

## On-surface evolution process from cysteine to cysteinato adsorbed on Au(111)

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### Abstract

Self-assembly of organic molecules on surfaces has attracted important attention due to their promising applications in nanotechnology and biotechnology. From these organised molecular units arise the possibility of complex functions like molecular recognition, sensing, electronic properties, conductivity, catalysis, chirality, magnetism and chemical reactivity that are important in nanoscience.

Understanding the adsorption, bonding and interaction of the simplest constituents of proteins, amino acids, on surfaces is a necessary step towards the broad application of the interdisciplinary emerging field of nano-biotechnology. Self-assembled monolayers of different amino acids on well-controlled surfaces provide, for instance, convenient models to understand chiral selection mechanisms in the formation of higher ordered molecular structures, [1-2] strategies to functionalize large molecular based nanostructures for solid state advanced biosensors [3] or organic-inorganic platforms for new devices. The formation of highly ordered molecular self-assembled networks of amino acids on well-controlled metal surfaces has been previously studied. These molecular layers have been structurally analyzed and their chemical adsorption forms derived from these studies. [4] However, very little is known about the mechanisms underlining the formation of those layers.

Amino acids contain a simple structure and can be used as model to study biomolecule-surface interactions, which can assist in the understanding of more complex systems. Among other amino acids, cysteine ( $\text{HS-CH}_2\text{-CH(NH}_3\text{)-COOH}$ ) presents a relevant role in nature, the side chain in cysteine often participates in enzymatic reactions and the high reactivity of the cysteine thiol group makes possible many biological functions related to metal binding in proteins. The chemical affinity of the  $\text{-SH}$  group has been used in nanobiotechnology to provide a way to anchor molecules, and large biomolecules, as alkenothiols, proteins or long nucleic acids (DNA,PNA) [5] to inorganic metallic supports.

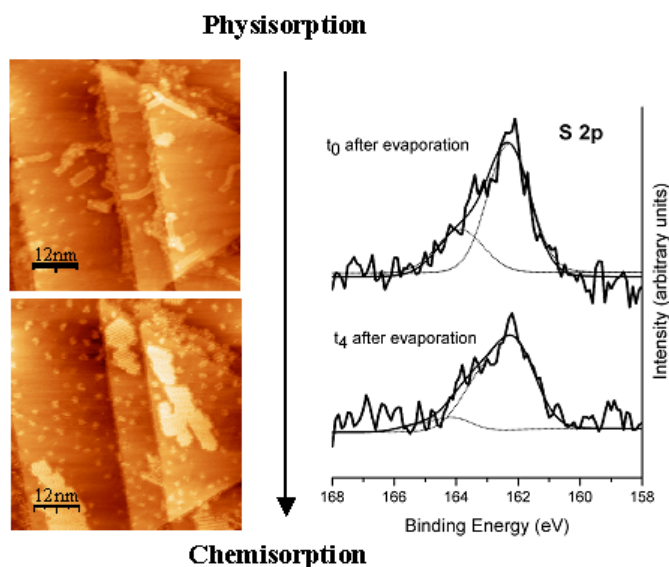
We have studied the first stages leading to the formation of self-assembled monolayers of S-cysteine molecules adsorbed on Au(111) surface. Density Functional Theory (DFT) calculations for the adsorption of individual cysteine molecules on Au(111) at room temperature show low energy barriers all over the 2D Au(111) unit cell. As a consequence, cysteine molecules diffuse freely on the Au(111) surface and can be regarded as a 2D molecular gas. The balance between molecule-molecule and molecule-substrate interactions induces molecular 'condensation' and 'evaporation' from the morphological surface structures (steps, reconstruction edges, etc.) as revealed by Scanning Tunneling Microscopy (STM) images. These processes lead progressively to the formation of a number of stable arrangements, not previously reported, like single-molecular rows, trimers and 2D islands. 'Condensation' of these structures is driven by aggregation of new molecules, stabilized by the formation of  $\text{NH}\cdots\text{O}$  hydrogen bonds, together with adsorption of the sulphur atom in the slightly more favourable site at the hollow-hcp site of the Au reconstruction, and one of the oxygen atoms of the carboxylate group sitting near a top site. [6] Furthermore, experimental STM images of the two dimensional molecular islands have been reproduced by DFT calculations, which allow us to present an atomic model for the self-assembled cysteine monolayer on the gold surfaces.

From the chemical point of view the interaction of S-cysteine on Au(111) surfaces, after being deposited under ultra high vacuum conditions, most of the molecules adsorb on the surface in the zwitterionic form, through the carboxylate group ( $\text{COO}^-$ ) and the sulphur atom ( $\text{S-Au}$ ). On the other hand, nearly 15% of the 1 Monolayer (ML) dosed molecules do not deprotonate directly on the surface, but they grow

forming a second layer before a first layer is completed. Cysteine molecules diffuse freely on the Au(111) surface after certain time, a transition process from these physisorbed cysteine molecules on the surface (SH do not get deprotonate) to chemisorbed (anchored through S-Au bond) occurs. Ordered molecular structures and spectral fingerprints provide evidence that this transition process has taken place (figure 1) [7]. Chemisorbed process is favoured at lower coverage. Finally, a short range of temperatures provokes dramatic changes, meaning the appearance of different molecular structures; therefore temperature performs as a crucial parameter promoting ordering structures. Then, both, molecular evolution with time and substrate temperature promotes molecular chemisorption and formation of long-range order molecular structures.

## References

- [1] Raval. R., Chem. Soc. Rev., **38** (2009) 707.
- [2] Kuhnle, A.; Linderoth, T.R.; Hammer, B.; Besenbacher, F. Nature, **415** (2002) 891.
- [3] Mateo-Marti, E.; Briones, C.; Pradier, C.M.; Martín-Gago, J.A., Biosensors and Bioelectronics, **22** (2007) 1926.
- [4] Mateo Marti, E.; Methivier, Ch .; Pradier, C.M., Langmuir, **20** (2004) 10223.
- [5] Mateo-Marti, E.; Briones, C.; Roman, E.; Briand, E.; Pradier, C.M.; Martín-Gago, J.A. Langmuir, **21** (2005) 9510.
- [6] Mateo Marti, E.; Rogero, C.; Gonzalez, C.; Sobrado, J.; De Andrés, P.; Martín-Gago, J.A., Langmuir, **26** (2010) 4113.
- [7] Mateo Marti, E.; Rogero, C.; Martín-Gago, J.A., submitted to Surface Science 2014.



**Figure 1.** It shows spectroscopic evidence from physisorption to chemisorption transition of cysteine molecules. STM images before and after the molecular diffusion process (chemical transition) and its corresponding XPS spectrums of S 2p to both stage during the time evolution progression, where  $t_0$  is 10 minutes after evaporation and  $t_4$  means 4 hours after evaporation.