



From Surface Science to Electrochemistry


Model Systems for Interface and Reaction Studies



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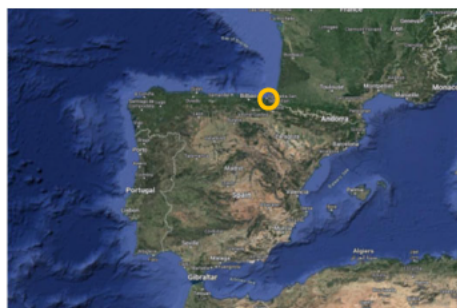


(Photo)- and electrocatalysis at the atomic scale





(Photo)- and electrocatalysis at the atomic scale

How can we build atomically defined model systems
to understand electrochemical reactions?



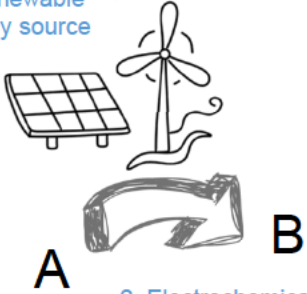
Faculty of Chemistry

<https://quantummile.basquequantum.eus/>

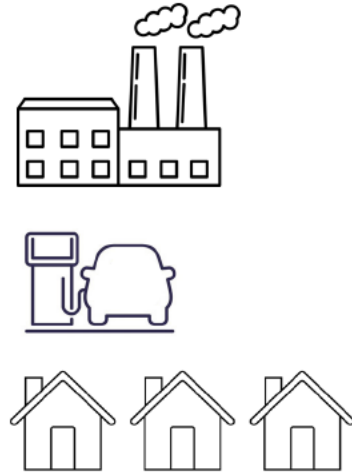
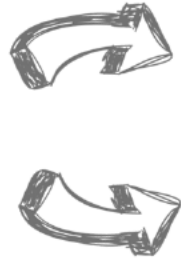
Decarbonize, electrify, and store

1. Renewable energy source



2. Electrochemical conversion

3. Energy storage/chemical

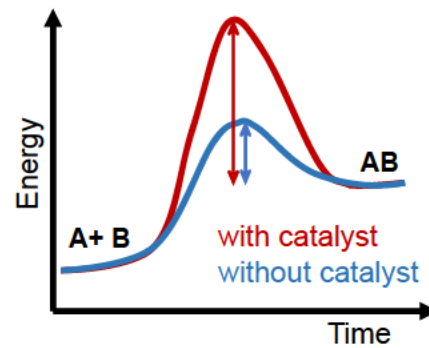
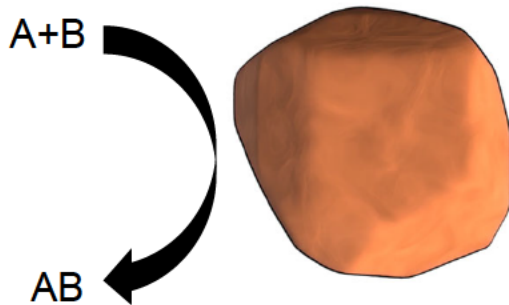


Why?

limited resources · geopolitical constraints · emissions

Electrochemistry enables the conversion of renewable electricity into chemical energy.

Catalysts lower activation barriers

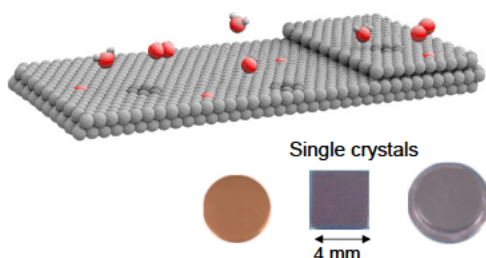


A catalyst accelerates reactions by changing the pathway (not the thermodynamic equilibrium)

The materials and pressure gap

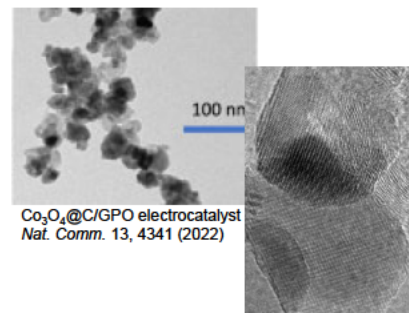
Surface science **model** systems

- Atomically defined surface
- Selected active sites
- Controlled environment
- Clean reference state



Real electrochemical catalysts

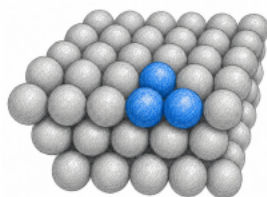
- Structural heterogeneity
- Multiple active-site candidates
- Electrolyte / solvent environment
- Operando dynamics



To retain **atomic precision** while approaching **reaction-relevant** conditions.

From atomic structure to catalytic trends

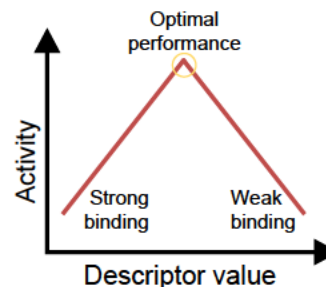
Atomic-scale properties (structure & electronics)



Descriptors (quantitative bridge)

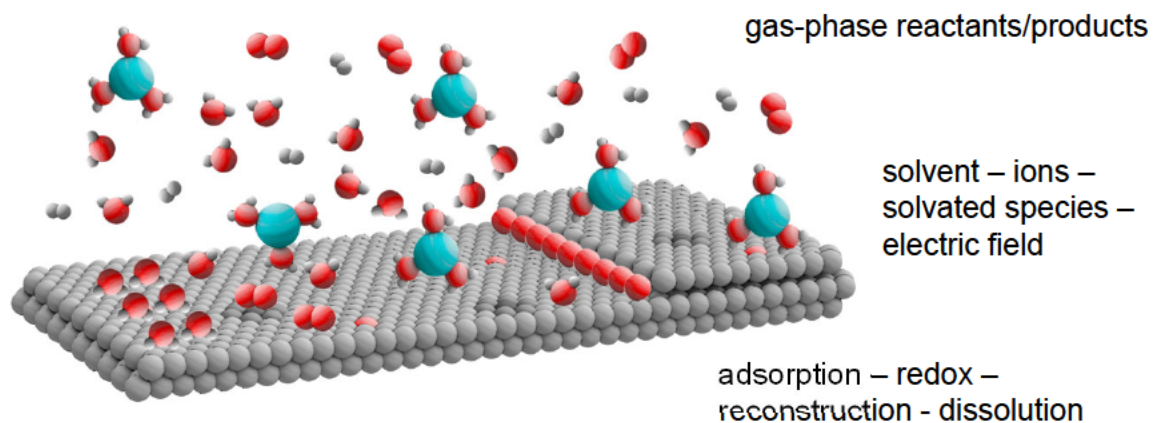
- Adsorption energy
- Electronic structure
- Coordination environment
- ...

