Direct Observation of Perchlorate Incorporation Induced by Redox Reaction of Ferrocene Terminated Self-Assembled Monolayer Studied by *in situ* FT-Surface Enhanced Raman Spectroscopy

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The incorporation of ClO_4^- into 8-ferrocenyloctanethiol (8FT) self-assembled monolayer (SAM) induced by the redox reaction at a gold wire electrode was demonstrated using *in situ* FT Raman spectroelectochemistry. Upon oxidation of the 8FT SAM, a band attributed to ClO_4^- was clearly observed and the band disappeared in its reduced state. On the other hand, when HNO_3 was used as a supporting electrolyte, the band attributed to NO_3^- was not observed in the oxidized form of 8FT.

For preparing functional modified electrodes, the surface electrochemistry of self-assembled monolayers (SAMs) of various thiols and sulfides on gold electrodes has been actively studied.[1] Ferrocene is one of most popular organic molecules exhibiting reversible electron transfer reactions. Recently, SAMs having ferrocene as a redox center have been studied using electrochemical and spectroelectrochemical techniques such as cyclic voltammetry,[2–6] FTIR,[4,6] and electrochemical quartz microbalance (EQCM)[5,6] to understand the mechanism of the redox reaction and surface properties of the SAM.

Shimazu et al. reported the structural changes and mass transport accompanying the redox reaction of a ferrocenylundecanethiol SAM using the *in situ* FTIR reflection absorption spectroscopy/EQCM combined system. They concluded that the uptakes of perchlorate anion and water molecule depended on the degree of packing extent of the SAM bearing ferrocene moiety.[6]

Surface enhanced Raman scattering (SERS) is one of the most powerful techniques to study the structure and structural change in the SAM induced by the redox reaction. Recently, we have reported that the structural change in SAMs of anthraquinone derivatives was controlled by the position of the butylsulfide moiety acting as an anchor to the substrate.[7] In addition, SERS can detect stretching bands of typical inorganic anions such as ClO_4^-, CO_3^{2-}, NO_3^-, and SO_4^{2-}, which are used as supporting electrolytes in electrochemistry.

In the present paper we report the uptakes of ClO_4^- induced by the redox reaction and structural changes in ferrocene terminated SAM using FT-SERS. It was reported that the uptake of ClO_4^- for the ferrocene terminated SAM using cyclic voltammetry[3] or EQCM,[6] however, direct detection of ClO_4^- complexed with the ferrocenium moiety in the SAM has not been reported to our knowledge.

8-Ferrocenyloctanethiol (8FT) was a kind gift of the Dojin Chemical Co. Ltd. (Kumamoto, Japan) and used without further purification. A gold rod (1 mm of diameter) polished with 0.3 µm Al_2O_3 powder was used as the working electrode. The surface was roughened by oxidation and reduction cycles (ORC) to make the surface active for SERS by potential scanning 40 times between –0.2 V and 1.2 V in a 0.1 M KCl aqueous solution.[7] A

platinum plate and Ag|AgCl (saturated KCl) electrodes were used as a counter and reference electrodes, respectively. FT Raman and SERS spectra were recorded with a Bio-Rad FTS-175c spectrophotometer equipped using a Raman accessory unit. The 1064 nm line of a YAG laser was used as the excitation line. Modification of the gold electrodes was made in a 100 µM 8FT ethanolic solution for 20 min. The electrodes were then rinsed with pure ethanol followed by pure water (Milli-Q) to remove any excess modifier. All measurements were carried out at room temperature (25 ± 1 °C) under an N_2 atmosphere.

