Potential driven phase transition in the self-assembled monolayers of N-heteroaromatic thiols on Au(111) electrode: an electrochemical scanning tunneling microscopy study

Dong Wang, Bo Cui, Ting Chen, Li-Jun Wan
Institute of Chemistry, the Chinese Academy of Sciences
No.2 Zhongguancun North 1 Street, Beijing, 100190
e-mail address: wangd@iccas.ac.cn

Surface modification with molecular self-assembled monolayers (SAMs) offers a simple, versatile, and effective way to tune the surface composition, structure, and physical/chemical properties. SAMs of organothiols on metal surfaces are among the most extensively studied systems and have found applications in numerous fields including corrosion inhibition, electrocatalysis, chem/bio sensors, and molecular electronic devices. Recently, increasing research efforts have been devoted to thiol SAMs containing aromatic backbones. The involvement of $\pi$-electrons, and heteroatoms in the case of heterocyclic thiols, in substrate-molecule interactions makes the SAMs of aromatic thiols have diverse adsorption geometries and structures. In this report, we present the adsorption and assembly of several N-heteraromatic thiols on Au(111) surface by combining electrochemistry, in situ scanning tunneling microscopy (STM) and theoretical simulation. All the SAMs show disordered structures at the open cell potential. The potential driven phase transition to highly ordered lamella SAMs is observed upon scanning the electrode potential negatively. The adsorption geometry and structures of molecules in the ordered SAMs are revealed by high resolution STM and theoretical calculations. These results provide direct evidence for understanding the electrochemical behavior and the adlayer structures of the N-heteroaromatic SAMs on Au electrode.