

Adsorption and structure of methyl mercaptoacetate on Cu(111) surface by XPS and NEXAFS spectroscopy

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Abstract

Methyl mercaptoacetate (MA) on Cu(111) surface was investigated using synchrotron radiation-based X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. MA adsorbs on the surface via thiolate formation and weak interaction of the carbonyl group with the surface. Two different adsorption states previously reported for methanethiolate and ethanethiolate were confirmed, besides atomic sulfur. NEXAFS measurements support gauche-type conformation of MA whose skeleton lies on the surface.

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1. Introduction

Interaction of thiol molecules with metal surfaces has attracted considerable attention especially for the formation of self-assembled monolayers (SAMs) during the past two decades [1,2]. As SAMs are densely packed and well-ordered organic monolayers which can be variously formed by substituting end functional groups, they can be applied to easily modify surface properties with respect to wetting, adhesion, lubrication, and corrosion. Nevertheless, there was some controversy regarding the adsorption state or adsorption structure of thiol molecules on metal surfaces. Thiol molecules chemisorb on surfaces by strong S–metal bonding (thiolate formation) via experiencing deprotonation of thiol groups. Most of the studies for this reaction are aimed at the simplest alkanethiolate to clarify thiolate formation mechanism in detail. Initially, two distinct thiolate states were found for the methane adsorption on Ni(111) surface and were interpreted as differently coordi-

nated adsorption sites (twofold bridge and threefold hollow sites) [3]. Recent studies of methanethiolate on Cu(111) have clarified noteworthy dynamical behaviour accompanying the reconstruction of Cu surface layer in adsorption at room temperature [4–8].

Our further interest regarding SAMs is focused on research in soft X-ray induced chemical reaction on ideal surfaces where highly oriented functional groups are prepared on the topmost surfaces. As core electron excitation takes place within a quite local area differently from valence excitation because of a special localization of the core electron, site-selective bond breaking can be achieved in the vicinity of the primary excited atom. Recently, we have successively demonstrated that the obvious site-selective ion desorption occurred in methyl ester-terminated SAM ($-\text{S}(\text{CH}_2)_{15}\text{COOCH}_3$ on Au or Ag) [9,10]: CH_n^+ ($n = 0-3$) and OCH^+ ions desorb dominantly in specific resonant core excitations as a consequence of selective ionic dissociation of the methyl ester group; *i.e.*, selective $\text{O}-\text{CH}_3$ and $\text{C}-\text{OCH}_3$ bond scissions. On the contrary, methyl ester-terminated SAM which consists of shorter methylene chain ($\text{Ag}-\text{SCH}_2\text{COOCH}_3$, MA) hinders selective OCH^+ ion desorption [10]. The investigation suggests that geometrical

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orientation of the functional group plays an important role to embody site-selective properties.

In this study, adsorption of methyl mercaptoacetate (MA), which has two reactive functional groups to metal surfaces, thiol and carbonyl groups, on a clean Cu(111) surface has been studied using synchrotron radiation-based soft X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. Adsorption site and the structure of MA have been discussed.

2. Experimental

XPS and NEXAFS measurements were carried out on the soft X-ray beamline BL13 at HiSOR of Hiroshima University. Soft X-ray photoelectron spectra were obtained by using a concentric hemispherical electron analyzer (Omicron EA125) with resolving power ($E/\Delta E$) of ca. 1000, and NEXAFS spectra in the C 1s and O 1s regions were obtained by measuring sample drain current at various incident angles. During measurements, the experimental chamber had a base pressure of 2×10^{-10} Torr. Photon energy and binding energy were calibrated by $\pi^*(C=O)$ resonant states of PMMA thin film [9] and $2p_{3/2}$ and $3p_{3/2}$ photoelectron peaks of Cu, respectively.

A Cu(111) single crystal (99.9%) mounted on a rotatable sample holder [11] was cleaned by argon ion bombardment and annealing cycles. The cleanliness of the surface was checked by low-energy electron diffraction (LEED) and XPS using a Mg X-ray source. MA (Tokyo Chemical Industry, 98%) was used after purification by freeze-pump-thaw method. Multilayer coverage of MA at low temperature (100–120 K) was obtained by dosing with a few tens of Langmuirs ($1 \text{ L} = 10^{-6} \text{ Torr s}^{-1}$), while the saturated monolayer of MA on the Cu(111) surface at room temperature (300 K) was obtained by annealing the multilayer up to room temperature or overdosing with several hundreds of Langmuirs at room temperature.

