Communications

Electrochemical Evaluation of Electron Tunneling Constant in Self-Assembled Monolayer of ω-Mercaptoalkylhydroquinone on Gold

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Self-assembled monolayers (SAMs) on electrode surface are attractive as model systems for studies of interfacial electron transfer[1] because they are stable and structurally well-defined interfacial monolayer with a controllable thickness and desirable function. This characteristics of SAMs affords an opportunity to study fundamental issues such as the effects of distance and interfacial structure on the long-range electron transfer kinetics between a redox active species and an electrode. The first direct information on electron-tunneling distance relationship was obtained for reduction of penta-amine-cobalt(III) complexes anchored to gold and mercury surface by Weaver and Li.[2] After Chidsey[3] reported heterogeneous electron transfer rates and electron tunneling constant (β) for the ferrocene-terminated alkanethiol monolayers with different alkyl chain length, a number of groups have reported β values for SAMs containing redox couples such as pentaamine (pyridine) ruthenium complex,[4] osmium bipyridyl complex,[5] viologen,[6] naphtoquinone,[7] and azobenzene.[8]

In this communication, we report the determination of the electron tunneling constant for long range electron transfer in the ω-mercaptoalkylhydroquinone SAMs on gold electrode. The electrochemical properties of the hydroquinone/quinone derivatives in solution have been extensively studied because of their important biological activities over a few decades.[9] Several groups including Hubbard and Soriaga and coworkers,[10,11] and Uosaki[12] have investigated the electrochemical behaviors of various quinone and mercaptohydroquinone derivatives adsorbed on metal surface. However, up to date, there has been no experimental data regarding electron tunneling constant of H_2Q-terminated SAM. In order to investigate distance dependence of electron transfer kinetics in hydroquinone (H_2Q) SAM, we have synthesized three derivatives of H_2Q with different spacer chain lengths, which were denoted as $H_2Q(CH_2)_nSH(n = 4, 8,$ and $12)$.

Figure 1 shows the typical cyclic voltammograms (CVs) for the spontaneously adsorbed $H_2Q(CH_2)_nSH(n = 4, 8,$ and 12) self-assembled monolayers on gold electrode, where the supporting electrolyte is aqueous 0.1 M $HClO_4$. These redox wave shapes are not changed to continuous potential cycling over 2 h period at room temperature, demonstrating that H_2Q-terminated monolayers are chemically and thermodynamically stable in acidic solution. As expected for the voltammetric behavior of the surface-confined redox centers,[13]

the redox peak currents for all of these H_2Q monolayers are linearly proportional to scan rate up to 10 V·s^{-1} (hired in this study). This indicates that the electroactive H_2Q monolayers were prepared in reproducible pattern. In each voltammogram, a pair of redox peaks was observed due to the oxidation and reduction of hydroquinone which follows a two-electron and two-proton transfer reaction mechanism. For the $H_2Q(CH_2)_4SH$ SAM shown in Figure 1(a), a quasi-reversible redox wave was observed and the peak-to-peak separation (ΔE_p) value was ca. 90 mV, suggesting a relatively fast electron transfer reaction kinetics. However, the value of ΔE_p in $H_2Q(CH_2)_{12}SH$ SAM becomes remarkably larger to ca. 540 mV (shown in Figure 1(c)) as the number of methylene groups (-CH_2-) within spacer chain is increased to twelve. As the alkyl chain length becomes longer, the electron transfer from the electrode to the redox center is forced to proceed at a larger distance, slowing the overall rate. The CVs in Figure 1(a-c) clearly demonstrate that the heterogeneous electron transfer kinetics of hydroquinone in SAM is dramatically transformed from reversibility to quasi-reversibility due to the longer spacer chain length in acidic condition. The faradaic charges estimated by the integration of redox peak area yield surface coverage values of $(4.5-5.6) \times 10^{-10}$ mole·cm^{-2}. These values are quite close to a coverage (5.7×10^{-10} mole·cm^{-2}) of full monolayer which was determined from the adsorption of 2,5-dihydrox-
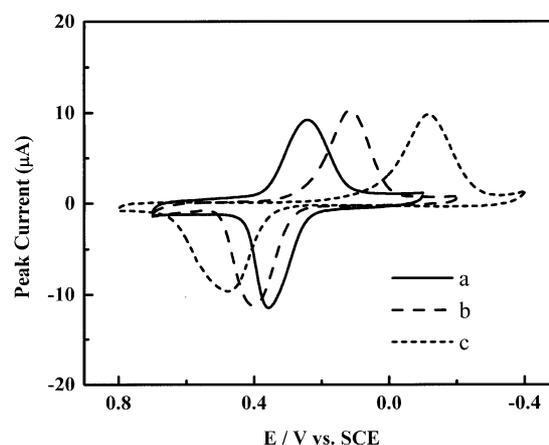

Figure 1. Cyclic Voltammograms of $H_2Q(CH_2)_nSH$ self-assembled monolayers on gold (a-c for n = 4, 8, and 12) in 0.1 M $HClO_4$. Scan rate was 100 mV·s^{-1}.

ythiophenol (H_2QSH) on gold.[11] For the H_2Q-SAMs on gold electrode, we also found that the surface coverage of hydroquinone increases with the spacer chain length increasing. This fact implies the packing structure of a hydroquinone monolayer on the electrode surface becomes more ordered with longer alkyl chain spacer.