Figure 1 shows the cyclic voltammograms of the 8FT SAM modified gold electrode. The redox potentials of 8FT in 0.1 M
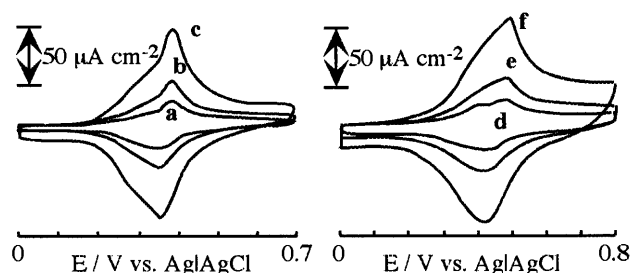

Figure 1. Cyclic voltammograms of Au electrodes modified with 8FT SAM in 0.1 M $HClO_4$ (a - c) and 0.1 M HNO_3 (d - f). Scan rates: 10 (a,d), 20 (b,e), 50 (c,f) mV s^{-1}.

$HClO_4$ and 0.1 M HNO_3 were 0.38 and 0.50 V, respectively. The redox potentials were independent of the scan rate up to 200 mV s^{-1} and the peak currents were proportional to the scan rate. Taking into account the roughness factor (4.1 ± 0.2) of the ORC treated electrode and the area occupied by one molecule of 8FT estimated from a space filling model, 8FT would form the monolayer under the conditions used. Surface coverage evaluated from the reduction wave of the voltammogram was $(6.1 ± 0.2) × 10^{-10}$ mol cm^{-2} and independent of the supporting electrolytes used. The difference in the redox potential was explained by the extent of the complexation of ferrocenyl moiety with anions used.[3]

Figure 2 shows the Raman spectra of 8FT in powder (a), 1.0 M $HClO_4$ (b), and SERS spectra of the 8FT SAM on a gold electrode in 0.1 M $HClO_4$ as a function of applied potential (c–g). As shown in Figure 2(a), a strong band at 1106 cm^{-1}, attributed to the breathing band of the cyclopentadienyl ring of ferrocene was observed. Also, another strong band at 320 cm^{-1}, corresponding to the stretching band of the Fe(II)-cyclopentadienyl ring,[9] was clearly seen. In Figure 2(b) a strong band at 933 cm^{-1}, attributed to Cl–O stretching band[9,10] was observed clearly. Since the Cl–O stretching band is inactive for the IR
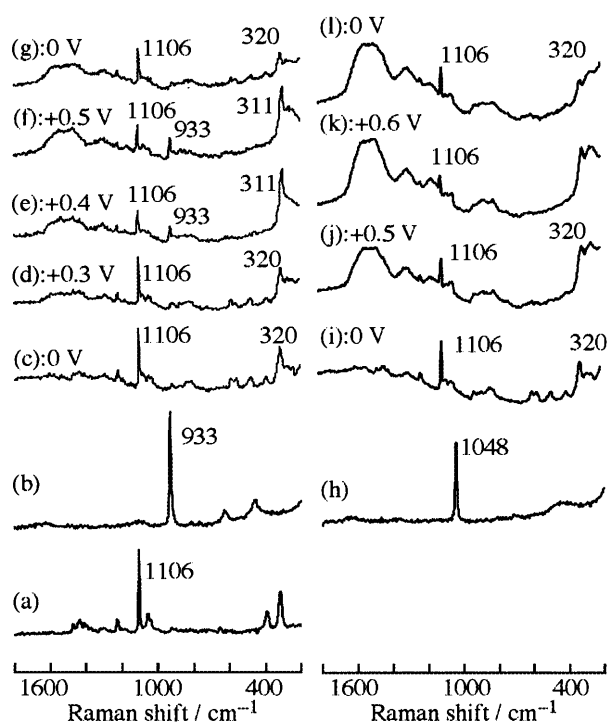
Figure 2. Raman spectra of 8FT in powder (a), 1.0 M HClO$_4$ (b), and 1.0 M HNO$_3$ (h) aqueous solutions, and *in situ* SERS spectra of Au electrodes modified with 8FT SAM in 0.1 M HClO$_4$ (c-g) and in 0.1 M HNO$_3$ (i-l). Potentials are indicated in the figure.

