EC tip-enhanced Raman spectroscopy for nanoscale detection of gold oxide

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Motivation: Nanoscale understanding of electrocatalytic processes

- The rational design of improved catalytic materials for energy conversion devices, such as fuel cells or metal-air batteries, requires detailed understanding of the relation between nanoscale surface structure, reactivity and reaction pathways. Two questions are of particular importance:
  - **At which nanoscale surface defects the reaction occurs?**
  - **Which reaction intermediates occur at the specific surface sites?**

➡ **Highly sensitive in-operando mapping of chemical reactions on the nanoscale is therefore required!**

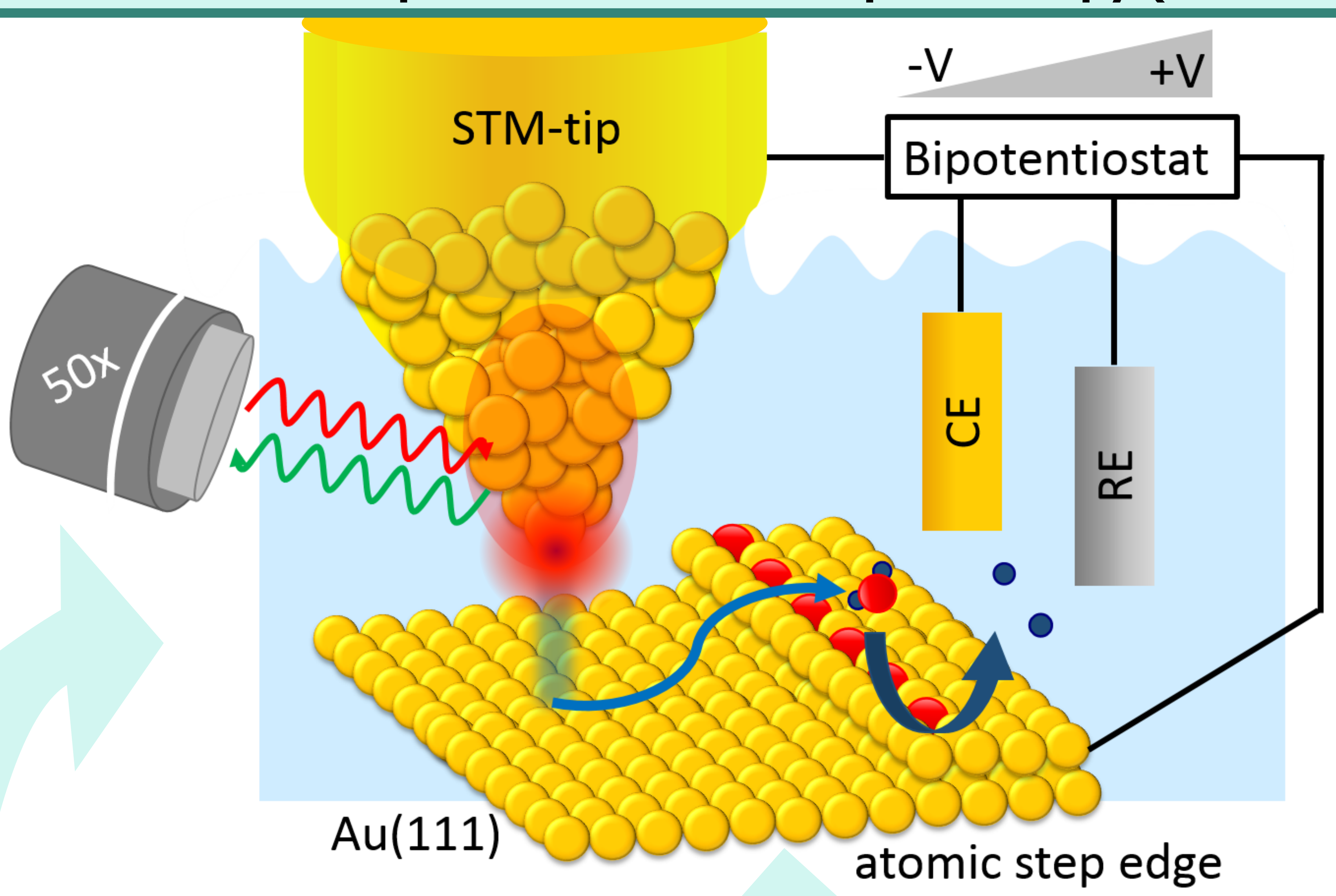
Electrochemical tip-enhanced Raman spectroscopy (EC-TERS)

