Effects of Alkyl Chain as a Spacer on Electrochemical Reaction and SEIRA Spectra for Self-assembled Monolayers Having Anthraquinone Redox Center

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Self-assembled monolayers (SAMs) of 1-mercaptoanthraquinone (AQSC0), bis(3-(1-anthraquinonylthio)propyl)disulfide (AQSC3), and bis(6-(1-anthraquinonylthio)hexyl) disulfide (AQSC6), on a gold electrode were investigated by cyclic voltammetry and surface enhanced infrared absorption spectroscopy (SEIRAS). A redox wave was observed for all the anthraquinone (AQ) derivatives studied and the redox potential shifted *ca.* -60 mV pH^{-1} in the pH region from 1 to 7. The peak separation of the voltammograms depended on the spacer length of the AQ derivatives, and the heterogeneous electron transfer rates of AQSC0, AQSC3, and AQSC6 at pH 1 were 7.5, 2.3×10^{-1} , and $3.1 \times 10^{-3} \text{ s}^{-1}$, respectively. For the SEIRA spectra of AQSC0 and AQSC3, the C=O stretching and C-C stretching bands of the AQ ring are clearly observed, suggesting that the AQ ring plane is perpendicular or tilted to the electrode surface. The SEIRA signal of the AQ derivatives decreased with an increase in the alkyl chain length, indicating that the AQSC3 and AQSC6 molecules are adsorbed on the electrode not by the sulfide S atoms but by the thiolate S atoms.

Key Words : SEIRAS, Surface Structure, Anthraquinone, Self-assembled Monolayer (SAM)

1 Introduction

For preparing functional modified electrodes, the surface electrochemistry of self-assembled monolayers (SAMs) of various thiols, sulfides, and disulfides on gold or silver electrodes has been actively studied.¹⁾ The electrochemical reactions of SAMs having a quinone redox center, which is an important redox moiety in some enzymes and proteins, have been studied.²⁻⁷⁾ Recently, we reported the electrochemically-induced structural change of the SAMs of anthraquinone derivatives by *in situ* SERS.⁶⁾ Also, by *in situ* STM, a structural change due to the redox reaction was demonstrated for the bis(2-anthraquinonyl)disulfide modified Au(100)-(1×1) electrode.⁷⁾ Surface vibrational spectroscopies such as SERS and IR-RAS can provide detailed information about a molecule at an interface.⁸⁾ Recently, surface enhanced IR absorption spectroscopy (SEIRAS),⁹⁾ of which the S/N ratio is hundreds times higher than that of IR-RAS, has been developed and applied to study SAMs on a gold evaporated electrode.^{10,11)} Both SEIRAS and SERS are sensitive to the structure and structural change in the SAMs on electrodes, and the distance between the electrode surface and the molecule is one of the most important factors to determine the enhancement factors.⁸⁾ However, to our knowledge, no paper on the effect of a spacer for SEIRAS has been published.

In the present study, we report the effects of the alkyl chain length for the SAMs having an AQ moiety as the redox center on evaporated gold electrodes using SEI-

RAS and cyclic voltammetry.

2 Experimental

SEIRAS coupled with attenuated-total-reflection of the adsorbed anthraquinone derivatives on Au(111) surfaces was carried out using a Bio-Rad FTS-6000 FT-IR spectrometer with a HgCdTe (MCT) detector at the resolution of 4 cm^{-1} and a homemade spectroelectrochemical cell. Gold was evaporated at the rate of *ca.* $6.7 \times 10^{-3} \text{ nm s}^{-1}$ onto a basal plane of a semi-cylindrical silicon prism.⁹⁻¹¹⁾ The prepared gold thin film (*ca.* 20 nm thick) was used as the working electrode. A platinum plate and Ag|AgCl (saturated KCl) electrodes were used as the counter and reference electrodes, respectively. All potentials in this study are referred to the Ag|AgCl. A Toho Giken PS-06 potentiostat was used for the electrochemical measurements. All electrochemical and SEIRAS measurements were carried out at room temperature ($25 \pm 1^\circ\text{C}$) under a N_2 atmosphere. The E° was obtained from the midpoint of the reduction and oxidation peak potentials in the cyclic voltammograms. An 0.1 M ($\text{M} = \text{mol dm}^{-3}$) HClO_4 aqueous solution or a Britton-Robinson buffer solution were used as the electrolytes. Gold electrodes were modified by immersion in a AQ derivatives saturated ethanolic solution for 20 min. The electrodes were then rinsed with pure ethanol followed by pure water (Milli-Q) to remove any excess modifier.

1-Mercaptoanthraquinone (AQSC0), bis(3-(1-anthraquinonylthio)propyl)disulfide (AQSC3), and bis(6-(1-anthra-

quinonylthio)hexyl)disulfide (AQSC6) were synthesized by a previously reported similar methods.^{6, 7, 12)} The final products were analyzed by ¹H NMR (400 MHz), elemental analysis, and mass spectroscopy.

