

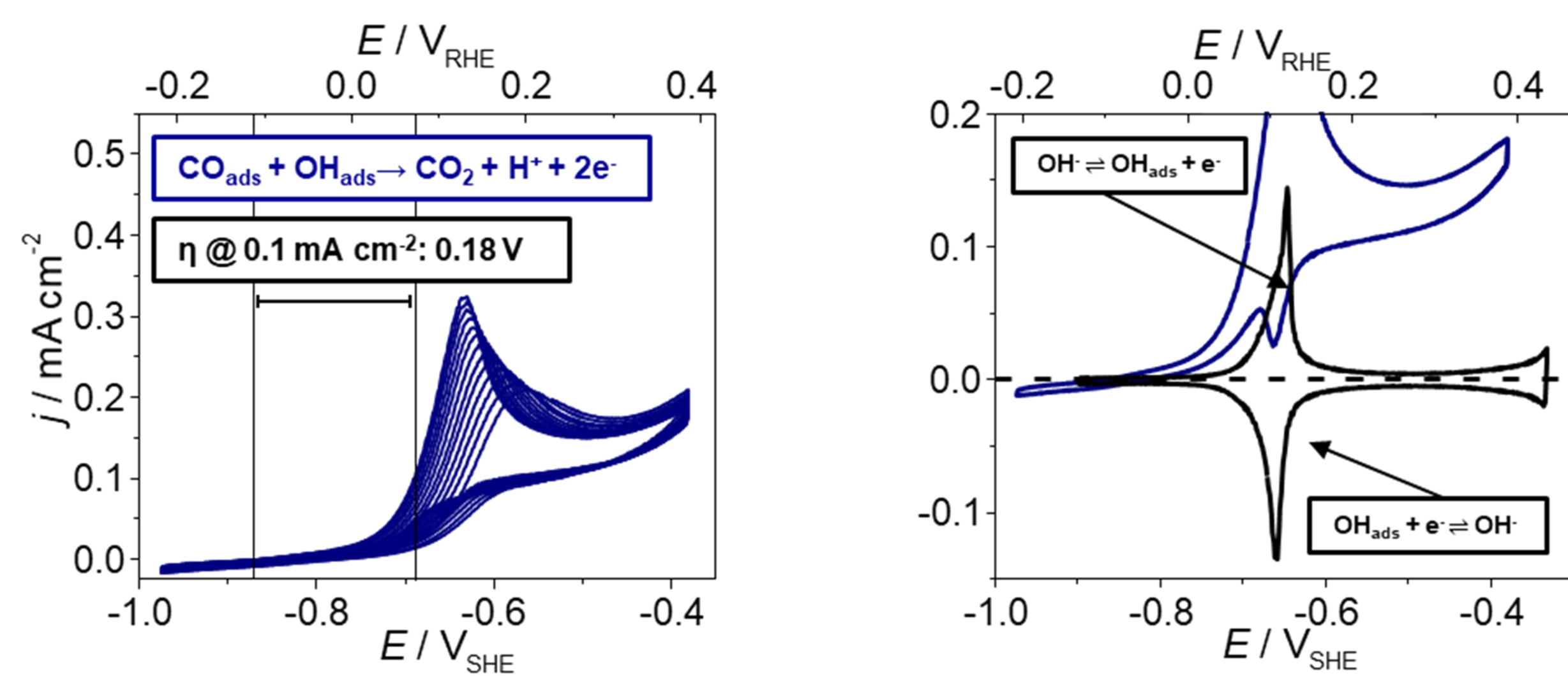
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In recent years, fundamental understanding of the electrochemical interface has strongly advanced, which can help to significantly promote the development of alternative systems for clean energy production and storage. Understanding the electrochemical Cu/liquid interface is of special interest, since Cu has been shown to be the sole transition metal which is able to reduce CO₂ and CO to valuable hydrocarbons and alcohols with reasonable Faradaic efficiencies.¹ More recently, we showed for the first time that CO is also oxidized to CO₂ at low overpotentials on Cu(111) electrodes, which self-activate through the quasi-reversible formation of high-energy undercoordinated Cu nanostructures in alkaline electrolyte.² This means that Cu is particularly intriguing in terms of its ability to act as a bidirectional electrocatalyst. **The aim of this project is to provide a systematic model study, i.e. investigation of morphological changes of the electrode surface under realistic reaction conditions and product selectivity, of different Cu single crystal systems for a detailed mechanistic understanding of CO(2) electro-activation by combining state-of-the-art *in situ* electrochemical analysis methods, such as electrochemical scanning tunneling microscopy (EC-STM), infrared spectroscopy (IR) and differential electrochemical mass spectrometry (DEMS).**

