Modeling Cu-based catalysts under eCO_2R conditions

Dr. Federico Dattila, 73rd Annual ISE meeting, 12/09/22

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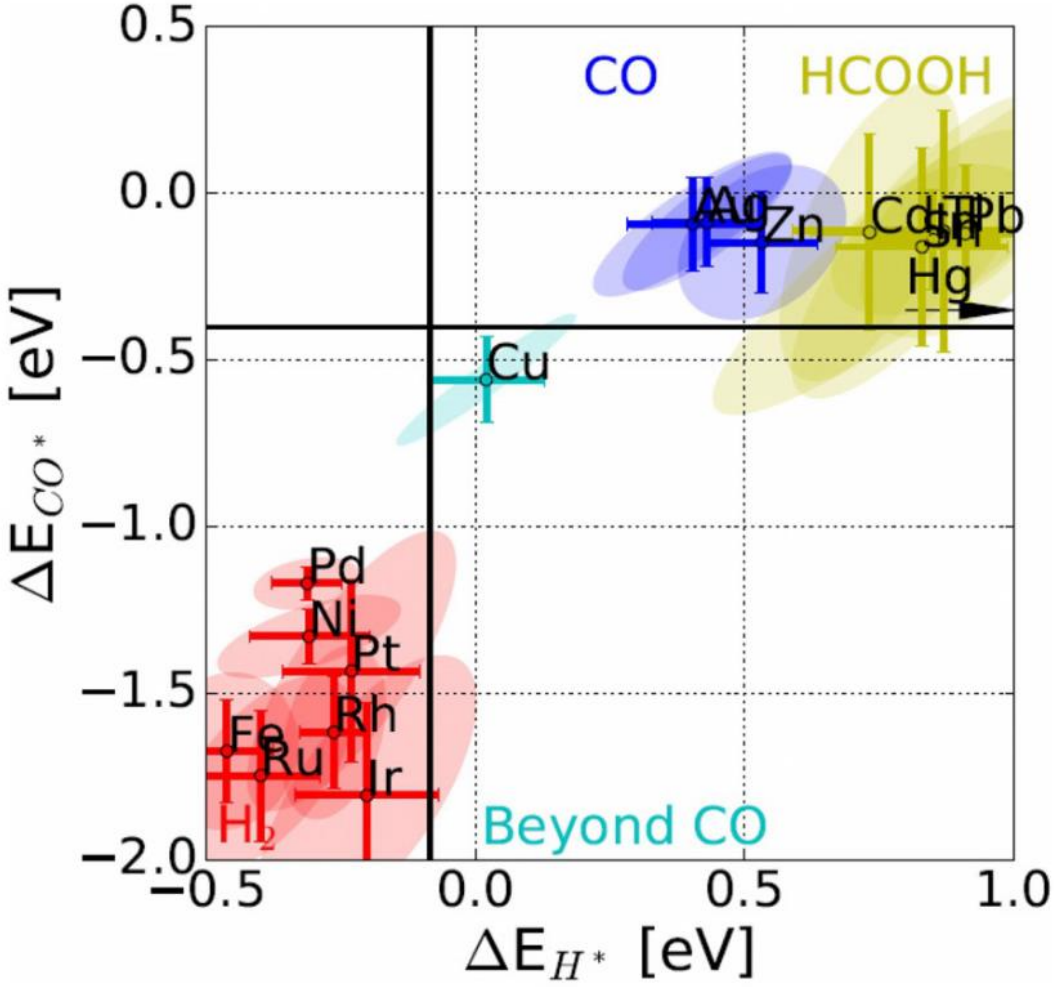
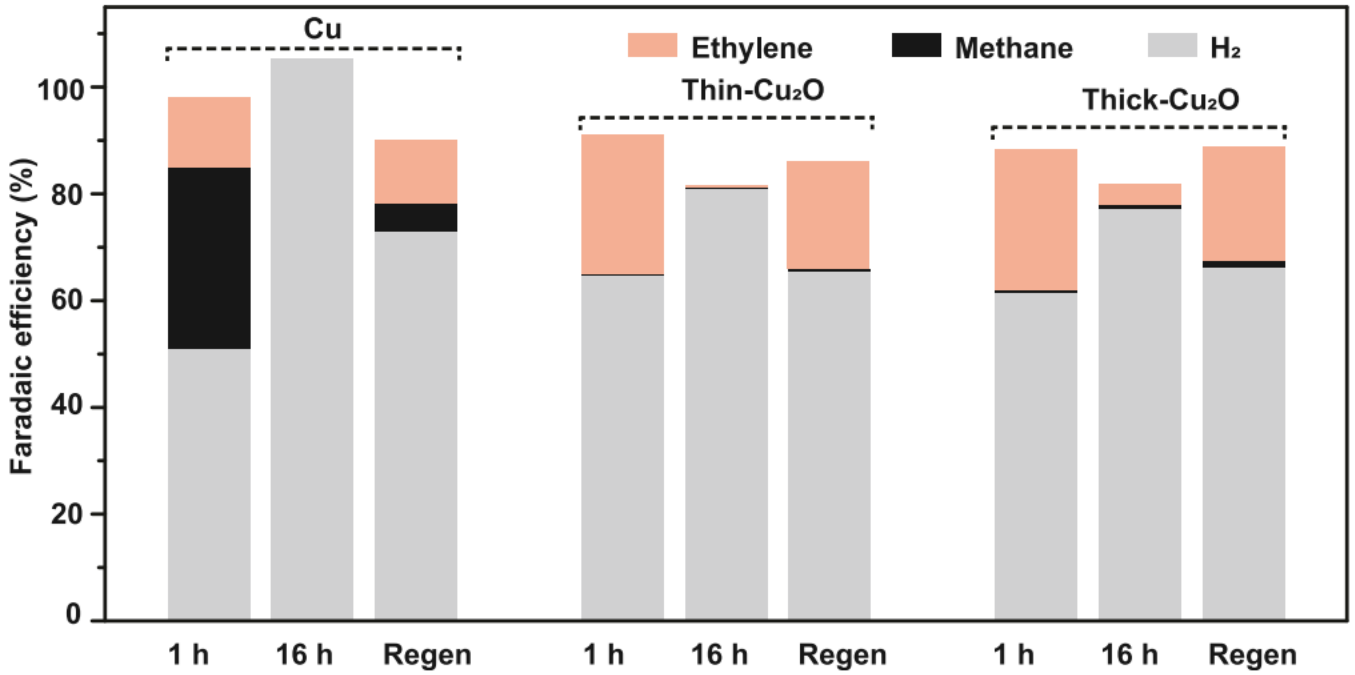
Expectation vs reality





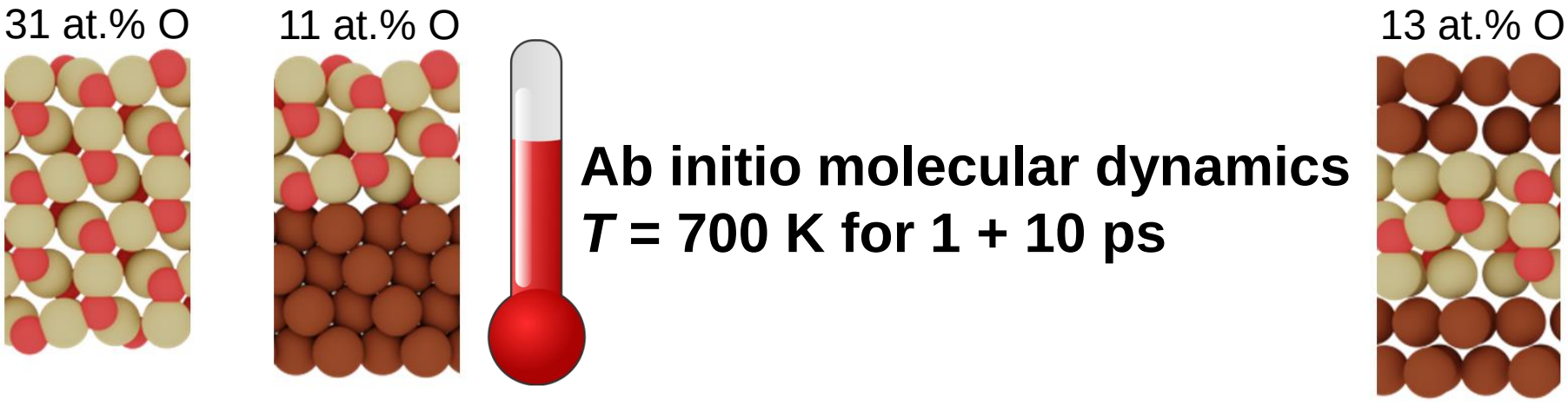
CO_2-saturated 0.1 M K_2CO_3 electrolyte (pH 7)

