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Adsorption Dynamics and Self-Assembled L-cysteine on Au(100)

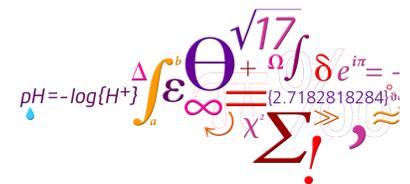


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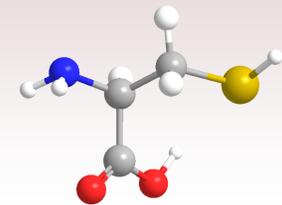
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As the only amino acid with a functional thiol group, L-cysteine offers a strong perspective both for binding to gold and other metals, and for gentle immobilization of biomolecules. Binding to single-crystal, atomically planar surfaces offers the additional perspective that bound L-cysteine can be structurally mapped at the single-molecule level. In this work, we have followed the adsorption of L-cysteine on single-crystal Au(100) by measuring the electrode potential dynamics during the adsorption process. In situ STM revealed the structure of the self-assembled ordered layers. The molecular assemblies were studied through simulated STM image contrast based on density functional theory (DFT) including solvation effects. The adsorption kinetics showed clearly a complex pattern with at least one intermediate state. The modelling disclosed details of the interaction of all functional groups with the Au(100)-substrate.

L-CYSTEINE

Figure 1. The molecular structure of the natural amino acid L-cysteine. C, N, O, S and H are represented in grey, blue, red, yellow and white, respectively. The molecule contains three functional groups; amine, carboxylic acid and thiol.



ELECTROCHEMISTRY

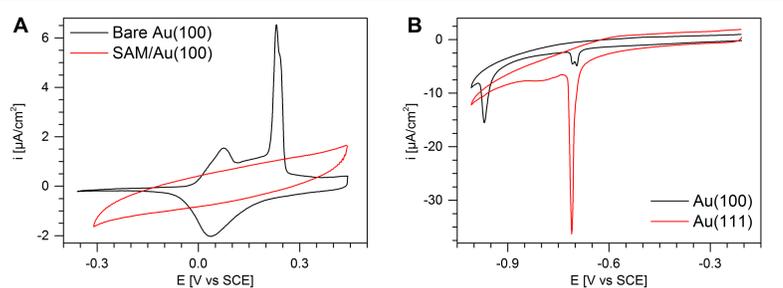
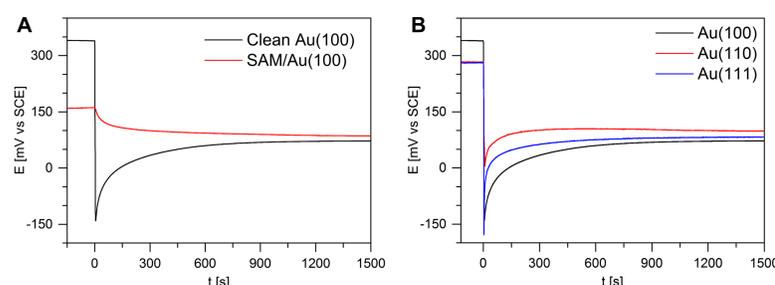


Figure 2. (A) Cyclic voltammograms of bare Au(100) (black) and L-cysteine covered Au(100) (red) in 25 mM KH_2PO_4 (pH 4.7). Scan rate 50 mV/s. (B) Reductive desorption of L-cysteine on Au(100) (black) and Au(111) (red) in 0.1 M NaOH. Scan rate 10 mV/s.

Cyclic voltammetry of the Au(100) electrode displays sharp anodic peaks characteristic for single-crystal Au(100). After adsorption of L-cysteine these features disappear and the capacitance increases due to the complete coverage of L-cysteine. At negative potentials the L-cysteine layer is desorbed in a reduction process. Au(111) shows one very sharp peak at -0.7 V vs SCE. A second and dominating peak appears on Au(100) at -0.95 V because of drastically different adsorption modes and structure of the SAMs on the different Au surfaces.