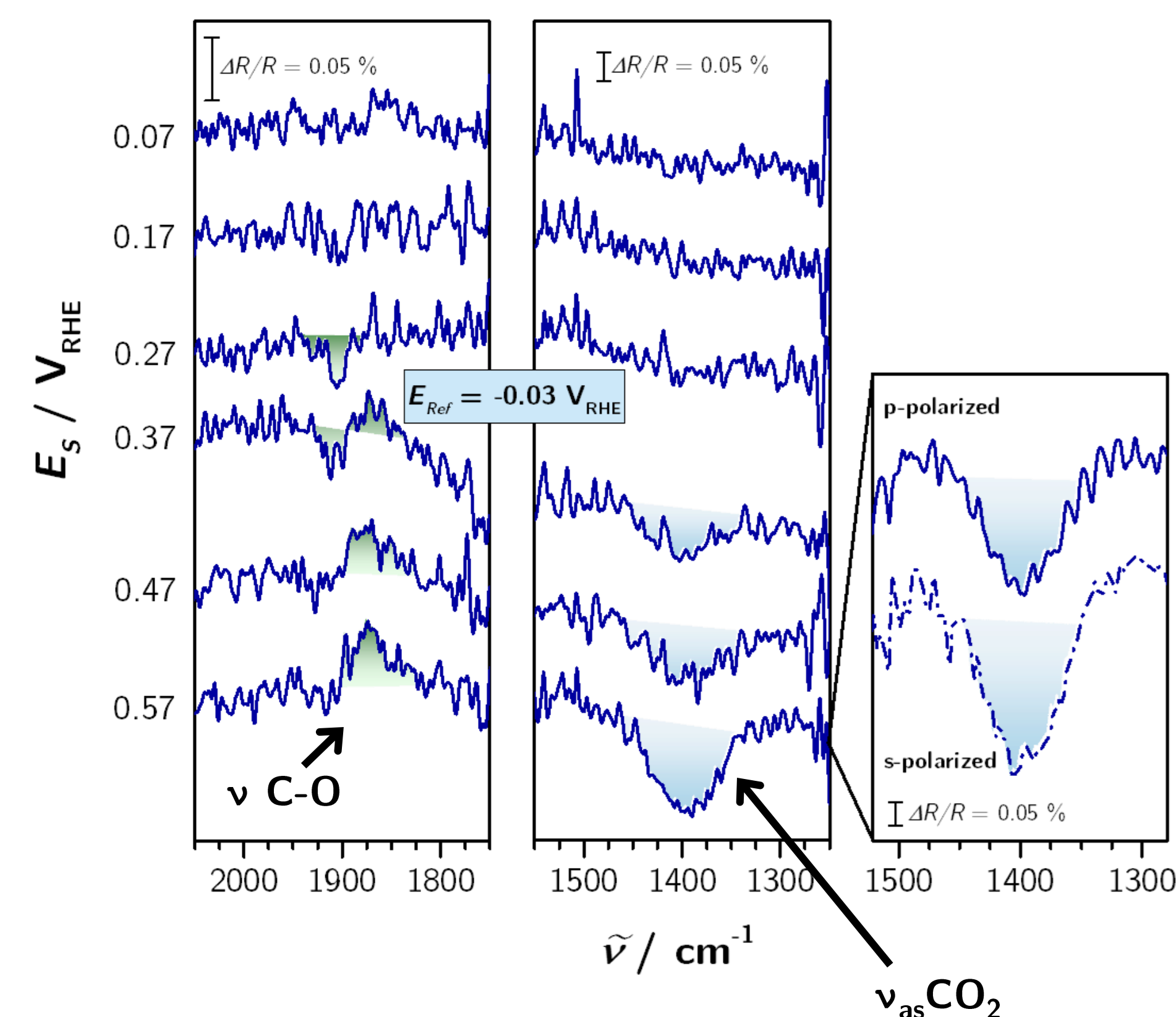
CO oxidation on Cu(111) in 0.1 M NaOH²

Electrocatalytic activity

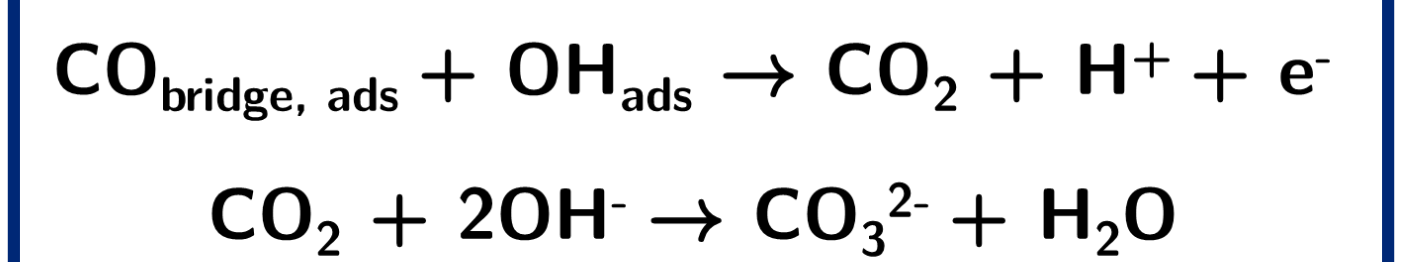


- CO bulk oxidation on Cu(111) at low overpotentials.
