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Packing State and Stability of Self-Assembled Monolayers of 11-Ferrocenyl-1-undecanethiol on Platinum Electrodes

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Synopsis. Self-assembled monolayers of 11-ferrocenyl-1-undecanethiol on Pt have been characterized with an electrochemical quartz crystal microbalance and X-ray photoelectron spectroscopy. Well-packed monolayers were defect-free, but less compact than on Au. The high affinity of Pt for oxygen made the monolayer relatively unstable compared with monolayers on Au.

Self-assembled monolayer films of alkanethiol and their derivatives have been extensively examined in order to obtain fundamental information for the construction of surfaces with structures and functions controlled at the molecular level.[1] These monolayers are known to be very stable because of chemical bonding between the substrate and the sulfur atom of alkanethiols. Alkanethiol molecules are well packed and highly oriented. These attractive properties of the monolayers have been confirmed for the monolayers on Au. The self-assembly method with alkanethiol can be also used with the other substrates such as Ag,[2] Cu,[3] Pt,[4] and ITO.[5] To establish the general usefulness of the self-assembly method, however, it is essential to evaluate the packing state and stability of the monolayers on these substrates.

Monolayers of ferrocene derivatives of alkanethiol have attracted particular attention in recently published papers[6—8] including ours[7,8] because the monolayers should provide suitable interfaces to study fundamentals of electron transfer process. In this paper, we have constructed self-assembled monolayer films of 11-ferrocenyl-1-undecanethiol ($FcC_{11}SH$) on platinum surfaces. The packing state such as density and existence of defect was examined using a highly sensitive electrochemical quartz crystal microbalance (EQCM).[8] The stability of the films on Pt in an aqueous solution was evaluated also with X-ray photoelectron spectroscopy and cyclic voltammetry.

Experimental

Experimental procedures were basically the same as those described previously.[8] Briefly, monolayer films of $FcC_{11}SH$ were constructed on platinum and gold films vacuum-evaporated on 5 MHz AT cut quartz crystals (Maxtek Inc.), by immersing the metal-coated crystals into hexane containing 5 mM (1 M=1 mol dm^{-3}) $FcC_{11}SH$[9] for a desired time. EQCM measurements were performed in an aqueous 0.1 M $HClO_4$ solution using a sodium-saturated calomel electrode (SSCE) as a reference electrode. X-Ray photoelectron spectra (XPS spectra) were measured with a VG model ESCALAB MKII Spectrometer with Al Kα radiation.

Results and Discussion

A typical cyclic voltammogram (CV) of a monolayer prepared by the immersion of a Pt-coated crystal for 5 h is shown in Fig. 1a. A pair of peaks due to the redox of the ferrocenyl moiety of the monolayer was observed clearly, and integration of the peak gives the number of molecules attached to the surface as 1.9×10^{14} molecules/cm^2, demonstrating the formation of a mono-

