

Anionic Surfactant Organized Film Formation on a Viologen Thiol SAM-Modified Polycrystalline Au and Au(111) Electrodes

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Introduction

Self-assembled monolayers (SAMs) of alkanethiol derivatives on a metal electrode surface act as a platform for a higher-ordered overlayer film formation. When a hybrid film is formed in a combination of a spontaneously developed overlayer with an underlying functional SAM, not only intrinsic properties of the SAM but also synergistic functions of the stratified film may emerge. Norman and Badia have reported anionic surfactant assembling process on a ferrocene-terminated alkyl thiol SAM [1]. On the other hand, Hagi and Sagara have studied the structure and electrochemical behavior a SAM of viologen-thiol, in which the viologen moiety is positioned at the midway of the alkyl chain, and achieved an anionic surfactant overlayer formation [2]. In the film, the amount of surfactant molecule depends on the oxidation state of viologen, dication form (oxidized form: V^{2+}) or mono-radical mono-cation form (one electron reduced form: $V^{\bullet+}$). When using dodecyl sulfate, the overlayer formation is found to be due to twofold interactions; one is the electrostatic interaction between anionic head group and cationic viologen moiety in the film interior with a low electric permittivity and the other is the chain-chain interaction.

In the present study, we aimed at clarifying in more detail the structure and function of the hybrid films at a molecular level on both polycrystalline Au and single crystal Au(111) electrodes. On a well-defined Au(111) electrode surface, the significance of the ordering should be made clear.

Experimental

Both polycrystalline Au (poly-Au) and single-crystalline Au(111) electrodes were modified with a SAM of *N*-heptyl-*N'*-10-bromodecyl-4,4'-bipyridinium dibromide in its ethanolic solution. Electrochemical measurements were conducted in the presence and the absence of the alkyl sulfates. The state of the viologen thiol (VT) SAM on a

poly-Au was characterized by *ex-situ* X-ray photoemission spectroscopy (XPS) measurements. The Au(111) electrode with a VT-SAM was brought into horizontal contact with 0.1 M KF or 0.1 M KF + 300 μ M sodium dodecyl sulfate (SDS) solutions and set in a hanging meniscus (H-M) configuration. Electrochemical measurements were carried out by the use of a Ag/AgCl/sat-KCl reference electrode in Ar gas atmosphere at room temperature.

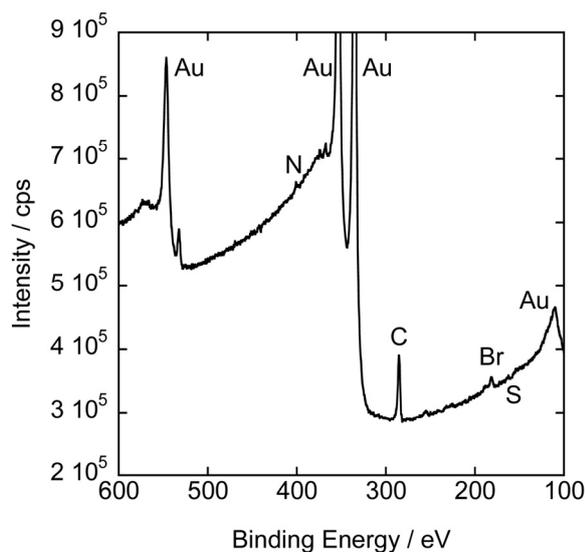


Fig. 1 XPS spectrum for VT-SAM after redox reaction experience in 0.1 M KBr solution.

Results and Discussions

In the presence of the alkyl sulfate with different alkyl chain lengths, measurements of cyclic voltammograms (CV) were used to elucidate the ratio of the binding equilibrium constants ($K_{\text{ox}}/K_{\text{red}}$) at a poly-Au electrode, where K_{ox} is the constant for the binding of two alkyl sulfate ions to V^{2+} and K_{red} for the binding of one alkyl sulfate ion to $V^{\bullet+}$. The alkyl chain length dependence of $K_{\text{ox}}/K_{\text{red}}$ revealed that the SAM-surfactant interaction involves an inter-chain interaction of 498 cal mol⁻¹ per one -CH₂-.

When a VT-SAM-modified poly-Au electrode was first subjected to CV measurements in 0.1 M KBr, rinsed with a copious amount of pure water, and left dried, it gives XPS signals of the constituents of the VT-SAM and counter anions (Fig. 1). We are now underway of XPS characterization in order for the anion exchanges to be quantitatively evaluated.

A VT-SAM-modified Au(111) electrode showed CV in 0.1 M KF with redox potential of -245 mV and surface excess of viologen (Γ) of 3.8×10^{-10} mol cm⁻². This redox potential is more negative than that at a poly-Au. The value of Γ is greater than that at a poly-Au. These differences may reflect a higher order of the SAM structure on a better defined Au(111) electrode surface. We are currently analyzing the structure of surfactant overlayers at the Au(111) electrode.

References

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