- Onset coincides with OH adsorption in Ar-sat. NaOH.

In-situ infrared spectroscopy



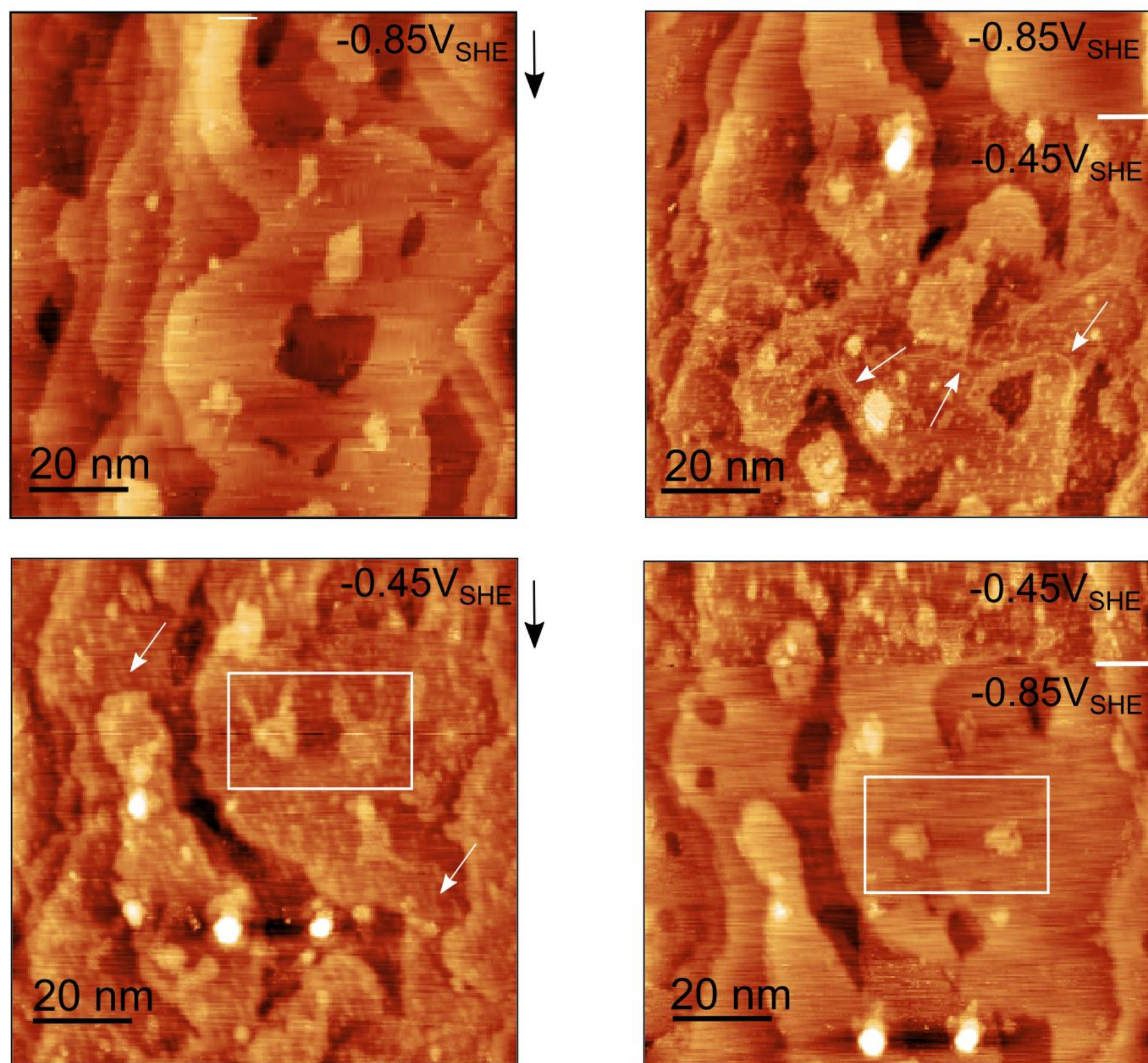
- IR confirms weak adsorption of CO and the formation of carbonate upon CO oxidation.