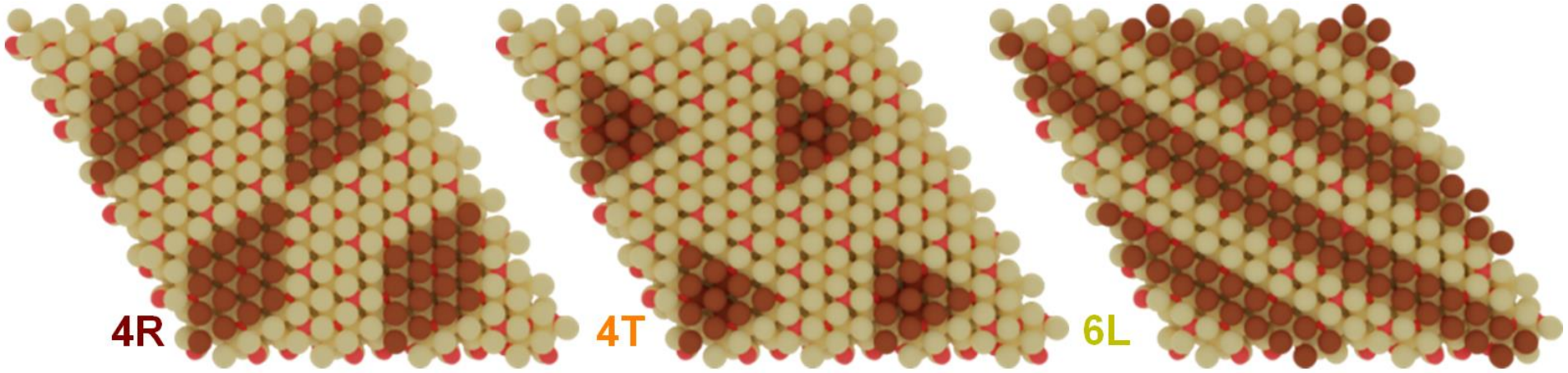
ChemPhysChem **2017**, *18*, 3266–3273.
Proc. Natl. Acad. Sci. U.S.A. **2021**, *118*, e2012649118.

Modeling surface reconstruction on OD-Cu catalysts

ACS Energy Lett. **2020**, *5*, 3176–3184.

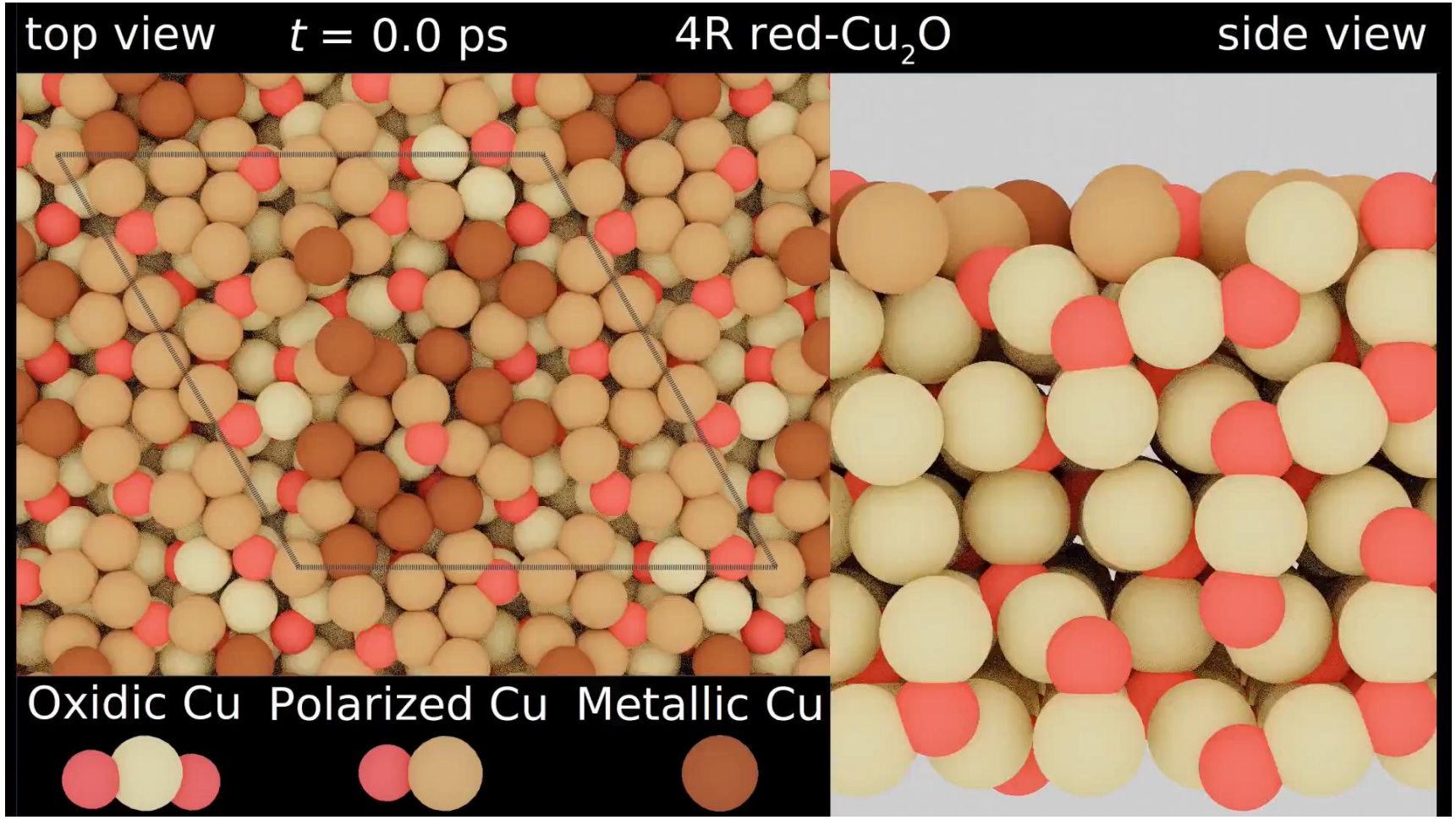
OD-Cu models





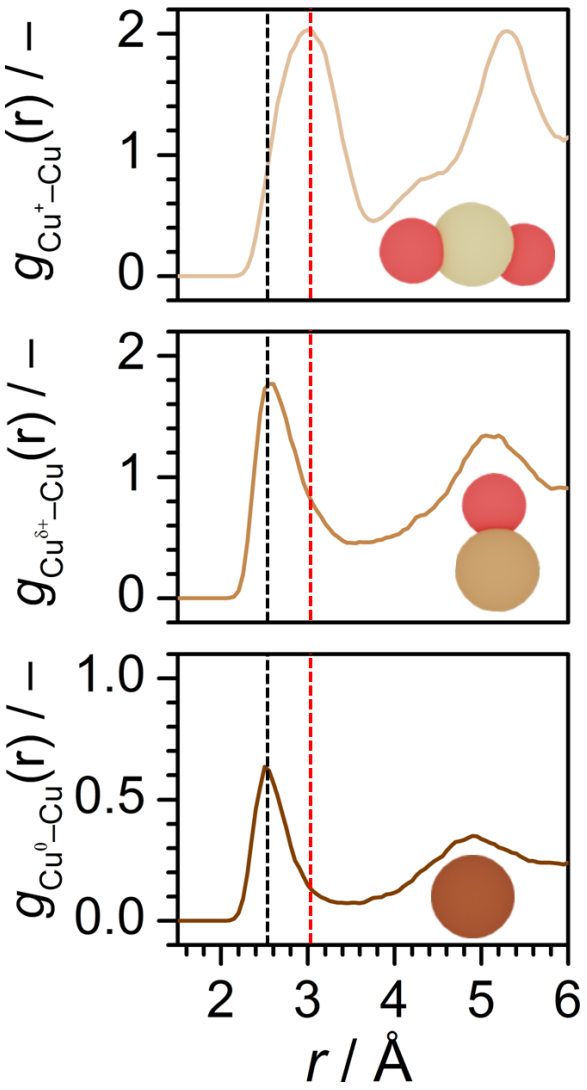
ACS Energy Lett. **2020**, *5*, 3176–3184.