Catalytic performance (activity, selectivity & stability)



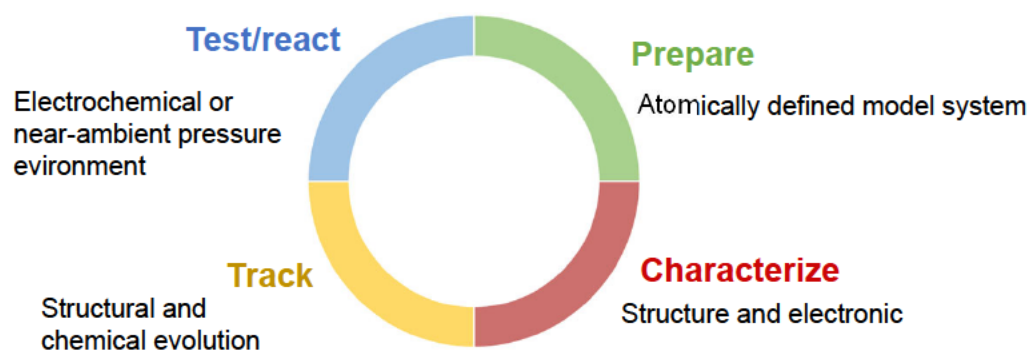
Descriptors condense local atomic and electronic properties into variables that rationalize catalytic performance.

Electrocatalysis is governed by the active interface



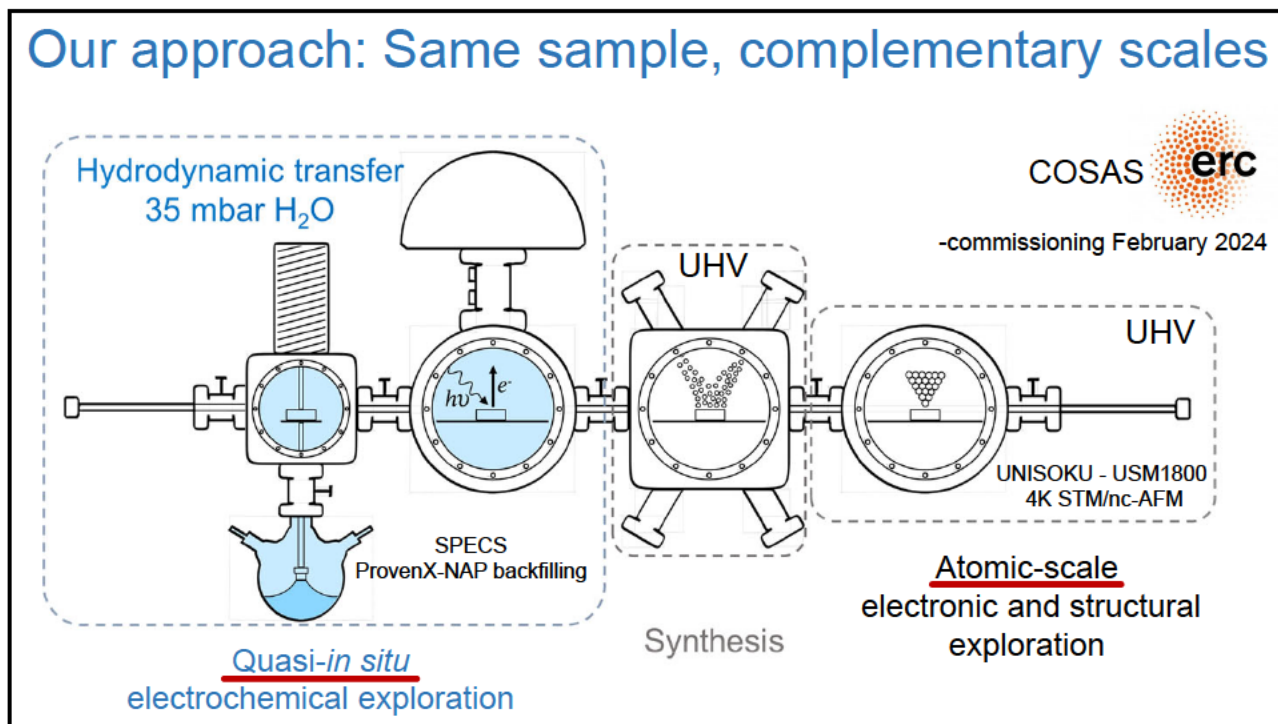
During reaction, the relevant descriptor may be a property of the operating surface, not of the pristine material.

Our approach: Same sample, complementary scales (from atomic-scale structure to electrochemical response)

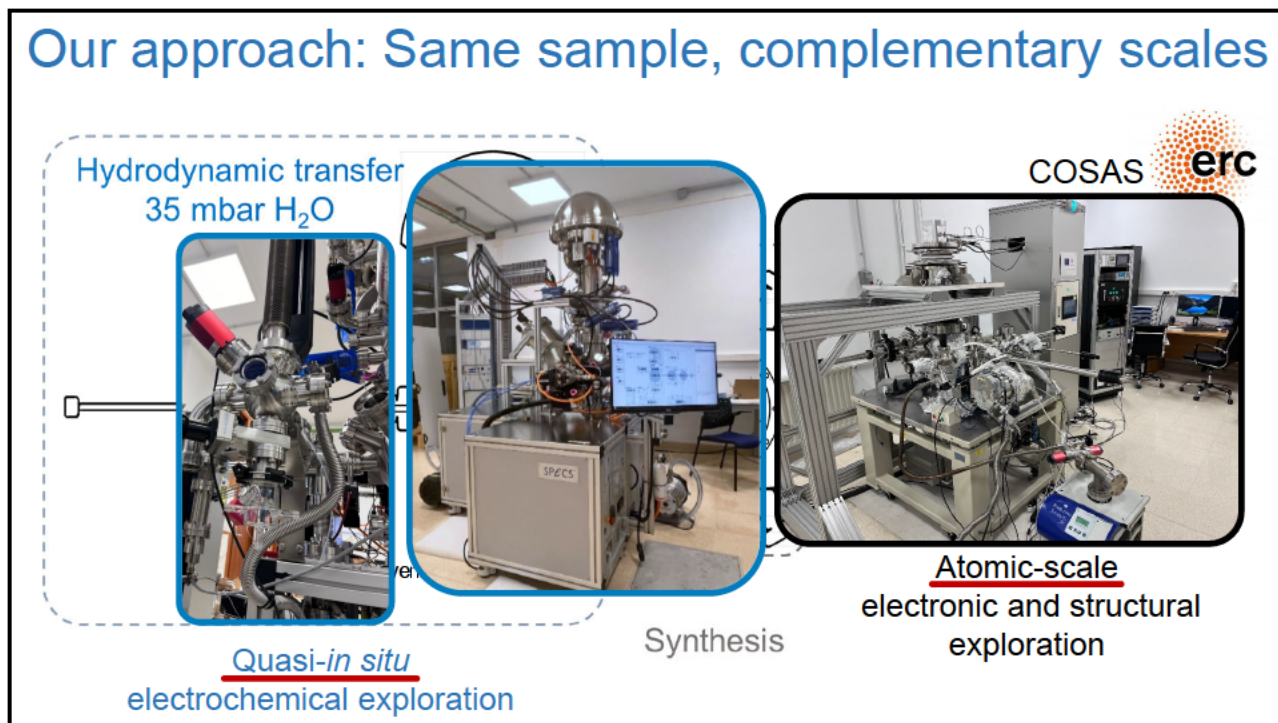


Identify, prepare and test the right model active site as it evolves into the active interface.

