Electrochemical Behavior of the Naphtoquinone Anchored onto a Gold Electrode through the Self-Assembled Monolayers of Aminoalkanethiol

Fumihiko Mukae, Hiroyuki Takemura, and Kô Takehara*

Department of Chemistry, Faculty of Science, Kyushu University, 4-2-1, Ropponmatsu, Chuo-ku, Fukuoka 810

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2,3-Dichloro-1,4-naphtoquinone (NQ) was anchored to a gold electrode surface through the self-assembled monolayers of aminoalkanethiols (AAT, $HS(CH_2)_nNH_2$: $n=2$, 5, and 8). The effect of the alkyl chain length of the AAT monolayer, which also acts as the spacer between the NQ molecule and the gold electrode surface, on the redox behavior of the immobilized NQ has been studied by using a voltammetric technique. The surface coverage of the anchored NQ was estimated to be 3.8×10^{-10} mol cm^{-2} in the case that 2-aminoethanethiol ($HS(CH_2)_2NH_2$) was used as the monolayer constituent. The electron-transfer rate constant, k_{et}, associated with the redox process of anchored NQ decreased from 9.7 s^{-1} at $n=2$ to 0.78 s^{-1} at $n=8$, with increasing the chain length of the AAT monolayer, though the redox potential of NQ was scarcely affected by the chain length. The tunneling barrier coefficient, β, of the electron transfer was estimated to be 0.36 Å^{-1}, from the observed linear relationship between the k_{et} value and the monolayer chain length.

Spontaneous adsorption of long-chain alkanethiols from solution onto gold surface has proven a convenient means for producing well-defined, structurally organized monolayers, known as self-assembled monolayers.[1—5] As reviewed by Xu and Li,[6] recent efforts in this area has been concentrated on the potential applications of this technique for new functional monolayers ranging from microfabrication technology to biological model systems.[7—11] The immobilization of redox active species onto a monolayer surface is one of the major attempts in this field to control the electron-transfer rate between the redox site and electrode surface separated by a self-assembled monolayer.[12—15] In connection with the electron transfer mechanism across biomembranes, Katz demonstrated that the biologically important quinone unit can be immobilized onto a gold surface through the self-assembled monolayer of aminoethanethiol.[16] As is well known, quinone plays a very important role in the charge transfer processes in the biological system. Therefore, it is worthwhile to make clear the redox characteristics of the quinone unit by controlling the charge transfer distance. However, there have been no quantitative analysis on the effect of the separation distance between the redox site and electrode surface on the electron-transfer rate for the anchored quinone unit.

In the present work, we prepared several aminoalkanethiols having different alkyl chain lengths and modified them onto a gold surface by the self-assembling method. Then the NQ molecules were linked to the terminal amino unit of the aminoalkanethiol monolayer assembly. The mechanism of the charge transfer between the anchored NQ molecule and gold surface is discussed in relation to the chain length of the monolayer assembly.

Experimental

2,3-Dichloro-1,4-naphtoquinone (NQ) and 2-aminoethanethiol (AET, $HS(CH_2)_2NH_2$) were purchased from Tokyo Kasei Co. and used as supplied. All inorganic chemicals used were of analytical reagent grade and were used without further purification. 5-Amino-1-pentanethiol (APT, $HS(CH_2)_5NH_2$) and 8-amino-1-octanethiol (AOT, $HS(CH_2)_8NH_2$) were synthesized in a way similar to that described previously.[17]

The modification of NQ on a gold electrode was done in the following way. A gold disk electrode (BAS Inc., 1.6 mm diameter) was polished with 0.05 μm alumina slurry on a felt pad (Buhler, Illinois), sonicated in distilled water, and air-dried. Then the electrode was immersed in ethanolic solution of 0.01 M (1 M = 1 mol dm^{-3}) AAT for 30 min to form the self-assembled monolayer of AAT on the gold electrode.[18] The gold electrode modified with the AAT monolayer (AAT/Au) was rinsed thoroughly with ethanol and then soaked in refluxing ethanol solution of 0.01 M NQ, to immobilize the NQ molecule through the terminal amino unit. Finally the NQ-modified electrode (NQ-AAT/Au) thus obtained was rinsed, first with ethanol and then with distilled water, and used for the voltammetric measurement.

