

Construction of Highly Oriented Self-assembled Monolayer of Alkyldithiol with Ferrocene on Gold (111) Using Underpotentially Deposited Lead Submonolayer as a Template

Toshihiro Kondo,* Saori Sato, and Wakana Maeda

Graduate School of Humanities and Sciences, Ochanomizu University, Ohtsuka, Bunkyo-ku, Tokyo 112-8610

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Highly oriented self-assembled monolayer (SAM) of alkyldithiol with a ferrocene group was constructed on Au(111) surface using underpotentially deposited (UPD) Pb submonolayer as a template. Orientation of this SAM was confirmed by comparing amounts of ferrocene moiety and Au–S bonding.

Self-assembly (SA) technique is one of the most promising methods to construct highly oriented molecular layers with a molecular dimension, and self-assembled monolayer (SAM) of alkyldithiol on gold has been extensively studied in various fields such as molecular devices.^{1–3} SA multilayer should be more useful to construct molecular devices. Although many studies on highly oriented SAMs were reported, ordered SA multilayers have hardly been studied because, during multilayer formation, yield of surface reactions for the bond between the molecular layers is relatively low as compared with that for the Au–S bonding between the SAM and gold. For example, Duevel and Corn reported⁴ that alkylcarboxylic acid layer was constructed on the amine-terminated SAM on gold through amide bonding but adsorbed amount of the second layer of alkylcarboxylic acid molecule was low, and, therefore, the orientation of alkylcarboxylic acid layer should be low. Kim et al. and Kohli et al. constructed covalently coupled disulfide multilayer on gold using (α,ω)-dithiol derivatives with relatively longer alkyl chain.⁵ However, a dithiol molecule with a longer alkyl chain often adsorbs on gold surface not only through one terminated thiol, which is so called as a rod type, but also through both terminated thiol groups, which is so called as a bridge type. If the rod-type SAM is constructed with a dithiol molecule, we can get a well-ordered SA multilayer using a disulfide bonding.

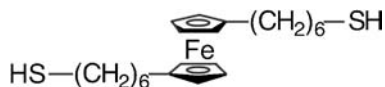
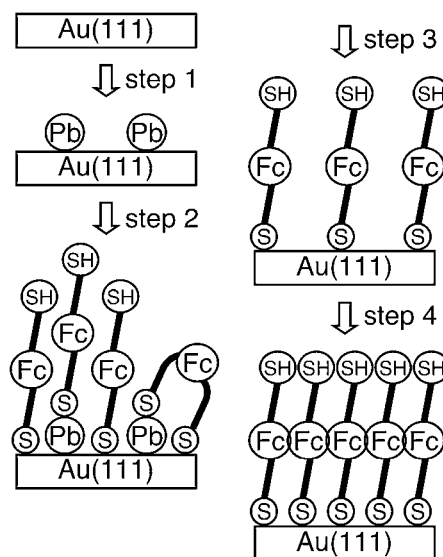


Figure 1. $\text{Fc}(\text{C}_6\text{SH})_2$ molecule.

On the other hand, Shimazu et al. constructed the highly oriented mixed SAMs on Au(111) using underpotentially deposited (UPD) Pb submonolayer as a template.⁶ As a first, Pb submonolayer (coverage, $\theta = 0.6$) was UPD on Au(111), followed by the formation of a SAM of an alkyldithiol. In this stage, the pinstripe structure was observed by STM. Spacing of each row was ca. 0.87 nm, and then this pinstripe was considered as a row of Pb. UPD Pb was then oxidatively desorbed from the gold surface to create a vacant site, where another thiol molecule was adsorbed to finally form the highly oriented mixed SAMs. In this final stage, the pinstripe structure was also observed, and spacing of each row was ca. 0.87 nm, which was matched well with the previous one. If a dithiol SAM is constructed on this UPD Pb

submonolayer on Au(111), SAM of both rod and bridge types should form. The bridge-type SAM connects both to Au and Pb atoms because the alkyldithiol and alkyldithiol SAMs were generally closed-packed and the spacing of 0.87 nm is too small that both terminated S atoms of the dithiol molecule adsorbed only on Pb atoms or only on Au atoms. After Pb is oxidatively desorbed, only a rod-type dithiol SAM should remain. When this substrate is dipped in the solution containing the same dithiol molecule, it is expected to form the highly oriented dithiol SAM with a rod-type. Here, we report the formation of the rod-type SAM of the dithiol molecule with a ferrocene group on Au(111) using UPD Pb submonolayer as a template. It was confirmed that this SAM is very highly well-ordered by comparison of amounts of ferrocene moiety and Au–S bonding.



Scheme 1.

Bis(6-mercaptohexyl)ferrocene ($\text{Fc}(\text{C}_6\text{SH})_2$, shown in Figure 1) was synthesized by the previously reported procedures.⁷ Formation procedures of $\text{Fc}(\text{C}_6\text{SH})_2$ SAM is shown in Scheme 1 and described in the followings. After commercially available Au(111) disk (SPL, surface area: 0.875 cm^2)⁸ was annealed by a gas flame and quenched under air, Pb was UPD with θ of 0.6 by scanning the potential from +0.65 V (vs. Ag/AgCl) to -0.15 V in the electrolyte solution containing 1 mM Pb^{2+} (step 1 in Scheme 1). Amount of UPD Pb was confirmed by the electrochemical crystal microbalance (EQCM) measurement. During keeping the potential of -0.15 V , ethanol solution of $10 \text{ mM Fc}(\text{C}_6\text{SH})_2$ was added to the electrolyte solution to construct the $\text{Fc}(\text{C}_6\text{SH})_2$ SAM until total concentration of

