

**IN SITU STUDY OF THE ELECTRONIC PROPERTIES OF ALKANETHIOL SAMs ON AU(111) BY ELECTROCHEMICAL TUNNELING SPECTROSCOPY**

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The potential applications of Self- Assembled Monolayers (SAMs) for the development of molecular electronic devices have increased the interest in the study of electron transport across alkanethiol molecules in electrical contact with metallic or semiconducting solids. Several techniques have been used to study these molecular junctions, including conductive AFM, STS and break junction measurements [1, 2]. Results obtained from different groups are quite dissimilar, probably because of the very different experimental setups, especially in what regards the electrical contacts.

However, while most of the studies have been performed in air (under different moisture conditions) [3] or in vacuum [4], to our knowledge no experiments have been done in aqueous media, although many of the thiol SAMs applications involve such environments. Thus, studies of electron transport at a local level, or even at a single molecule level (like those attained with scanning probes) performed in electrolytes under electrochemical control would provide new insight into this subject.

Recently, after several experimental improvements, our group has successfully performed Electrochemical Tunneling Spectroscopy (ECTS) measurements of the iron passivation process [5]. The main requisites for reliable ECSTS measurements are (a) an accurate and independent control of both tip ( $U_t$ ) and sample ( $U_s$ ) potentials by use of a 4- electrode configuration commanded by a bipotentiostat, (b) the use of real reference electrodes (like a miniaturized SSC electrode) to control  $U_s$  and  $U_t$  along the experiment, and (c) suitable STM probes that provide a wide electrochemical energy range and a low current level during fast tip voltage scanning.

Here we report the ECTS first measurements of decanethiolate SAMs on Au(111) single crystals in alkaline solutions, a model system among alkanethiol SAMs. We have performed two types of measurements: (1) tunneling current ( $I$ ) vs. tip- substrate distance ( $Z$ ) curves and (2)  $I$  vs.  $U_t$  curves. Both types of spectra have been recorded for different  $U_s$  values ( $-1.2 \text{ V} \leq U_s \leq -0.1 \text{ V}$ ). The use of single crystals ensures that the tip will be placed on flat, defect-free regions when the feedback is disconnected to record the tunneling spectra.

In the case of  $I$  vs  $Z$  curves, the tip is initially placed inside the SAM and then, when the feedback is disconnected, the tip- sample distance is increased. From the  $\ln I$  vs  $Z$  plots, recorded for different  $U_s$  and  $U_t$  values, two linear regions of different slope can be clearly identified. The linear region with a higher slope would correspond to the thiol SAM and the other one to the solution [4, 6]. The point where the slope changes would thus correspond to the  $Z$  position at which the tip is in contact with the terminal groups of the thiol SAM. For  $Z$  values larger than that, the tip is completely outside the SAM. From the linear relationships the local electron barriers  $\Phi$  corresponding to each region have been calculated for different  $U_s$  and  $U_t$  values. The barrier height displays a strong dependence with the tip potential and can be reduced to a few hundred meV under suitable conditions. This suggests that electron transfer with low conductance organic molecules is possible by using the independent control of tip and sample potential provided by electrochemical STM.

On the other hand,  $I$  vs  $U_t$  spectra are linear in a wide potential range. From the experimental curves it can be seen that, as  $U_s$  is made more negative, there is a reversible change in the

slope of the  $I$  vs  $U_t$  curves (the conductance) at  $U_s \approx -0.6$  V that cannot be related to alkanethiol desorption (which occurs at  $U_s \leq -1$  V and can be detected from further changes in the ECTS curves and also by ECSTM).

Based on our experimental data we will present an electronic model of the alkanethiol layer and discuss possible conduction mechanisms.

**References:**

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