Composition Control of Mixed 2-Aminoethanethiol/Octadecanethiol Monolayers by Underpotentially Deposited Lead on Gold

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The mixed aminoethanethiol/octadecanethiol monolayers, the surface composition of which was predetermined by the initial coverage of Pb underpotentially deposited on a bare gold electrode during the first step of the preparation, were constructed.

The self-assembled monolayers (SAMs) of functionalized alkanethiols have attracted particular attention in various fields.[1,2] To optimize the surface and catalytic properties of the SAMs, it is very important to prepare mixed monolayers. In most studies, the mixed monolayers were prepared by immersing the substrate in mixed thiol solutions.[1–5] Although this is very convenient method, it required a considerable number of trial and error experiments to prepare the mixed monolayers with the desired compositions due to the difference in the adsorbability between the thiols. An alternative method is based on the molecular structure of the thiol. Namely, asymmetric disulfides provide mixed monolayers of thiol fragments formed on the adsorption.[6–8] In this case, however, the surface composition is limited to 1:1. In addition, part of the fragments were not adsorbed on the electrode surface. The control of the composition in mixed monolayers is, therefore, hard to attain by either the immersion or disulfide method. In this paper, we propose a novel method to prepare mixed monolayers with controlled compositions using underpotentially deposited Pb (upd Pb), as exemplified here with 2-aminoethanethiol (AET)/octadecanethiol (ODT) monolayers.

All chemicals including AET (Wako) and ODT (Wako) were of reagent grade. Absolute ethanol (Wako) was used as the solvent for both the SAM preparation and reductive desorption experiments. Milli-Q water was used for the preparation of the aqueous solutions. The substrate electrode was a 200-nm gold thin film evaporated in vacuo onto a Ti-coated slide glass held at 300 °C. The gold film shows the typical characteristics of a Au(111) surface. Electrochemical measurements were performed in solutions sufficiently deaerated with argon of 5N purity prior to use. All potentials in the text are referred to a Ag/AgCl(sat'd KCl) electrode. The X-ray photoelectron spectra (XP spectra) were obtained using a Rigakudenki model XPS-7000 X-ray photoelectron spectrometer with Mg Kα radiation. The take-off angle was 90°.

The mixed monolayers were prepared according to the following procedures: (1) upd of the lead ion, (2) formation of ODT SAM, (3) desorption of upd Pb and (4) adsorption of AET. The underpotential deposition was performed in 1 mM $PbCl_2$ + 0.2 M $NaClO_4$ using the potential step method. The deposition amount was determined by a stripping voltammogram taken after holding the potential for 5 min. The surface coverages of Pb (hereafter referred to as the initial Pb coverage), defined as the ratio of the desorption charge to the saturated value at –0.4 V, are 0.60 and 0.30 at the deposition potentials of –0.2 V and –0.1 V, respectively.

After the underpotential deposition, the electrolyte solution was replaced with a fresh 0.2 M $NaClO_4$ solution. The electrode potential was held at the same potential during the replacement to avoid any unexpected desorption of Pb. The ODT solution was then injected into the 0.2 M $NaClO_4$ solution to form the SAM of ODT. The surface coverage of Pb on the electrode covered with ODT-SAM was determined from the Pb 4f signals in the XP spectra. These values (0.64 and 0.27) are approximately the same as the initial Pb coverages (0.60 and 0.30).

In order to create the adsorption sites for AET, Pb was removed from the electrode surface by oxidation at 0.5 V. The XP spectra showed that only a trace amount of Pb (< 0.02 in coverage) remained on the electrode. The adsorption amount of ODT can be determined by reductive desorption voltammetry, since it is well established that the Au–S bond is cleaved by a one-electron reduction.[9,10] To accurately estimate the charge, the contribution from the double layer charging and faradaic process (reduction of solvent) was subtracted from the total charge according to a previously reported procedure.[10] It should be mentioned that the contribution of the double layer charge often reaches 30% of the total change and is not negligible. The potential of zero charge (pzc) and capacitance of the partially and fully covered ODT adlayers and bare gold, which are necessary to estimate the double layer charge, were separately obtained and will be reported elsewhere.[11] The desorption charge for a full monolayer of ODT was 100 μC cm^{-2}, which is approximately consistent with that expected from the well-known $(\sqrt{3} \times \sqrt{3})R30°$ structure. The surface coverages of ODT were 0.48 and 0.73 for the samples of the initial Pb coverages of 0.60 and 030, respectively. Therefore, the same fraction (coverages) of vacant sites as the initial Pb coverages can be formed.