Figure 3. Chronopotentiometric data for L-cysteine adsorption. (A) bare Au(100) (black) and L-cysteine covered Au(100) (red). (B) single-crystal Au(100) (black), Au(110) (red) and Au(111) (blue). All measurements carried out in 25 mM KH_2PO_4 (pH 4.7). L-cysteine conc. 250 μM .



Addition of L-cysteine to the pure electrolyte solution with a bare Au(100) electrode instantly causes the potential to drop almost 0.5 V before starting to increase. The kinetics reveal a complex process with at least one intermediate state. This behaviour is not observed when the Au(100) surface is already saturated with L-cysteine, where only a modest decrease is detected. L-cysteine shows different adsorption behaviour on Au(100), Au(110) and Au(111) while no adsorption occurs on "inert" substrates such as basal-plane and edge-plane pyrolytic graphite and Au(100) with pre-formed L-cysteine SAM.

IN SITU STM STUDY

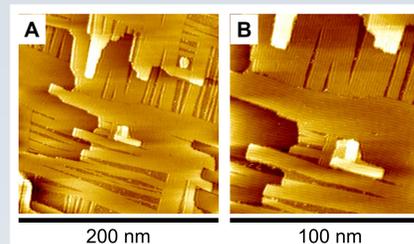


Figure 4. In situ STM images of Au(100) in 25 mM KH_2PO_4 (pH 4.7). The surface is reconstructed into (5x20).

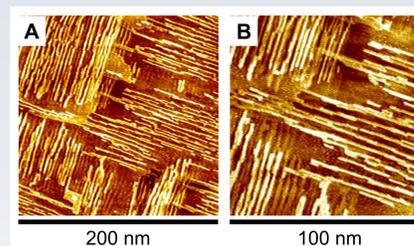


Figure 5. In situ STM images of L-cysteine monolayer on Au(100) in 25 mM KH_2PO_4 (pH 4.7), showing long-range ordered L-cysteine monolayers.

In situ scanning tunneling microscopy (STM) was used to study the structure of the self-assembled L-cysteine layer at the molecular level. High-resolution STM images revealed chain structure caused by the packing of individual L-cysteine molecules which reflects the symmetry of the underlying Au(100) substrate.

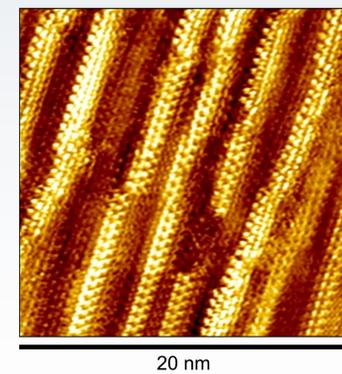


Figure 6. High resolution in situ STM images of L-cysteine monolayer on Au(100) in 25 mM KH_2PO_4 (pH 4.7).

MODELLING BASED ON DFT CALCULATIONS

The interactions between L-cysteine and the single-crystal Au(100) surface were investigated from a theoretical perspective using DFT. Periodical calculations (Figure 7) of different adsorption orientations of L-cysteine radicals showed that the orientation in C was most favourable though the energy difference between A, B and C were insignificant. It was noted that only the "vertical" orientation (A) provided sub-molecular resolution. Adsorbed L-cysteine in its zwitterionic form and "vertical" orientation is shown in Figure 8 was more stable than any radical forms considered due to lateral electrostatic interactions. The sub-molecular resolution was also found for the zwitterionic form. Dimers forming on the surface was also considered. Dimers of two L-cysteine radicals (Figure 9A) or two zwitterions (-9B) led to different STM model images the radical form being most asymmetrical. Asymmetry was also found for mixed dimers of protonated and deprotonated species (-9C and -D) where hydrogen bonds formed and the protonated molecule being "brightest" in the STM image. The orientation in Figure 9C was preferred. The formation of dimers blocks the surface, slows down the adsorption process and cause the appearance of "strips" and "zigzag" structures as seen with STM.

