Cysteine Self-Assembly on Au(100) Studied by In Situ STM, Voltammetry and DFT

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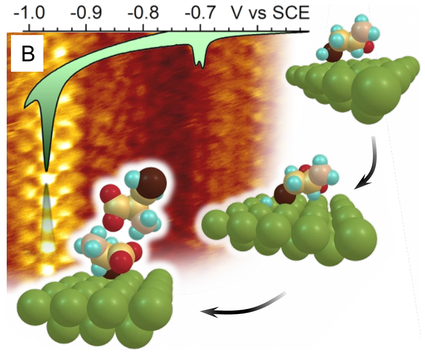

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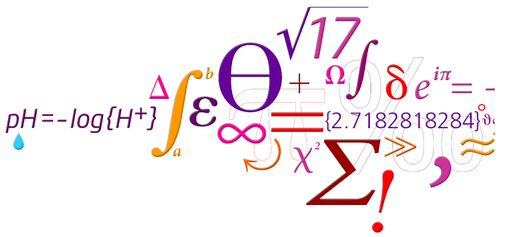
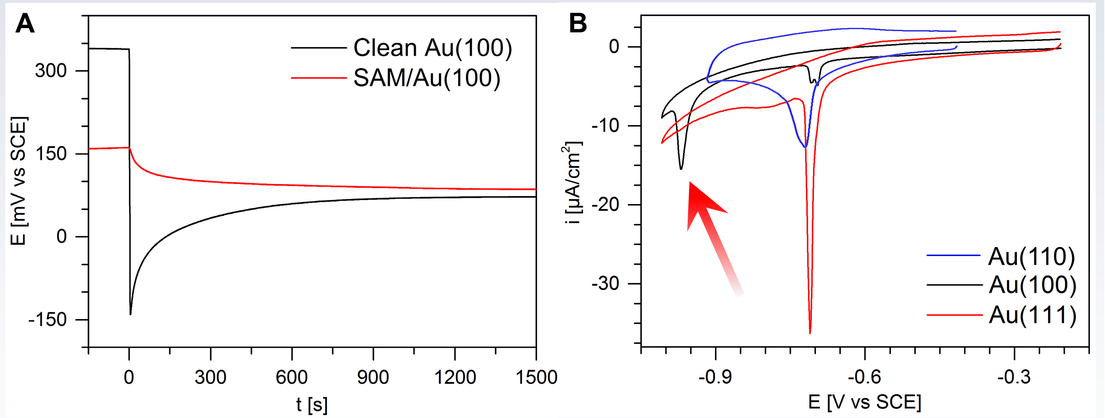


As the only amino acid with a thiol group, L-cysteine offers a strong perspective both for binding to gold and other metals, and for gentle immobilization of biomolecules. Binding to single-crystal, atomically planar surfaces offers the additional perspective that bound L-cysteine can be structurally mapped at the single-molecule level. In this work, we have followed the adsorption of L-cysteine on single-crystal Au(100) surfaces by electrode potential dynamics and in situ STM revealing the structure of the self-assembled monolayers (SAMs). The SAMs were further studied computanionally through density functional theory (DFT) including solvation effects and Monte Carlo simulations. The adsorption kinetics showed a complex pattern with at least one intermediate state. Unique chain-like cysteine dimer structures were found on Au(100).