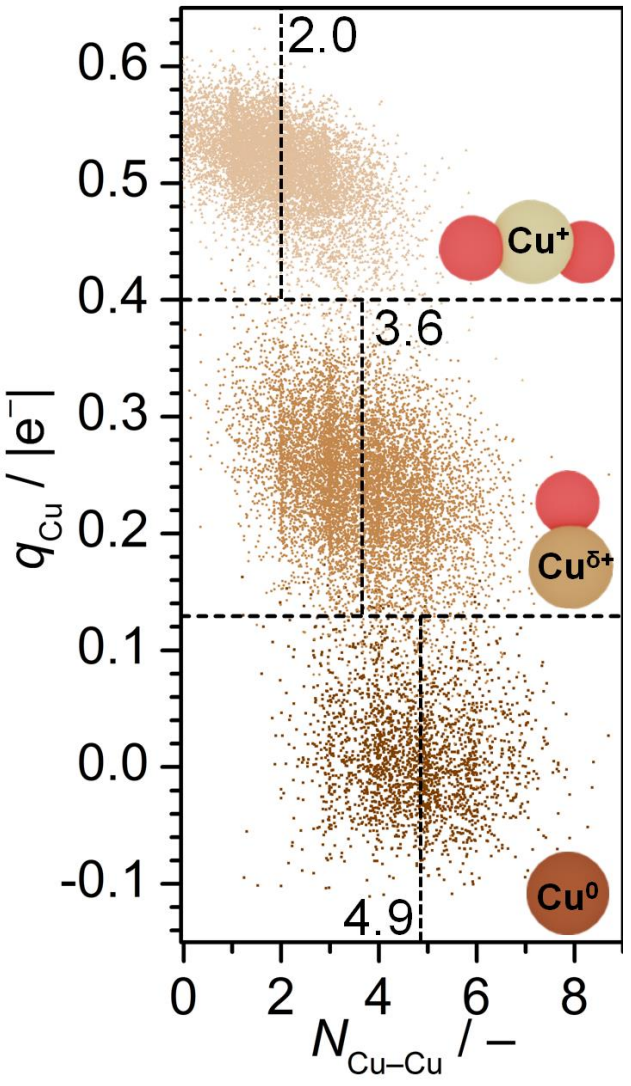
Ab initio molecular dynamics



ACS Energy Lett. **2020**, *5*, 3176–3184.

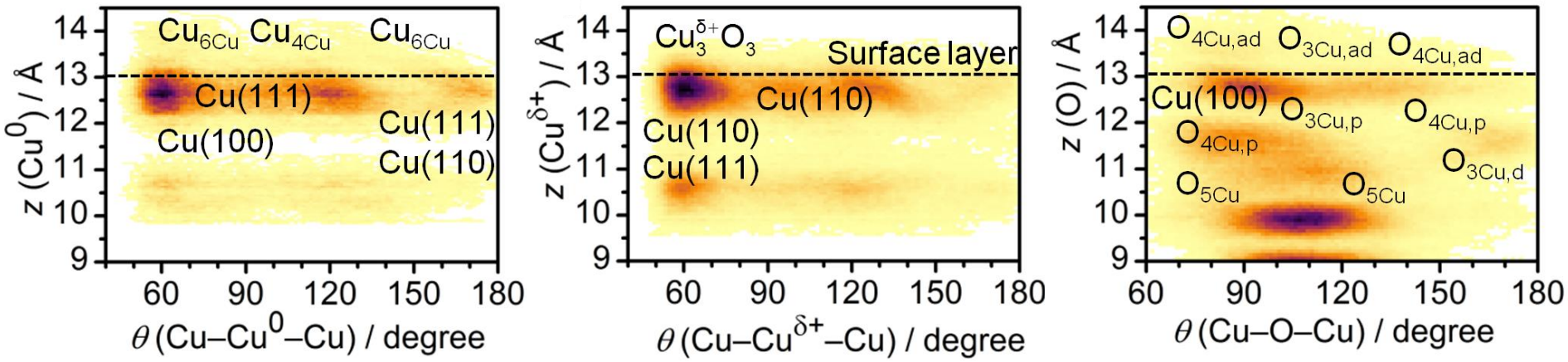
Evolution toward three main copper species





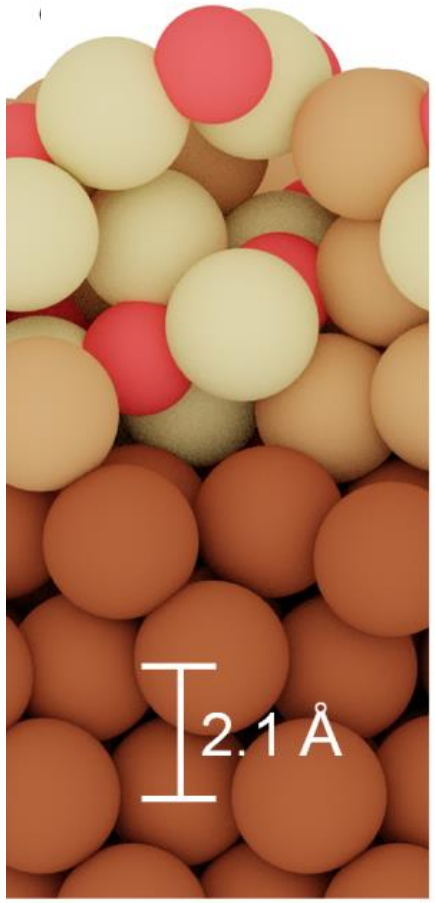
ACS Energy Lett. **2020**, *5*, 3176–3184.

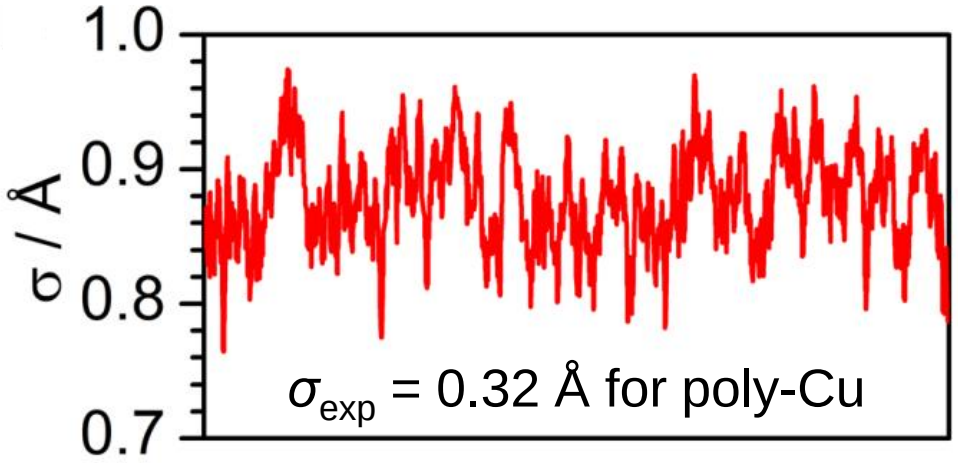
Identification of recurrent ensembles



Benchmarks with Hubbard (U_{eff} = 6 eV) and T = 300 K and 500 K bear same results.