Characteristics of EC-TERS

- In-operando working conditions
- Chemical specificity
- Surface-molecular sensitivity
- Nanoscale spatial chemical and topographic resolution

The model system

- Au(111) in 0.1 M H_2SO_4
- Oxidation/reduction of Au/AuOx

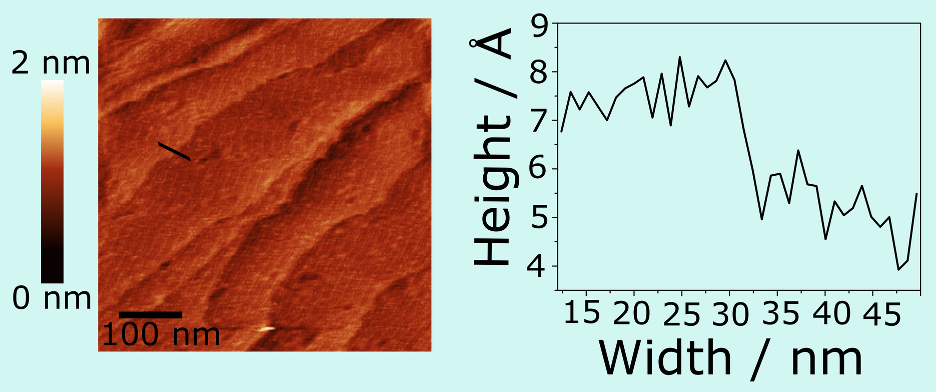


The goal

- Local detection of gold oxide
- Nanoscale mapping of oxidized Au(111) at different potentials
- Discrimination between defect and terrace oxidation to distinguish the reactivity of different nanoscale surface sites