3 Results and Discussion.

Figures 1(a–c) show cyclic voltammograms of the AQSC0, AQSC3, and AQSC6 SAMs on gold electrodes in 0.1 M HClO₄ aqueous solution. All AQ SAMs showed a couple of redox waves and the peak currents were proportional to the scan rate (*i.e.*, the reaction is due to an adsorbed species). The surface excess evaluated from the cyclic voltammetric re-oxidation peak areas were 2.7 ± 0.3 , 3.0 ± 0.3 , and $3.5 \pm 0.3 \times 10^{-10}$ moles cm⁻² for AQSC0, AQSC3, and AQSC6, respectively. Taking into account the area occupied by one molecule of the anthraquinone ring estimated from a space filling model (0.5 to 0.6 nm² molecule⁻¹), the surface coverages of the AQ derivatives are a monolayer or submonolayer on the electrode. In the pH region from 1 to 7, all the voltammograms were stable for repeated scans. The redox potential (midpoint of the reduction and reoxidation peak potentials) changed with pH by *ca.* -60 mV pH⁻¹ for all AQ SAMs as shown in Fig. 1(d), suggesting the 2-electron-2-proton reaction like other quinone SAMs on gold^{3, 6)}:

where AQ and AQH₂ are the oxidized and reduced forms, respectively.

The peak separations for the AQSC0, AQSC3, and AQSC6 SAMs at a scan rate of 50 mV s⁻¹ were 30, 110, and 300 mV, respectively. The peak separation of the voltammogram is related to the electron transfer rate constant of adsorbed redox molecules:

$$\log k_s = \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha - \log(RT/nFv) - \alpha(1 - \alpha)nF\Delta E_p/2.3 RT^{13)} \quad (2)$$

Fig. 1 Typical cyclic voltammograms of (a) AQSC0, (b) AQSC3, and (c) AQSC6 SAMs on an Au/Si electrode in 0.1 M HClO₄. Scan rate was 50 mV s⁻¹ (d) Plots of *E*^o vs. pH. *E*^o were obtained from cyclic voltammograms of the AQ SAMs in B&R buffer solutions.

Table 1 Comparison of heterogeneous electron transfer rates for AQ derivatives SAM in pHs 1,3,5 and 7 solutions.

AQ derivatives	<i>k</i> ^o /s ⁻¹ a)			
	pH 1	pH 3	pH 5	pH 7
AQSC0	7.5	3.0	1.4×10^{-1}	7.9×10^{-1}
AQSC3	2.3×10^{-1}	1.0×10^{-1}	8.6×10^{-2}	3.9×10^{-2}
AQSC6	3.1×10^{-3}	5.4×10^{-4}	1.3×10^{-3}	2.6×10^{-3}

a) Calculated using Laviron's equations assuming $\alpha = 0.5$.

where *k*_s, Δ*E*_p, and *v* represent the electron transfer rate constant, a peak separation in volts, and a scan rate in volts, respectively. α is a transfer coefficient. *R*, *T*, *n*, and *F* represent usual meanings. Table 1 shows the electron transfer rates of the AQ SAMs in various pH solutions calculated from eq. (2), assuming $\alpha = 0.5$. Although the authors will not go into the detail concerning the electron transfer theory, the distance between the electroactive species and the electrode surface is one of the important factors to determine the rate. Here, we would like to emphasize that for the evaluated AQ SAMs, the alkyl chain length significantly affected the electron transfer rate. All pH regions studied (pH 1 to 7), the electron transfer rates of AQSC6 were smaller by three orders of magnitude than those of AQSC0. AQSC0 has just one thiol group, therefore, it is quite reasonable that the AQSC0 was adsorbed by its thiolate group. On the other hand, AQSC3 and AQSC6 have sulfide groups and a disulfide group in one molecule and both groups are active on the gold surface.¹⁴⁾ Indeed, in our previous paper, we reported⁶⁾ that the sulfide group of the AQ derivative acted as the anchor to the electrode. For the 1-anthraquinonylbutylsulfide and 2-anthraquinonylbutylsulfide SAMs, where these molecules were fixed to the electrode via their sulfide moiety, the peak separations of the voltammograms were very similar values to that of AQSC0. If the AQSC3 and AQSC6 molecules adsorbed on the electrode at the sulfide S atoms, the electron transfer rate would be independent of the chain length. However, the electron transfer rate is strongly dependent on it. Therefore, for AQSC3 and AQSC6, only the thiolate group produced by the dissociation of the disulfide

Fig. 2 Typical SEIRA spectra of (A) AQSC0, (B) AQSC3, and (C) AQSC6 SAMs on an Au/Si electrode in 0.1 M HClO₄ at different potentials, together with FT-IR spectra of the samples dispersed in KBr.

group¹⁴⁾ acted as the anchor to the electrode surface, which indicates that the AQ moiety is located away from the electrode surface by the alkyl chain.