Voltammetric measurements were performed by using a Fuso Model 312 Polarograph with a Fuso Model 321B potential sweep unit. Cyclic voltammograms (CVs) were recorded on either a Riken Denshi F-5C X–Y recorder or a Yokogawa Model 3655 digital recorder. The NQ-AAT/Au electrode, an Ag/AgCl/3 M NaCl (aq) and a platinum wire were used as the working electrode, the reference electrode and the counter electrode, respectively. All potential values were reported versus the Ag/AgCl reference electrode. All the measurements were done in deoxygenated aqueous solution containing 0.1 M KCl as the supporting electrolyte and at 25±0.5°C. The pH of the electrolyte solution was adjusted by Britton–Robinson buffer.

To confirm the reproducibility of the voltammetric response, the preparation of the NQ-AAT/Au electrode and the voltammetric measurement were repeated at least three times for all of the experimental conditions examined. Although the voltammetric peak current was somewhat distributed from measurement to measurement, essentially the identical peak potential was observed for the

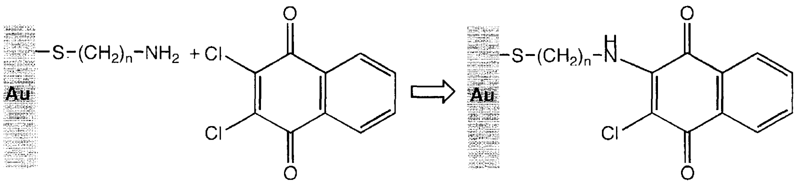

Fig. 1. Schematic illustration of the NQ immobilization to the self-assembled AAT monolayer formed onto a gold surface.

same type of modified electrodes.

Results and Discussion

The Reaction Mechanism and the Surface Coverage of NQ-AAT/Au. Long-chain alkanethiols have been known to form a stable self-assembled monolayer on a gold surface.[1] As reported by Katz and Solov'ev,[16] on the other hand, redox active NQ unit can be modified on the amino-terminated monolayer surface in the scheme shown in Fig. 1. In this case, the AAT molecule acts as an anchor for the NQ molecule and therefore the distance of the NQ molecule from the gold surface can easily be controlled by changing the alkyl chain length of the AAT monolayer.

Figure 2 shows the CVs of the NQ-AAT/Au electrodes having different chain lengths of the AAT monolayer. At the potential scan rate of 0.1 V s^{-1}, the change of the monolayer chain length scarcely affected the peak potential of the anchored NQ, though the peak current decreased with increasing the chain length. Figure 3 shows the dependence of the surface coverage of the immobilized NQ molecules (Γ_{NQ}) on the soaking time of the AET/Au electrode in ethanolic

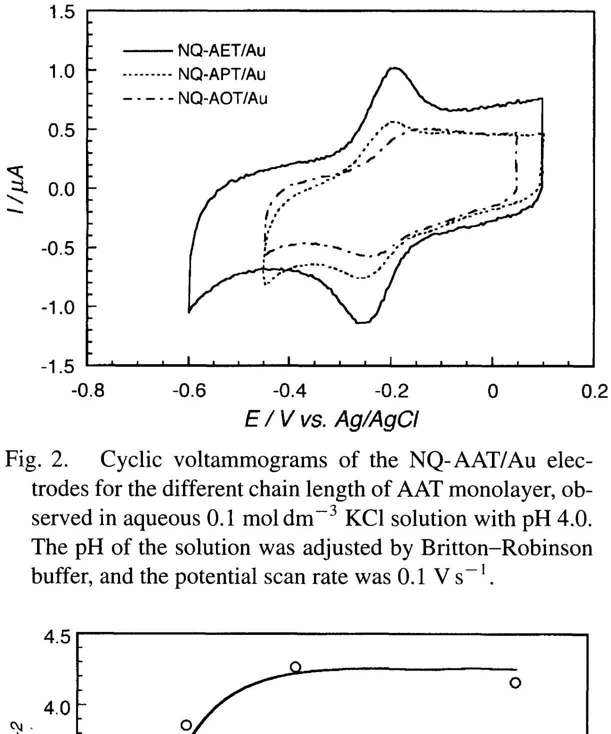

Fig. 2. Cyclic voltammograms of the NQ-AAT/Au electrodes for the different chain length of AAT monolayer, observed in aqueous 0.1 mol dm^{-3} KCl solution with pH 4.0. The pH of the solution was adjusted by Britton–Robinson buffer, and the potential scan rate was 0.1 V s^{-1}.