Our approach: Same sample, complementary scales



Our approach: Same sample, complementary scales



Two levels of the same problem

1- Atomic-scale descriptors

What is the local structure and electronic fingerprint of an active site?



Single defects as atomic-scale active centers



UHV – STM/STS

2- (Quasi)in situ dynamics

How does this site evolve into the active interface under reaction conditions?

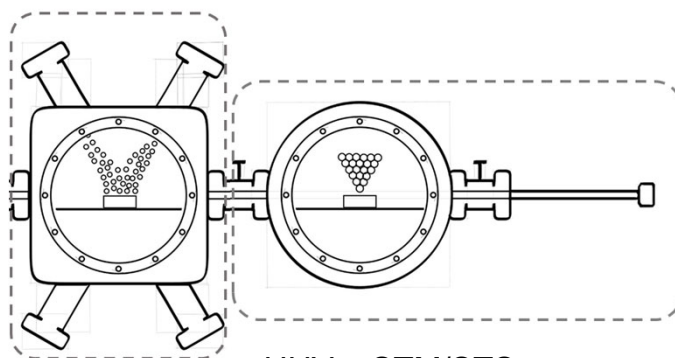


Following chemical state and reaction dynamics under realistic environments

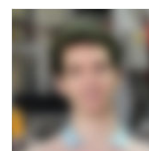


NAP-XPS / electrochemistry

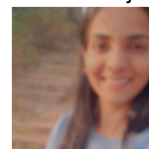
1- Atomic-scale descriptors: Point defects in MoSe₂ and WS₂



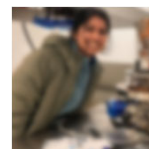
UHV – STM/STS



Guillermo Tajuelo



Tarushi Agarwal



Sruthibhai P V

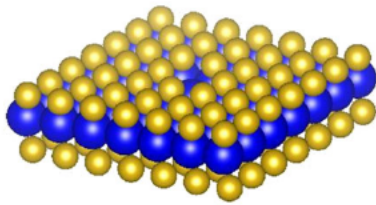
How does the local atomic and electronic structure of an individual defect define its potential role as an active site?



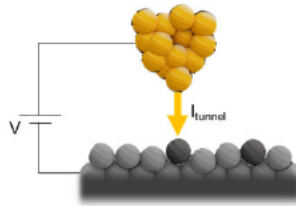
Example 1 - Atomic-scale descriptors at single defects

Question
 Model System
 Probe
 Observation
 Mechanism
 Take-home

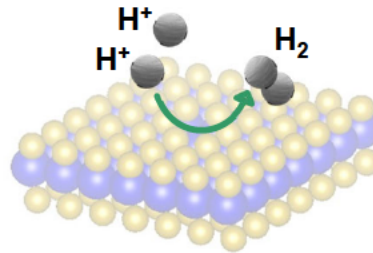
How does a single atomic defect control local reactivity?



atomic defect



electronic fingerprint



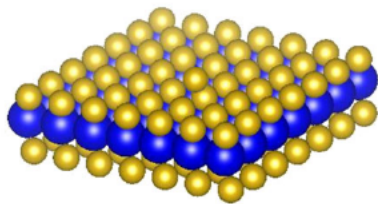
reaction pathway

Can the atomic and electronic structure of one defect define its role as an active site?

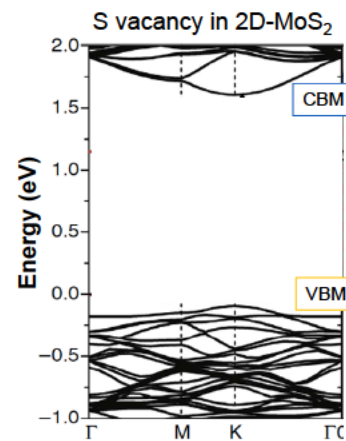
Example 1 - Atomic-scale descriptors at single defects

Question
 Model System
 Method
 Observation
 Mechanism
 Take-home

Point defects in monolayer TMDs as model active-site for H_2 production



- MoS_2 , WS_2 , MoSe_2 , WSe_2 : semiconductors
- No chemical reactivity on basal plane

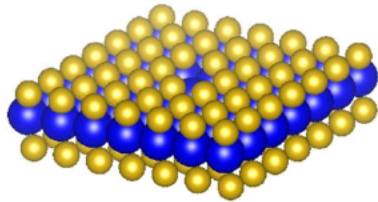


Qiu. Nat. Commun. 4, 2642 (2013)

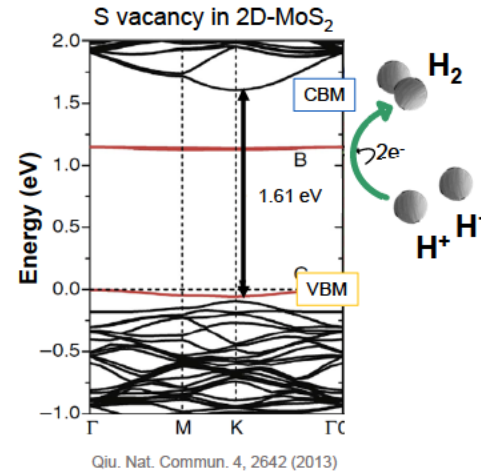
Example 1 - Atomic-scale descriptors at single defects

○ Question ● Model System ○ Method ○ Observation ○ Mechanism ○ Take-home

Point defects in monolayer TMDs as model active-site for H₂ production



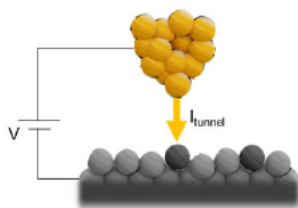
- S, Se vacancy: in gap state at Fermi level
- Lowest energy formation point defect
- Local active-site candidates for H⁺ adsorption



Example 1 - Atomic-scale descriptors at single defects

○ Question ○ Model System ● Method ○ Observation ○ Mechanism ○ Take-home

STM/STS resolves structure and electronic states locally

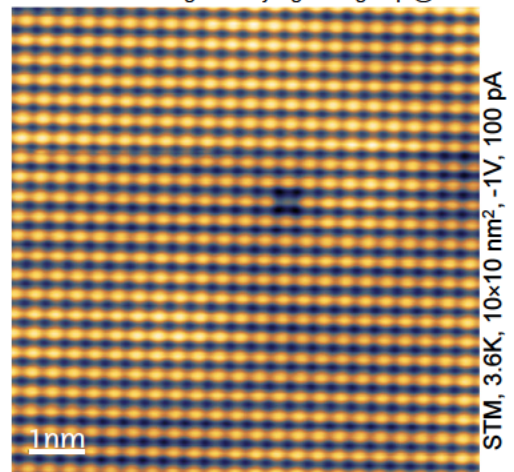


Scanning Tunneling Microscope (STM)

$$I \propto \int_0^{eV} \rho_s(\vec{r}_s, E) \rho_t(\vec{r}_t, E - eV) T(E, eV, d, \phi) dE$$

$$\frac{dI}{dV} \propto \rho_t(0) \rho_s(eV) T(eV, eV, d, \phi)$$

FeSe/BLG - MBE growth by Ugeda's group @ DIPC

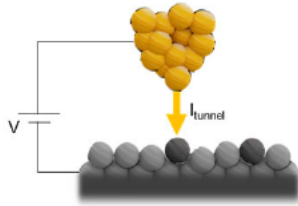


Wang, Phys. Rev. Research 7, 023288 (2025)