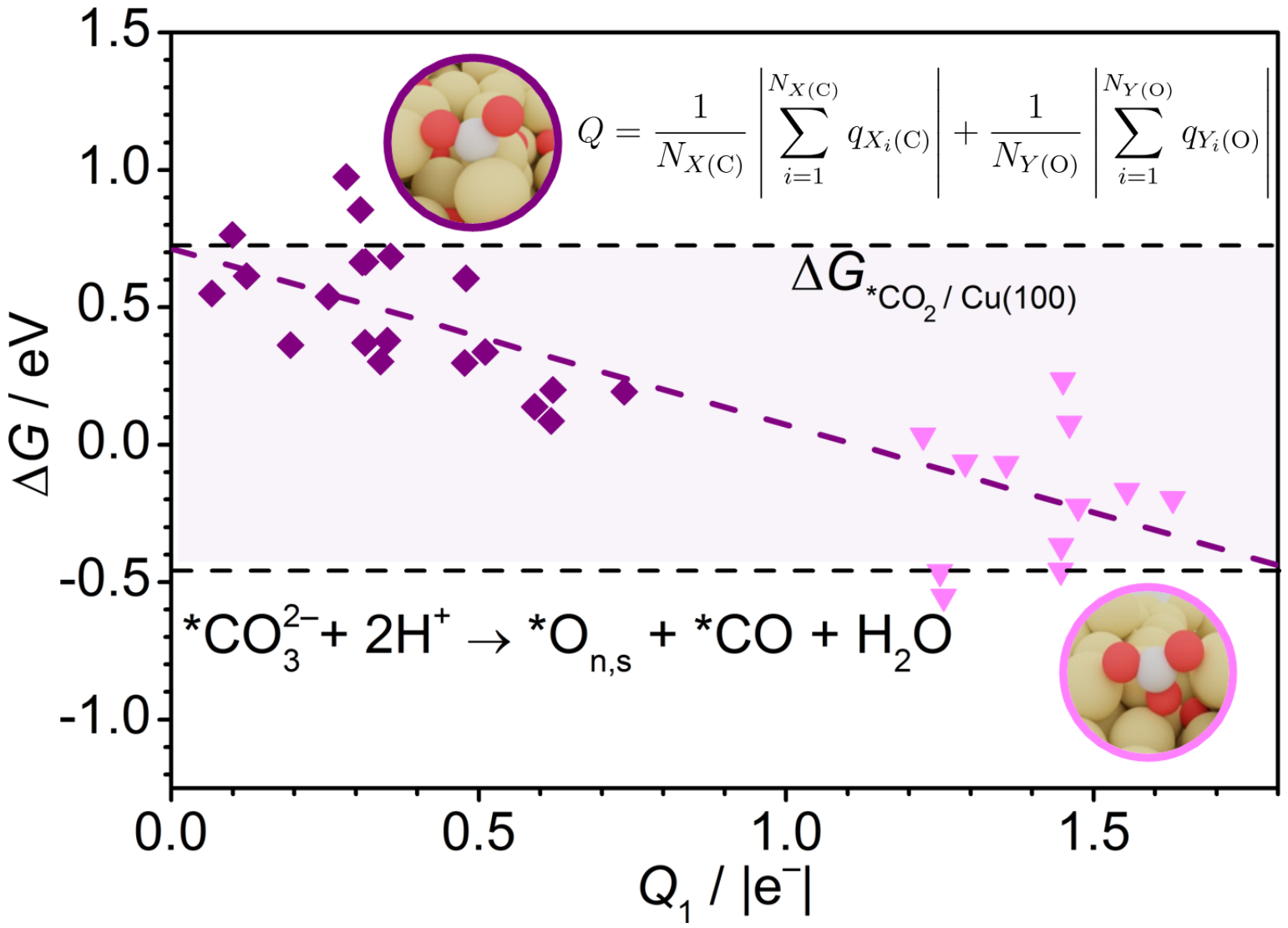
Increased roughness and active area



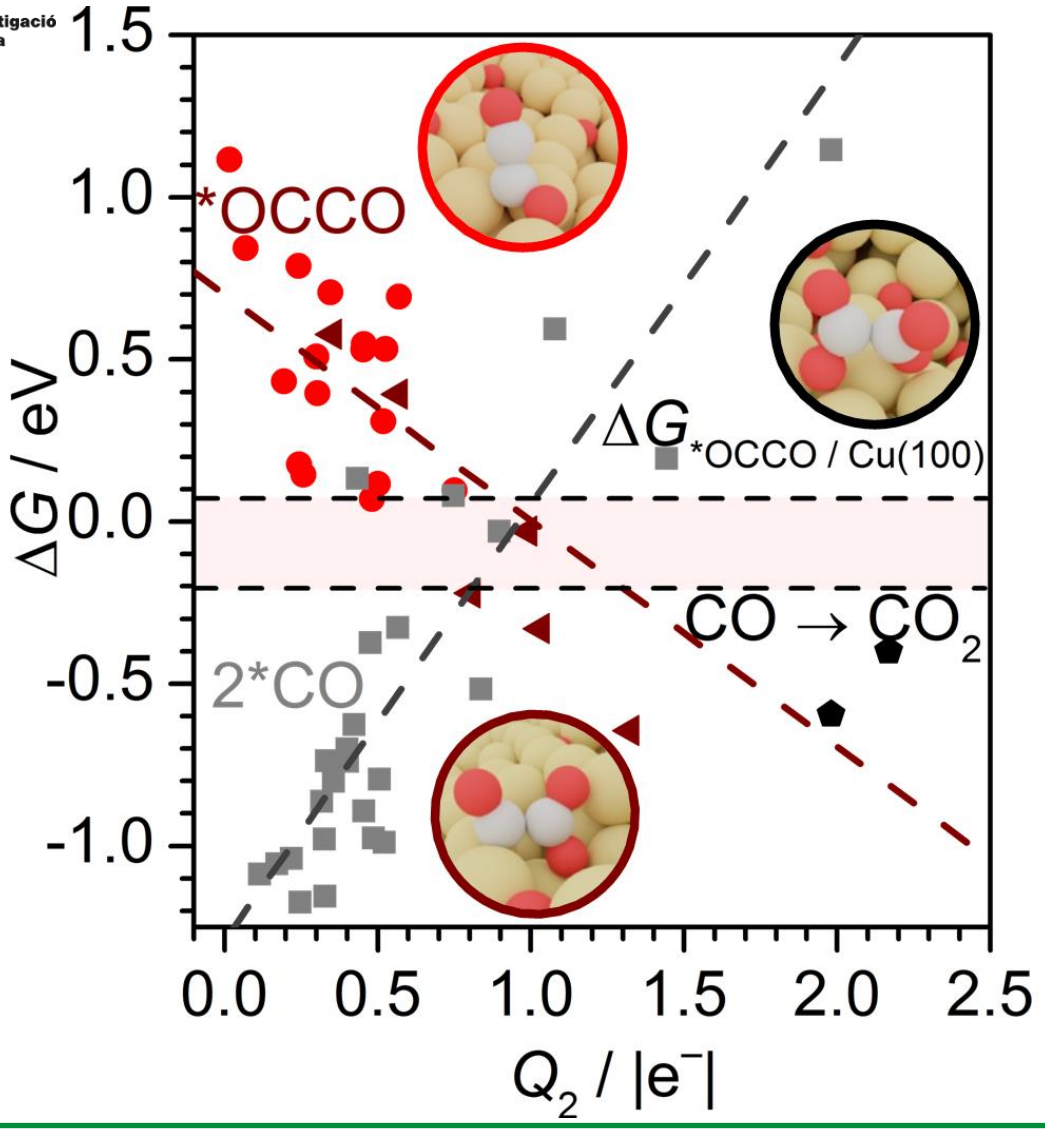


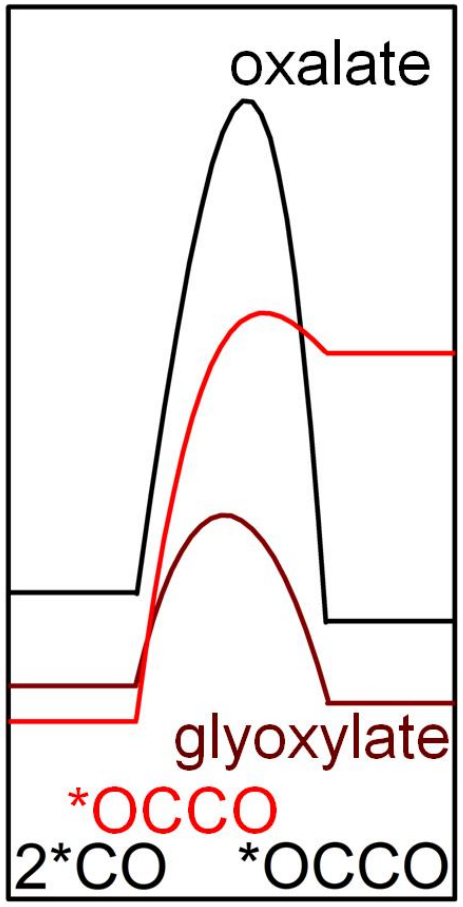
Appl. Phys. Lett. **1998**, *73*, 3607–3609.

Surface polarization enhances CO_2 activation



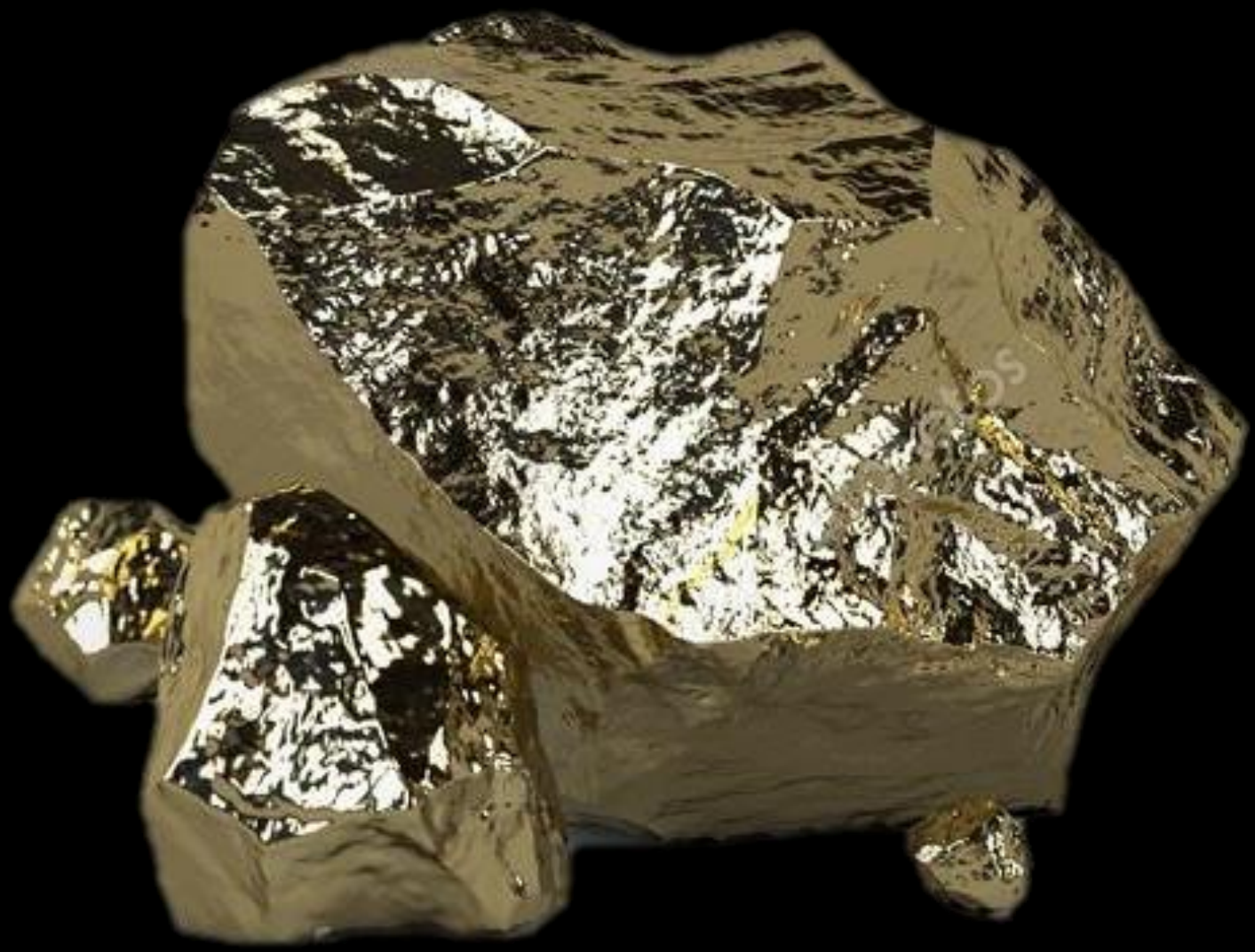
Surface polarization enhances C_{2+} selectivity