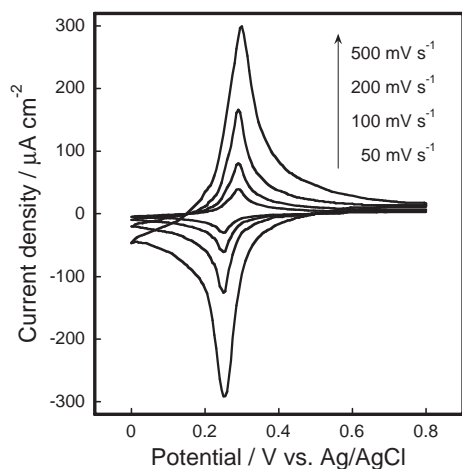


Figure 2. CVs of $\text{Fc}(\text{C}_6\text{SH})_2$ -SAM-modified Au(111) electrode measured in 0.1 M HClO_4 with various scan rates.

$\text{Fc}(\text{C}_6\text{SH})_2$ became 1 mM. After that, the substrate was directly immersed in the ethanol solution of 1 mM $\text{Fc}(\text{C}_6\text{SH})_2$ for 1 h to form complete $\text{Fc}(\text{C}_6\text{SH})_2$ SAM on UPD Pb/Au(111) substrate (step 2). UPD Pb was then oxidatively desorbed in the electrolyte solution without Pb^{2+} by scanning the potential from -0.15 V to $+0.65$ V (step 3). Finally, the substrate was immersed again in ethanol solution of 1 mM $\text{Fc}(\text{C}_6\text{SH})_2$ (step 4).

Figure 2 shows cyclic voltammograms (CVs) of the $\text{Fc}(\text{C}_6\text{SH})_2$ -SAM-modified Au(111) electrode, which was prepared by the above procedures. Relatively sharp wave due to the redox of ferrocene moiety was observed at $+0.27$ V. Linear relationship between peak current and sweep rate showed that this peak is due to the redox of the attached ferrocene moiety on electrode surface. Amount of Fc moiety, i.e., surface concentration of $\text{Fc}(\text{C}_6\text{SH})_2$ molecule, was estimated from the integrated anodic charge of the redox peak to be ca. $7.1 \times 10^{-10} \text{ mol cm}^{-2}$ ($4.3 \times 10^{14} \text{ molecules cm}^{-2}$). Redox potential and surface concentration observed in the present study were matched well with those previously observed at the ferrocenylalkyl thiol SAM on gold.^{7,9} Fwhm (full width at half maximum) of the peak and the peak separation were 0.07 and 0.04 V, respectively. Although the former value was quite similar to, the latter was slightly larger than those at the previous one,⁹ indicating that the ferrocene moiety should be placed inside the alkyl chain; namely, this SAM is highly oriented as a rod type.

Figure 3 shows a linear sweep voltammogram (LSV) of $\text{Fc}(\text{C}_6\text{SH})_2$ -SAM-modified Au(111) electrode, which was prepared by the above procedures. A relatively sharp cathodic peak was observed at -1.05 V, which is due to electrochemically reductive desorption of the $\text{Fc}(\text{C}_6\text{SH})_2$ SAM from the Au surface. Amount of Au–S bonding estimated from reductive charge of this cathodic peak was ca. $8.1 \times 10^{-10} \text{ mol cm}^{-2}$ ($4.9 \times 10^{14} \text{ molecules cm}^{-2}$). When we consider the charge required to establish the double layer of the unmodified electrode (ca. $10\%^{10}$), real value of the amount of Au–S bonding (90% of the observed value) is calculated to be $7.3 \times 10^{-10} \text{ mol cm}^{-2}$, which is matched well with that of the amount of adsorbed $\text{Fc}(\text{C}_6\text{SH})_2$ molecule. This result indicated that the $\text{Fc}(\text{C}_6\text{SH})_2$ SAM prepared in the present study should be connected with

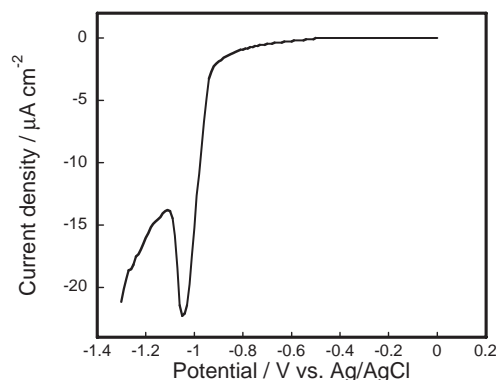


Figure 3. LSV of $\text{Fc}(\text{C}_6\text{SH})_2$ -SAM-modified Au(111) electrode measured in 0.1 M KOH with a scan rate of 20 mV s^{-1} .

a single Au–S bond, namely, is constructed as a rod-type. When the $\text{Fc}(\text{C}_6\text{SH})_2$ SAM was prepared just by the dipping of Au(111) substrate into the $\text{Fc}(\text{C}_6\text{SH})_2$ solution, the amount of Au–S bonding was 1.7 times larger than that of the adsorbed $\text{Fc}(\text{C}_6\text{SH})_2$ molecule. Thus, it is concluded that the present $\text{Fc}(\text{C}_6\text{SH})_2$ SAM is highly oriented on the Au(111) surface.

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