Example 1 - Atomic-scale descriptors at single defects

○ Question ○ Model System ● Method ○ Observation ○ Mechanism ○ Take-home

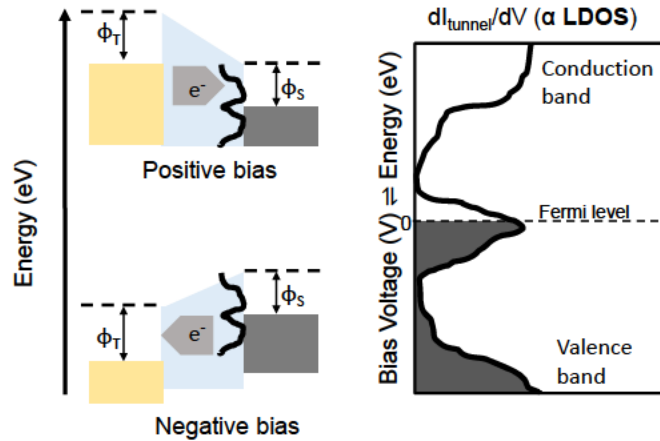
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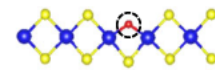
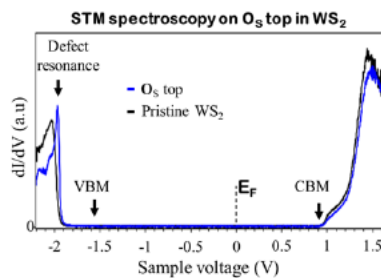
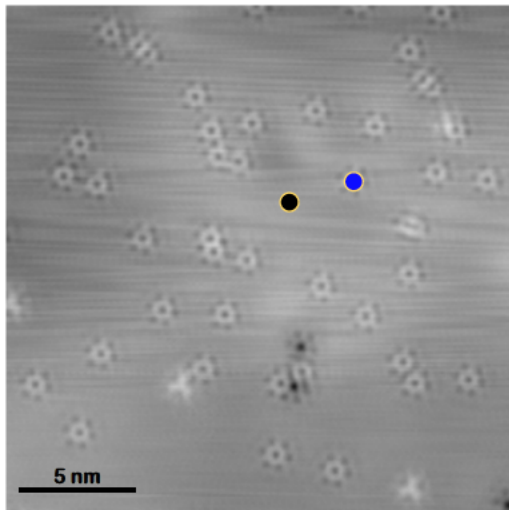


Ultra high vacuum (<math>< 1 \cdot 10^{-10}</math> mbar) – low temperature (<math>< 4</math>K)

Example 1 - Atomic-scale descriptors at single defects

○ Question ○ Model System ○ Method ● Observation ○ Mechanism ○ Take-home

Defect chemistry controls the electronic descriptor



Bare WS_2 :

- Semiconductor gap

Defect:

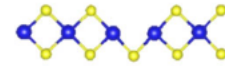
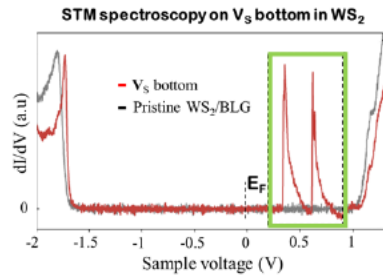
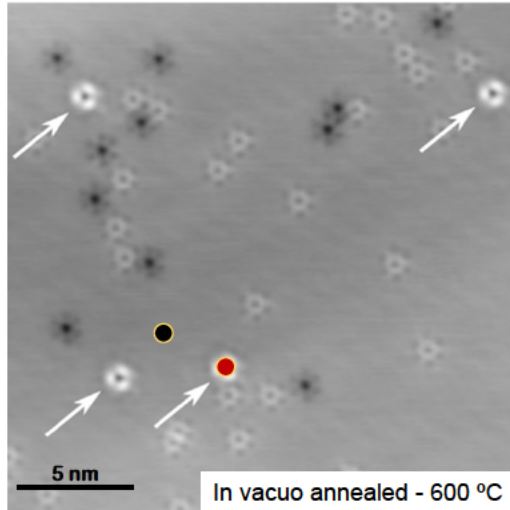
- Shallow state at the valence band
- No deep in-gap states

Barja, Nature Comm. 10, 3382 (2019), Schuler, PRL 123, 076801 (2019)

Example 1 - Atomic-scale descriptors at single defects

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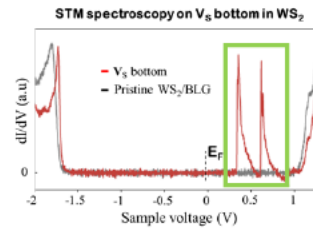
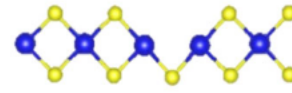
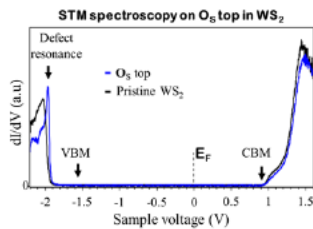
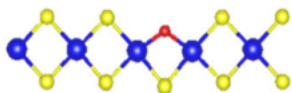
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Example 1 - Atomic-scale descriptors at single defects

○ Question ○ Model System ○ Method ● Observation ○ Mechanism ○ Take-home

Defect chemistry controls the electronic descriptor

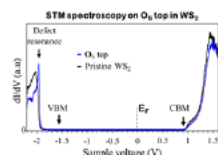
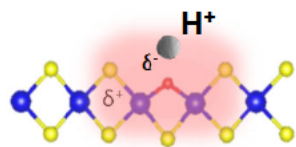


Similar-looking defects can have different electronic fingerprints depending on their chemical termination.