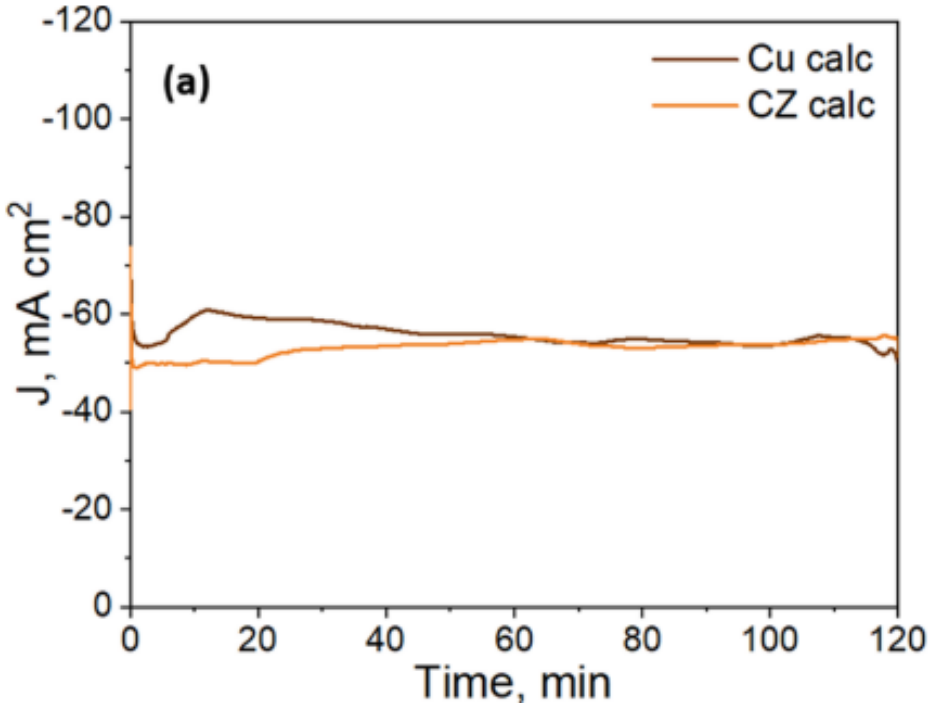
$$Q = \frac{1}{N_{X(C)}} \left| \sum_{i=1}^{N_{X(C)}} q_{X_i(C)} \right| + \frac{1}{N_{Y(O)}} \left| \sum_{i=1}^{N_{Y(O)}} q_{Y_i(O)} \right|$$

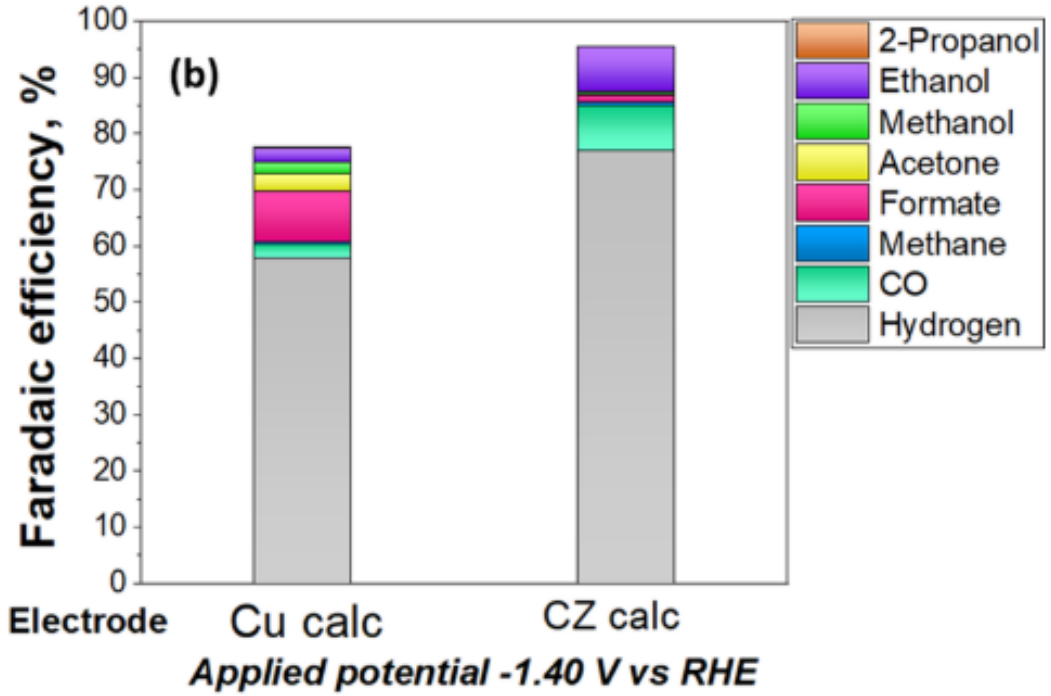
Modeling surface reconstruction on Cu-Zn catalysts



In preparation

Experimental results

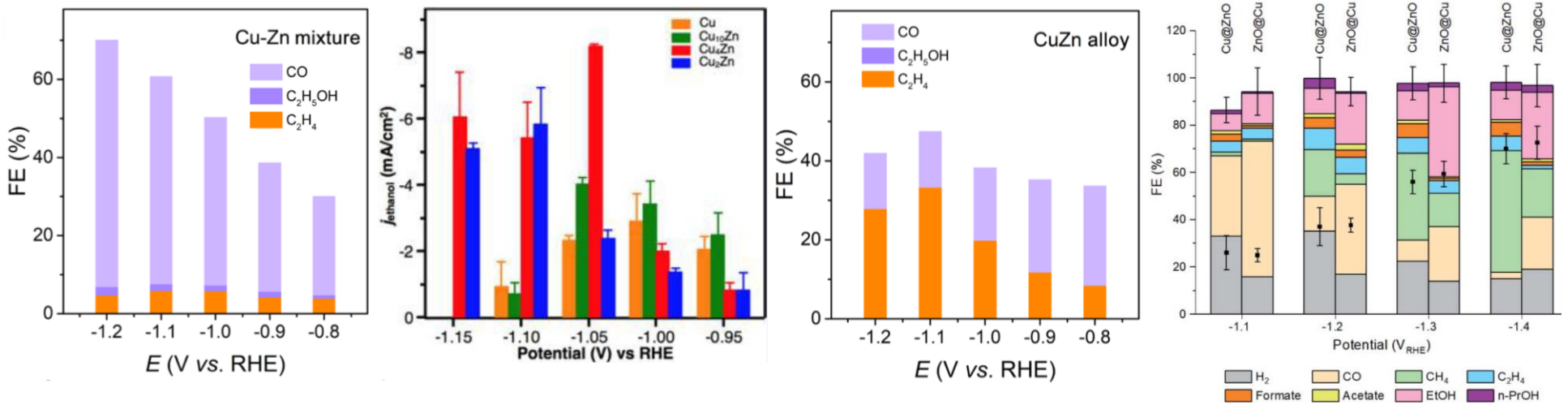




CO_2-saturated 0.1 M $KHCO_3$ aqueous

CO_2R selectivity of Cu-Zn catalysts

CO	Ethanol	Ethylene	Methane



ZnO phase stabilizes $Cu^{\delta+}$ sites

CO spillover from Zn to Cu

$CO\text{-}CH_x$ coupling vs CO-CO coupling

Strong C_x binding

$Zn^{\delta+}$ impurities

Electron-rich Cu

Langmuir **2018**, *34*, 13544–13549.

ACS Catal. **2016**, *6*, 8239–8247.

Chem. Sci. **2021**, *12*, 14484–14493.