Structure-activity relation:
In-situ electrochemical STM inside an Ar-filled glove box was performed.

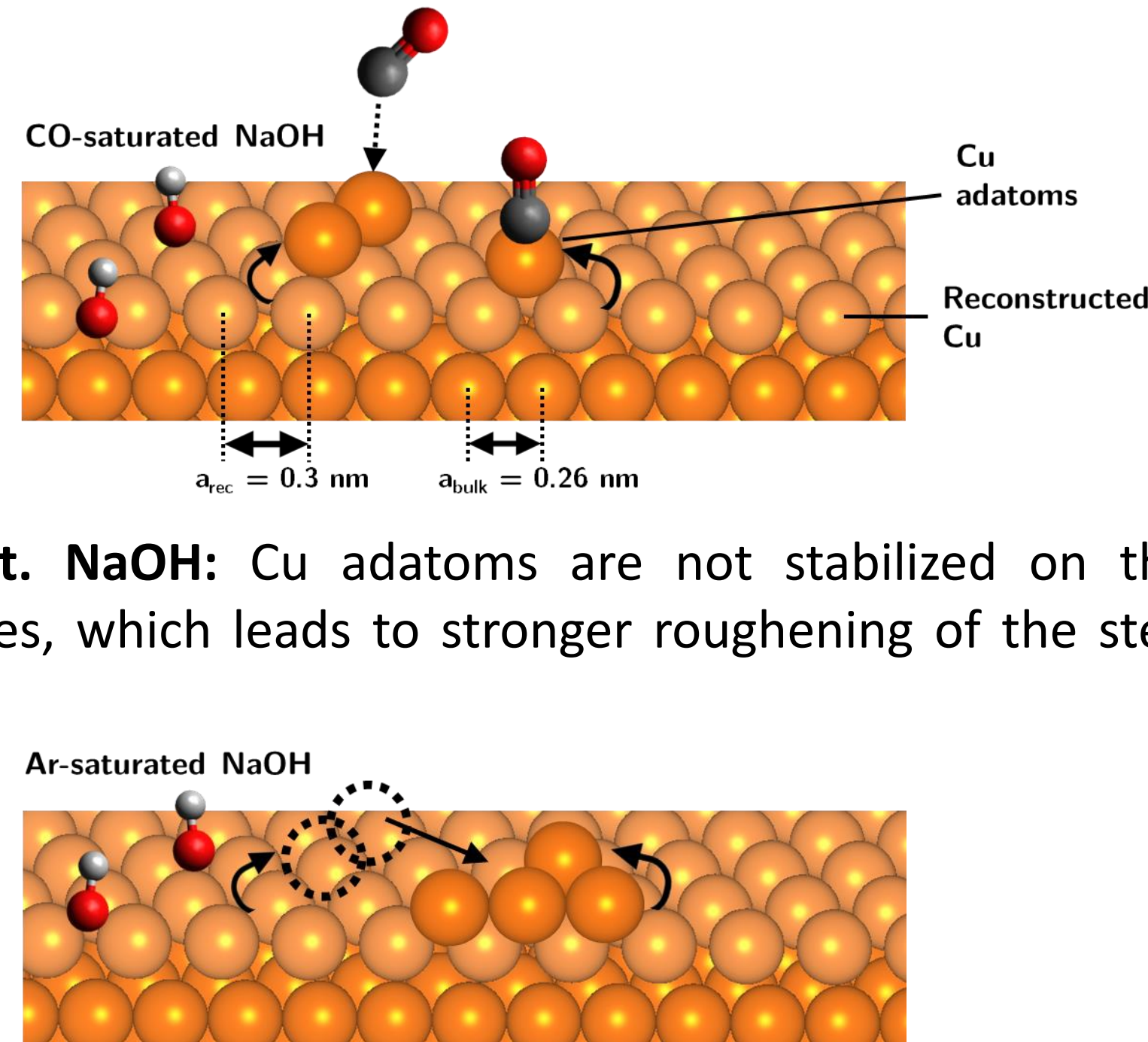
Electrochemical STM during CO oxidation²