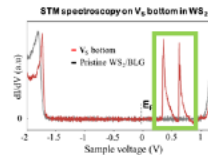
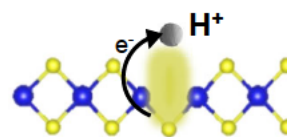
Example 1 - Atomic-scale descriptors at single defects

○ Question ○ Model System ○ Method ○ Observation ● Mechanism ○ Take-home

Electronic structure defines the H⁺ adsorption mechanism



O-passivated vacancy
Occupied M–O hybrid states
H⁺ adsorption via bond polarization

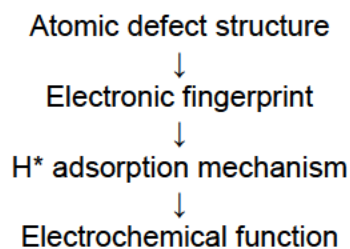


Bare chalcogen vacancy
Unoccupied M–d in-gap states
H⁺ adsorption via electron transfer

Example 1 - Atomic-scale descriptors at single defects

○ Question ○ Model System ○ Method ○ Observation ○ Mechanism ● Take-home

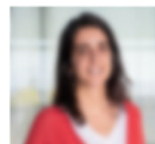
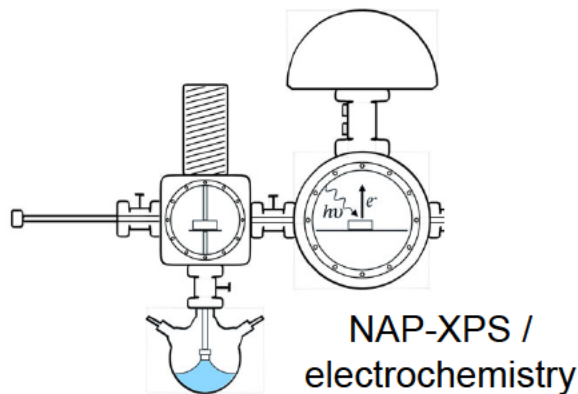
Local descriptors determine reaction pathways



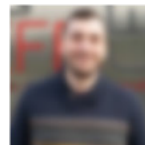
The same type of atomic defect can lead to different mechanisms depending on its chemical termination and in-gap electronic states.

Barja, Nature Comm. 10, 3382 (2019); Schuler, PRL. 123, 076801 (2019)

2- (Quasi)in situ surface dynamics: Au(111) electrooxidation



Ane Etxebarria



Jesús Redondo



Josef Mysliveček's group
(Charles University)



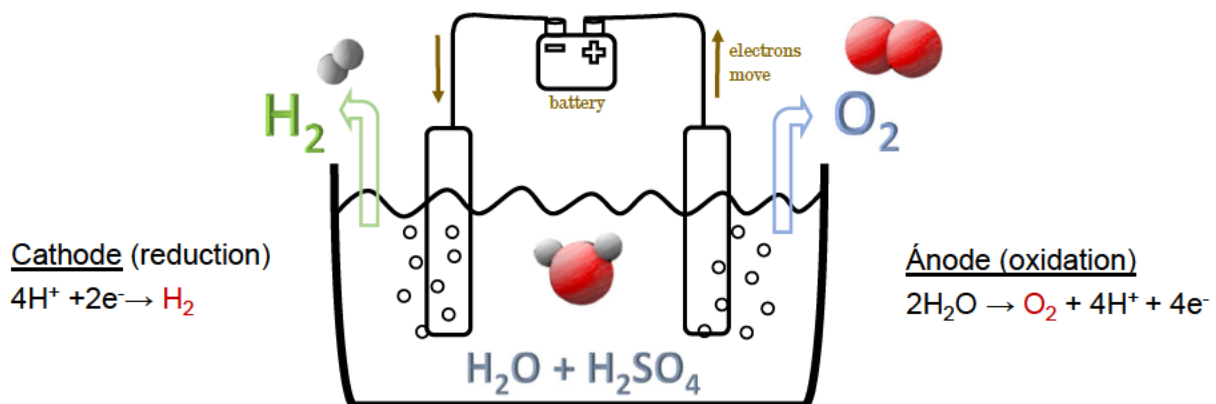
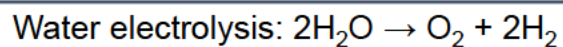
Pankaj K. Samal

How does the catalyst surface evolve under electrochemical reaction conditions?

Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

- Question
- Model System
- Method
- Observation
- Mechanism
- Take-home

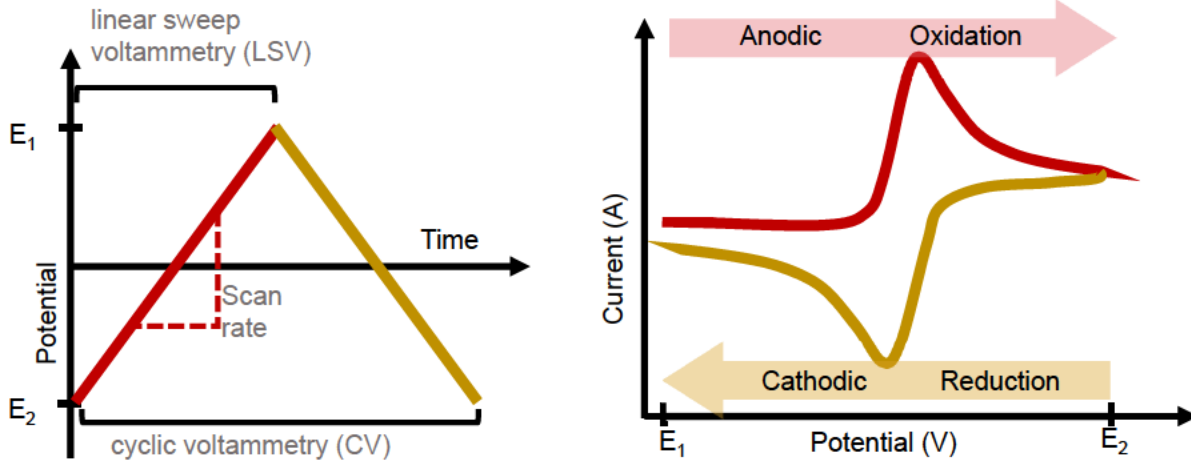
Which chemical states form under anodic potential?



Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

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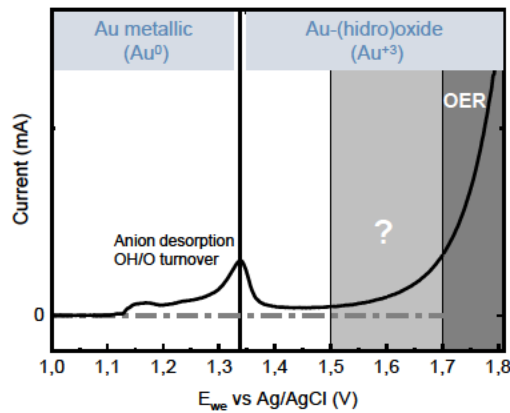
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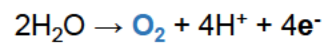
Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

- Question
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Au(111) electro-oxidation acidic media



Oxygen Evolution Reaction



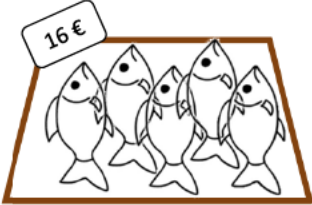
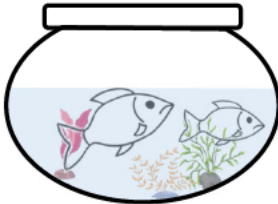

- Reaction mechanism
- Actual OER active phase

Anodic Oxidation

Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

○ Question ○ Model System ● Method ○ Observation ○ Mechanism ○ Take-home

Why quasi-in situ?