Structural input for models

Bulk composition (EDS)

	Average atomic %			
Sample	O	Cu	Zn	K
Cu calc Fresh	69.87	30.13	-	-
Cu calc Tested	30.03	61.74	-	8.23
CZ calc Fresh	42.24	35.92	21.84	-
CZ calc Tested	58.66	12.86	26.14	2.34

Surface composition (XPS)

Electrode	Cu	O	C	Zn	K	F	S	Cu/O	Zn/Cu
Cu calc Fresh	1.9	4.8	62.9	-	-	29.8	0.6	0.4	
Cu calc Tested	0.9	7.4	65.4	-	1.7	24.2	0.4	0.1	
CZ calc Fresh	1.6	7.3	70.1	1.3	-	19.5	-	0.2	0.8
CZ calc Tested	3.8	43.1	37.9	13	2.1	-	-	0.1	3.4

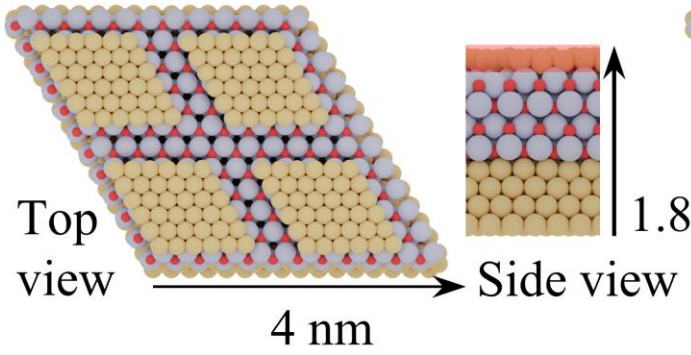
CZ: Mixture of calcinated Cu NPs and ZnO NPs.
Tested: 2h CO_2R at −1.4 V vs RHE.

ACS Appl. Mater. Interfaces **2022**, *14*, 517–530.