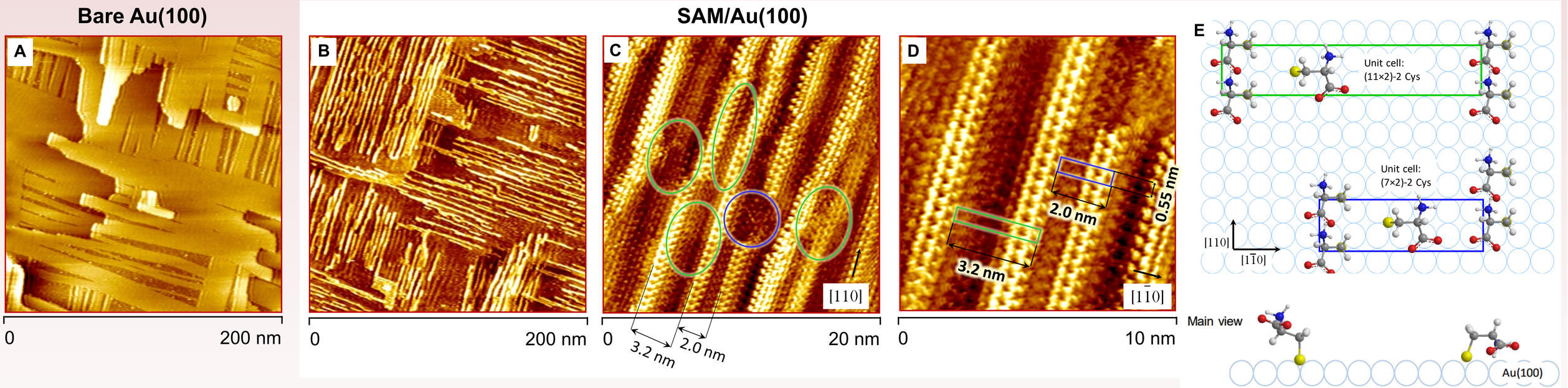
Electrochemistry

Figure 1. (A) Dynamics of cysteine self-assembly on bare Au(100) (black) and already coated Au(100) (red) in 25 mM KH_2PO_4 (pH 4.7). [Cys] = 250 µM. (B) Reductive desorption of cysteine on low-index Au surfaces in 0.1-0.5 M NaOH. Scan rate 10 mV/s.



Chronopotentiometry of cysteine adsorption on Au(100) shows biphasic behaviour indicating that several processes are involved in the SAM formation. Reductive desorption of SAMs on low-index Au surfaces shows clear differences in (1) coverage and (2) binding energies of cysteine. The additional peak for Au(100) suggest a widely different binding mode believed to relate to adsorbed cysteine dimers.

in situ STM study



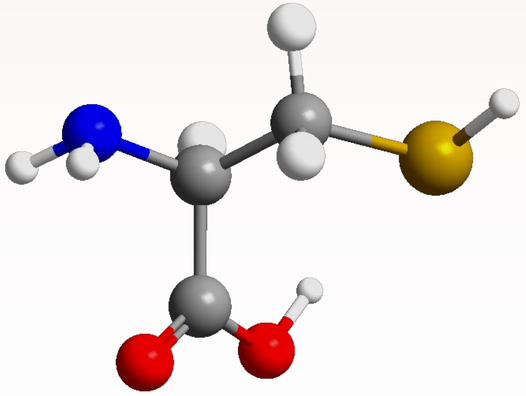


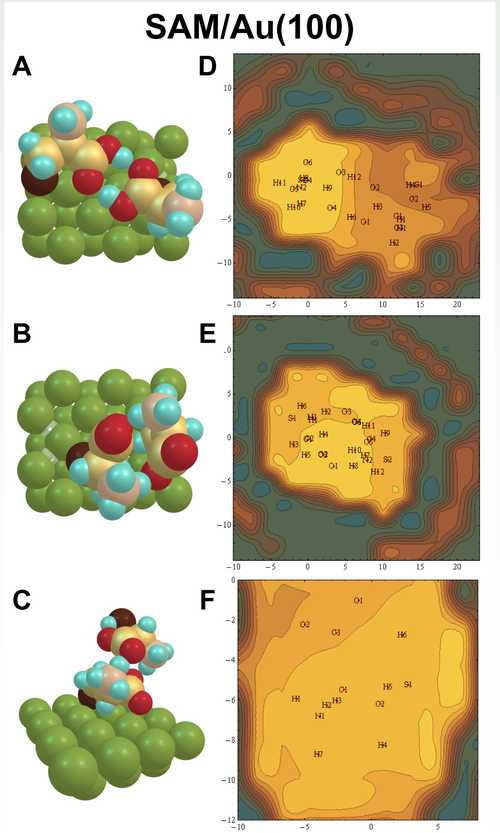
Figure 3. Molecular structure of the neutral form of L-cysteine

