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Layer by Layer Construction of Metal–Organic Molecule Bilayer on a Au(111) Surface

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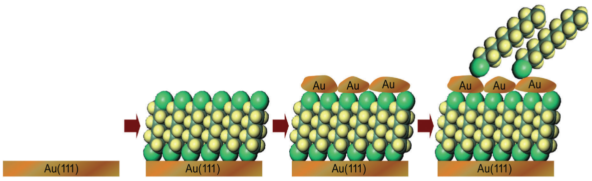
A thiolate self-assembled monolayer (SAM) was formed on a metallized dithiol SAM, resulting in a new kind of metal–organic molecule bilayer. 1,6-Hexanedithiol (HDT) was adsorbed on a Au(111) surface followed by adsorption and electrochemical reduction of $\mathrm{AuCl_4}^-$ on the HDT SAM, and then by adsorption of 1-decanethiol. The formation of the bilayer was confirmed by Fourier transform infrared spectroscopy, sum frequency generation, and electrochemical measurements.

Self-assembled monolayers (SAMs) of organic thiol molecules provides a useful method for constructing organic interfacial structure on metals, especially gold, and a highly reproducible model system for understanding organic and biological interfaces.[1] Although self-assembly of organic multilayers is important as such a system has a wide variety of potential applications such as molecular electronics and sensors because materials with complicated structure can be fabricated in molecular level resolution, only limited number of reports are available.[2]

In this study, we propose a novel approach to layer-by-layer construction of an organic bilayer on a Au(111) surface as shown in Scheme 1. We already demonstrated that a metal layer can be formed on top of an arenedithiol SAM.[3,4] Here, we employed a similar way to form a gold layer on top of an alkanedithiol SAM/Au surface and used it as a substrate for second molecular layer. The formation process and the formed bilayer were characterized by electrochemical methods, infrared reflection absorption spectroscopy (IRAS), and sum frequency generation (SFG) spectroscopy.

1,6-Hexanedithiol (HDT) was self-assembled on a Au(111) surface by immersing the Au(111) substrate in an ethanol solution containing 1 mM HDT. A cyclic voltammogram (CV) of the HDT/Au(111) electrode obtained in a 0.1 M KOH solution shows a sharp cathodic peak corresponding to reductive desorption of the HDT at −0.97 V (vs. Ag/AgCl) with the reductive charge of $98\,\mu\mathrm{C\,cm^{-2}}$ without double-layer charge correction, which is in good agreement with the value for the reductive desorption of an alkanethiolate SAM with saturated coverage of the $(\sqrt{3} \times \sqrt{3})\,R\,30°$ structure on a Au(111) surface,[5–7] showing the formation of well-ordered HDT SAM on a Au(111) surface.



Scheme 1. Schematic illustration of bilayer formation.

The HDT-modified Au(111), after being sufficiently rinsed with ethanol and deionized water, was immersed in a 0.5 M KOH solution for 3 min in order deprotonate the surface thiol group and was then incubated in a 5 mM $\mathrm{KAuCl_4}$ solution for 20 min. The gold substrate was transferred to a 50 mM $\mathrm{H_2SO_4}$ solution, and the electrode potential was set to +0.4 V, which is more negative than the redox potential of $\mathrm{AuCl_4}^-$/Au, i.e., ca. +0.8 V,[8] so that adsorbed gold complex was electrochemically reduced to a metallic gold layer on top of the HDT SAM resulting in a Au/HDT SAM/Au(111) structure. Previous study showed that the electrochemically deposited metallic gold film on an HDT SAM is a submonolayer with respect to the Au(111) substrate.[3,4]

Finally, a 1-decanethiol (DT) monolayer was formed as the second molecular layer on top of the Au/HDT SAM/Au surface by immersing the Au/HDT SAM/Au substrate into an ethanol solution containing 1 mM DT.

This stepwise formation of the DT/Au/HDT/Au(111) bilayer was followed by SFG spectroscopy. A detailed description of the SFG measurements has been given elsewhere.[9] In the present experiment, polarizations of the SFG, vis, and IR beams to obtain SFG spectra were all p, and SFG spectra were analyzed by using the following equation,[10]

$$I_{\mathrm{SFG}} = \left| \chi_{\mathrm{NR}}^{(2)} + \frac{A_0 e^{i\varphi}}{\omega - \omega_0 + i\Gamma_0} \right|^2 \tag{1}$$

where ω is the infrared frequency, $\chi_{\mathrm{NR}}^{(2)}$ is the nonresonant contribution to the surface nonlinear susceptibility, and ω_0, A_0, φ, and Γ_0 are the resonant frequency, transition amplitude, phase difference between resonant and nonresonant term, and homogeneous width, respectively.

Figure 1 shows the SFG spectra of (a) HDT/Au(111), (b) Au/HDT/Au(111), (c) DT/Au/HDT/Au(111), and (d) DT/Au(111). The solid lines were the least-squares fitting results by using eq 1.

No clear peak was observed in the spectrum of HDT SAM on Au(111) surface (Figure 1a) in contrast to the SFG spectrum of DT SAM on Au(111) surface (Figure 1d) where three peaks

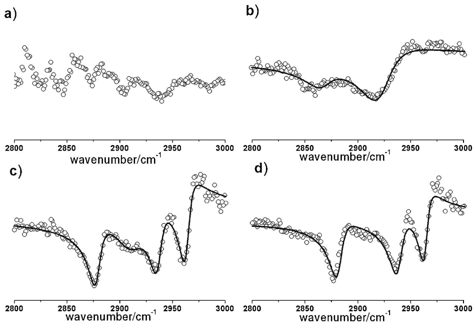


Figure 1. SFG spectra of (a) HDT/Au(111), (b) Au/HDT/Au(111), (c) DT/Au/HDT/Au(111), and (d) DT/Au(111).