CO-saturated NaOH



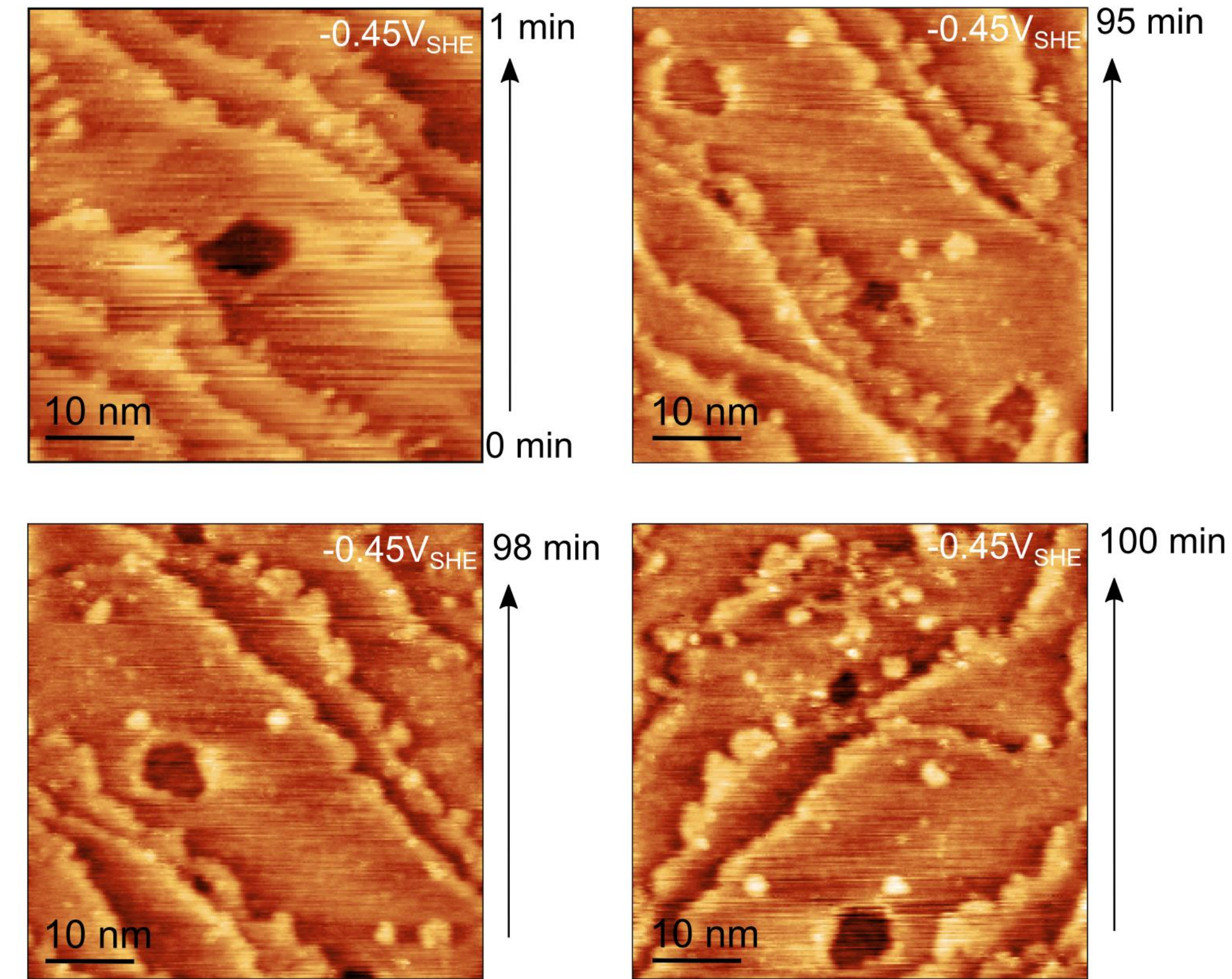
Reconstruction of Cu(111)

- CO-sat. NaOH: Self-activation process of Cu(111) by forming 1D threadlike and subsequently 2D Cu adatom nanostructures, stabilized by adsorbed CO.



- Ar-sat. NaOH: Cu adatoms are not stabilized on the terraces, which leads to stronger roughening of the step edges.

