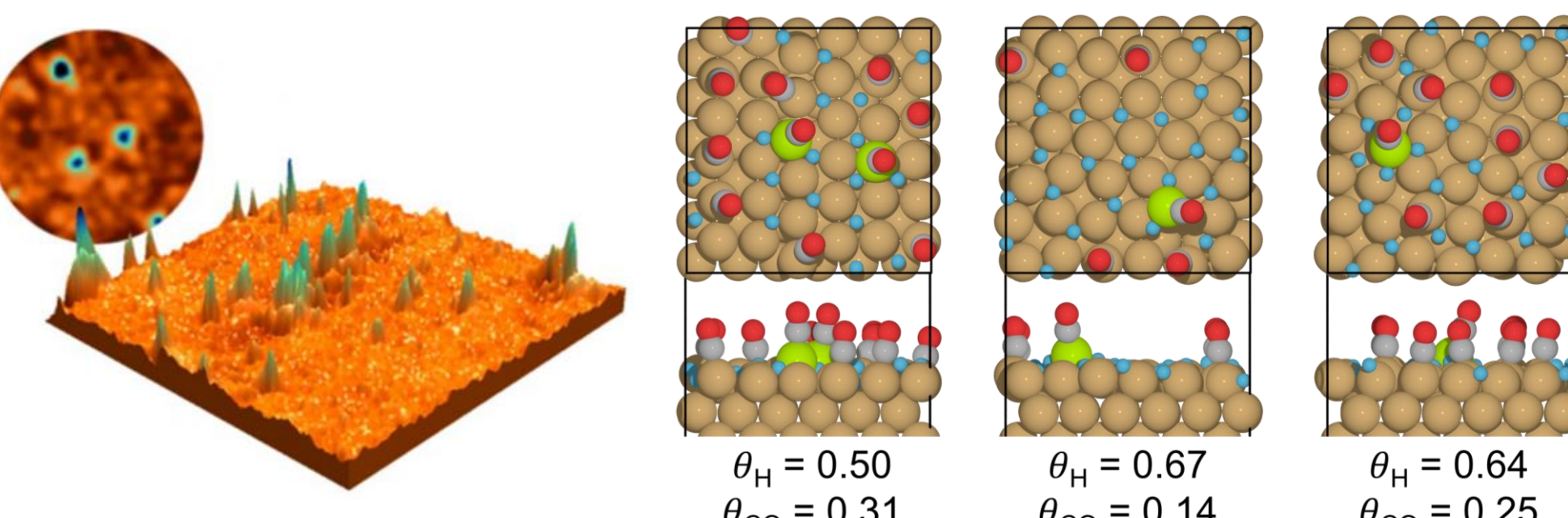
Roughening only under mixed coverage  $\rightarrow$  inaccessible regime?



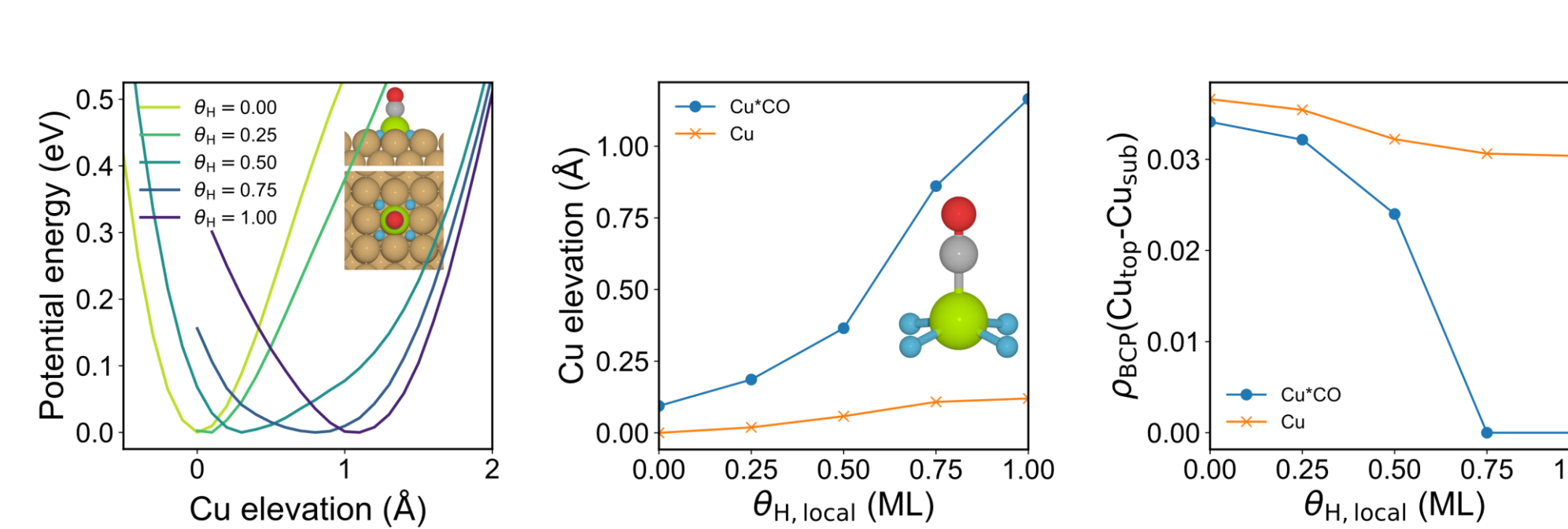
As FES shifts, the system must cross a bumpy metastable region