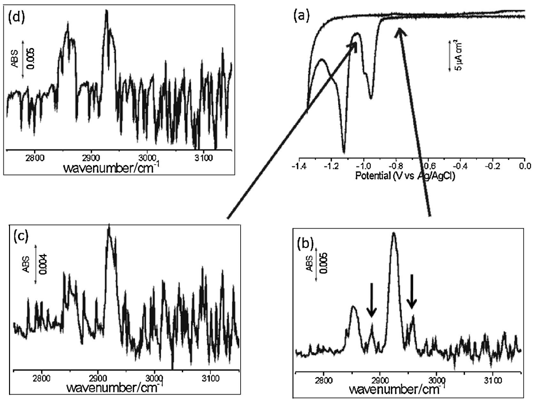


Figure 2. (a) CV of a DT/Au/HDT/Au(111) electrode in a 0.1 M KOH solution. Scan rate of 20 mV s^{-1}. FT-IR spectra of (b) DT/Au/HDT/Au(111), (c) DT/Au/HDT/Au(111) after the reductive desorption of DT by negative potential scan to −1.05 V, and (d) Au/HDT/Au(111).

corresponding to CH stretching of methyl group were observed at 2880 (ν_s, CH_3), 2939 ($\nu_{s,FR}$, CH_3), and 2965 ($\nu_{a,ip}$, CH_3) cm^{-1}, suggesting the alkyl chain of HDT is in *all trans* conformation.[11,12] However, two peaks were observed at 2855 and 2914 cm^{-1}, which can be assigned to CH_2 symmetric and asymmetric vibration, respectively (Figure 1b), after gold was electrodeposited on top of the HDT SAM, indicating that the structure of alkyl chain was no longer in an *all trans* conformation, i.e., structural perturbation by deposited gold.[13] When the layer of DT formed on Au/HDT/Au(111) surface, in addition to CH_2 asymmetric vibration mode at 2913 cm^{-1}, three peaks corresponding to methyl group were detected at 2876, 2935, and 2962 cm^{-1}, showing that the DT layer was successfully formed on top of Au/HDT SAM/Au(111) surface.

Figure 2a shows CV of a DT/Au/HDT/Au(111) electrode recorded in a 0.1 M KOH solution. The CV of the DT/Au/HDT/Au(111) electrode in a 0.1 M KOH solution shows two cathodic peaks at −0.97 and −1.12 V (Figure 2a). The reductive charges of these two peaks were found to be 35 and 101 μC cm^{-2} without double-layer charge correction, respectively. Since the total charge was much larger than that for the reductive desorption of a full-monolayer alkanethiolate SAM on a Au(111) surface, the possibility of these two peaks to be due to the binary SAMs as a result of the partial replacement of Au/HDT SAM by DT SAM is ruled out.[14] The reductive charge of the former peak was 34% of that of the latter peak. Since the coverage of thiol SAM was only 1/3 of Au(111) surface[1] and one HDT molecule is expected to form a complex with one $AuCl_4^-$,[15] the number of gold atoms on top of the HDT SAM available for the DT SAM formation should be 1/3 of that of Au(111) surface for the HDT SAM formation. Thus, the peak at −0.97 V is assigned to the reductive desorption of DT from the DT/Au/HDT/Au(111) surface.

The charge for another peak at −1.12 V, 101 μC cm^{-2}, is similar to that for the reductive desorption of an alkanethiolate SAM with saturated coverage of the $(\sqrt{3} \times \sqrt{3})\,R\,30°$ structure on a Au(111) surface, but the peak position is more negative than that of the reductive desorption of HDT from Au(111), −0.97 V. This is because not HDT but Au/HDT was reductively desorbed in this case. The presence of Au overlayer should make the reductive potential more negative.

The selective desorption of the DT SAM from DT/Au/HDT/Au(111) surface at the first cathodic peak was confirmed by ex situ IRAS measurements (Bio-Rad FTS-30). Figures 2b and 2c are the IR spectra of the DT/Au/HDT/Au(111) surface obtained by using p-polarized light with an incident angle of 80° before and after, respectively, the negative potential scan to −1.02 V, i.e., reductive desorption of the DT SAM. A freshly prepared gold film was used to obtain reference spectra. While two bands corresponding to the symmetric and asymmetric stretching of CH_3 group at 2885 and 2958 cm^{-1}, respectively, were observed in Figure 2b as indicated by arrows, they are absent in Figure 2c, which is identical to the spectrum of the Au/HDT/Au(111) shown in Figure 2d. These results indicate that the DT SAM on top of the Au/HDT/Au(111) was successfully removed after negative potential scan to −1.05 V.

In conclusions, a novel method to construct a thiolate bilayer on a Au(111) surface in a layer-by-layer fashion is proposed. HDT was adsorbed on a Au(111) surface followed by adsorption and electrochemical reduction of $AuCl_4^-$ on the HDT SAM to a Au/HDT/Au(111) structure. DT was then adsorbed on a metallic gold layer on top of the HDT SAM so that an organic bilayer, DT/Au/HDT/Au(111), structure is formed. The formation of the bilayer was confirmed by IRAS, SFG, and electrochemical measurements. The amount of DT in the top layer was 1/3 of that of HDT in the bottom layer. The top and bottom layers can be reductively removed in layer-by-layer fashion by sweeping the potential negatively.

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15 Although it is not possible to prove the complexation in this case since both substrate and metal ion contain Au, the coordination of S atom of thiol to Pt of $PtCl_4^{2-}$ was confirmed by XAFS.