Ar-saturated NaOH

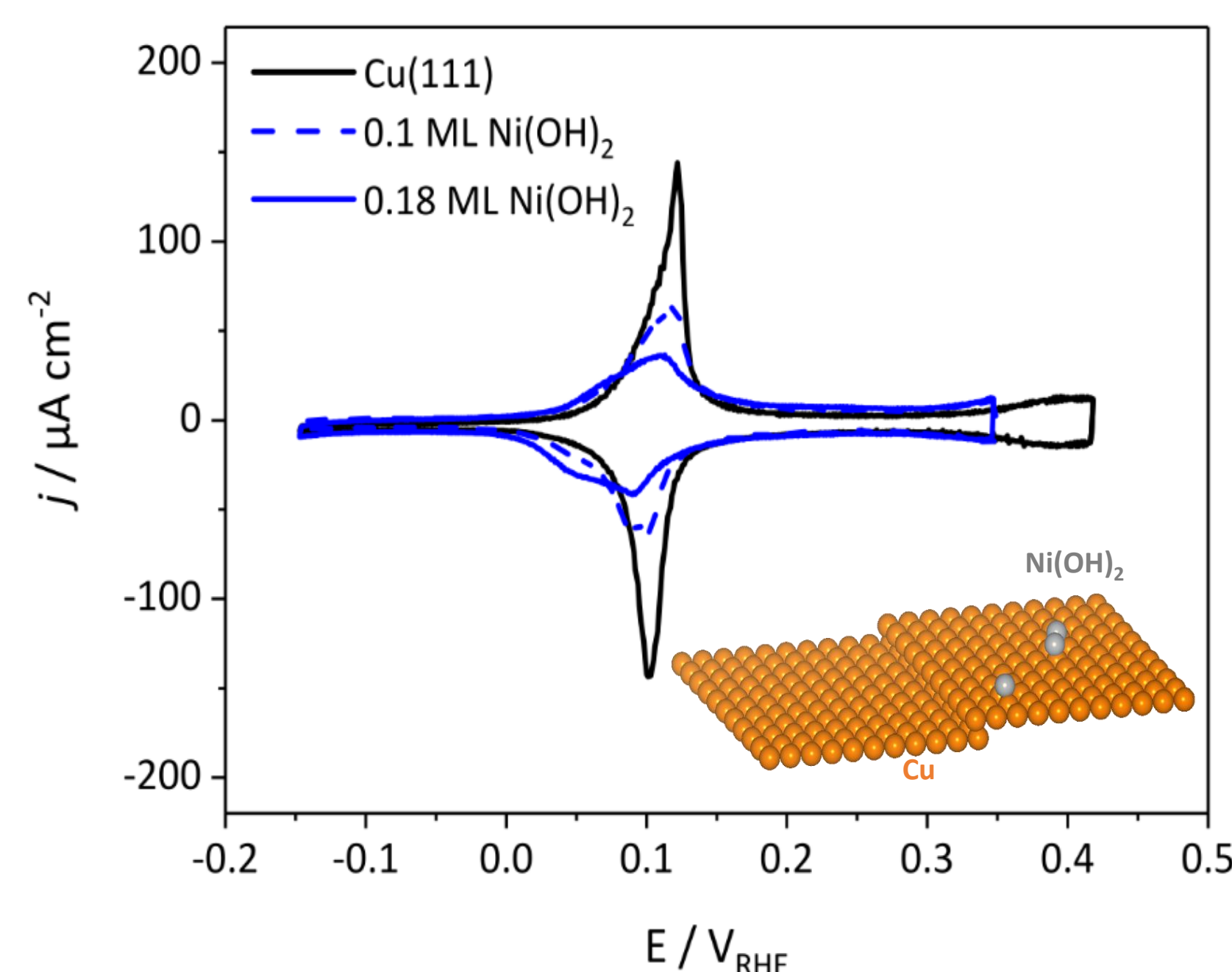


Cu(111) is monitored during CO oxidation reaction by *in situ* electrochemical scanning tunneling microscopy (EC-STM), which reveals **strong surface morphological changes** as well as a **high degree of mass transport** during the reaction. This relates the observed high activity to the **continuous formation of new low-coordinated active Cu sites** in the presence of CO and OH.²