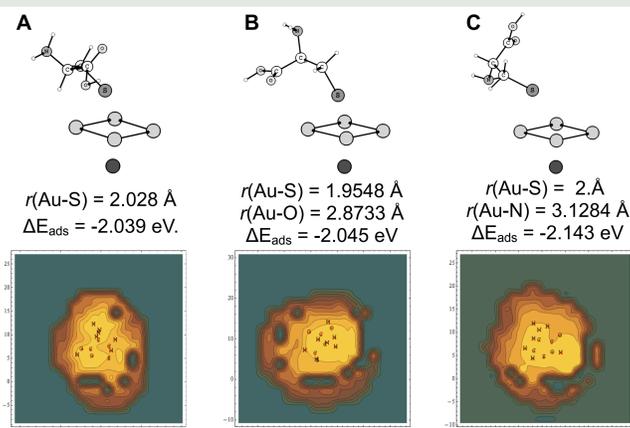


Figure 7. Optimized structure of a single L-cysteine radical adsorbed on Au(100) in (A) "vertical", (B) "COO" and (C) "NS" orientations from periodical DFT calculations. Corresponding model STM contrasts are shown below.

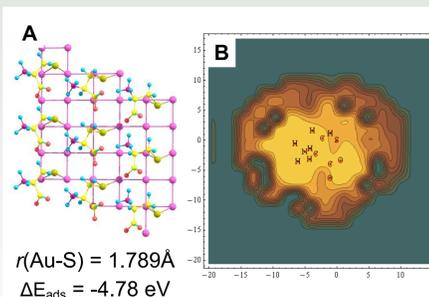


Figure 8. (A) Optimized structure of a row of L-cysteine zwitterions adsorbed on Au(100) in the "vertical" orientation (see Figure 7) from periodical DFT calculations. (B) The model STM contrast of a single zwitterion in this row.

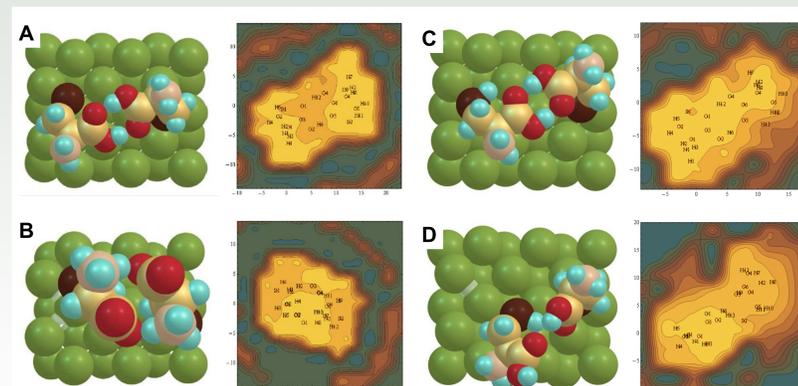


Figure 9. Optimized structure and STM model contrast of most stable dimers of (A) two L-cysteine radicals, (B) two zwitterions and (C-D) mixed (one radical and one zwitterion) in different orientations on Au(100) from cluster calculations.

DFT methods: Periodical and molecular DFT versions were employed. Details are reported in our previous work (Langmuir, 2009, 25, 2232-2240). In molecular calculations, a two-layer cluster Au_{30} (15+15) was used to describe the Au(100) surface. All calculations were performed using the Gaussian 09 and SIESTA program suites. The model STM contrasts were built in the framework of an original approach developed by us earlier (Langmuir, 2006, 22, 7556-7567). All scales are in Bohrs.

CONCLUSIONS

The kinetics of L-cysteine monolayer formation on Au(100) was studied by electrochemistry which suggests that adsorption proceeds by more than a single process. The reductive desorption of the monolayer showed two distinct adsorption modes. In situ STM demonstrated

a non-trivial structure of the monolayers (chain-like features). This was confirmed by DFT calculations provides some evidence of in favour of stable L-cysteine dimers adsorbed on the electrode surface.

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