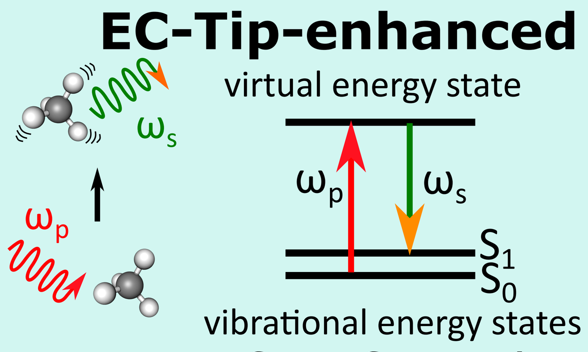
EC-Scanning tunneling microscopy

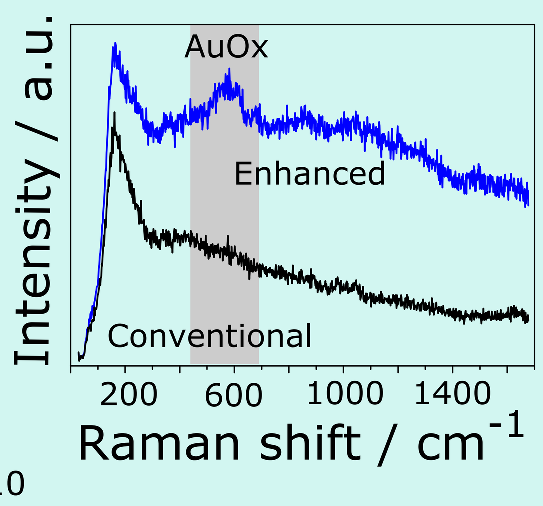
Au(111) in 0.1 M H_2SO_4



- Nanoscale topography: Monoatomic step edge

EC-Tip-enhanced Raman spectroscopy

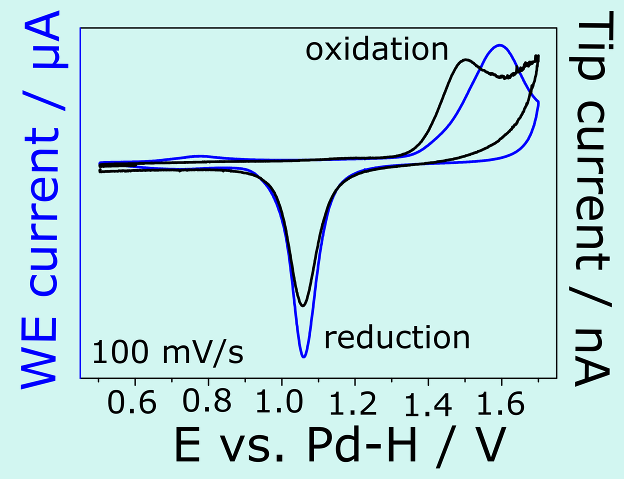




- Excitation of surface plasmons in nanometric tip creates localized nearfield at tip appex
- Raman enhancement of up to 10^{10}
- Chemical specificity: AuOx band at ~600 cm^{-1}