Ni(OH)₂ modified Cu(111) electrocatalysts

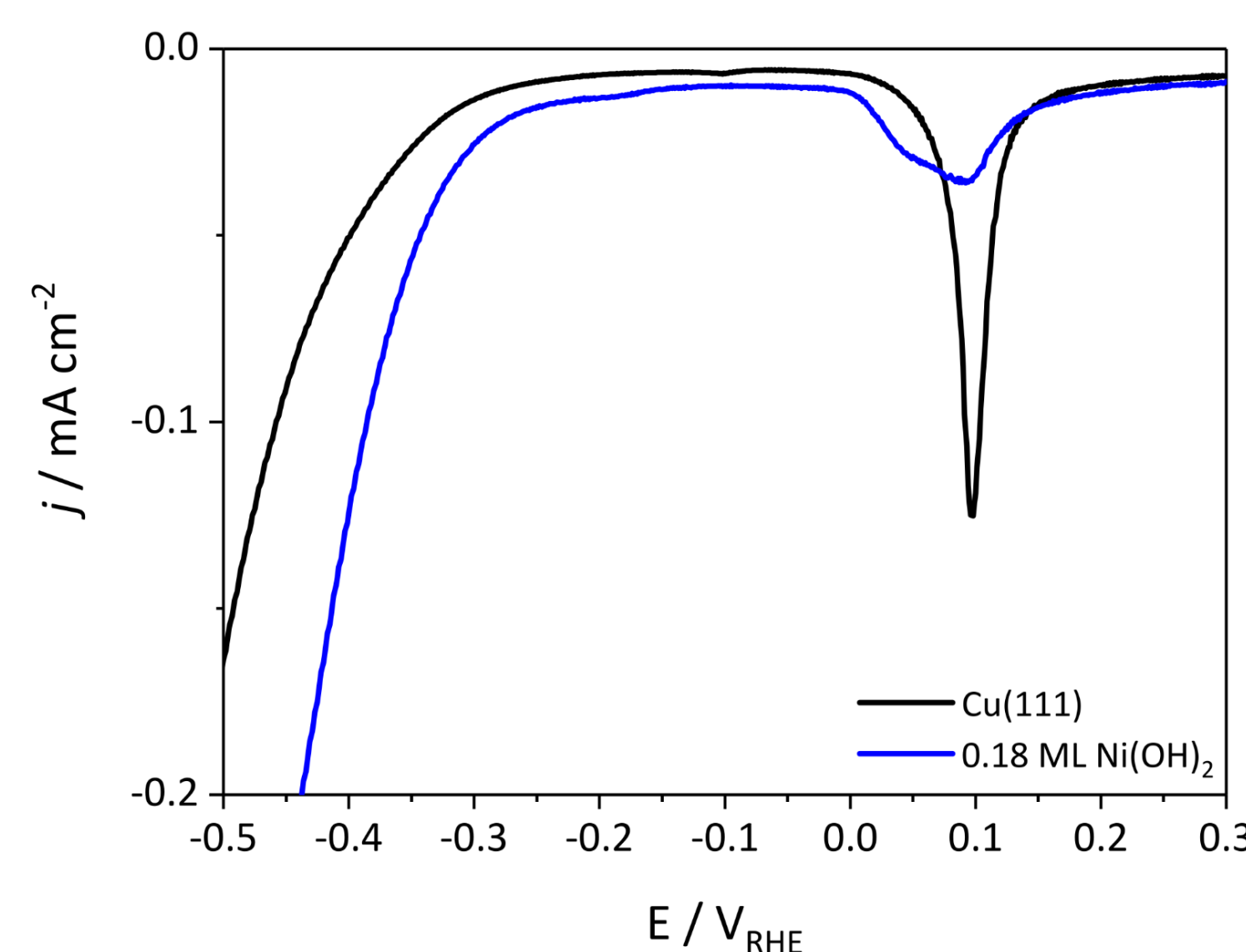
Adatom-modification of Cu(111) electrodes in 0.1 M NaOH

- Ni(OH)₂ is deposited on Cu(111) electrodes by irreversible adsorption³.