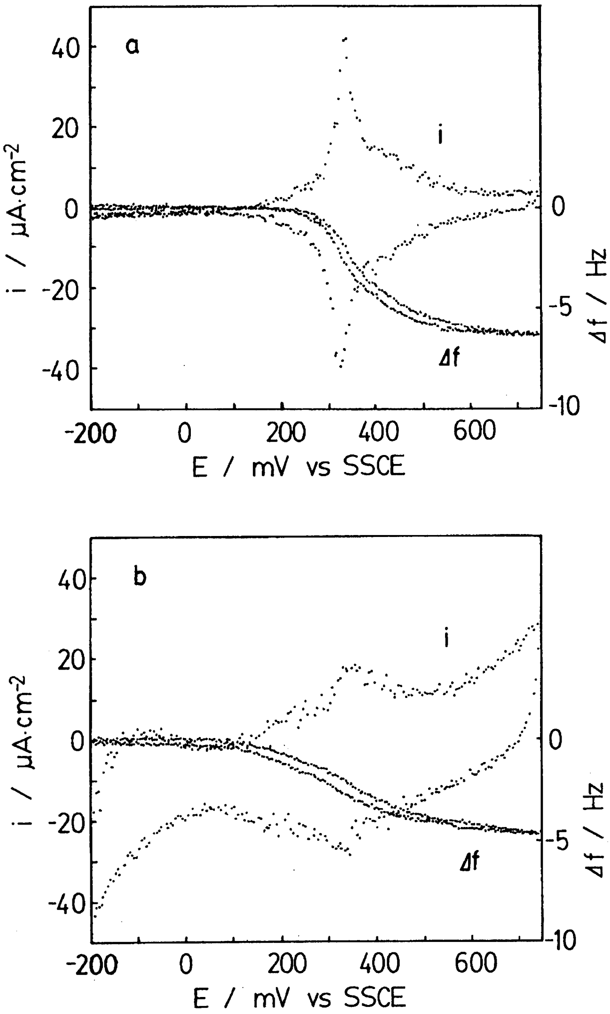

Fig. 1. Cyclic voltammograms and simultaneously recorded frequency response of $FcC_{11}SH$ monolayers prepared on Pt EQCM electrodes by (a) 5 h and (b) 0.5 h immersion in 5 mM $FcC_{11}SH$. Measurements were carried out in 0.1 M $HClO_4$ with a sweep rate of 50 mV s^{-1}.

layer of $FcC_{11}SH$ on Pt. Complete depletion of the hydrogen adsorption/desorption peaks within so-called hydrogen region (−0.2—0.1 V) indicates that there do not remain defects to which oxonium ion could have access to form adsorbed hydrogen.

Shorter immersion of the Pt-coated crystal gives lower coverage of $FcC_{11}SH$. Figure 1b shows the CV of the monolayer formed by 0.5 h immersion. The number of attached $FcC_{11}SH$ molecules was estimated to be 0.22×10^{14} molecules/cm^2. This value is much smaller than that at 5 h immersion. In addition, hydrogen adsorption/desorption peaks were observed in the CV. These results show that the $FcC_{11}SH$ molecule is packed much more loosely when the immersion time is shorter.

The packing density expected for hexagonal close packing of ferrocene is 2.7×10^{14} molecules/cm^2, and this value was obtained for a monolayer of $FcC_{11}SH$ on Au.$^{7)}$ However, the highest packing density on Pt obtained so far (1.9×10^{14} molecules/cm^2) is smaller than this value. The ratio of the observed to the expected packing densities gives the surface coverage and is 0.70. If the rest of the surface is $FcC_{11}SH$-free and hydrogen atoms can be adsorbed on this surface, the number of adsorbed hydrogen atoms can be calculated to be 3.9×10^{14} atoms/cm^2. This value is larger than the packing density of ferrocene and therefore redox peaks in the hydrogen region of the CV should be larger than those of ferrocene. However, such larger peaks were not observed as mentioned above. Similar discrepancy was also observed for more loosely packed monolayers. This discrepancy and smaller packing density compared with that on Au can be explained by the orientation of the monolayer film on Pt being more tilted than that on Au. To confirm the tilted orientation, IR and ellipsometric measurements are under way.

The oscillation frequency of quartz crystal, recorded simultaneously during the potential, decreased upon the oxidation of ferrocene, demonstrating that oxidation accompanies anion association with the monolayer. There hold linear relations between the frequency change and the charge passed during the oxidation. The slope gives mass change when the charge equivalent to one Faraday passes. We denote this mass change as mpe (mass per electron). The mpe's are 159 and 200 g for the cases in Figs. 1a and b, respectively. A simple association of ClO_4^- and ferricinium cation should give 100 g, the molar mass of ClO_4^-. At a densely packed monolayer on Au, actually, the mpe was observed to be 108 g.$^{8b)}$ The large mpe values on Pt are explained by simultaneous uptake of water molecules upon the anion association. For a loosely packed monolayer, a large amount of water uptake into the space between the surface-attached thiol molecules is likely. Therefore, the packing of $FcC_{11}SH$ on Pt is not so compact, even for a monolayer prepared by 5 h immersion, as that of a densely packed monolayer on Au.

Results presented above show that a higher concentration and longer immersion time were required to construct a well-packed monolayer on Pt, compared with the formation of a monolayer on Au.$^{7)}$ This difference may be due to the stronger affinity of Pt for oxygen. We speculate that displacement of preadsorbed oxygen species by thiol molecules is slow, so that stronger conditions are required to form the monolayer.

