Construction of Nanostructured Thiol Monolayers Using UPD Pb as a Design Element

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In order to optimize the function of the electrode, it is very important to control the amount and distribution of functionalized molecules on the electrode surface. The most popular approach is the construction of mixed monolayers by the self-assembly of two different thiol molecules from their mixed solution. However, this approach requires a number of trial and error experiments to obtain the desired composition because of the difference in adsorbability between component thiols. In addition, each component thiol is hardly mixed homogeneously and often forms a domain. Recently, we have proposed a new method for controlling the amount of mercaptopropionic acid (MPA) or aminoethanethiol in their mixed monolayers with alkanethiol on Au using the underpotentially deposited Pb (UPD Pb) as a template.[1-3] Here we report the distribution of thiols at each stages of preparation of mixed MPA/alkanethiol monolayers, and the construction of mixed monolayers of ferrocenyl-octanethiol (FcC8SH) and alkanethiol.

The mixed monolayers were prepared according to the procedure reported in a previous paper.[3] Briefly, the lead ion was deposited on Au(111) at -0.2 V or -0.1 V vs. Ag/AgCl from a 1 mM $PbCl_2$ + 0.2 M $NaClO_4$ solution. A 2 mM ethanolic solution of the alkanethiol was injected to form the self-assembled monolayer (SAM) on Au partially covered with UPD Pb. The UPD Pb was stripped from the electrode by electrooxidation at 0.5 V vs. Ag/AgCl. During the final step of the preparation, the electrode was immersed in a 1 mM ethanolic solution of the functionalized thiol (MPA or FcC8SH) for 1 h to form the mixed monolayers.

The surface coverages of UPD Pb, alkanethiol and functionalized thiol, and the total numbers of thiols were determined using an electrochemical quartz crystal microbalance (EQCM) and reductive desorption voltammetry. The results show that the surface coverage of the functionalized thiol in the mixed monolayers is determined by the initial coverage of UPD Pb. The observed single peak in the cyclic voltammogram for the reductive desorption shows that the functionalized thiol and alkanethiol do not form their single-component domains. For the mixed FcC8SH /alkanethiol monolayers, the mass change accompanying the redox was determined using an EQCM; it increased with an increase in the chain length of alkanethiol and with a decrease in the surface coverage of FcC8SH. This mass change is interpreted by the model that anion and water are incorporated upon oxidation into the pocket surrounded by alkanethiol molecules and a FcC8SH molecule at the bottom. These results contrast with those obtained for the mixed monolayers formed from mixed solutions; the mass was independent of the surface coverage of FcC8SH. The latter observation is consistent with that expected for the domain formation.

The scanning tunneling microscope images showed the single row pinstripe structure for all the thiol adlayers formed during each step of the preparation. This shows that the surface structure of the mixed monolayers is determined by the structure of the initially formed SAM on Au partially covered with UPD Pb.

References

1. K. Shimazu and T. Kawaguchi, 197th Electrochemical Society Meeting, Abstract No. 586, Toronto, Canada, 2000.
2. T. Kawaguchi and K. Shimazu, Chem. Letters, 2001, 90.
3. K. Shimazu, T. Kawaguchi and T. Isomura, J. Am. Chem. Soc., in press.