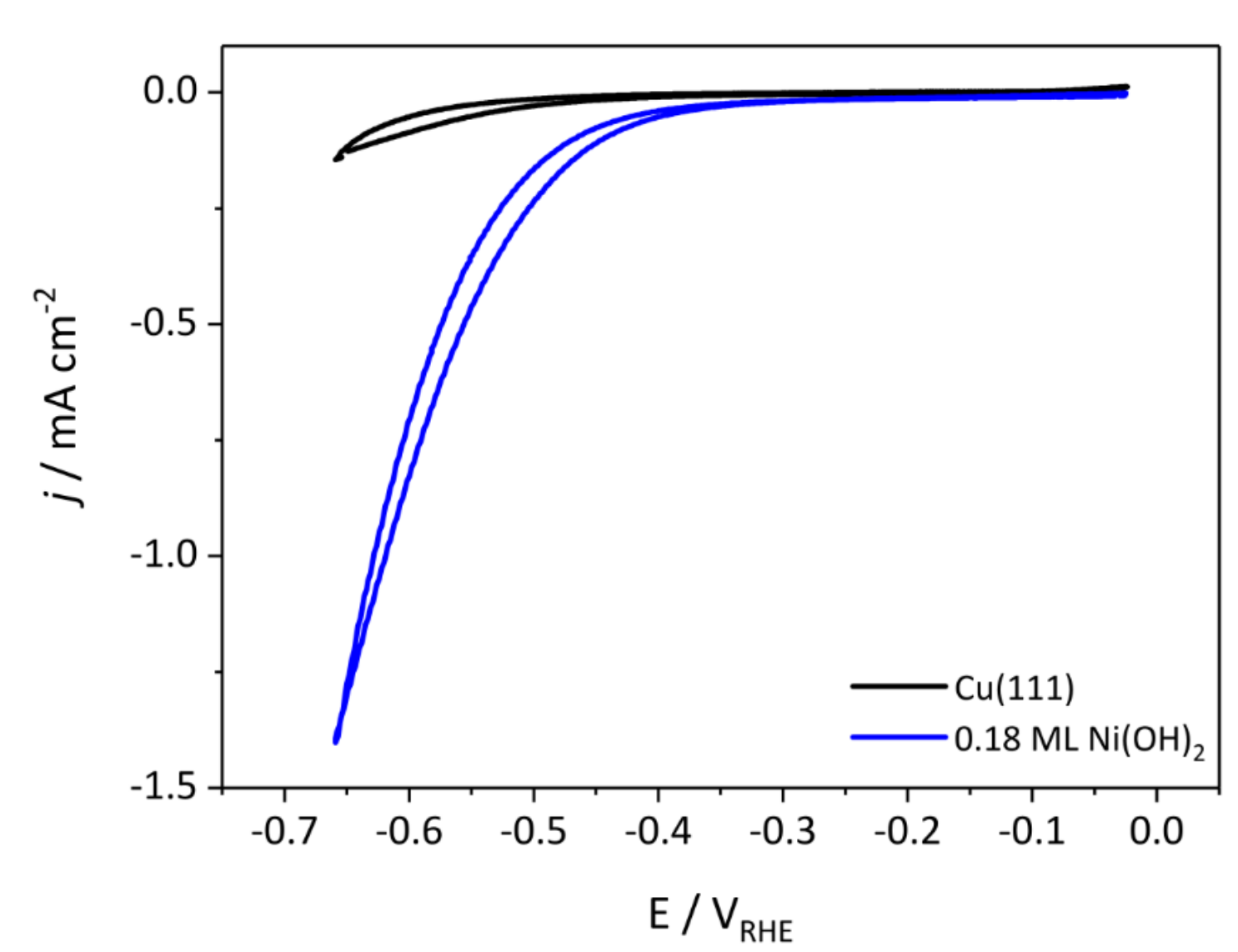


Electrocatalytic activity

Hydrogen evolution reaction



CO reduction reaction



- Linear sweep experiments indicate that Ni(OH)₂ deposition on Cu(111) enhances both reduction reactions, i.e. hydrogen evolution and CO reduction, presumably due to a weakening of the electric field^{3,4}

One key tactic to alter or enhance the catalytic performance of Cu electrodes is the preparation of **bimetallic systems**.¹ Here, irreversible adsorption of Ni²⁺ ions was applied to Cu(111) to prepare **Ni(OH)₂ modified Cu(111) electrodes** with a tunable coverage. Preliminary electrochemical measurements show the **enhancement of reduction reactions**, i.e. hydrogen evolution as well as **CO reduction** of these bimetallic model electrocatalysts.

References

[1] I. Chorkendorff, et al., Chem. Rev. **2019**, 119, 7610–7672.

[2] A. Auer, M. Andersen, E.-M. Wernig, N. G. Hörmann, N. Buller, K. Reuter, J. Kunze-Liebhäuser, Nat. Catal. **2020**, doi.org/10.1038/s41929-020-00505-w.

[3] I. Ledezma-Yanez, et al., Nature Energy **2017**, 2, 17013.

[4] F. J. Sarabia, P. Sebastián-Pascual, M.T.M. Koper, V. Climent, J. Feliu, ACS Appl. Mater. Interfaces **2019**, 11, 613-623.