3. Results and discussion

Soft X-ray photoelectron spectra of MA on Cu(111) have been measured for C 1s, O 1s, and S 2p regions in the saturated monolayer and multilayer phases. Fig. 1 shows C 1s spectra for (a) the monolayer at room temperature and (b) the multilayer at low temperature measured at photon energy of 390 eV together with deconvoluted fitting curves (Gaussian fitting). The monolayer indicates discriminating three peaks and almost identical yields, which indicates that these originate from three kinds of carbon atoms composing MA. The peak at the highest binding energy of 289.3 eV is attributed to the most electron-deficient carbon atom in the ester group. This binding energy is in good agreement with the reported value of 289.1 eV for the carbon (C_{COO}) bonded to carbonyl and hydroxyl oxygen atoms in the carboxy group of 3-mercaptopropionic acid ($HS(CH_2)_2COOH$, 3-MPA) adsorbed on Au(111)

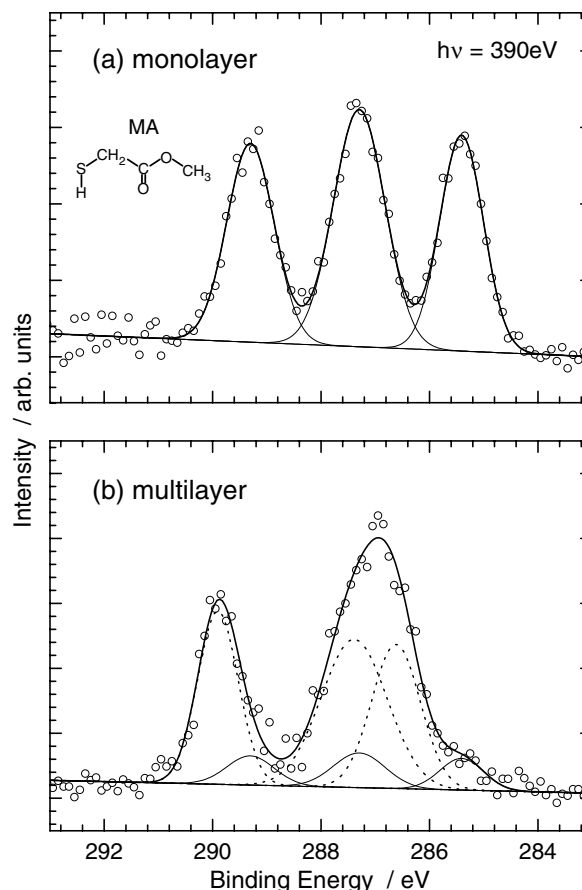


Fig. 1. C 1s photoelectron spectra of MA on Cu(111) for (a) the saturated monolayer at room temperature and (b) multilayer at liquid N_2 cooled condition. The spectra were measured at photon energy of 390 eV. Deconvoluted curves are also drawn for monolayer components (thin lines) and multilayer components (dotted lines) together with best fitted profiles (thick lines).

[12]. The peak at the lowest binding energy of 285.4 eV is assigned to the carbon (C_{CS}) bonded to the thiolate sulfur, which is reported to be at 285.2 eV for 3-MPA. The middle peak at 287.3 eV can be assigned to the carbon (C_{OCH_3}) in the methoxy group. In the multilayer phase where the monolayer components can also be observed for easy and precise comparison, the latter two peaks overlap in the higher energy region so that the spectrum consists of two main peaks. From the deconvolution procedure as shown in Fig. 1b, binding energies are 289.9, 287.4, and 286.6 eV for C_{COO} , C_{OCH_3} , and C_{CS} , respectively. The large energy shift (+1.2 eV) of C_{CS} from the monolayer to the multilayer supports the MA adsorption onto the Cu(111) surface by forming the S—Cu bonding (thiolate formation). This chemisorption is more directly confirmed in S 2p photoelectron spectra. On the other hand, although the energy shift for C_{OCH_3} is negligible within the resolution in this experiment, relatively large shift of +0.6 eV for C_{COO} may be considered that MA is also affected weakly by the Cu surface through the carbonyl group.

In the O 1s XPS, only one broad peak was obtained for both layer phases, although MA consists of two different

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