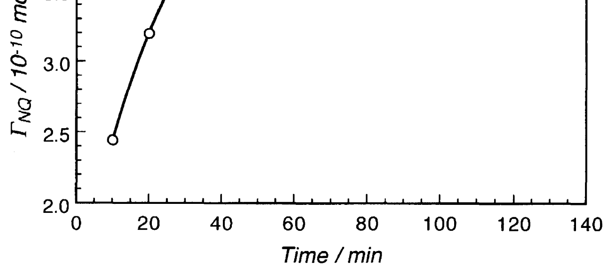

Fig. 3. Plot of the surface concentration of NQ, Γ_{NQ}, as a function of an adsorption time, t, obtained for the NQ-AET/Au electrode. The Γ_{NQ} values were calculated by the graphical integration of the voltammetric cathodic peak current.

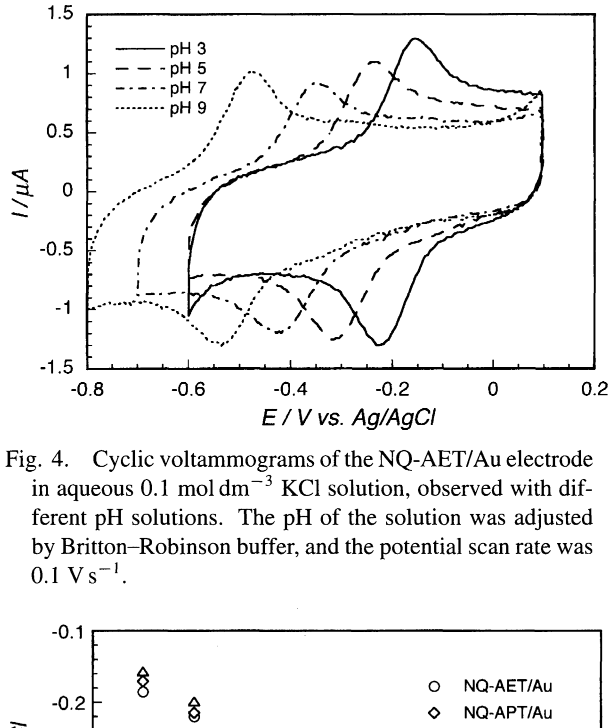

Fig. 4. Cyclic voltammograms of the NQ-AET/Au electrode in aqueous 0.1 mol dm^{-3} KCl solution, observed with different pH solutions. The pH of the solution was adjusted by Britton–Robinson buffer, and the potential scan rate was 0.1 V s^{-1}.

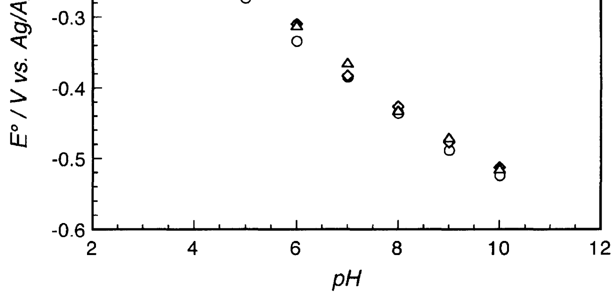

Fig. 5. Plot of the formal potentials, E°, of NQ-AAT/Au electrodes as a function of solution pH. The E° values were obtained as the midpoint potential between the anodic and cathodic peak potentials.

