AN ATOMIC SCALE MODEL FOR S-CYSTEINE SELF-ORGANIZED ON Au(111)

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Abstract:

Biomolecules interaction on metal surfaces is of a great relevance due to the wide number of scientific and technological areas in which are involved. Among them, biosensors, biomaterials, biocatalysis and biocompatibility. Due to its simple structure, amino-acids can be used as a good model system to study biomolecule-surface interaction, which can indeed assist in the understanding of more complex systems. It has been found that a number of amino-acids self-organize to form well ordered-two-dimensional structures at metal surfaces [1]. The local adsorption geometry and the two-dimensional self-assembly of *S*-cysteine are of particular interest because it is the only amino-acid having a thiol side group. Previous studies on Cu(110) surface have shown the interaction of cysteine-metal through the COO^- and SH- group [2]. It is well-known the affinity of thiol groups for noble metals, therefore, cysteine can be used as a bonding group for self-assembled monolayers formation.

We present a characterization of cysteine adsorption on Au(111) at submonolayer coverage performed by a combination of experimental techniques: Scanning Tunnelling Microscopy-(STM), X-ray Photoemission Spectroscopy (XPS) and Ultraviolet Photoemission Spectroscopy (UPS) and theoretical *ab-initio* methods. XPS data show the adsorption of the zwitterionic form of S-cysteine molecule on Au(111) surface, meaning the desprotonation of the carboxylic group (COO^-) and the protonation of the amino group (NH_3^+). Furthermore, the interaction of the amino-acid on the surface goes through the COO^- and the thiol group (S-Au), which is the anchoring point of the molecule. The STM characterization performed under UHV conditions at room temperature reveals an structural evolution with time of the Cys/Au(111) system. Just after cysteine dosing at room temperature, the diffusion of molecules on the surface is very high. These diffusing molecules coexist with both, molecular islands lacking of internal order, which appear mainly anchored to the step edges, and with long ordered molecular rows. After a period of time, the long molecular rows evolve to develop ordered molecular networks of *S*-cysteine. By means of video-STM we show that after a period of time, the long molecular rows evolves to develop an ordered molecular network of *S*-cysteine. The row separation is 12 Å, and the molecules interact with each other along the $[\bar{1}\bar{1}0]$ surface direction, in good agreement with works from other authors [3]. An example of this growth is shown in figure 1. We show that the self-organized molecular island formation is related to the vanishing of the disordered areas due to surface diffusion. Thus, the interaction between molecules plays an important role, driving the formation of the self-organized structure.

This process can be fully explained by Density Functional Theory (DFT) calculations, which show that the on-top site is the most stable for the sulphur adsorption, being the carboxylate group also on-top. The diffusion barrier through the bridge site is small enough to lead diffusing molecules on the surface at room temperature. The optimized molecular geometry by

DFT reproduces the main features described by XPS and infrared spectroscopy, i.e, interaction to the surface through the COO^- and the thiol group. The cysteine molecule is deformed on the surface, adopting a flattened geometry and H-bridge bonding stabilizes the molecular rows imaged by STM.

Therefore, the above mentioned multi-technique approach let us to propose an atomic scale model for the interaction of the molecule with the surface (see figure 2), which accounts for the self-organization of the S-cysteine on Au(111).

References:

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Figures:

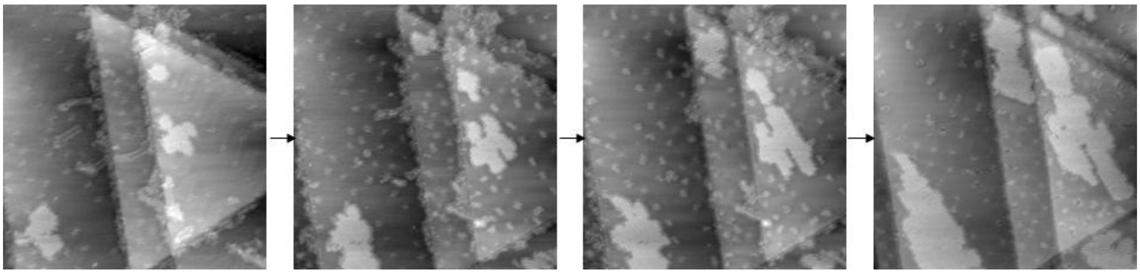

Figure 1: Subsequent serie of STM images of *S*-cysteine adsorbed on Au(111) surface, where the growth of the islands is observed.

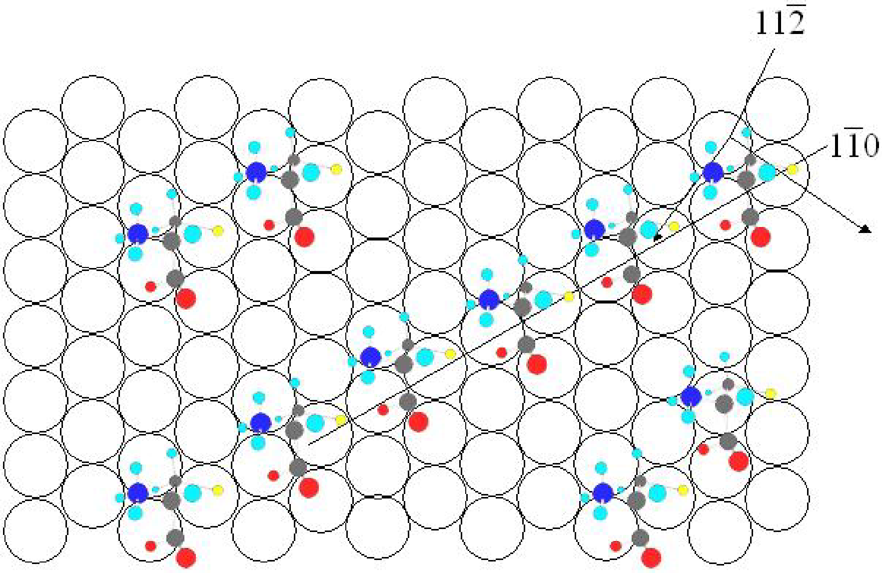

Figure 2: Scheme of a proposed model of self-organized molecular rows of S-cysteine adsorbed on Au(111) surface.