Electrochemical AFM

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This report demonstrates the capability of the FlexAFM in studies of charged solid-liquid interfaces. In order to carry out electrochemical (in-situ) AFM experiments, a conductive sample was mounted in an electrochemical liquid cell and connected to a lab-build bipotentiostat. We employed Clavilier-type Au(111) single crystal bead crystal electrodes with facets of micrometer-wide terraces. As examples, we studied the lifting of the Au(111)-(pxv3) reconstruction, surface oxidation as well as the growth and dissolution of copper clusters in sulfuric acid solution.

Experimental Details: The AFM imaging was carried in dynamic mode employing NCHAuD cantilevers (Nanosensors) and an Au(111) bead single crystal sample immersed in the liquid cell in 0.1 M H_2SO_4 solution. 1 mM $CuSO_4$ was added for copper deposition experiments. The bead crystal sample was connected to the potentiostat as a working electrode, while Pt wires immersed into liquid cell served as a counter electrode and as a reference electrode in Cu-free solution. A Cu wire was used as a reference electrode in the Cu-containing solution.

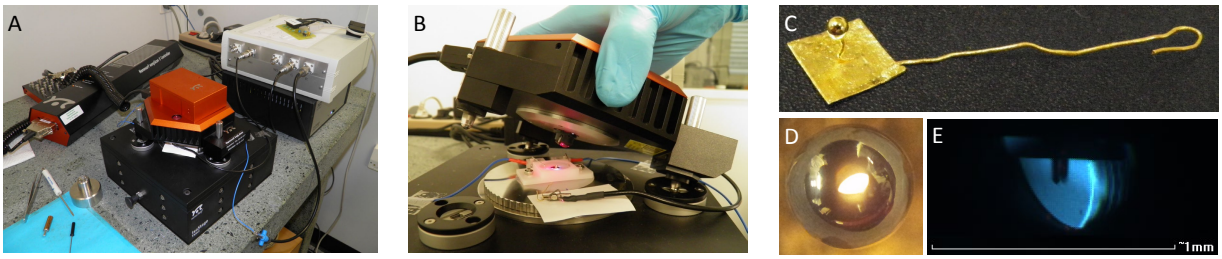

Figure 1: **Experimental Setup.** (A) Overview showing the Nanosurf EasyScan 2 controller, the FlexAFM scan head as positioned on an isoStage table and the lab-build potentiostat. (B) Electrochemical liquid cell mounted below the FlexAFM scan head. (C) AFM sample : A bead single crystal attached to supporting gold plate. (D) Facets of the bead crystal as observed with an optical microscope. (E) AFM cantilever aligned on the upper Au(111) facet of the bead crystal as seen through the camera integrated into the FlexAFM scan head.

Au(111) in sulfuric acid solution: The EC-AFM experiment started with a freshly annealed Au(111)-(pxv3) surface under potential control at E = –0.6 V vs. Pt. The reconstructed surface as formed during flame annealing is preserved at this potential, and large, atomically smooth terraces were observed (Fig. 2B). Upon increasing the potential to 0 V, the reconstruction was lifted, and a number of small gold clusters and two big clusters are formed on the surface (Fig. 2C). Increasing the potential to E > 0.6 V results in the formation of a rough surface oxide, which was reduced upon returning the potential to E < 0.2 V (Fig. 2D).

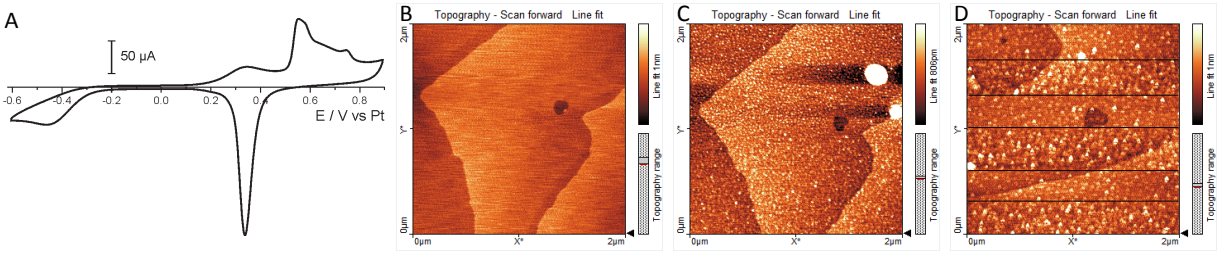

Figure 2: **Au(111) in 0.1 M H_2SO_4.** (A) Cyclic voltammogram of the bead crystal as attached to the gold sheet in 0.1 M H_2SO_4. AFM images: (B) atomically-flat terraces, E = –0.6 V; (C) same area after lifting of the reconstruction, E = 0 V; (D) roughening and smoothing of the gold surface upon several subsequent oxidation and reduction cycles.

3D copper deposition on Au(111): The EC-AFM experiment in Cu-containing solution was carried out on Au(111) in 0.1 M H_2SO_4 containing 0.1 mM Cu^{2+} using a Cu reference electrode. In this potential scale E = 0 V corresponds to the equilibrium between metallic copper and dissolved Cu^{2+} ions. At negative substrate potentials, overpotential (3D) Cu-deposition takes place. The nucleation of the new phase and its growth are strongly affected by the substrate potential. The experiment illustrated in Fig. 3 shows the formation of a single nucleus on an atomically flat Au(111) surface after stepping the potential from 0 to –50 mV, and its subsequent growth at –10 mV after a nucleation time of 0.2 s. The growth of the Cu cluster was followed in real time. Some snapshots are shown in Fig.3. Finally, the potential was stepped to 15 mV, which leads to a quick dissolution of the cluster.

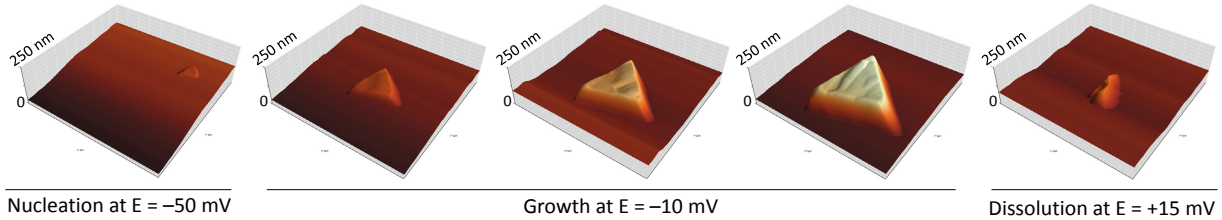

Figure 3: 3D deposition and dissolution of copper on Au(111). 3D AFM images (time series) showing the growth and dissolution of a single Cu cluster. All images have a lateral size of 2 µm × 2 µm and a normalized vertical scale of 250 nm.

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