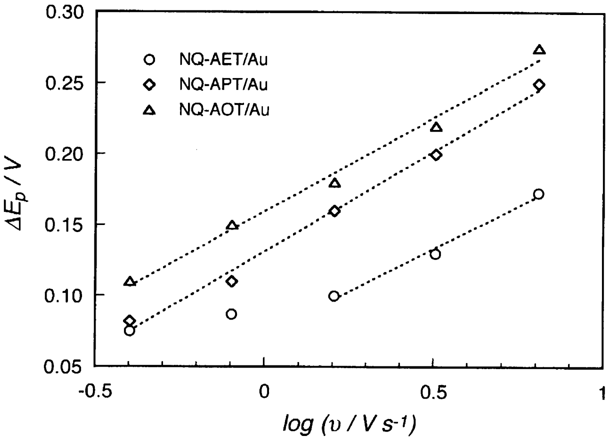

Fig. 6. Plot of the peak-to-peak separations, ΔE_p, as a function of logarithmic values of scan rates, $\log v$, obtained at pH 4.0. The ΔE_p values were obtained as the potential difference between the anodic and cathodic peaks, $\Delta E_p = E_{p,a} - E_{p,c}$.

NQ solution. In this figure, the Γ_{NQ} value was estimated by the graphical integration of the cathodic peak current of NQ, by assuming the two-electron- and two-proton-transfer reaction to form a hydroquinone, $NQ + 2e^- + 2H^+ \rightarrow NQH_2$, where NQH_2 is the hydroquinone form of the NQ. This assumption is supported by the pH dependence of the formal potential (E°) of the anchored NQ, as shown in Fig. 4 and summarized in Fig. 5. For all of the NQ-AAT/Au electrodes examined, the value of the $\partial E^\circ/\partial \mathrm{pH}$ slope was obtained to be -0.052 ± 0.002 V in the pH range between 3 and 10. This $\partial E^\circ/\partial \mathrm{pH}$ slope is close to the theoretical value of -0.059 V for the $2e^- + 2H^+$ process, and the slight deviation is probably caused by the incomplete electrochemical reversibility of the redox process, as also reported by Katz.[16)]

The limiting Γ_{NQ} value was achieved after 60 min soaking time, as shown in Fig. 3 for the case of NQ-AET/Au. The saturated surface coverage of the NQ-AET/Au was obtained to be $\Gamma_{NQ} = 3.8 \times 10^{-10}$ mol cm^{-2}, which corresponds to a molecular area of 44 Å^2 per NQ molecule. By taking into account the roughness factor of 1.44 reported for a polished gold surface, the obtained molecular area is about two times larger than the calculated area of ca. 26 Å^2 for the close-packed NQ molecules orientated perpendicular to the electrode surface.[19)] From these results, we concluded that the surface coverage of the NQ on the AET/Au is nearly a full coverage but less than for a close-packed monolayer. In the cases of NQ-APT/Au and NQ-AOT/Au, the limiting Γ_{NQ} values decreased to 8.02×10^{-11} mol cm^{-2} and 2.73×10^{-11} mol cm^{-2} for NQ-APT/Au and NQ-AOT/Au, respectively. Although the limiting Γ_{NQ} value decreased with increasing the alkyl chain length, the soaking time required to reach the limiting Γ_{NQ} value was not affected by the chain length. Therefore, we applied the soaking time of 60 min to immobilize the NQ molecules on an AAT/Au electrode. On the other hand, the voltammetric response of the NQ-AAT/Au scarcely changed for several days when the NQ-AAT/Au electrode was stored in distilled water.

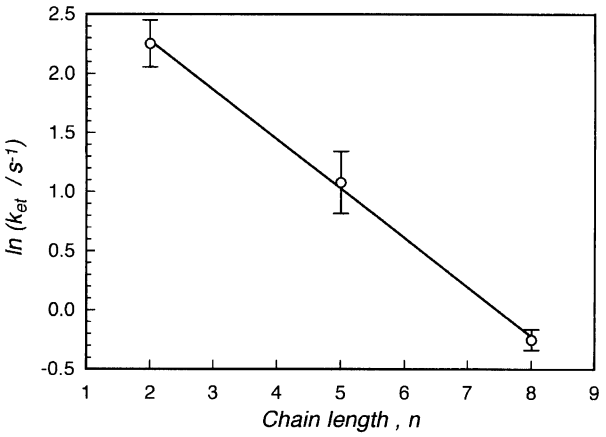

Fig. 7. Plot of the logarithmic value of rate constant, $\ln k_{et}$, as a function of the alkyl chain length of the AAT monolayer, n. The k_{et} values were estimated from the ΔE_p values in Fig. 6, by using Laviron's equation.