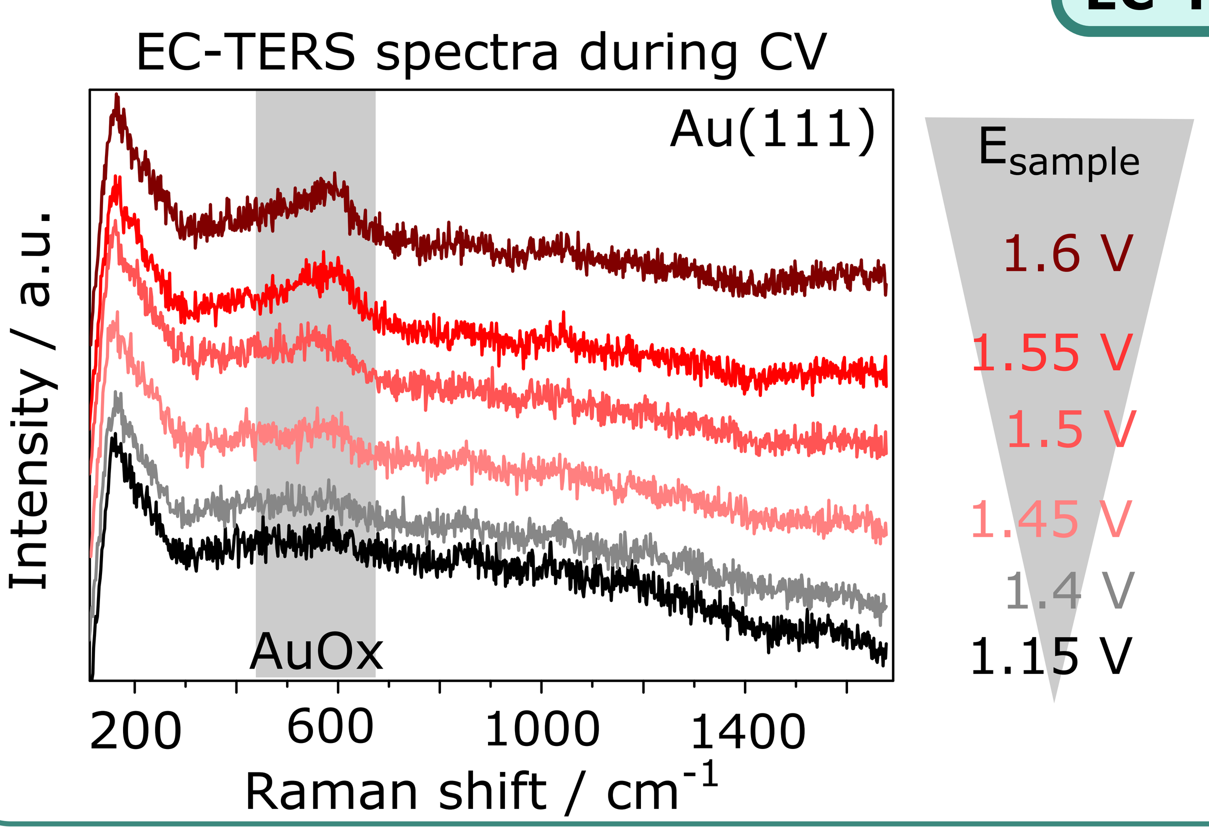
In-operando conditions

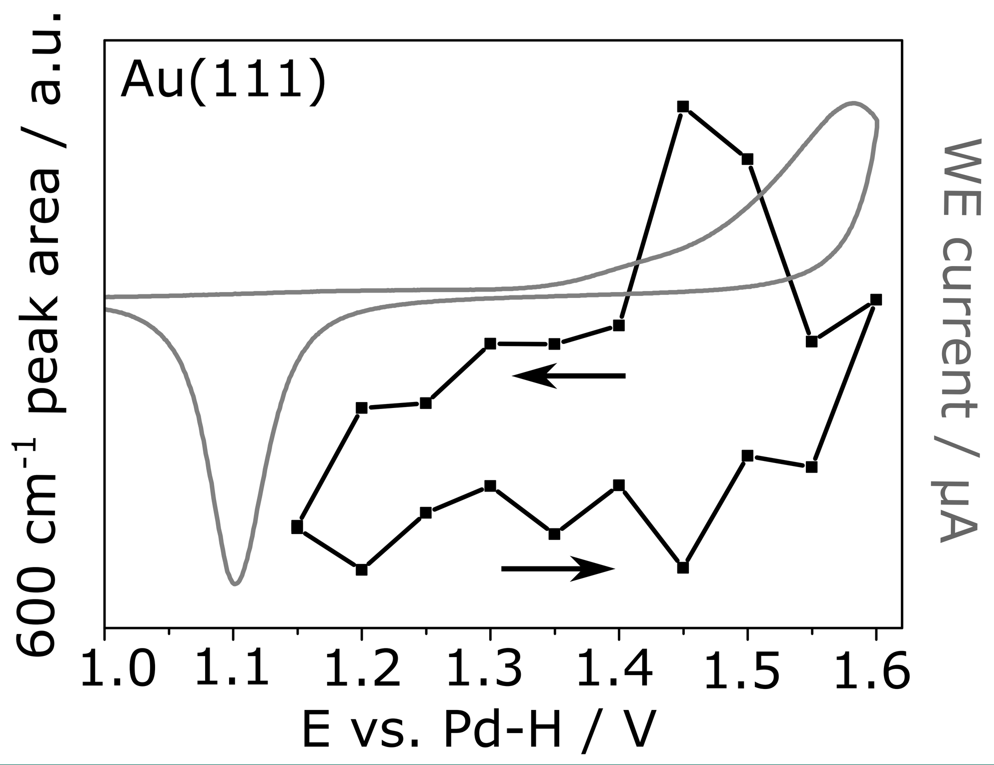
Tip vs. Au(111) CV



- Potential control (tip and WE)