Ex situ	Emersed electrode	In situ	Operando
<ul style="list-style-type: none"> • After reaction • Air exposure • Possible loss of transient states 	<ul style="list-style-type: none"> • After electrochemical polarization • Controlled transfer • Preserves reaction-induced surface chemistry 	<ul style="list-style-type: none"> • During reaction • Most realistic • Instrumental challenge (surf. sensitive) XPS 	
			

E. Pastor et al., *Complementary probes for the electrochemical interface*, Nature Reviews Chemistry 8,159–178 (2024)

Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

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Why quasi-in situ?

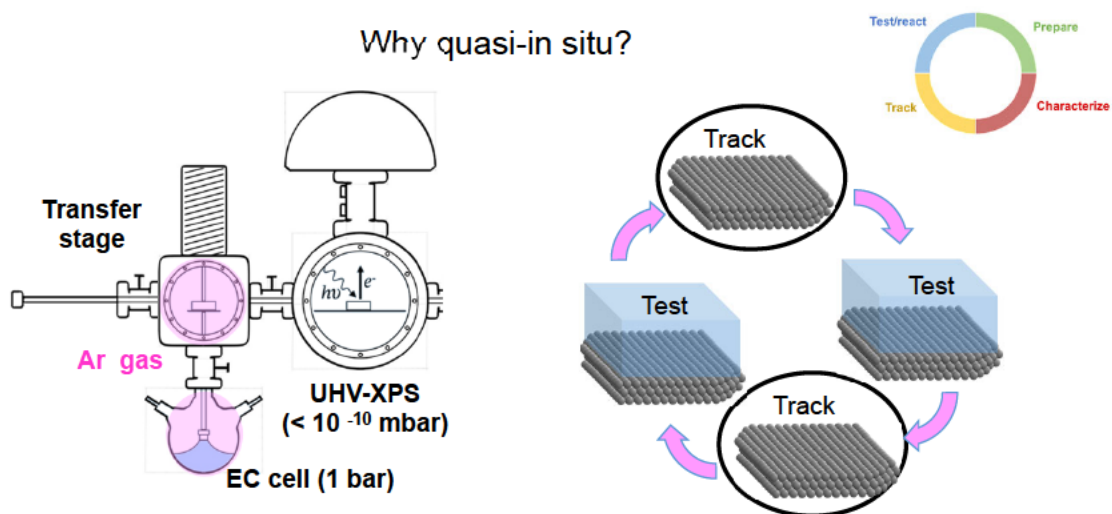
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	<div style="text-align: center;">  <p>Dry/Inert gas (UHV) Humid/Vapor H₂O (NAP)</p> </div>		

E. Pastor et al., *Complementary probes for the electrochemical interface*, Nature Reviews Chemistry 8,159–178 (2024)

Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

○ Question ○ Model System ● Method ○ Observation ○ Mechanism ○ Take-home

Why quasi-in situ?



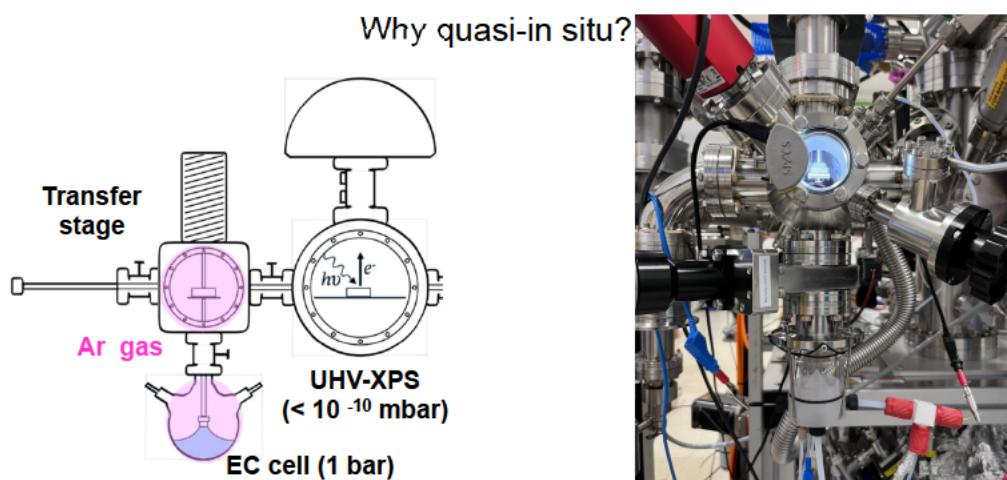
Redondo, J Am Chem Soc . 148, 12587 (2026)

Other ex-situ cells: Nat. Comm. 4 , 2904 (2013); 17, 592 (2018); Rev.Sci.Instrum. 91, 125101 (2020); Rev Sci Instrum 92, 094101 (2021)

Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

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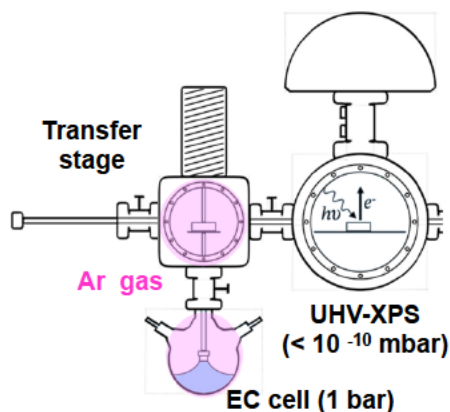
Cell design by
Josef Mysliveček's group (Charles University)



Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

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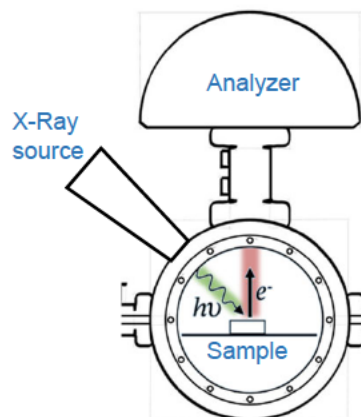
XPS follows the surface chemical state

Photon in → electron out → binding energy → oxidation state

- Core-level shifts identify chemical states.
- Surface sensitivity probes the top few nm.
- NAP-XPS adds controlled gas/vapor environments.

$$K.E. = h\nu - B.E. - \Phi$$

K.E. kinetic energy of the photoelectron
 $h\nu$ photon energy
 B.E. binding energy of the electron
 Φ work function of the spectrometer



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- Surface sensitivity probes the top few nm.
- NAP-XPS adds controlled gas/vapor environments.

