

Adsorption of hexanethiolate on Au(111) in the 'striped' phase

Toru SHIMADA, Hiroshi KONDOH, Ikuyo NAKAI, Masanari NAGASAKA
Reona YOKOTA, Kenta AMEMIYA and Toshiaki OHTA*
Department of Chemistry, Graduate School of Science, The University of Tokyo,
Hongo, Tokyo 113-0033, Japan

Introduction

Self-assembled monolayers (SAMs) have attracted wide attention in recent years because they have potential applications in such fields as corrosion inhibition, tribology, molecular recognition and biosensors, where thorough understanding of the molecular structure of SAMs is necessary for effective applications. In this work, the adsorption structure of the 'striped' phase of hexanethiolate on Au(111) was studied by near-edge X-ray absorption fine structure (NEXAFS), X-ray photoelectron spectroscopy (XPS) and scanned-energy photoelectron diffraction (PD).

Experimental

The experiments were performed in ultrahigh vacuum (UHV) chamber (the base pressure of less than 2×10^{-10} Torr) which was equipped with a hemispherical analyzer. All the measurements were carried out at the soft X-ray beamline BL-7A. An Au(111) surface was cleaned by repeated cycles of Ar ion sputtering and annealing at 820 K. To prepare the hexanethiolate 'striped' phase, the clean surface was exposed to 200 L gaseous hexanethiol at room temperature. All the C K-edge NEXAFS and S 2p PD measurements were performed at 300 K. The C K-edge NEXAFS spectra were recorded in the partial electron yield mode with a retarding voltage of -200 V. The molecular structure was determined by the *R*-factor analyses.

Results and discussion

In S 2p XPS, only one S component was observed with spin-orbit split peaks, $2p_{3/2}$ and $2p_{1/2}$ at 161.8 and 163.0 eV, respectively, which agreed well with those for alkanethiolate. This shows that no disulfide-like structure was formed with two different adsorption sites.

The polarization dependence of C K-edge NEXAFS spectra from hexanethiolate adsorbed on Au(111) indicates that the -C-C-C- plane is almost parallel to the substrate.

Figure 1 shows a modulation of the normal emission S 2p peak as a function of the wavenumber in the range of 3-10 \AA^{-1} . To determine the adsorption structure, the experimental curve was compared with theoretical simulations, using the multiple scattering calculation of diffraction (MSCD) package developed by Chen and van Hove [1]. The reliability factor (*R*-factor) analyses were performed for several possible adsorption sites to obtain the optimum structure model. Among several high symmetry adsorption sites, the atop site gives the

minimum of the *R*-factor at the S-Au distance of $2.40 \pm 0.05 \text{ \AA}$, which agrees well with the previous observation [2]. This finding provides firm evidence for the atop adsorption, in agreement with the previous X-ray standing wave (XSW) study for octylthiolate adsorbed on Au(111) in the lying down phase. The S-Au distance also agrees with that reported value in XSW study ($2.50 \pm 0.05 \text{ \AA}$) [3].

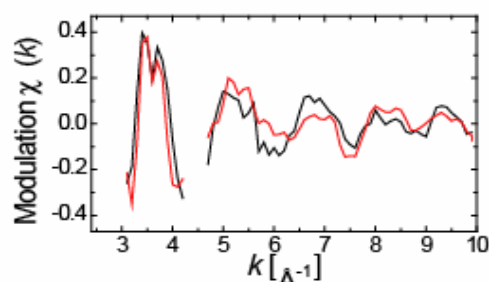


Fig. 1 Normal emission S 2p PD modulation (solid line). Dashed line is a simulation curve for the best-fit atop adsorption model.

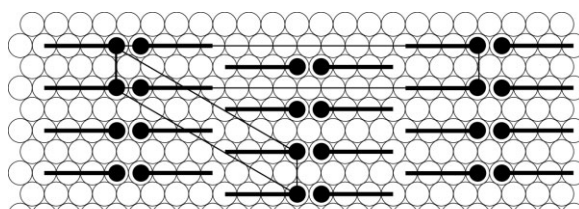
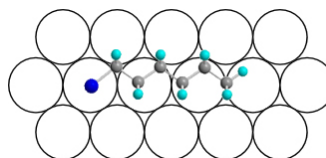


Fig. 2 Schematic view of the best-fit adsorption geometry of C₆H₁₃S and its arrangement on Au(111).

References

- [1] Y. Chen et al., MSCD package, Lawrence Berkeley National Laboratory (1998)
- [2] T. Hayashi et al., J. Chem. Phys. 114, 7615 (2001).
- [3] M.G. Roper et al., Chem. Phys. Lett. 389, 87 (2004)

* ohta@chem.s.u-tokyo.ac.jp