Self-Assembled Monolayers of Ferrocene-terminated Thiol on Gold: Reorientation Induced by Coadsorption of Dodecanethiol

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Received October 29, 1998

Since the introduction by Sagiv,[1] self-assembly method has been emerged as one of the most powerful methods to fabricate organic monomolecular layers on metal surfaces.[2] Especially, alkanethiols on evaporated gold and/or silver surfaces have been studied extensively.[3] Molecular recognition, nonlinear optics, microelectronic application, surface wetting control, and corrosion protection are some of the applications of the recently developed monolayers.[4] Many studies have been reported on chemical methods of derivatizing monolayer structure to prepare well defined new structures with novel properties.[5] Among many different approaches leading to the development of the self-assembled monolayer, potential dependent reorientation of mercaptoalkanenitrile monolayers on gold has been reported.[6] However, the structural reorientation by coadsorption of other molecules has not been reported yet.

In the process of studying the coadsorption and exchange in self-assembled monolayers, we found that the structure of a self-assembled monolayer could be changed by the coadsorption of other molecules. This paper describes the structural reorientation of a ferrocene-terminated undecanethiol monolayer by the coadsorption of dodecanethiol. Ferrocene-terminated alkanethiol monolayers on a gold surface have been a valuable probe for the study of electron-transfer kinetics. The distance from the redox center to the electrode surface was controlled by changing the chain length in the molecule used and the coadsorption with an unsubstituted alkanethiol was used to control the electron transfer properties.[7] The electrochemically active ferrocene moiety was also used to measure the surface coverage of monolayers.[8]

For our study, a monolayer of 11-sulfidoundecyl ferrocenecarboxylate[abbrev. $FcCOO(CH_2)_{11}S$] was fabricated on the gold substrate (Au/Ti/Glass) by self-assembly from the 1mM ethanol solution of $FcCOO(CH_2)_{11}SH$. After taking the FT-IR spectrum, this substrate was immersed into the 1 mM ethanol solution of dodecanethiol, $CH_3(CH_2)_{11}SH$. The substrate was taken out and rinsed with ethanol before taking another spectrum. This procedure was repeated at certain interval.

The structure of the $FcCOO(CH_2)_{11}S$ monolayer has been studied by FT-IR external reflection spectroscopy with the *p*-polarized light. Figure 1 shows the infrared spectra of the monolayer before and after the coadsorption of $CH_3(CH_2)_{11}S$ along with the KCl dispersed DRIFT spectrum of $FcCOO(CH_2)_{11}SH$. Peak positions, intensities, and shapes for the monolayer were similar to the previously reported data.[8] Peak assignments based on previous works,[8~10] and peak positions for the spectra in Figure 1 are listed in Table 1. Insight into the presence of reorientation of monolayer can be inferred from the disappearance of the carbonyl stretching peak. The peak at 1713 cm^{-1} which was assigned as ν(C=O) was quite intense on the spectrum of the $FcCOO(CH_2)_{11}S$ monolayer shown in Figure 1(b). The intensity of this peak was consistent with previously reported spectra of $FcCOO(CH_2)_8S$ and $FcCOO(CH_2)_{11}S$

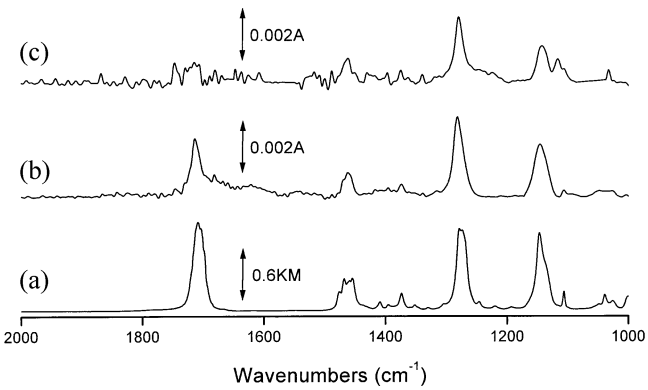

Figure 1. Comparison of the FT-IR spectra of $FcCOO(CH_2)_{11}SH$ powder dispersed in KCl(DRIFTS) (a), the monolayer of $FcCOO(CH_2)_{11}S$ on gold (b), and the monolayer of $FcCOO(CH_2)_{11}S$ on gold treated with $CH_3(CH_2)_{11}SH$ (c).