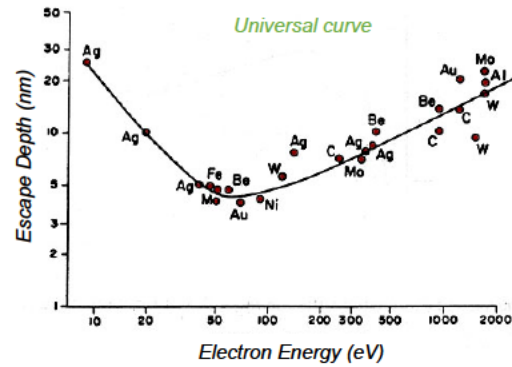
$$K.E. = h\nu - B.E. - \Phi$$

$Al_{K\alpha} = 1486.6 \text{ eV}$

X-Ray penetration depth ~ 1 nm

K.E.: 5-1500 eV

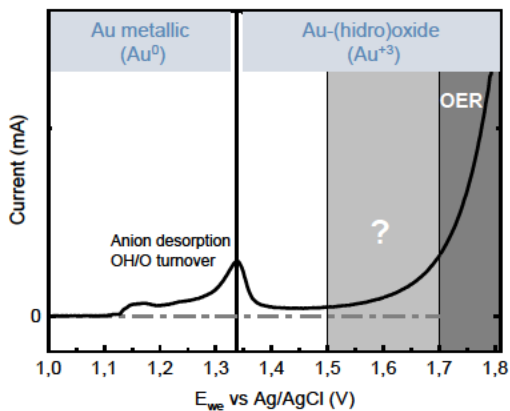
Electrons escape length ~ 10 nm



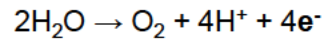
Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

○ Question ○ Model System ● Method ○ Observation ○ Mechanism ○ Take-home

Experimental workflow on the same sample



Oxygen Evolution Reaction



Chronoamperometry:

$1.4 \text{ V} < E_{ap} < 2.0 \text{ V}$

$\Delta t = 30 \text{ s}, 300 \text{ s}, 30 \text{ min}, 90 \text{ min}$

- UHV-prepared Au(111)
- Anodic polarization
- Controlled time and potential
- XPS after emersion

Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

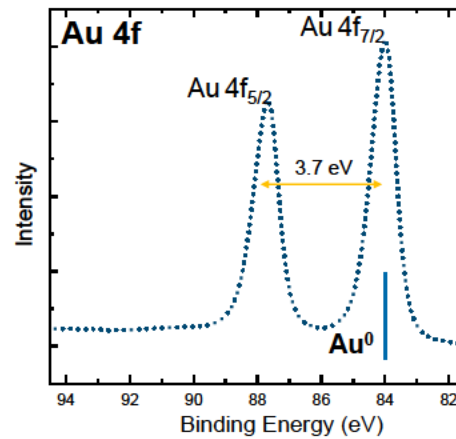
○ Question ○ Model System ○ Method ● Observation ○ Mechanism ○ Take-home

A transient $\text{Au}^{\delta+}$ state appears before Au^{3+} oxide formation

- Clean (metallic) Au(111): surface reference
- Spin-orbit doublet (same chemical information)

What do we learn?

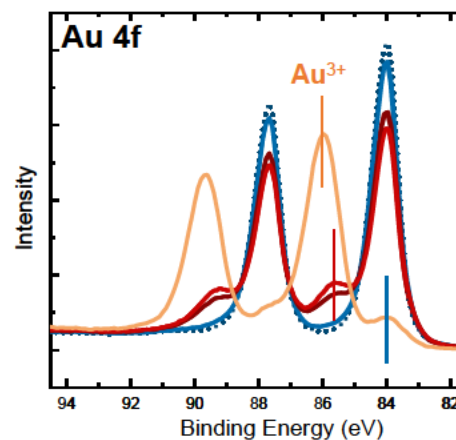
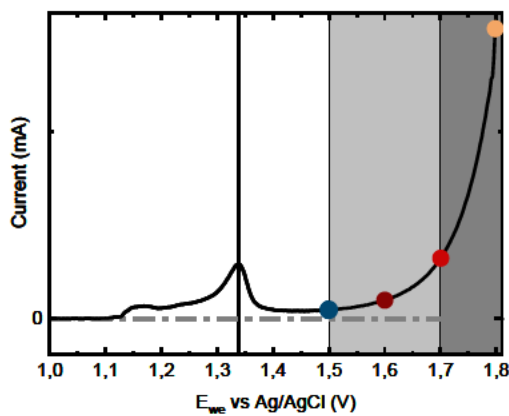
- Peak position → oxidation state/charge transfer
- Intensity → coverage/attenuation by overlayers



Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

○ Question ○ Model System ○ Method ● Observation ○ Mechanism ○ Take-home

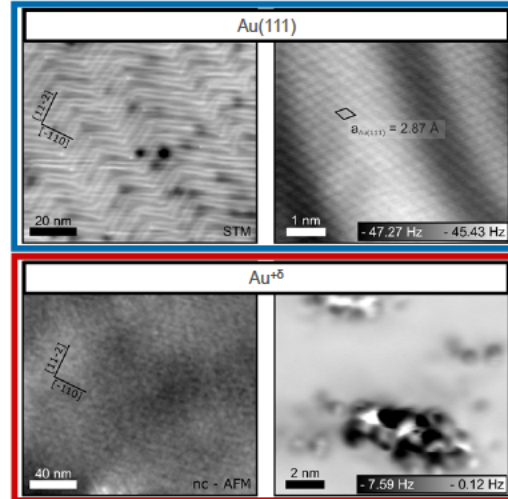
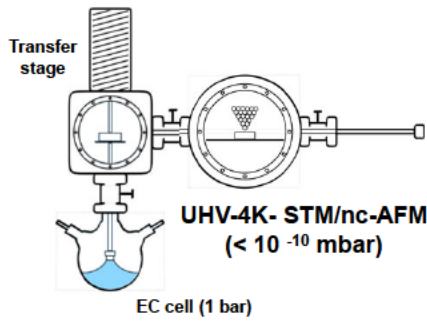
A transient $\text{Au}^{\delta+}$ state appears before Au^{3+} oxide formation



Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

○ Question ○ Model System ○ Method ● Observation ○ Mechanism ○ Take-home

Chemical oxidation is accompanied by surface restructuring

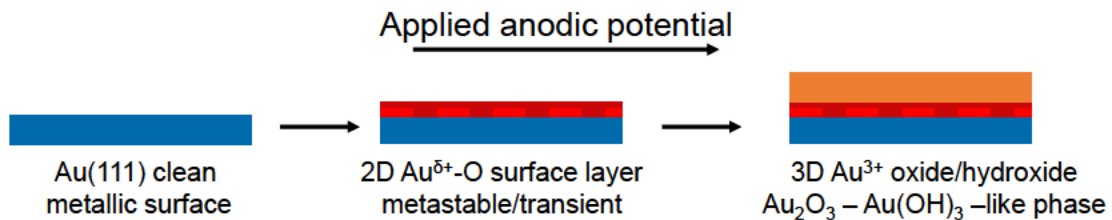


- Au^{δ+}: thin Au–O surface layer
- Au³⁺: oxide/hydroxide-like phase
- Surface becomes amorphous / cluster-like

Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

○ Question ○ Model System ○ Method ○ Observation ● Mechanism ○ Take-home

Oxidation proceeds through a transient Au^{δ+} surface state

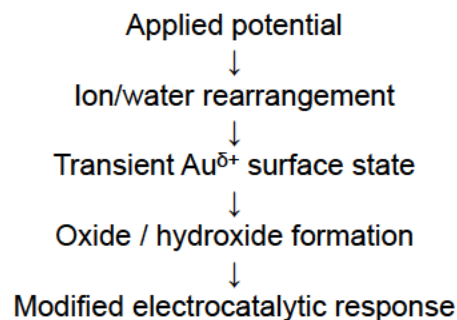


Transient states, not only stable end states, can govern electrocatalytic behavior.