spectroscopy, the detection of the ClO$_4^-$ is one of the distinct features for Raman spectroscopy. As shown in Figure 2(c) a strong band at 1106 cm^{-1} and the band at 320 cm^{-1} were clearly observed, which indicates that the ferrocenyl moiety is reduced at 0 V. The SERS spectra were independent of the applied potential when the 8FT was reduced. Upon oxidation of 8FT (Figure 2(e,f)), pronounced changes in the SERS spectrum were seen. A new band appeared at 933 cm^{-1}, which corresponds to the Cl–O stretching band. This means that the uptake of the ClO$_4^-$ into 8FT SAM was induced by the redox reaction. Also, the band at 320 cm^{-1} shifted to 311 cm^{-1}, corresponding to the Fe(III)–cyclopentadienyl ring vibration,[9] which clearly exhibits that the oxidation of the ferrocene moiety of 8FT occurred at the potential. In addition, the band at 1106 cm^{-1} became weak in intensity, which suggests that a conformational change in the ferrocene ring took place or the average distance between the ferrocene moiety and the electrode surface in the oxidized form became longer than that in the reduced form as reported.[6] When the potential was back to 0 V, the ferrocene moiety was reduced, the band at 933 cm^{-1} disappeared, and the intensity at 1106 cm^{-1} recovered to that in the reduced state as shown in Figure 2(g). The electrochemical reaction and spectral change induced by the redox reaction were essentially reversible.

Similar experiments were done in a 0.1 M HNO$_3$ to see the effect of anions used. Figure 2(h) shows the Raman spectrum of 1.0 M HNO$_3$ and Figure 2(i–l) show the SERS spectra of the 8FT SAM in 0.1 M HNO$_3$ as a function of the applied potential. A strong band at 1048 cm^{-1}, attributed to the N–O stretching band[9,11] was clearly seen shown in Figure 2(h). The SERS

spectrum of 8FT in reduced form in HNO$_3$ (Figure 2(i)) was essentially identical to that in HClO$_4$. On the other hand, the SERS spectrum in oxidized form was different from that in HClO$_4$. At 0.6 V the ferrocene moiety of 8FT is oxidized since the redox potential of 8FT SAM in HNO$_3$ was 0.5 V (see Figure 1(d–f)). The band at 1048 cm^{-1} attributed to the N–O stretching band was never seen as shown in Figure 2(j–k). The intensity of the N–O stretching band was ca. 80% of that of the Cl–O band (compare Figures 2(b) and 2(h)). Therefore, if NO$_3^-$ forms a complex with the ferrocenium cation as ClO$_4^-$, the N–O stretching band should be observed at 1048 cm^{-1}. In the SERS spectrum of 8FT SAM at 0.4 V in the mixed solution of 0.1 M HNO$_3$ with 0.01 M HClO$_4$, a clear Cl–O band was still observed at 933 cm^{-1}. When aminooctanethiol (8AT) SAM (no ferrocene moiety but cationic) was used instead of 8FT SAM, the N–O stretching band at 1048 cm^{-1} and Cl–O stretching band at 933 cm^{-1} were clearly seen in the SERS spectra in 0.1 M HNO$_3$ and 0.1 M HClO$_4$, respectively. Also, the ClO$_4^-$ band for 8FT SAM in the oxidized form was higher than that for the 8AT. These results suggest that ClO$_4^-$ was selectively incorporated into the 8FT SAM in the oxidized form, the interaction between the ferrocenium cation and NO$_3^-$ was weaker than ClO$_4^-$, and the average distance between the electrode and the ClO$_4^-$ for 8FT SAM was shorter than that for 8AT SAM. We also tried H$_3$PO$_4$, and H$_2$SO$_4$ as a supporting electrolyte. But the bands attributed to the anions were never seen. So, the interaction between these anions and the ferrocenium cation of 8FT would be weak.

In conclusion, by *in situ* SERS measurements the incorporation of ClO$_4^-$ into 8FT SAM and the structural change in the ferrocenyl moiety were demonstrated. This method is useful technique to detect the inorganic or organic ions used as supporting electrolytes for SAMs.

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