The strong affinity of Pt for oxygen also influenced the stability of the monolayer. We have reported that $FcC_{11}SH$ monolayers constructed on gold electrodes are very stable, as the storage of the monolayer-coated electrodes in air-saturated water for days gives reproducible electrochemical responses.$^{7)}$ In the case of the monolayer on Pt, however, the current decreased to a considerable extent. For example, the peak current became approximately half after the immersion in air-saturated water for 10 h. Disappearance of the ferrocene moiety from the film on Pt by immersion in air-saturated water is demonstrated clearly by XPS spectra. Figure 2a shows an XPS spectrum of a monolayer which was exposed to air for 1 d before measurement. A pair of peaks at 708 and 721 eV are assigned to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ of the ferrocenyl group,$^{10)}$ respectively. The shoulder at 711 eV indicates that a part of the Fe is in a more oxidized form. A broad peak at ca. 725 eV is of Pt, as shown clearly by an XPS spectrum for a bare Pt foil (Fig. 2e). Essentially the same spectrum was recorded after 3 d exposure to air (Fig. 2b). When

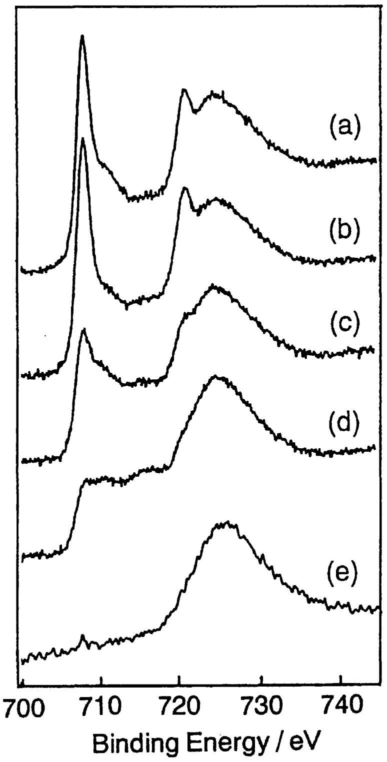

Fig. 2. XPS spectra of $FcC_{11}SH$ monolayers on Pt. After exposure to air (a, b) and water (c, d) for 1 d (a, c) and 3 d (b, d). (e) XPS spectrum of bare Pt.

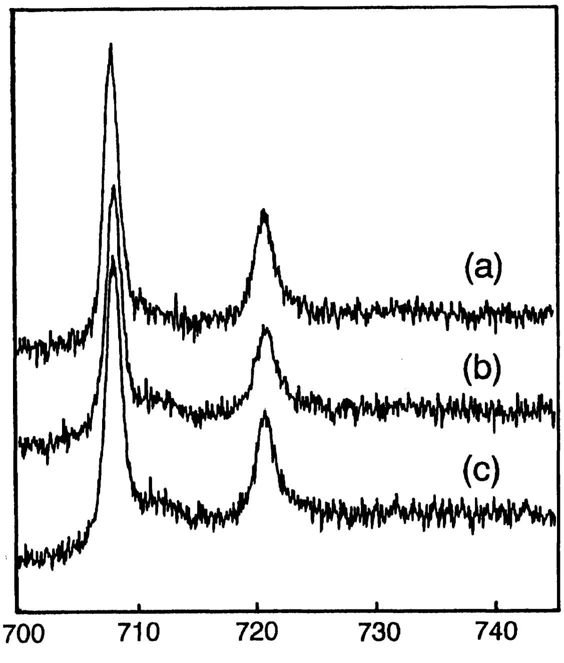

Fig. 3. XPS spectra of $FcC_{11}SH$ monolayers on Au. After exposure to air for 3 d (a), and to water for 1 d (b) and 3 d (c).

the monolayer film was immersed in water, the peaks at 708 and 721 eV became smaller (Fig. 2c). After 3 d immersion in water, only a small and broad peak remained (Fig. 2d). A similar trend was observed for the S 2p peak at ca. 163 eV. Therefore, it is clear that Pt–S bond was cleaved.

XPS spectra of monolayers on Au were also taken after immersion in water for the same periods. Peaks at 708 and 721 eV were observed clearly not only after the exposure to air for 3 d (Fig. 3a), but also after the immersion in air-saturated water for 1 and 3 d (Figs. 3b and c, respectively). Thus, the high stability of the $FcC_{11}SH$ monolayers on Au was confirmed.

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