With a view to evaluating electron tunneling constant, we have investigated the electron transfer kinetics for hydroquinone redox centers in $H_2Q(CH_2)_nSH$ SAMs by cyclic voltammetry. According to Laviron's procedure,[14] the standard rate constant and the electron transfer coefficient can be determined by measuring variation of peak potential splitting (ΔE_p) with scan rate *under totally irreversible condition*. Using this procedure, the obtained anodic and cathodic apparant rate constants (k_{app}) and their average values were plotted for each hydroquinone SAM of three different alkyl chain length in Figure 2.

The electron tunneling constant can be easily obtained from the slope of the plot of the logarithmic average value of k_{app} vs. the number of methylene group of $H_2Q(CH_2)_nSH$ SAMs on gold. The average slope in the plot shown in Figure 2 gives the β value of $0.92(\pm 0.11)$ per CH_2 unit using the number of methylene within alkyl chain spacer instead of absolute distance (Å) in our system. The difference between the anodic and cathodic apparent rate constant values might be due to asymmetric transfer coefficient values. Unlike the anodic transfer coefficient values, the obtained cathodic transfer coefficient value is slightly smaller than unity in hydroquinone monolayer with a relatively long alkyl chain spacer. It may be due to a small change in the cathodic formal potential of hydroquinone, which slightly changes with the spacer chain length in the monolayer. However, the sum of cathodic and andic transfer coefficient values is quite close to 2 (*i.e.*, the number(n) of transferred electron in the redox reaction of hydroquinone) in all hydroquinone SAMs.

Up to date, several reports on the determination of β value
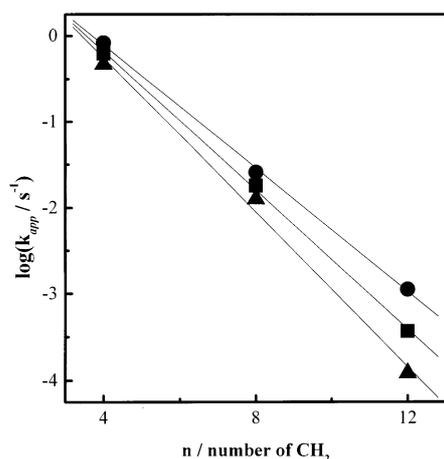
Figure 2. Distance dependence of log (k_{app}/s^{-1}) on the number of CH_2 group involved in the alkyl chain spacer of $H_2Q(CH_2)_nSH(n = 4, 8,$ and 12) SAMs on gold. The slope(β) values estimated from the cathodic (●), anodic (▲) and their average (■) apparent rate constants were determined to be 0.81, 1.03, and 0.92 per CH_2 unit respectively.

are available for only a few different electroactive SAM systems. The experimental β value of (0.92 ± 0.11) for our hydroquinone SAMs seems to be compatible with the value of $\beta - 1.06$ for ferrocene-SAM studied by Chidsey,[3] the value of $\beta - (1.06 \pm 0.04)$ for mixed SAM prepared with $Ru(NH_3)_5Py$ and diluent alkanethiols measured by Finklea,[4] and the values of β measured for nonelectroactive SAM systems with redox couples in solution: 0.90 for aqueous $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$, and $Fe^{3+/2+}$ with ω-hydroxyalkylthiol films,[15] and (1.02 ± 0.2) for aqueous $Fe(CN)_6^{3-/4-}$ and $Fe^{3+/2+}$ with alkanethiol films.[16]

Currently, we are investigating the effects of pH, temperature, solution, surface coverage, spacer chain length, and coadsorption with diluent thiols on the heterogeneous electron transfer kinetics for hydroquinone-SAM system.

The electrochemical measurements were carried out in a single compartment cell with home-made Au bead electrode as working electrode, platinum counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. Voltammetric experiments were performed with the use of a BAS 100B/W Potentiostat controlled by a HP 586 personal computer and a BAS 100B/W software package. The electrolyte solutions were prepared with deionized water purified to a resistivity of 18 MΩ/cm with UHQ II system (Elga) and deaerated by purging with nitrogen. All measurements were carried out at room temperature. The homolog series of $H_2Q(CH_2)_nSH(n - 4, 8,$ and 12) were synthesized according to the procedure reported by Hickman[17] *et al.*

The Au bead electrodes (*ca.* 2.1-2.4 mm diameter) was cleaned by immersion for 10 min in a "piranha" solution (3 : 1 mixture of concentrated H_2SO_4 and 30% H_2O_2) prior to use. After rinsing with deionized water, the Au electrode was cycled electrochemically in 0.5 M H_2SO_4 between -0.30 and 1.20 V *vs.* SCE until the typical cyclic voltammogram of clean gold was obtained. After rinsing with deionized water, ethanol and drying with nitrogen gas blowing, the gold electrode was immersed in 1 mM ethanol solution of H_2Q-$(CH_2)_nSH$ for 2-5 h. The electrode was rinsed with fresh ethanol and deionized water and then used for voltammetric studies.

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