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S K-edge X-ray absorption fine structure study of adsorbed alkanethiols on Ag(111)

Erika SAKO*, Akihiro NOJIMA, Jun MIYAWAKI,
Hiroshi KONDOH, Toshiaki OHTA
Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Introduction

Self-assembled monolayers (SAMs) of alkanethiols on noble metals have been extensively studied both from fundamental and technological points of view. Recently, Dooms et al. reported the total reflection XANES spectra from alkanethiols on Ag(111) and found an anomalous peak in octadecanethiol (C18) SAM, which might be associated with a specific adsorption structure, thus motivated us to study S K-edge XANES and SEXAFS to determine the adsorption structure of C_{18} on Ag(111).

Experiment

The experiments were performed at BL-7A and 11B. C K-edge NEXAFS spectra were measured at BL-7A by partial electron yield mode to confirm the orientation of alkyl chains. The S-K fluorescence-yield XAFS spectra were measured for the samples at 100 K by using a gas-flow proportional counter filled with the P10 gas. A mechanically and chemically polished Ag(111) surface was cleaned by repeated cycles of Ar^+ sputtering and annealing. The freshly cleaned substrate was then immersed into 1 mM ethanol solution of C_{18} for at least 48h, to form a saturated C_{18} SAM.

Results and Discussion

Fig. 1 shows the S K-edge NEXAFS spectra of the C_{18} on Ag(111) at three different angles. The sharp peak at 2473eV was assigned to the S1s → σ*(S-C) excitation. The small peak at around 2480 eV arises from oxidized sulfur because the Ag substrate is exposed to the air and dipped in the solution. The tilt angle calculated from the polarization dependence of the σ*(S-C) peak is about 40° from the surface normal. $k^2\chi$ (k) functions and their Fourier transforms (Δk=3.0−8.8 $Å^{-1}$) for two incident angles are shown in Fig. 2 (a) and (b), respectively. There are mainly two peaks at ~1.5 Å(observed at grazing angle) and ~2.5 Å ascribed to the S-C and S-Ag contributions. The S-Ag bond length obtained is 2.48 ±0.03Å, which is obviously shorter than that of previous study[1], 2.54±0.03Å.

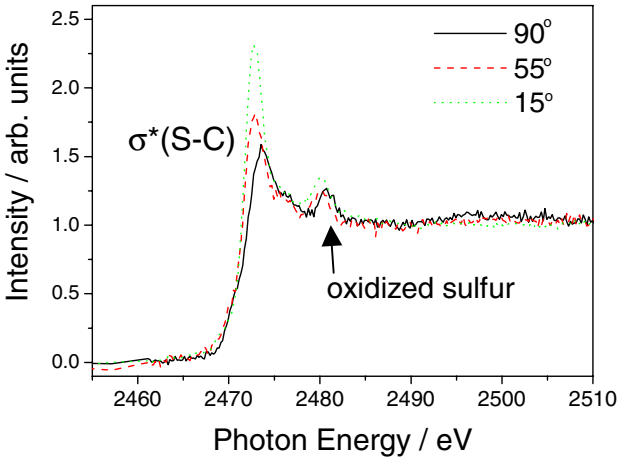

Fig. 1. S K-edge NEXAFS spectra of C_{18}/Ag(111)

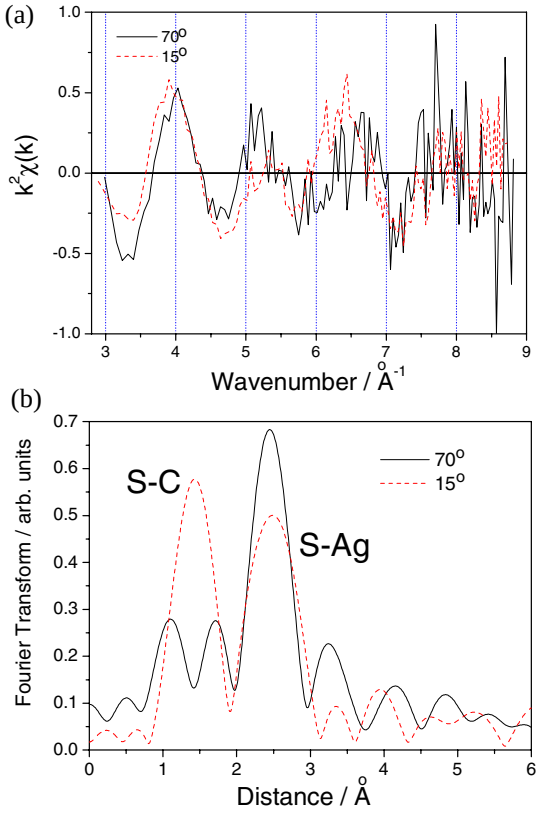

Fig. 2. S K-edge SEXAFS oscillation functionsχ (*k*) (a), and Fourier transforms (b) of C_{18}/Ag(111) .

References

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[2] E. E. Doomes et al., J. Phys. Chem. B 107, 10193 (2003).

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