Table 1. Peak positions and mode assignments for $FcCOO(CH_2)_{11}$-SH powder dispersed in KCl (DRIFTS) and $FcCOO(CH_2)_{11}S$ monolayers adsorbed on gold before and after the coadsorption of $CH_3(CH_2)_{11}S$

mode assignment	KCl (DRIFTS)	Monolayer[a]	
		$FcCOO(CH_2)_{11}S$ only	$FcCOO(CH_2)_{11}S$ with $CH_3(CH_2)_{11}S$
$\nu(C\text{-}H)_{Fc}$	3109, 3087	3129	3129
$\nu_a(CH_3)$	-	-	2956
$\nu_a(CH_2)$	2919	2922	2918
$\nu_s(CH_2)$	2851	2850	2850
ν(C=O)	1708	1713	1714, 1747
$\delta(CH_2)$	1468	1462	1462
ν(C-(C=O)O)	1279	1282	1279
ν(C-C-O)	1146	1146	1143
$\delta(C\text{-}H)_{\perp,Fc}$	1106	1106	1116
δ(C-H)	1039	n.o.	1033
$\delta(C\text{-}H)_{\parallel,Fc}$	1000	n.o.	n.o.

[a] n.o., not observed above the noise level of the monolayer spectrum.

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monolayers on gold.[8] By immersion of the $FcCOO(CH_2)_{11}S$ monolayer into the ethanol solution of $CH_3(CH_2)_{11}SH$ for 10 minutes, the intensity of this carbonyl peak decreased rapidly as shown in Figure 1(c). This implies that the carbonyl group is either removed completely from the monolayer or reoriented parallel to the surface. Nevertheless, C-O stretching peaks at 1282 cm^{-1} and 1146 cm^{-1} which were assigned as ν(C(C=O)-O) and ν(C-C-O) respectively, still existed with almost same intensities. This implies that the incoming $CH_3(CH_2)_{11}SH$ molecules are not replacing much of the existing $FcCOO(CH_2)_{11}S$ molecules but induce the reorientation of the structure. Although a previous work reported that the mixed monolayer of $FcCOO(CH_2)_{11}S$ with $CH_3(CH_2)_6S$ would give ~12 cm^{-1} shift in higher energy for the carbonyl peak,[8] the selective decrease of only carbonyl peak on the monolayer was never reported before. We think that this decrease of carbonyl peak is due to the reorientation of the ferrocene moiety induced by the coadsorption of alkanethiol.