In order to understand in detail the surface structure of these AQ SAMs on the electrode and their structural change induced by the redox reaction, the *in situ* electrochemical SEIRA spectra of the AQS SAMs on gold were measured.

Figure 2(a) shows the SEIRA spectra of the AQSC0 SAM in a 0.1 M HClO₄ solution as a function of the applied potential. The redox potential of AQSC0 on gold in the solution is -0.15 V. When 0.2 V is applied to the electrode, AQSC0 is oxidized, and a strong band at 1668 cm⁻¹, corresponding to the C=O stretching (*b_{1u}* mode),⁵⁾ was observed. The strong bands at 1324 cm⁻¹ and 1274 cm⁻¹, which are assigned to the C-C stretching mode (*b_{2u}* mode),⁵⁾ were also observed. SEIRA can observe the vibration mode perpendicular to the surface due to its selection rule. The observation of the bands attributed to the in-plane stretching of the AQ ring, indicated that the AQ ring plane would be relatively perpendicular to the electrode surface. The spectrum did not change between 0.2 and -0.1 V. Upon the reduction of the AQSC0 SAM at -0.15 V, the bands at 1668, 1324, and 1274 cm⁻¹ became weak and a new band at 1373 cm⁻¹ appeared. When -0.3 V was applied, the bands at 1668, 1324, and 1274 cm⁻¹ disappeared.

Figure 2(b) shows the SEIRA spectra of AQSC3 SAM in a 0.1 M HClO₄. At 0.2 V, where AQSC3 is oxidized, strong bands at 1669 cm⁻¹, corresponding to the C=O stretching (*b_{1u}* mode),⁵⁾ were observed. The strong bands at 1339, 1325, and 1276 cm⁻¹, which are assigned to the C-C stretching mode (*b_{2u}* mode),⁵⁾ were observed. Apparently, the SEIRA spectrum of AQSC3 is similar to that of AQSC0, however, the SEIRA signal of the AQSC3 assigned to the in-plane stretching bands was less than half of the AQSC0 signal. Upon the reduction of the AQSC0 SAM at -0.15 V, the bands at 1669, 1339, and 1276 cm⁻¹ became weak. When -0.3 V was applied, the AQSC0 was reduced completely. The bands at 1668, 1324, and 1274 cm⁻¹ disappeared and a new band at 1371 cm⁻¹, which is not assigned yet, appeared.

Figure 2(c) shows the SEIRA spectra of the AQSC6 SAM in 0.1 M HClO₄. The weak bands at 1669, 1339, and 1227 cm⁻¹ were observed at 0.2 V, where AQSC6 is oxidized (see Fig. 1(c)). Upon the reduction of AQSC6 at -0.4 V, a very weak band at 1372 cm⁻¹ appeared. Here, the bands are relatively broader than those of AQSC0 and AQSC3, which suggest that the AQ moieties of the AQSC6 SAM are randomly oriented.

For all the AQ derivatives SAMs studied here, the spectral change is fairly reversible for the repeated potential steps and the bands attributed to the in-plane stretching mode disappeared when the AQ moiety was reduced. The change in the orientation of the AQ plane induced by the reduction would be one of the reasons. In order to discuss the structural change induced by the redox reaction, the spectra of the isotropic AQ derivatives in the reduced form are needed. We are trying to take the spectra of the isotropic reduced AQ derivatives. The

Fig. 3 Possible orientations of (a) AQSC0, (b) AQSC3, and (c) AQSC6 SAMs on an Au/Si electrode. The AQSC0 was adsorbed on the electrode by the thiolate S atoms, while the AQSC3 and AQSC6 were adsorbed not by the sulfide S atoms but by the thiolate S atoms.

absorbance in the SEIRA spectra of a molecule depends on the surface coverage, orientation, enhancement factor, vibrational modes, and surface morphology.⁹⁾ As described earlier, the surface coverage of the AQ moiety of AQSC6 was higher than those of AQSC0 and AQSC3, however, the absorbances attributed to the in-plane stretching mode of the AQ ring of the AQSC6 SAM are considerably smaller than those of AQSC0 and AQSC3. The reason may be the distance between the AQ ring and the electrode surface, since the other factors are essentially identical. This result also suggests that the AQ moiety of AQSC6 would be widely separated from the electrode surface by the alkyl chain.

Taking into account the heterogeneous electron transfer rates and SEIRA spectra, the possible surface structures of AQSC0, AQSC3, and AQSC6 in the oxidized forms on gold are shown in Fig. 3. Because the bands assigned to the out-of-plane of the AQ ring were not clearly observed, the authors did not describe the precise configuration of the AQ ring. Here, the AQSC0 adsorbs the surface at the thiolate S atoms. On the other hand, AQSC3 and AQSC6 are fixed with the thiolate S atoms and AQ moieties located away from the electrode surface by the alkyl chain.

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