

## Electrochemical Stability of Octanethiol and Octanedithiol on Au (111) Surfaces

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During the last decades, the adsorption of alkanethiols on metal surfaces (Au, Ag) has provoked a huge interest since the resulting structures can be strategically used as templates for building functional molecular systems ranging from mimetic biological membranes, chemical sensors, to optic and electronic devices. They represent versatile materials for tailoring chemical properties of the surfaces by the incorporation of terminal groups which allows the control of the chemical and physical properties of the interfaces. That results very significant for electrochemists when making use of potential-controlled processes. Therefore a thorough study of the electrochemical stability of such organic layers on the metal surfaces is fundamentally required.

Some research groups have devoted their investigations to the electrochemical stability of Self-Assembled Monolayers (SAMs) based on thiols by using different techniques [1-6]. Nevertheless, there are still remaining unsettled issues and it is our aim to contribute with additional information. In such sense, we have followed mainly the reductive desorption 1-octanethiol and 1,8-octanedithiol layers on Au(111) by Cyclic Voltammetry (CV), Scanning Tunneling Microscopy (STM) and Electrochemical Impedance Spectroscopy (EIS) in electrolytes of different pHs.

With our CV measurements we characterized the package and density of thiolates on the surface in the potential region in which no faradaic processes occur. After that, the desorption of the thiols but also the oxidative readsorption processes were monitored. The area of the reduction peaks of the thiol and dithiol layers correspond to those when the SAMs are in the highest monolayer density. For the dithiols, such results are basically in agreement with those found for other dithiols (i.e. 1,6-hexanedithiol) [7,8]. In the oxidative thiol adsorption process, the area and the shape of the peaks depend on the pH and the nature of the thiol in correspondence with their different solubilities in the electrolyte.

EIS provided complementary information since it revealed more precisely the capacitance behavior of such system as the potential or the pH were changed. The double layer capacitance values for the freshly prepared SAMs were very low according to the formation of a quite close-packed layer.

From the STM measurements in the double layer potential region, we found for octanethiol layers ordered high density structures typical for alkanethiols on Au(111). However, in the case of the dithiol layers a disordered structure was observed at the potentials at which no redox processes occur. However, when the electrode was subjected to reductive dithiol desorption an ordered structure developed, at potentials slightly more positive than the reductive desorption peak. During this

desorption process areas with a high adsorbate mobility were detected, starting from defects, such as steps, vacancy island rims and domain boundaries. These areas grew with the time and additional aggregates were formed on them. These aggregates exhibited different shapes, and in some cases the formation of tube-like features following the substrate symmetry directions could be observed. These structures seem to result from some kind of micellization process [7] which resembles the (half-)cylindrical hemimicelles found by assembling surfactants on metal surfaces. On the other hand, during and after the reductive thiol desorption, it was also observed that the step edges became very rough, indicating that the gold substrate is quite involved in the process. Moreover, very stable gold islands with monoatomic height were formed from material extracted mainly from the steps. These islands kept stable after subjecting the electrode to more positive potentials, that is, in the potential region in which the SAM had been stable. That implies that subjecting the thiol modified electrode to reductive desorption only once is enough to induce morphological changes of the gold substrate resulting in rougher surfaces. We attribute this effect to strong interactions between Au and adsorbed thiolate.

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