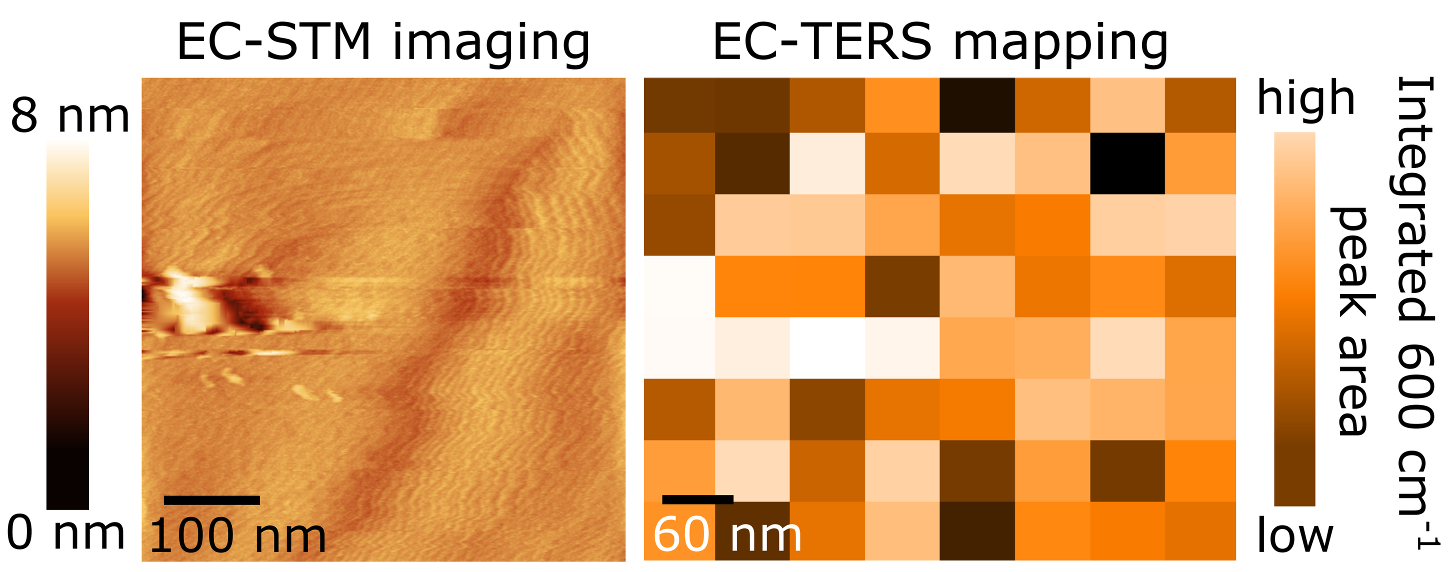
EC-TERS monitors in situ the oxidation of Au(111)





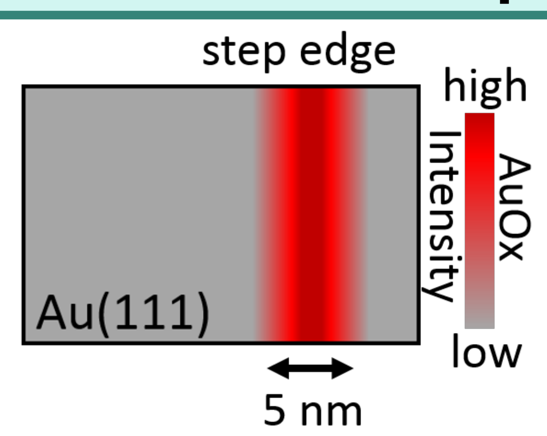
- Potential-dependent detection of Au(111) oxide in close proximity to gold STM-tip
- ~10-12 nm Raman resolution
- Correlation of the gold oxide peak area at ~600 cm^{-1} recorded by EC-TERS with CV
- EC-TERS signal of nanoscale AuOx reveals difference to macroscopic CV response

EC-TERS mapping of oxidized gold defects



- 500 nm x 500 nm EC-STM image recorded at 1.3 V
- Simultaneously acquired EC-TERS map (8 x 8 pixels, 5 s acquisition time per pixel)
- Oxidize Au(111) defects only at 1.45 V, while tip is retracted (12 µm)
- Approach tip to surface and image/map at 1.3 V
- Integrated 600 cm^{-1} AuOx region reveals highest intensity at defect structure
- EC-TERS mapping is indeed possible!

Outlook: Oxidized step edges



- Selective oxidation of **step edge defects**, while the (111) terraces will be kept oxide free
- Mapping **site-specific reactivity** is a major step towards the identification of electrocatalytically active surface sites

[1] Martin Sabanes N., Angew. Chem., 2017, 56, 9796-9801 [2] Pfisterer J.H.K., Curr. Opin. Electrochem., 2018

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