The specific control and local tailoring of the morphological and electronic properties of electrode surfaces at the nanoscale level provides access to tune reaction sites and pathways.

We have performed model studies with low index \((\text{Au}(111), \text{Au}(100))\) and stepped gold single crystals to selectively create nanostructures by in situ surface oxidation and reduction. The pattern formation was controlled by the applied field, the electrode geometry and the composition of the electrolyte. The mechanisms of these processes were monitored by electrochemical transient techniques in combination with in situ STM, infrared spectroscopy and measurements of the surface resistance. Selective oxidation starts at sufficiently positive potentials at step edges, and subsequently the reaction front grows onto terraces. The onset of terrace oxidation is critically determined by the interplay of OH - species with the ordered sulfate adlayers on both, \text{Au}(111) and \text{Au}(100) electrodes. The transitions involve a disordered potential region on \text{Au}(111), and, on \text{Au}(100), a rather continuous transformation into the oxide phase. The surface resistance increases with the onset of terrace oxidation. In situ current-distance tunneling spectroscopy reveals distinct differences in barrier height profiles within the various potential regions.

Reversing the potential and completion of the surface oxide reduction allows to create selectively nanoscale patterns employing the tunneling tip as a “tool”. The application of a variable potential/time regime upon multiple oxidation/reduction cycles enables to generate various island and monatomic vacancy arrangements. The geometry, size distribution and stability of these patterns reflects clearly the surface crystallographic properties of the used gold single crystal electrodes and the regime of potential perturbation. The growth and relaxation of these nanostructures was monitored by in situ STM and will be dicussed in detail. Mechanisms, such as Ostwald ripening, coarsening and cascade growth of hole pattern will be illustrated. First applications of selected pattern as active reaction sites and template structures to functionalize electrode surfaces will be also presented.

LITERATURE