

AN ATOMIC SCALE MODEL FOR THE SELF-ORGANIZATION OF S-CYSTEINE ON AU(111) SURFACES.

Eva Mateo-Martí⁽¹⁾, Celia Rogero⁽¹⁾, Pedro De Andres⁽²⁾, Jose-Angel Martín-Gago^(1,2)

⁽¹⁾ *Centro de Astrobiología. INTA-CSIC. Torrejón de Ardoz, 28850 Madrid. Spain.*

⁽²⁾ *Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco 28049 Madrid, Spain.*

mateome@inta.es

Understanding the interaction of biomolecules on metal surfaces is an issue of relevance due to the wide number of scientific and technological areas in which they 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. In addition, it has been found that a number of amino-acids self-organise 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. 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. In addition, cysteine is located on the outer side of proteins, being a potential linker to anchor these proteins to inorganic or organic supports.

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 the Au(111) surface (desprotonation of the carboxylic group and protonation of the amino group). Furthermore, the interaction of the amino-acid with the surface goes through the COO⁻ and the thiol group (S-Au), which is the anchoring point of the molecule. This adsorption chemistry is similar to the depicted for the adsorption on Cu(110) surfaces by infrared spectroscopy [2]. The STM characterization performed under UHV conditions at room temperature reveals a 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 molecular islands lacking of internal order, which appear mainly anchored to the step edges, and with long ordered molecular rows. By means of video-STM we show that after a period of time, the long molecular rows evolve to develop an ordered molecular network of *S*-cysteine. The row separation is 12 Å, and the molecules interact with each other along the [112] 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 to 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, which accounts for the self-organization of the S-cysteine on Au(111).

References:

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Figures:

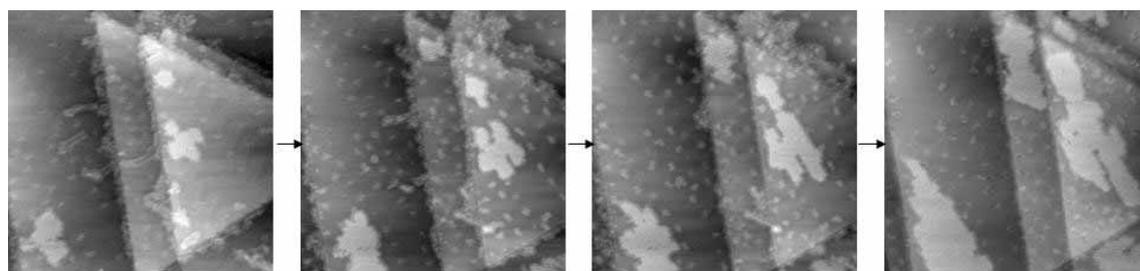


Figure 1: subsequent serie of STM images of S-cysteine adsorbed on Au(111) surface, where the growth of the islands is observed.