We are postulating that this behavior is dependent on the relative chain lengths of ferrocene-terminated thiol and unsubstituted alkanethiol. Our postulation is depicted in Figure 2. Even though these structures are oversimplified, these will show the relative orientation of carbonyl group with respect to the gold surface. The structure in Figure 2(a) shows the monolayer before the coadsorption of $CH_3(CH_2)_{11}SH$. The vibrational mode, ν(C=O) is perpendicular to the metal surface and its absorption intensity on the spectrum would be increased due to the surface selection rule. This can be confirmed by the fact that the 1713 cm^{-1} peak was very intense on the previously reported spectra of $FcCOO(CH_2)_8S$ and $FcCOO(CH_2)_{11}S$ on gold[8] as well as this work. With the addition of $CH_3(CH_2)_{11}S$ on the monolayer, the C-O single bond on the carbonyl side of ester would be rotated. This means that the coadsorbed $CH_3(CH_2)_{11}S$ molecules on gold would push the ferrocenyl group upward to make more room for themselves. The resulting structure is shown in Figure 2(b). If the coadsorbed alkanethiol was short enough such as $CH_3(CH_2)_6SH$, it would not induce the reorientation since it could be accommodated in the space among adjacent $FcCOO(CH_2)_{11}S$ molecules without any reorientation. This explains why Walczak *et al*. detected the peak shift instead of the disappearance of carbonyl peak for $CH_3(CH_2)_6S$ coadsorption.[8] The shift of ν(C=O) peak in the mixed monolayer with $CH_3(CH_2)_6S$ were thought to come from the interactions between neighboring end groups. The spectra for C-H stretching mode, although not shown here, gave consistent information for the structure postulated. By coadsorption of $CH_3(CH_2)_{11}S$, new peak appeared at 2956 cm^{-1} which corresponds to $\nu_a(CH_3)$. The peak at 2922 cm^{-1} associated with $\nu_a(CH_2)$ shifted to 2918 cm^{-1}. It is clearly established that the peak position of $\nu_a(CH_2)$ of densely packed polymethylene chains is roughly 5-6 cm^{-1} lower in energy than that of loosely packed ferrocene-terminated polymethylene chains.[10] The structure in Figure 2(a) can not give a densely packed monolayer and would provide more liquid like environment for the chains. On the other hand, the structure in Figure 2(b) would provide more crystalline environments. Though it is not clear why the carbonyl group prefer vertical position to horizontal one in the $FcCOO(CH_2)_{11}S$ monolayer, the same spectra were observed for $FcCOO(CH_2)_8S$ and $FcCOO(CH_2)_{11}S$ monolayers before.[8] For the structure of the coadsorbed monolayer of $FcCOO(CH_2)_{11}S$ and $CH_3(CH_2)_{11}S$, Chidsey and others proposed that the dipping of the $FcCOO(CH_2)_{11}S$ monolayer in the $CH_3(CH_2)_{11}SH$ solution would give exchange of $FcCOO(CH_2)_{11}S$ molecules at the domain boundary with $CH_3(CH_2)_{11}SH$.[7] According to their model, the peak intensity at 1713 cm^{-1} of the $FcCOO(CH_2)_{11}S$ monolayer should come from only those molecules at the domain boundary. On the observed spectra, the peak at 1713 cm^{-1} was almost completely disappeared but the intensities of other peaks at 1282 cm^{-1} and 1146 cm^{-1} remained almost the same after the exchange. This strongly suggests that the disappearance of carbonyl group is due to the overall reorientation rather than partial desorption.

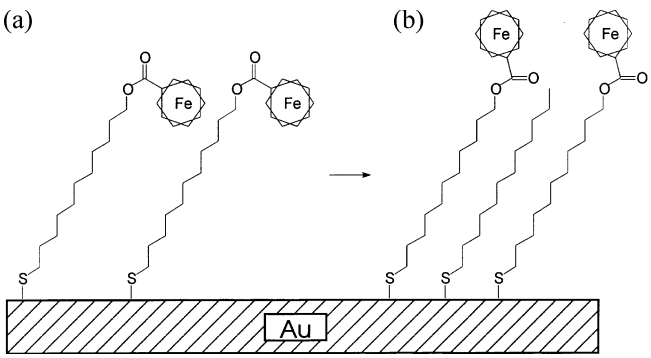

Figure 2. A schematic representation for the reorientation of the $FcCOO(CH_2)_{11}S$ monolayer self-assembled on gold before the coadsorption of $CH_3(CH_2)_{11}S$ (a) and after the coadsorption of $CH_3(CH_2)_{11}S$ (b).

We think that $CH_3(CH_2)_{11}S$ would adsorb at the vacant gold surface among $FcCOO(CH_2)_{11}S$ molecules and push the ferrocene moiety resulting in the overall reorientation of the $FcCOO(CH_2)_{11}S$ monolayer. For comparison, we performed another experiment. We made a mixed monolayer from ethanol solution containing both $FcCOO(CH_2)_{11}SH$ and $CH_3(CH_2)_{11}SH$, and took the infrared spectrum of the mixed monolayer. There was little difference on spectra of the monolayer from a mixed solution and the monolayer which immersed in the $FcCOO(CH_2)_{11}SH$ solution first and dipped in the $CH_3(CH_2)_{11}SH$ solution later. This implies that in the presence of $CH_3(CH_2)_{11}S$, the monolayer of $FcCOO(CH_2)_{11}S$ prefers the orientation shown in Figure 2(b).

In this work, it has been shown that in the presence of $CH_3(CH_2)_{11}SH$, either from the beginning or afterwards of the monolayer formation, the ferrocene moiety of the $FcCOO(CH_2)_{11}S$ monolayer is pushed to the outer layer to make a room for $CH_3(CH_2)_{11}SH$.

Studies for the coadsorption of various alkanethiols with different chain lengths would clarify this further and are still in progress.

Acknowledgement. This work was supported by the 1998 Keimyung University Graduate Student Research Scholarship.

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