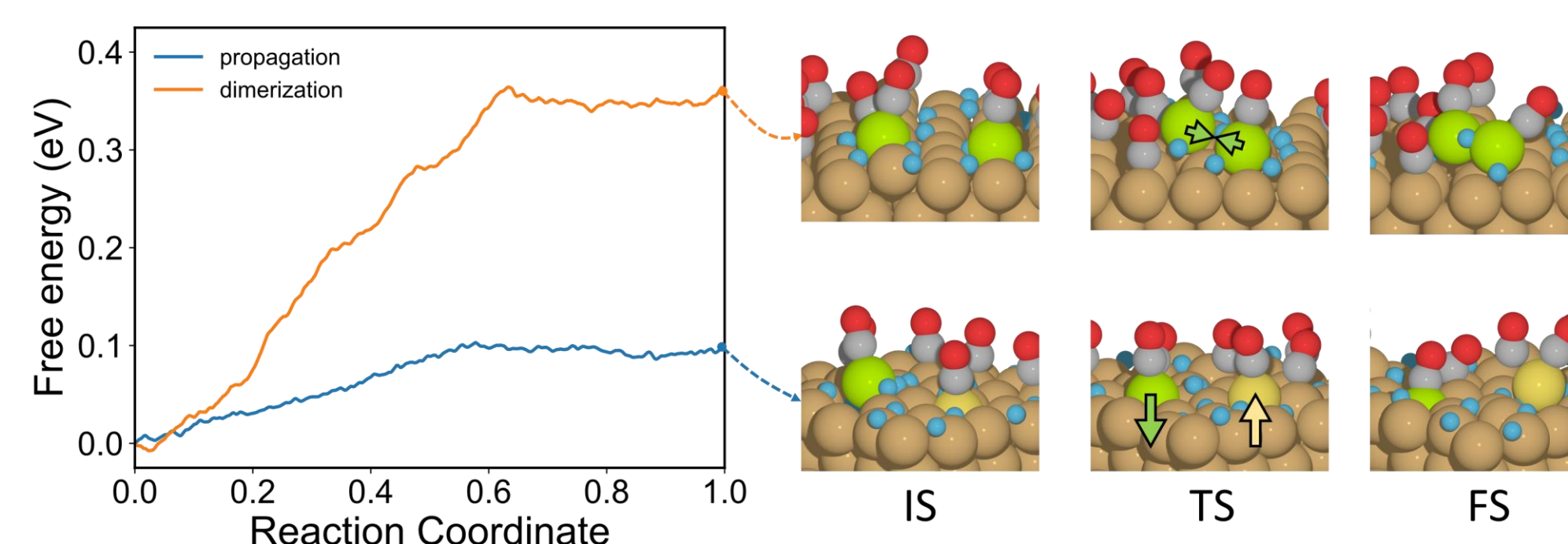
Revealing the kinetically limited path with MC simulation



Metastable mixed-coverage states with elevated Cu atoms



Co-influence of both H and CO on local bonding  $\rightarrow$  Cu elevation



## Summary

- Statistical ensemble representation & computational for sampling off-stoichiometric FES
- Dramatic restructuring of metal under coverage of the simplest adsorbate H.
- Adsorbate coverage influences the reactivity and the nature of active sites for electrochemistry.
- Complex adsorbate coverage leads to off-equilibrium behaviour (evolution in metastable regime)