$ZnO(0001)/Cu_2O(111)$ epitaxy on Cu

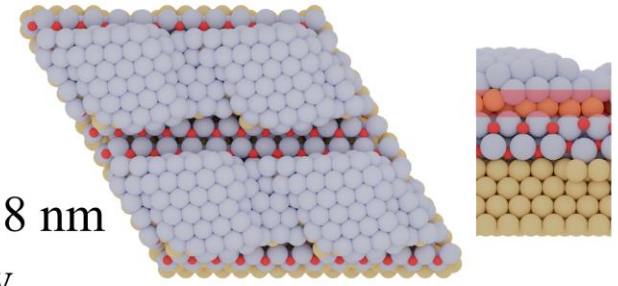
Cu_2O-1L

Zn: 25 at.% ; O: 25 at.%



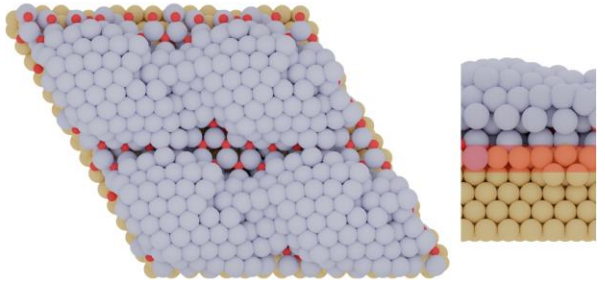
Cu_2O-2L

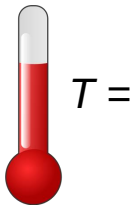
Zn: 28 at.% ; O: 14 at.%



Cu_2O-3L

Zn: 29 at.% ; O: 11 at.%



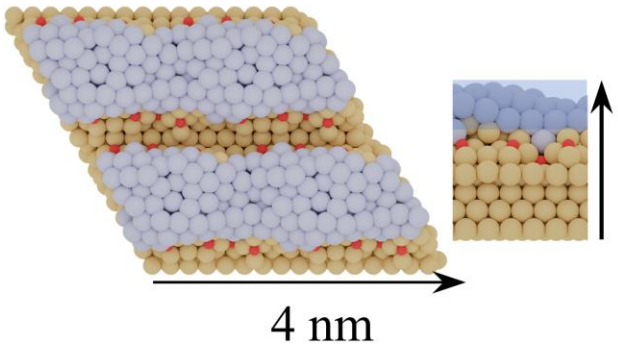


T = 700 K for 1 + 10 ps

U = –1.0 V vs RHE

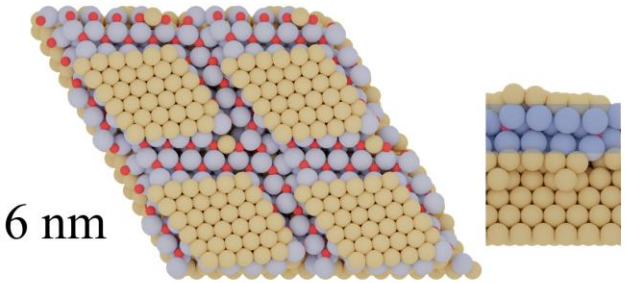
ZnO-1L

Zn: 17 at.% ; O: 4 at.%



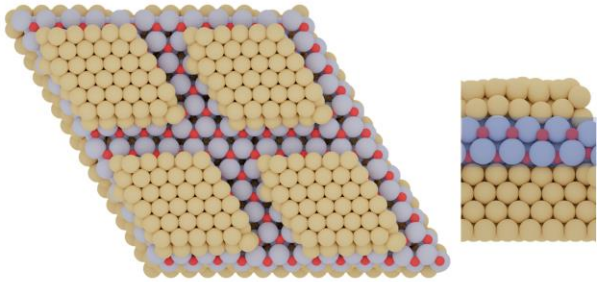
ZnO-2L

Zn: 16 at.% ; O: 12 at.%



ZnO-3L

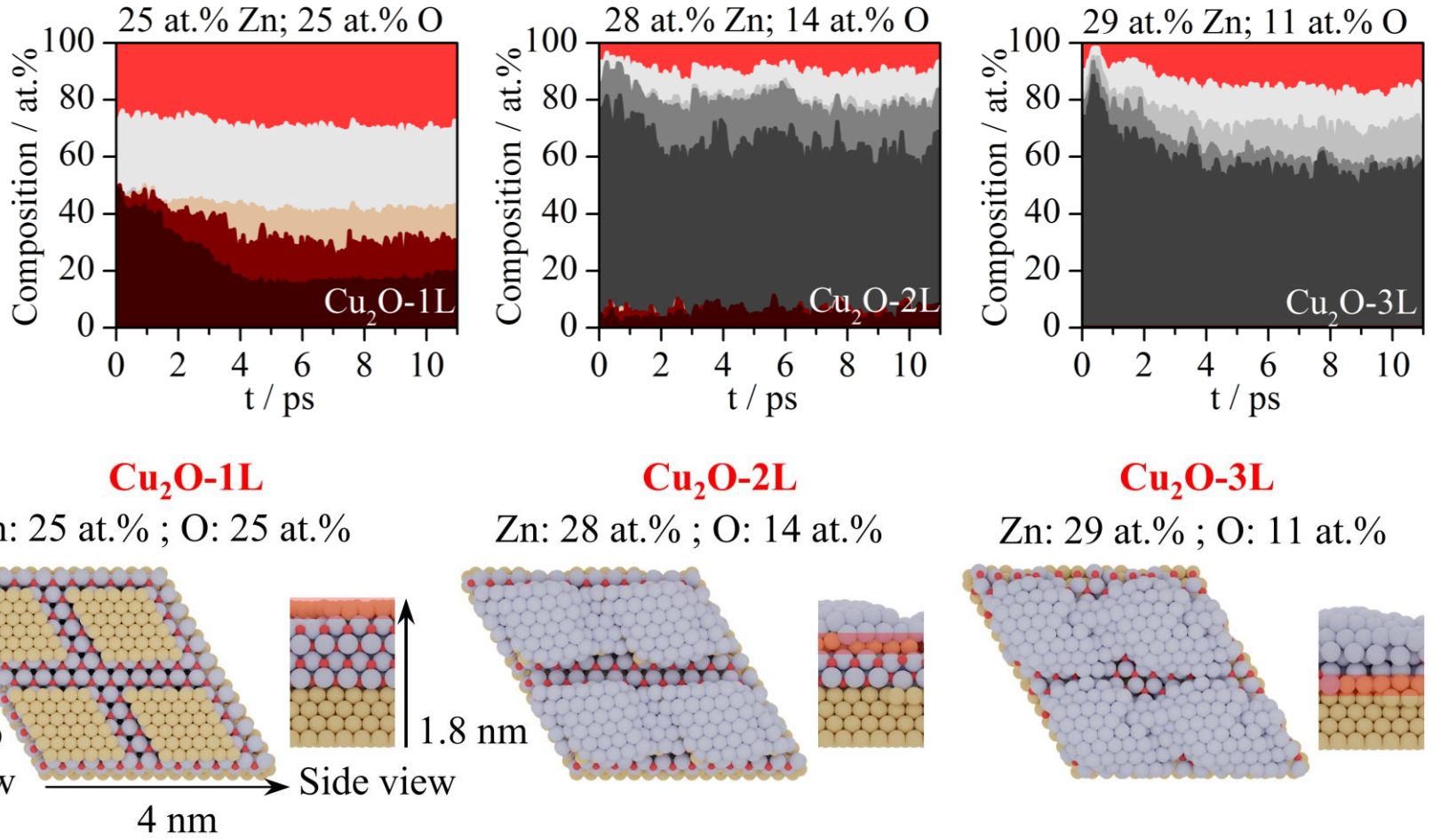
Zn: 15 at.% ; O: 15 at.%



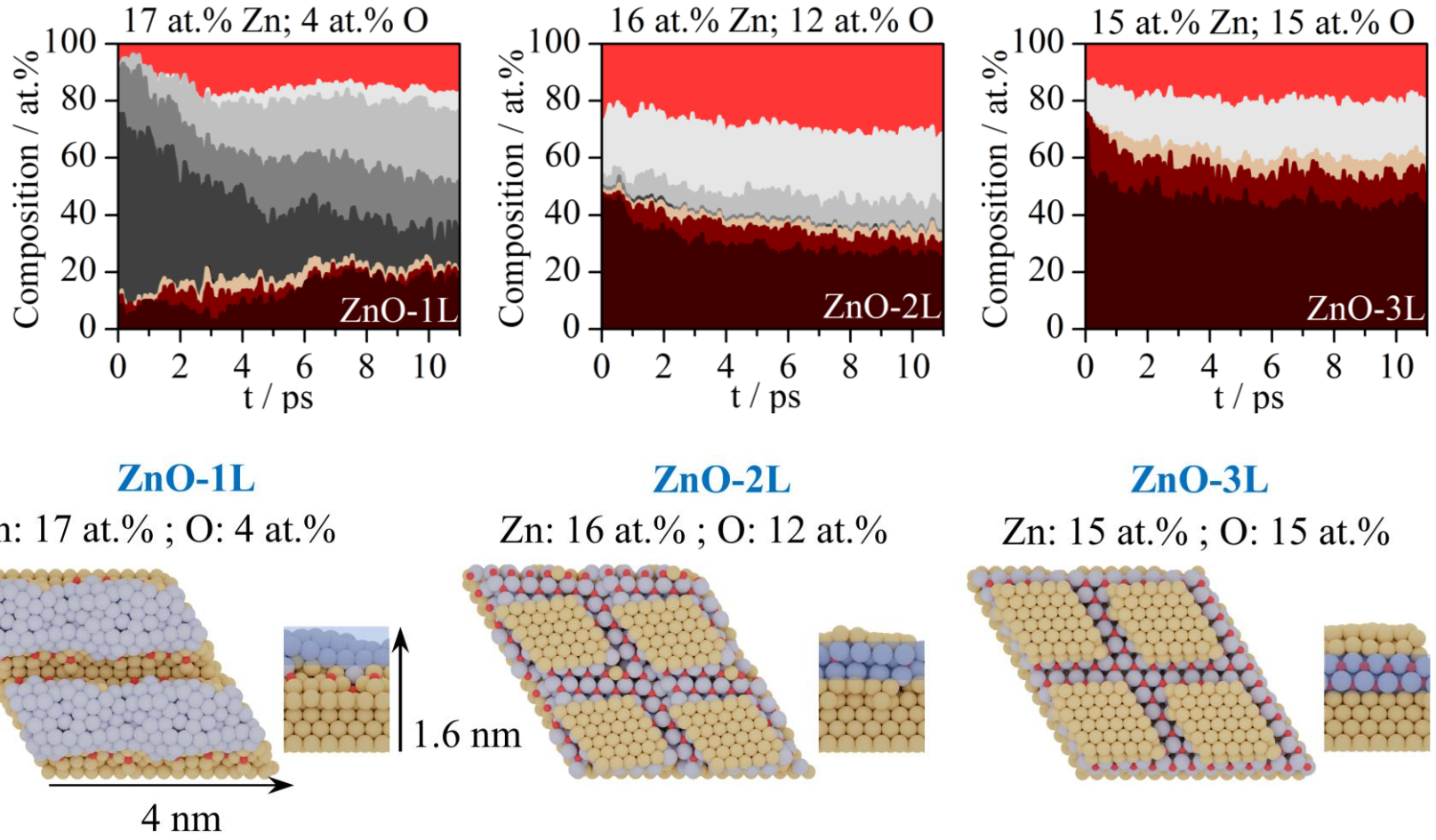
Legend Cu: Zn: O:

Bulk: 4 layers of 8 × 8 Cu(111).

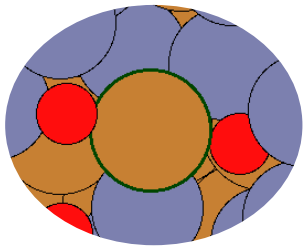
Surface composition vs AIMD time



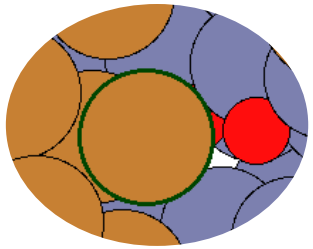
Surface composition vs AIMD time



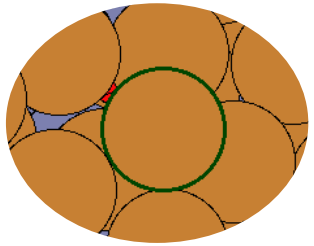
Surface reactivity



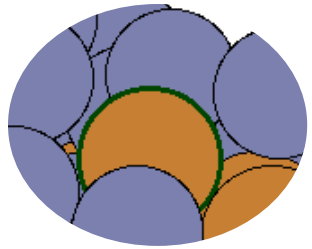
Cu^{+}; q = +0.6 |e^{-}|



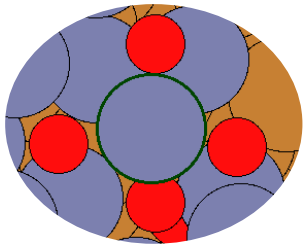
$Cu^{\delta+}$; q = +0.3 |e^{-}|



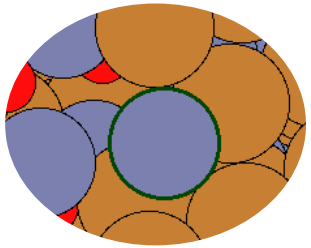
Cu^{0}; q = –0.1 |e^{-}|



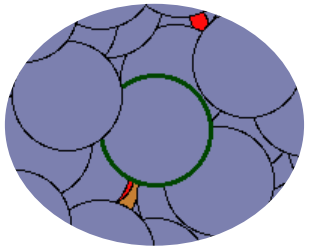
$Cu^{\delta-}$; q = –0.3 |e^{-}|



Zn^{2+}; q = +1.2 |e^{-}|



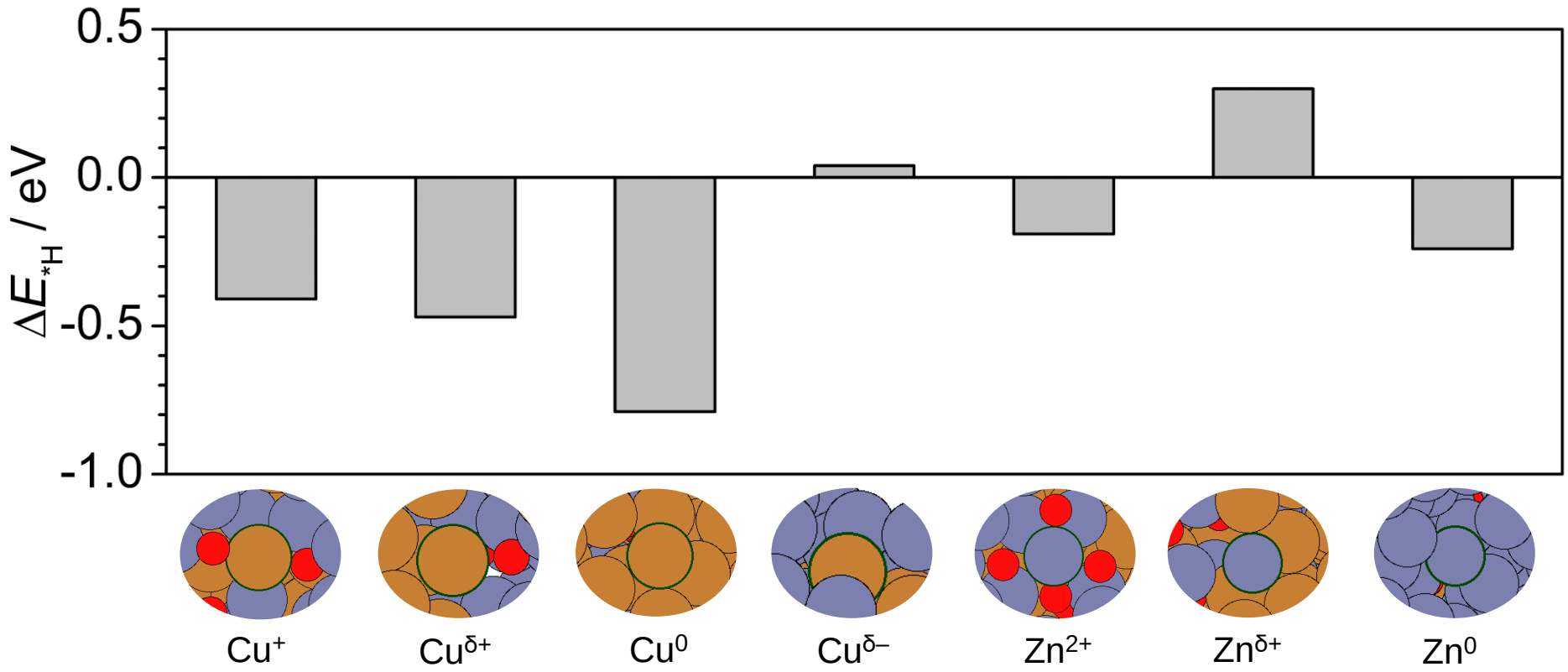
$Zn^{\delta+}$; q = +0.2 |e^{-}|



Zn^{0}; q = 0.0 |e^{-}|

Legend Cu: Zn: O:

