

High-Resolution X-ray Photoelectron Spectroscopy Study on CH₃S/Au(111): Evidence for Formation of Au-Adatom-Dithiolate Complex

Hiroshi Kondoh^{1,*}, Koichiro Nakaya¹, Kozo Mukai², Kazuhiko Mase³, and Jun Yoshinobu²

¹Department of Chemistry, Keio University, Yokohama 223-8522, Japan

²ISSP, The University of Tokyo, Kashiwa 277-8581, Japan

³Photon Factory, Tsukuba 305-0801, Japan

1 Introduction

The methylthiolate (CH₃S) monolayers adsorbed on Au(111) surfaces can be considered as prototypical self-assembled monolayers and have been extensively studied from the structural and electronic points of view. Although its structure has been long under controversy, a scanning tunneling microscopy (STM) study revealed that Au adatoms ejected from the surface contribute to stabilization of the methylthiolate monolayers via formation of a CH₃S-Au-SCH₃ complex as illustrated in Fig. 1 [1]. However, this Au-dithiolate complex model was not fully supported by a later high-resolution x-ray photoelectron spectroscopy (XPS) study, where a Au-monothiolate complex (CH₃S-Au) model was proposed based on the relative Au4f XPS intensity of the Au atoms with different chemical environments [2]. In this study, we conducted high-resolution XPS measurements for the CH₃S/Au(111) system to check the both models.

2 Experiment

The experiments were carried out at the high-resolution XPS station of BL-13A, which was equipped with a hemispherical electrostatic electron-energy analyser (PHOIBOS 100). A Au(111) single-crystal surface was cleaned by repeated cycles of Ar ion sputtering and annealing. The cleanliness and ordering were checked by XPS and LEED. A saturated methylthiolate monolayer was prepared by exposing the clean Au(111) surface to gaseous dimethyldisulfide at room temperature.

3 Results and Discussion

Fig. 2 shows Au4f XP spectra taken for clean and CH₃S-adsorbed Au(111) surfaces. The XP spectra were deconvoluted into several components by curve-fitting with the Doniach-Sunjić line shape convoluted by Gaussian functions. The clean surface spectrum exhibits two components from the bulk (B) and the surface layer (S), latter of which is significantly enhanced due to the high surface sensitivity of the Au 4f photoelectrons detected here ($E_{\text{kin}} \approx 50$ eV). The CH₃S-adsorbed Au(111) surface gives a higher-energy component (T_a) which is associated with the Au adatom [2] and instead the surface-layer component (S) is reduced in intensity. A part of the surface-layer Au atoms should be bound to the thiolate (T_s) and appear at the same binding energy as that of the bulk (B). The integrated intensity ratio T_a/S is obtained as 0.25. This ratio is in agreement with the Au-dithiolate model (0.25) but not with the Au-monothiolate model (0.33). This provides evidence for that the Au-

dithiolate complexes cover the Au(111) surface, which is consistent with a recent STM study on CH₃S-sturated Au(111) surfaces [3].

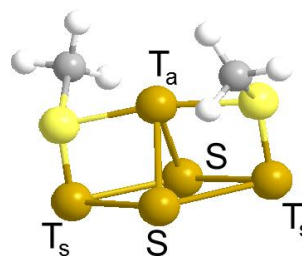


Fig. 1: Structure model for the CH₃S-(Au adatom)-SCH₃ dimer complex adsorbed on Au(111). T_a and T_s denote Au adatoms and surface Au atoms bound to the sulphur atom of the thiolate, respectively. S denotes surface Au atoms that are not bound to the thiolate.

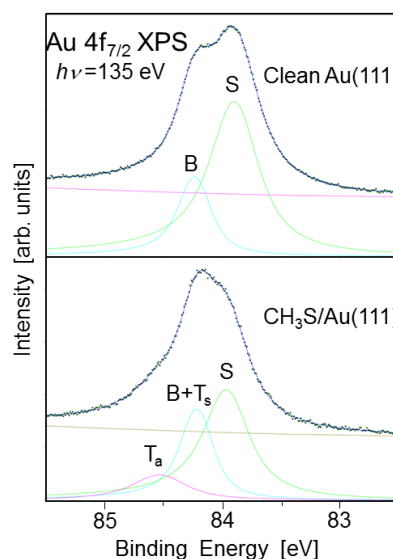


Fig. 2: High-resolution Au 4f_{7/2} XP spectra taken for clean and CH₃S-adsorbed Au(111) surfaces. T_a, T_s and S denote components corresponding to Au atoms shown in Fig. 1.

References

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* kondoh@chem.keio.ac.jp