

# Study of the ferrocenylalkanethiol self-assembled monolayers by electrochemical surface plasmon resonance

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## Abstract

In this work, redox-induced orientation changes of self-assembled monolayers (SAMs) of 6-ferrocenylhexanethiol ( $\text{FcC}_6\text{SH}$ ) and 11-ferrocenylundecanethiol ( $\text{FcC}_{11}\text{SH}$ ) were studied by the in situ electrochemical surface plasmon resonance (ESPR). There existed two mechanisms concerning the redox-induced structure change of the self-assembled monolayer of ferrocenylalkanethiols. First, upon electrochemical oxidation of the ferrocene group, the swinging of the alkyl chain farther away from the electrode lead to the orientation changes of the monolayers; second, the flipping of the Fc cyclopentadiene ring around the bond between the Fc group and the alkyl chain, during the oxidation of the ferrocene group, can also contribute to the film structure changes. In order to further clarify the mechanism about the reorientation, the high resolution ESPR was used to investigate the redox reaction of ferrocene groups in this paper. The characters of the cyclic voltammograms and the SPR dip shift confirmed that the ferrocenylalkanethiols were immobilized onto the gold substrates. The difference of the SPR signal between the monolayers of  $\text{FcC}_6\text{SH}$  and  $\text{FcC}_{11}\text{SH}$  had proved that the first mechanism plays an important role. The influence of the scan rate on the peak currents and SPR signal had also been investigated.

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**Keywords:** Ferrocenylalkanethiol SAMs; Electrochemical surface plasmon resonance; Mechanism of orientation change; Redox-reaction

## 1. Introduction

Self-assembled monolayers (SAMs) of alkanethiols bearing different functional groups [1–6] have been widely used in studies of the intelligent modification of solid surface. Alkanethiol SAMs terminated with electroactive groups were considered to be ideal for understanding the fundamentals of the electron transfer (ET) process at an electrode/solution interface [7–16] and received a great deal of attention [7,17–28]. Among which the ferrocenylalkanethiol monolayer has been used as a model system to study the electrons exchange between ferrocenyl groups and gold electrodes, because of the simple and good electrochemical characters of the ferrocene groups. In order to investigate the ET mechanism more detailedly and to know the changes on the electrode surface during the ET, it is important to clarify the actual structure change of the prepared monolayers. There were many reports on the orientation/structural

change of the alkanethiol molecules (redox-induced orientation change [19,21,29–34]), which occurred during the redox reactions of the terminal groups. Uosaki and coworker, have systematically characterized the redox-induced orientation change of ferrocene (Fc)-terminated alkanethiol SAMs [29,30,34] with a wide range of surface techniques. Based on in situ infrared reflection absorption spectral peaks, Ye et al. suggested that the tilt angle of the alkyl chain would decrease with respect to the surface normal as the Fc groups were oxidized to the positively charged ferrocenium cations [29]. Such a reorientation is reasonable for alleviating the electrostatic repulsion among the adjacent ferrocenium cations and that between the ferrocenium cations and the positively charge electrode. While Viana et al. have carried out a similar voltammetric and infrared spectroscopic study and concluded that instead of a decrease of the tilt angle, the cyclopentadiene (Cp) ring of the Fc molecule would flip around the Fc–C bond at the end of the SAM. For comparison, the schemes of these two different routes are reproduced in Fig. 1. As can be deduced from the two schemes, the swing of the alkyl chain towards the surface normal would cause a different change in the SPR dip shift between different chains

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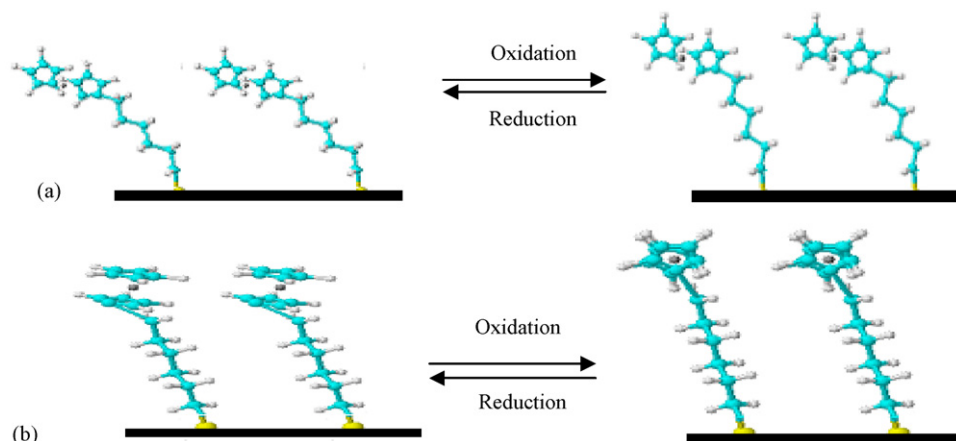