Example 2 – Quasi/in situ dynamics during Au(111) electro-oxidation

○ Question ○ Model System ○ Method ○ Observation ○ Mechanism ● Take-home

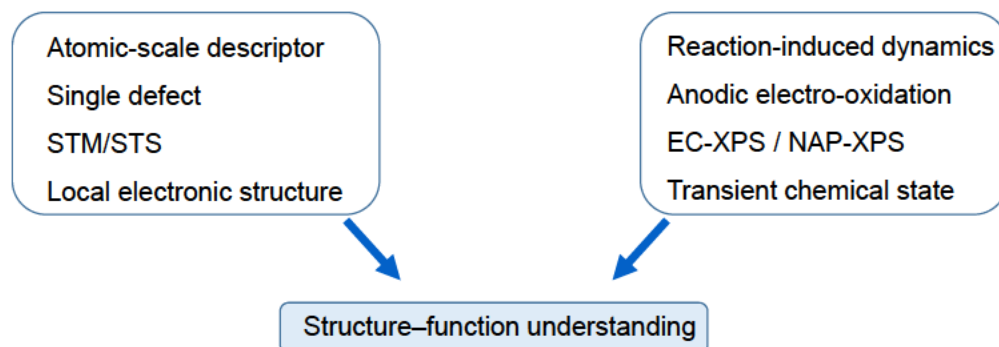
Reaction conditions create the active surface



The relevant surface is not the pristine Au(111), but the reaction-induced chemical state formed under electrochemical polarization.

Redondo et al. *J Am Chem Soc.* 148, 12587 (2026)

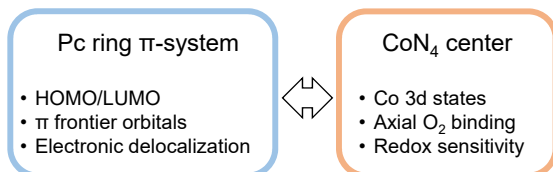
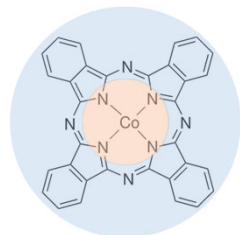
Two examples, one approach



Controlled model systems allow us to connect:

- local atomic/electronic descriptors,
- surface-averaged electrochemical response,
- and reaction-induced evolution of the active interface.

Complex model case CoPc/Au(111) (combining both approaches to make ORR descriptors measurable)



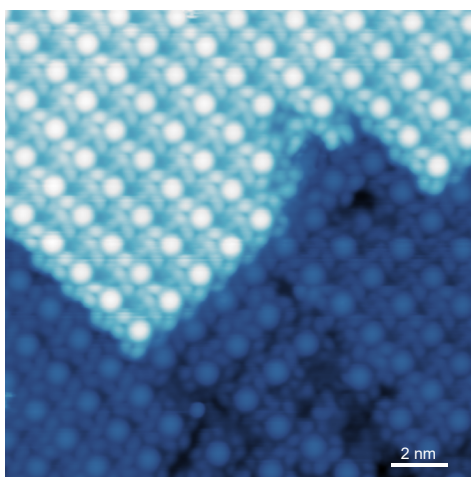
Oxygen reduction descriptors

1. Number of d-electrons in the metal center
2. Donor-Acceptor Intermolecular Hardness (HOMO-LUMO gap)
3. Redox potential
4. M-O₂ binding energy (E_b , E_{ad})

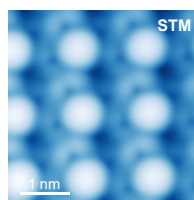
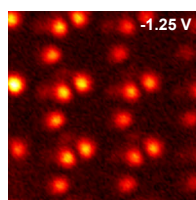
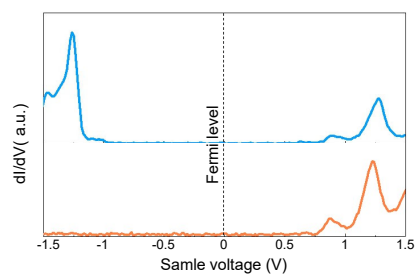
Many ORR descriptors remain indirect, lacking a direct local measurement at the active interface.

Angew Chem Int Ed, 55, 47, 14510-14521 (2016), Journal of Electroanalytical Chemistry 922, 116799 (2022), ACS Electrochem. 1, 5, 617 (2025)

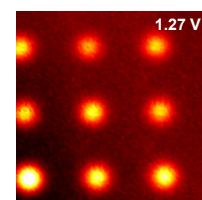
CoPc/Au(111) before O₂ electro-reduction (defining the electronic reference state)



$I_t = 50$ pA, $V_s = 2$ V, 3.4 K



$I_t = 20$ pA, $V_s = 1.7$ V, 3.4 K

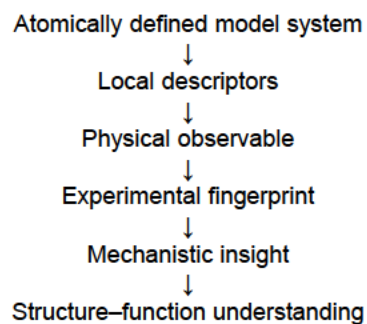
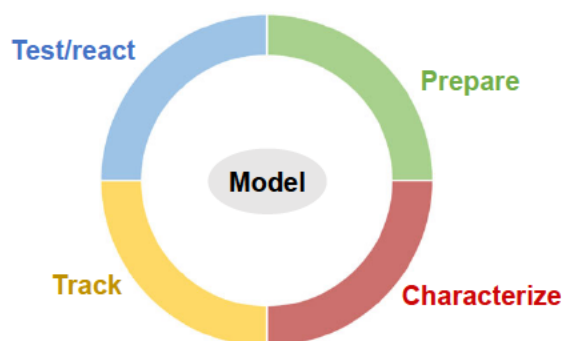


CoPc/Au(111): O₂ electro-reduction





1. What is the initial electronic structure?
2. Which electronic features respond to oxygen or reaction?
3. Is the electronic response accompanied by chemical change?
4. Does the local descriptor correlate with catalytic response?
5. Which observable tracks activity?

Turning CoPc ORR descriptors into measurable local observables

From atomic-scale structure to electrochemical response




Atomically defined model systems help us identify which local properties control catalytic function, and how they evolve under reaction conditions.











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Atomic-scale Reaction-relevant



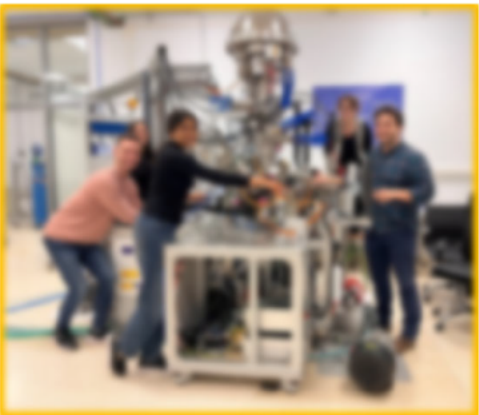
Descriptors

Unified Experimental Protocols

Model systems



Pressure & Materials gap



Thanks!