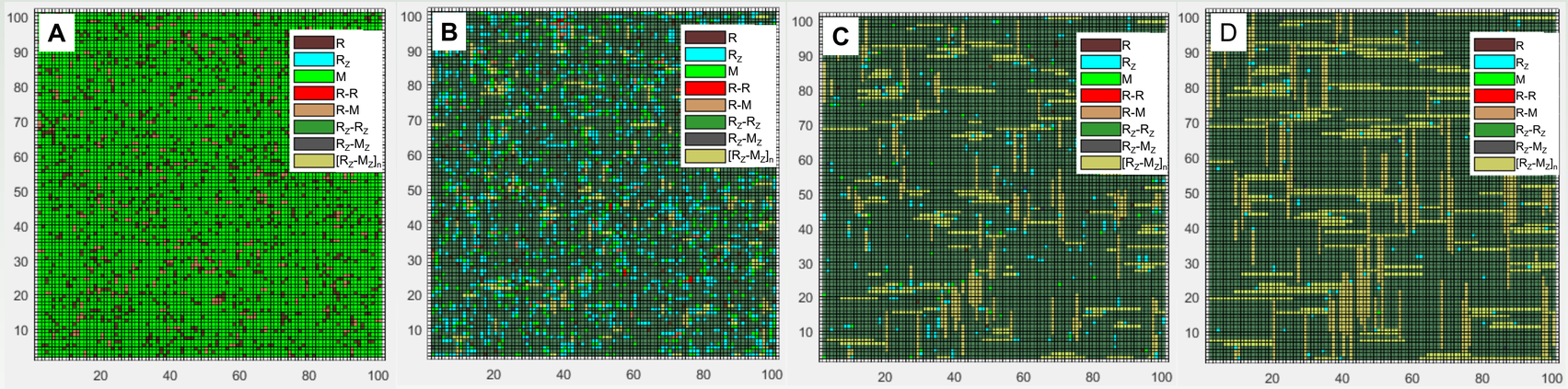
In situ scanning tunneling microscopy (STM) studies showed the molecular level structure of the L-cysteine SAMs. High-resolution STM images disclosed well-defined and highly surface-specific molecular assemblies. Chain-like structures following the underlying gold substrate surface structures were found on Au(100), which have not been observed in previous studies of cysteine SAMs on Au(111) and Au(110). Dense cysteine monolayers were found between the chain structures with lower contrast indicating two different adsorption modes. The bright chains are believed to arise from vertical cysteine dimers.

Figure 4. In situ STM images of (A) the bare Au(100) substrate and (B-D) L-cysteine SAMs on Au(100) in 25 mM KH_2PO_4 (pH 4.7). (E) Scheme of proposed unit cells of adsorbed L-cysteine matching the dimensions observed in the in situ STM images. L-cysteine is believed to adsorb in both an upright and planer configuration.

DFT and Monte Carlo computational study

Figure 4. (A-C) Optimized structure and (D-F) STM model contrast of most stable dimers. (top) Two radicals, (middle) zwitterions planar, (bottom) zwitterions vertical.





The interactions between L-cysteine and the Au(100) surface were investigated from a theoretical perspective using DTF, including periodical and cluster calculations of different adsorption orientations of L-cysteine in radical and zwitter ionic forms. Formation of cysteine dimers is favourable on Au(100), where a combination of planar and vertical dimers result in dark and bright lines in the STM images.

Kinetic Monte Carlo simulations of L-cysteine self-assembly on Au(100) showed that the monolayer goes through several phases and finally reproduced the chain-like pattern observed with *in situ* STM.

Figure 5. 2D pictures illustrating four different stages of the formation of a cysteine adlayer on Au(100) from kinetic MC simulations. M, R, and RZ are cysteine molecules, radicals, and radical zwitterions, respectively. R–R, R–M, RZ–RZ, and RZ–MZ are dimer species. $[RZ–MZ]_n$ indicates rows of vertical dimers.

CONCLUSIONS

In situ STM, electrochemistry and computational studies were employed to investigate the assembly of cysteine on low-index Au(100) surfaces. The orientation of the adsorbed cysteine molecules and the SAM structure are controlled by interaction with the Au substrates. The structural differences of the low-index Au surfaces lead to drastically different SAMs. Unique adsorbed vertical dimers are formed by hydrogen bonding between cysteine molecules on Au(100) giving rise to bright chain-like structures in *in situ* STM images.

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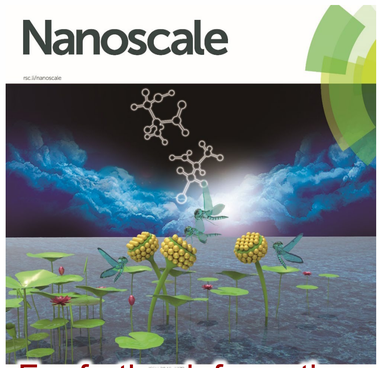

For further information:
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