Fig. 1. The sketch of the two possible mechanisms concerning the orientation change of the 6-ferrocenylundecanethiol SAMs accompanying with the Fc oxidation. In (a) the electrostatic repulsion between the positively charged surface and the ferricenium cation and that among the cation led to a decrease in the tilt angle of the alkanethiol chain. In (b) upon Fc oxidation, the Fc group rotates from a tilted conformation to a position where the cyclopentadiene plane becomes perpendicular to the electrode.

length of the monolayers, but the flipping of the Cp ring would not.

In recent years, electrochemical surface plasmon resonance (SPR) has emerged as a powerful tool for investigating extremely small changes of various adsorbate films at the metal/solution interface [24,35–39]. The high-resolution surface plasmon resonance (SPR) spectrometer have already been homemade and used for the study of conformational and electronic changes of redox proteins [40] or for flow injection analysis to detect the DNA hybridization reactions at ultrasensitive level [41,42]. It was found that the electrochemical SPR (ESPR) can detect a change of as little as 0.05 nm for redox-induced cytochrome *c* film [40]. Moreover, with the flow injection SPR, an attomole quantities of oligonucleotide and polynucleotide adsorption onto surfaces can be quantified [41,42]. Such a remarkable sensitivity to surface adsorption or adsorbate structural change is attributing to the utilization of a bi-cell detector that can measure infinitesimal variation of the SPR dip shift associated with the surface processes. Since the orientation change caused by the oxidation of the terminal Fc groups of the SAMs is considered to be only in sub-nanometer range [18,29,34,43], the advantage of using such a highly sensitive SPR for addressing this problem becomes evident. In this work we have studied the SAM of  $C_6FcSH$  by ESPR. Electrochemical data were used to assess the packing and the degree of order of the monolayers, and in situ SPR was used to probe structural and orientational changes induced by the redox activity of the ferrocene end group, the influence of the hydrocarbon chain lengths of the monolayers have also been studied. The electrochemical reaction results indicated that the ferrocene have been immobilized onto the surface of the gold substrate and formed a relatively packing monolayers. If the mechanism is only due to the flip of the Fc cyclopentadiene ring around the bond between the Fc group and alkyl chain, as the second mechanism described, the SPR dip shift should be equal for the two SAM. In our work reported previously [44], we have quantified the thickness change of  $FcC_{11}SH$  SAMs during the redox reaction by ESPR and electrochemical quartz crystal

microbalance (EQCM). In this paper, the SPR signal of  $FcC_{11}SH$  and  $FcC_6SH$  are compared, which show that the SPR dip shift of  $FcC_{11}SH$  SAM is much bigger than that of  $FcC_6SH$  SAM during the redox reaction. Then the experiment results proved further that the orientation change of the SAM is due to the tilt angle of the alkyl chain, which would decrease with respect to the surface normal.

## 2. Experimental

### 2.1. Chemicals

6-Ferrocenylhexanethiol ( $FcC_6SH$ ) was synthesized as reported [27]. 11-Ferrocenylundecanethiol ( $FcC_{11}SH$ ) was obtained from Dojindo Co. (Atlanta, GA). 1-Hexanethiol was purchased from Acros organics (Belgium). Perchloric acid and hexane (Beijing Reagent Co.) were of reagent grade and used without further purification. The water treated by a purification system (Simplicity Plus, Minipore Inc.). All experiments were carried out in room temperature.

### 2.2. Instruments and electrodes

BK7 glass slides (Fisher) were heated in a piranha solution (30%  $H_2O_2$  and 70% concentrated  $H_2SO_4$ ) at 80 °C for 30 min (Note: This is dangerous cleaning solution, and care must be taken in solution handing). After cooled, the glass slides were thoroughly cleaned with water, then sonicated in the solution of  $H_2O:NH_4OH:30\% H_2O_2 = 5:1:1$  (v/v/v) for 60 min. After rinsed with water, the slides were stored in water before using. Before preparation of the gold substrate, the slides were dried by  $N_2$  steam. The gold substrate was obtained by evaporating 50-nm-thick gold on glass slides which had been previously coated with a 2 nm Cr layer by a sputtering coater (Model 108, Kert J. Lester Inc., Clairton, PA). The underlying Cr layer was used to improve the adhesion of gold to glass slides. The gold-coated glass slides were modified with  $FcC_6SH$  or  $FcC_{11}SH$ . An Ag/AgCl electrode

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