

Structural Studies of Binding Group Terminated Self-Assembled Monolayers on Au(111) for Construction of Flatly Adsorbed Porphyrin Layers

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Introduction.

Porphyrin derivatives are well-known to have unique photochemical and electrocatalytic properties and then have extensively used as a functionality building block in a construction of molecular devices [1,2]. Since the photo-absorption vector of porphyrins is inside their ring plane, porphyrin ring should be arranged parallel to the solid surface in order to construct photo-device using porphyrin with higher efficiency. Since the substrate binds to porphyrin along the direction of the normal to the ring plane, porphyrin ring also should be arranged parallel to the solid surface in order to construct catalytic device using porphyrin with higher efficiency. Previously, Yoshimoto et al. reported well-arranged flatly-adsorbed porphyrin monolayers in order on the solid substrate surface [3]. However, the porphyrins were just physisorbed on the solid surface and it appeared to easily desorb from the surface by external perturbations such as photo-irradiation and/or potential applying.

On the other hand, the self-assembly technique is one of the best methods to chemisorb and to arrange the molecule in order onto the solid substrate surface and the self-assembled monolayers (SAMs) on gold have been widely used because of their high stability, high packing density, and high orientation [4]. We succeeded to flatly chemisorb the porphyrin derivatives with 4 thiol groups as binding group on the Au(111) surface [5]. But these porphyrin derivatives were too difficult to synthesize and very unstable.

Thus, in this study, we tried that the highly oriented 4-mercaptobenzoic acid (4-MBA) and 3-mercaptopropionic acid (3-MPA) SAMs were constructed on the Au(111) surface as a first and then, metallo-porphyrin was fixed on those SAMs using a coordinate bonding to achieve the construction of flatly adsorbed porphyrin layers, as shown in Fig. 1.

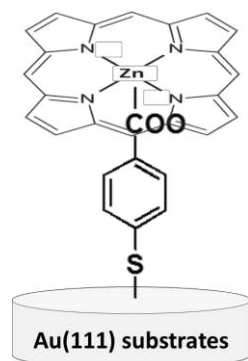


Figure 1. Model illustration of the flatly adsorbed porphyrin layer on 4-MPA SAM on Au(111).

Experimentals.

The Au(111) substrates were annealed by a gas burner and quenched with ultrapure water and after that, they were immersed in ethanolic solutions containing 1 mM 4-MBA or 1 mM 3-MPA for certain periods. Their self-assembly processes were investigated by electrochemical measurements for the reductive desorption and X-ray photoelectron spectroscopy (XPS) measurements in order to find the preparation conditions of the densely-packed and well-oriented SAMs. After that, metallo-porphyrin was fixed on their SAMs and their structures were investigated by XPS measurements.

Results and Discussion.

Figure 2 shows LSVs of Au(111) electrodes modified with the 4-MBA SAMs, which were prepared for several dipping periods. We can clearly see cathodic peaks, due to the reductive desorption of 4-MBA, around -0.60 V. With increasing of the dipping period, the peak potential shifted to negative and the surface coverage of 4-MBA increased. However, full width half maximum (fwhm) of the cathodic peak, which shows degree of the orientation of the SAM, decreased until the dipping period of 1 h and then increased with increasing of the dipping period. This result indicated that repulsion interaction between carboxylate groups should increase with increasing of the dipping period. For 5 h dipping, the surface coverage was saturated to 0.518 nmol cm⁻². XP spectrum of the 4-MBA SAM prepared by the dipping period of 5 h showed that this 4-MBA SAM is well-packed and highly oriented. Constructing of the flatly adsorbed metallo-porphyrin layers on these SAMs is now under investigation.

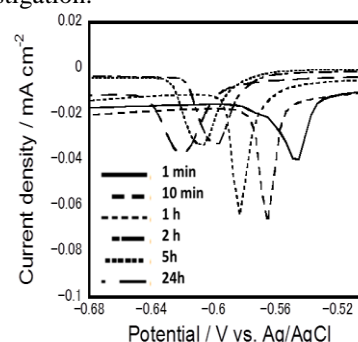


Figure 2. LSVs of the Au electrodes modified with the 4-MBA SAM, which were prepared for several dipping periods, measured in deaerated 0.1 M KOH with a scan rate of 20 mV s⁻¹

References.

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