

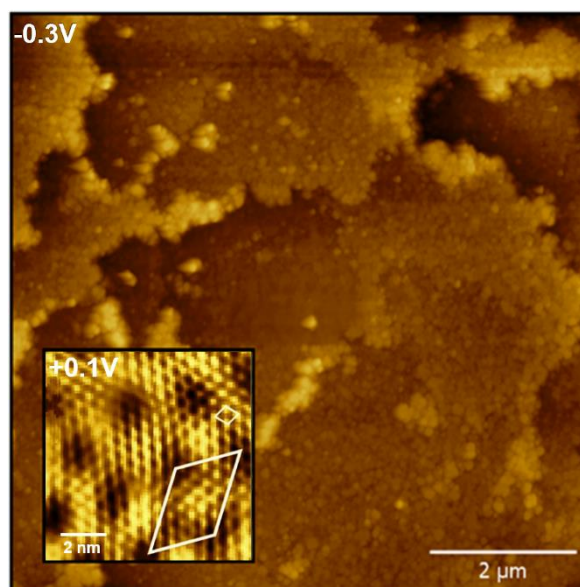
Nanoelectrochemistry: mechanisms of sulphate adsorption on vicinal Cu (111) electrode surfaces studied by EC-STM and EC-AFM

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Research in electrochemical processes is usually based on (sub-)millimetric (mesoscopic) description by looking at average charge fluxes and reaction rates. Nonetheless the advent of methods for preparing, studying and interacting with matter of dimensions close to single molecules brings new fundamental insights and experimental potentialities. In addition, there is much to be learned from probing the behavior of single redox molecules, individual catalytic sites, and single-electron-transfer events. Despite these facts, systematic studies on the so-called nanoelectrochemistry (i.e., the influence and even the processes related to nanometric structures) are still missing.

In this talk, we propose an original approach where molecules adsorption (namely, sulphates) on the electrode surface is influenced by the presence of steps, as naturally observed in vicinal copper (Cu) surfaces. The electrochemical scanning tunneling microscopy (EC-STM) locally detects the formation of a well-ordered sulphate superstructure (Moiré pattern) in case that the copper terrace size is larger with respect to the Moiré lattice parameter. If the potential applied to the Cu electrode is close to- or within- the anodic corrosion regime, i.e., when copper undergoes a dissolution process that releases copper ions (Cu^{2+}) into solution, EC-STM acquisition becomes difficult, due to the significant detriment of the electrode surface flatness. In the corrosion regime, we successfully exploit the EC-atomic force microscopy (EC-AFM) to prolong the surface characterization towards relatively high anodic potentials. The combined experimental investigation, which is able to follow the electrode morphology on different length scales, highlights the effect of the redox processes and the role of steps during the sulphate molecules adsorption and desorption processes at the Cu surface.



Picture: (8×8) μm^2 EC-AFM image of the Cu (111) surface after the dissolution and then the Cu re-deposition process (at 0.15V).

Blow-up: EC-STM image of the Moiré pattern (larger unit cell) and of the sulphate superstructure (smaller unit cell).