The mixed AET/ODT monolayers were finally prepared by immersing the electrode partially covered with ODT in the AET solution. Figure 1 shows the reductive desorption voltammograms of the mixed monolayers together with those of the single component SAMs. A single wave was observed for desorption of the mixed monolayers. The desorption charge, Q_{des}, was determined after consideration of the double layer charge using the pzc and capacitance data.[12] Because the charge required for the reductive desorption of ODT, Q_{ODT}, is known, the surface coverage of AET can be given by $(Q_{des} - Q_{ODT})/Q_{AET}$, where Q_{AET} represents the desorption charge for AET-SAM. In this equation, it is implicitly assumed that the electrode area occupied by one AET molecule in the mixed monolayers is the same as that in the single component AET-SAM. The AET coverages of 0.68 and 0.29 are close to the initial Pb coverages. The XPS N1s spectra were also used to estimate the surface coverage of AET. The signal intensity, I_N, linearly increased with the increase of the initial Pb coverage (Figure 2). This shows that the coverage obtained

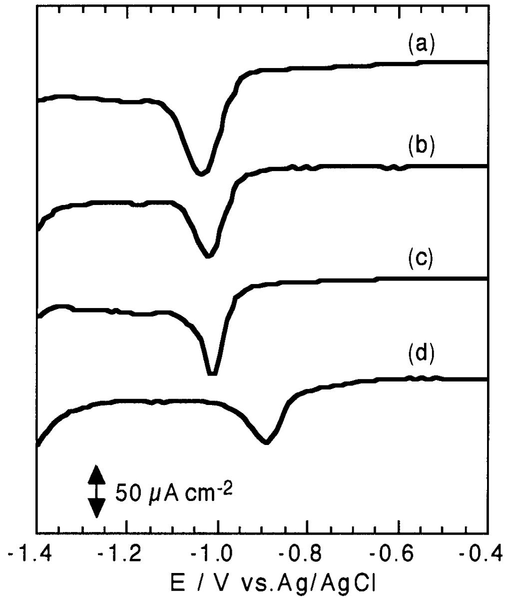

Figure 1. Reductive desorption voltammograms for (a) ODT-SAM, (b, c) mixed AET/ODT monolayers and (d) AET-SAM. The initial Pb coverage: (b) 0.30 and (c) 0.60. Solution: 0.1 M KOH/ethanol, sweep rate: 0.1 V s^{-1}.

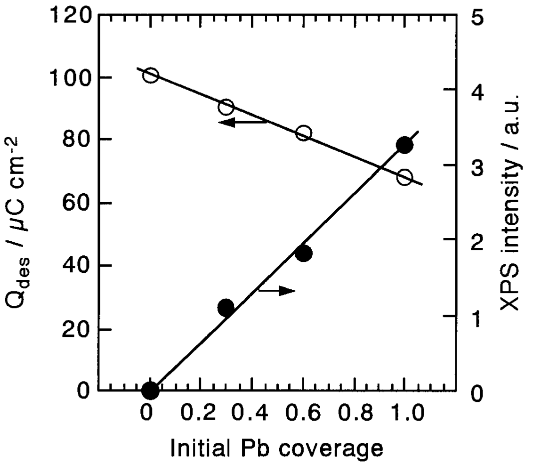

Figure 2. Desorption charge (open circle) and XPS N1s intensity (solid circle) as a function of the initial Pb coverage.

from the XP spectra, which is given by $I_N/I_{N,AET}$ ($I_{N,AET}$ represents the intensity for AET-SAM), is also the same as the initial Pb coverage. Therefore, both the reductive desorption voltammetry and XPS demonstrate that the surface coverage of AET can be determined by the initial Pb coverage.

The single wave is usually used as a diagnosis for no domain formation. However, in the case that the peak potentials of the single component SAMs are very close to each other like the present case (the difference in the peak potential is 0.15 V), a single peak is formed even when the domain is formed. Therefore, we have conducted desorption in aqueous 0.5 M KOH, in which a single component AET- and ODT-SAMs were desorbed at –0.72 and –1.14 V, respectively. Although the mixed monolayers formed from the mixed solution showed two waves, which are attributed to single component SAMs, only a single wave was observed for desorption of the mixed monolayers prepared by the present method. These results show that single component domains were not formed. The accurate determination of the desorption charge was not possible in aqueous solutions due to the overlapping currents caused by the desorption and hydrogen evolution reaction. This is the reason that ethanolic solutions were used to quantify the desorption charge of the mixed monolayer.

In summary, the upd Pb was used to control the surface coverage of AET in its mixed monolayers with ODT. Since the AET was adsorbed on vacant sites formed by the desorption of Pb, no Pb remained in the finally formed mixed monolayers. Recently, several studies have been reported on the upd into the SAM.[13–15] Most of these studies were conducted to examine the effect of SAM on the upd process. The construction of mixed monolayers after the upd into SAMs was also proposed.[15] In this case, however, it is hard to control the surface composition and distribution at a molecular level, because the upd process is strongly affected by the structure and interaction with the SAM. In contrast, the present method has a superior ability to control the surface composition and distribution of the mixed monolayers because upd on bare electrodes is very easily controlled. Further detailed examination is now under way.[11]

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