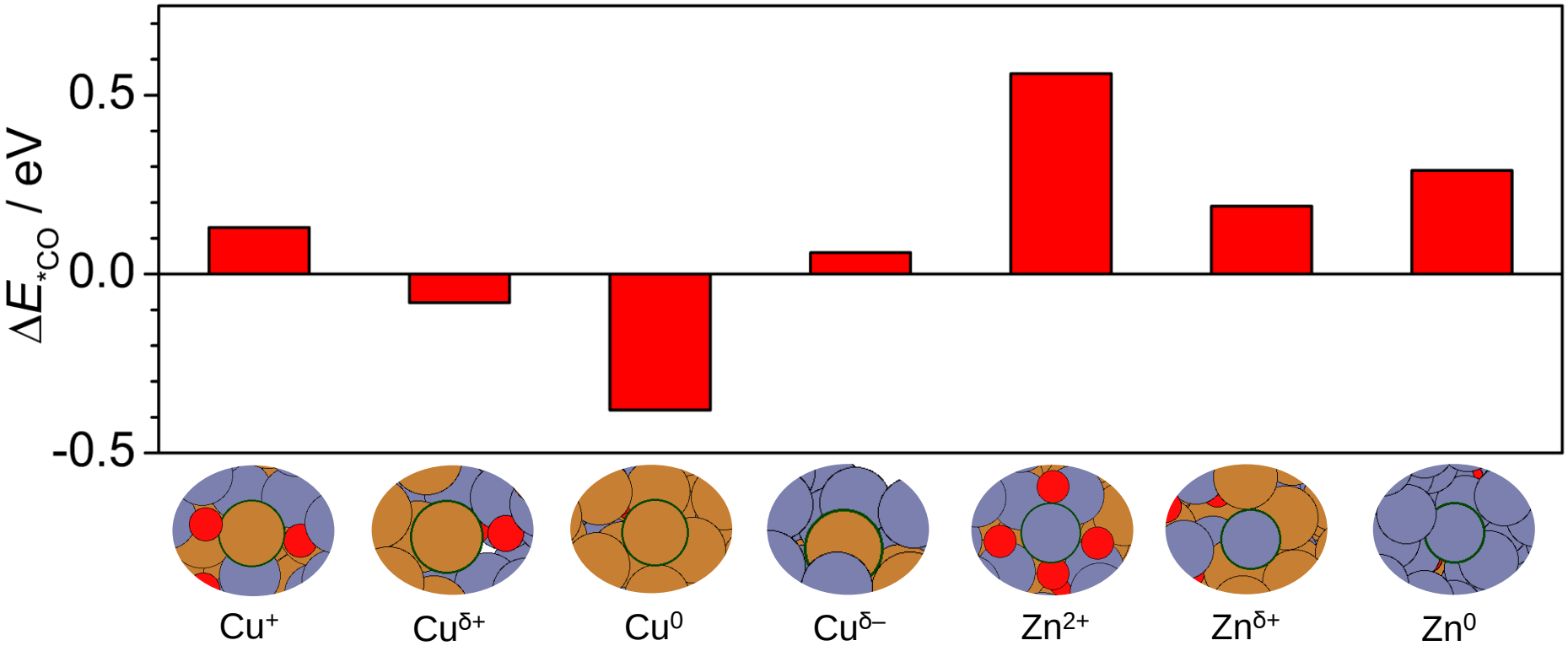
Selectivity descriptor toward HER



Strong *H binding on Cu sites. In presence of Zn, *H binding is weakened

Legend Cu: Zn: O:

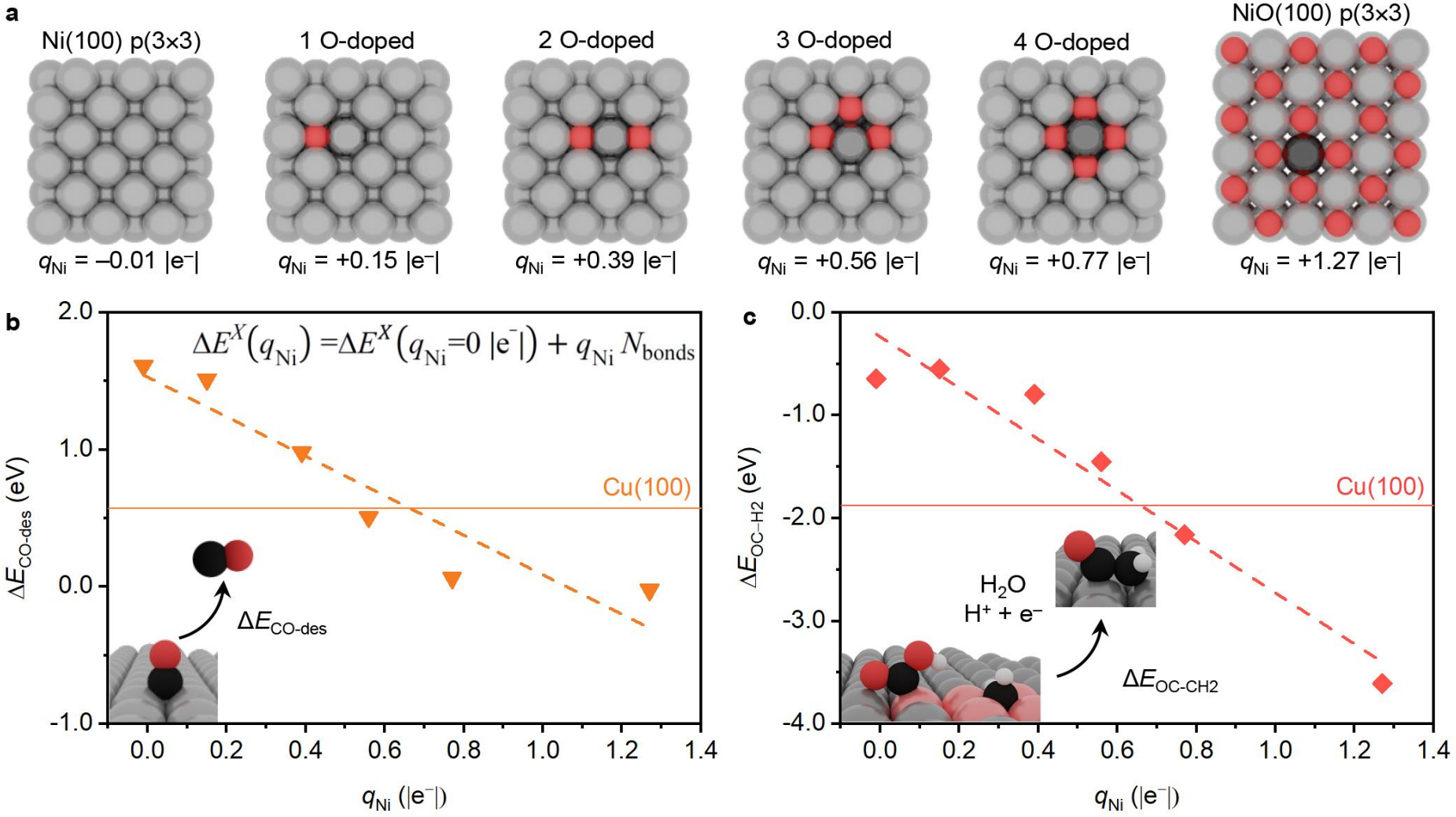
Selectivity descriptor toward CO



Cu^0 strongly binds CO, while CO desorption is favored on Cu$^+$, Cu$^{\delta+}$, and Zn

Legend Cu: Zn: O:

*q*LSR formalism



Yeo, B. S; Pérez-Ramírez, J.; López, N. *et al. Nat. Catal.* **2022**, *5*, 545–554.
Chem. Rev. **2022**, *122*, 11085–11130.

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Thank you all for your kind attention!