The Effect of the AAT Monolayer Chain Length on the Kinetics of the Electrode Process. The dependence of the voltammetric response on the potential scan rate v was measured to obtain the kinetic information on the effect of monolayer chain length on the electrode process of NQ. As shown in Fig. 6, the peak-to-peak separation ($\Delta E_p = E_{p,a} - E_{p,c}$) between the anodic peak potential ($E_{p,a}$) and cathodic peak potential ($E_{p,c}$) of the immobilized NQ molecule increased linearly with $\log v$, except in the case of NQ-AET/Au at lower potential scan rates. In the CVs of NQ-AET/Au at lower scan rates, the deviation from the linear dependence can be ascribed to the increasing electrochemical reversibility of the redox process of the anchored NQ unit. At the same potential scan rate, on the other hand, the ΔE_p value increased with increasing the monolayer chain length, indicating the decrease of the electrochemical reversibility with increasing the monolayer chain length. In spite of the change of the ΔE_p, the formal potential E° obtained as $E^\circ = (E_{p,a} + E_{p,c})/2$ was scarcely affected by the potential scan rate, for the all of NQ immobilized electrodes examined. The absence of change of the E° value is due to the fact that the values of the electron-transfer coefficients α_a and α_c for anodic and cathodic processes are similar ($\alpha_a \approx \alpha_c \approx 0.5$).

Form the observed linear dependence of the ΔE_p value on $\log v$, the electron-transfer rate constant k_{et} associated with the redox process of the immobilized NQ molecule was estimated by using Laviron's equation, which was derived for the electrode process of adsorbed species.[20,21)] Based on this analysis, the dependence of the peak-to-peak separation ΔE_p on the potential scan rate v is written, assuming $\alpha_a = \alpha_c = 0.5$, as

$$\Delta E_p = \frac{4RT}{2.303nF} \log \left(\frac{nF}{2RTk_{et}} |v| \right) \tag{1}$$

where n is the number of electrons transferred in one electron-transfer. The k_{et} value was obtained from the best fitted line of the ΔE_p versus $\log v$ plot in Fig. 6. Figure 7 shows the plot of the $\ln k_{et}$ value as a function of the alkyl chain length of the AAT monolayer. The observed $\ln k_{et}$ slope of -0.42 per unit methylene group corresponds to the slope of -0.36 per unit angstrom increase of the monolayer thickness, if one uses the reported value of 1.25 Å for the increase of monolayer thickness with the addition of each methylene group.[1,3,22]

The effect of the separation distance between redox site and electrode on the electron-transfer rate is predicted by the Marcus model as Eq. 2 and Eq. 3 in simplified forms,[23,24] where k_0 is the electron-transfer rate constant at closest approach, β is the tunneling barrier coefficient, r is the distance of the redox unit from the electrode surface, Z is the pre-exponential factor including collision number, and ΔG° and λ are the standard free energy change and the reorganization energy, respectively, associated with the electron-transfer process.

$$k_{\mathrm{et}} = k_0 \exp(-\beta r) \tag{2}$$

and

$$k_0 = Z\exp[-(\Delta G^\circ + \lambda)^2/4RT\lambda] \tag{3}$$

The ΔG° value of the anchored NQ is not changed by the monolayer chain length, as reflected by their similar redox potentials. The observed linear dependence of the $\ln k_{\mathrm{et}}$ value on the monolayer chain length indicates the similar λ values for all NQ-AAT/Au electrodes, and therefore it also indicates that the distance of the NQ unit from the gold surface is well controlled by the AAT monolayer assemblies. The β value was estimated to be 0.36 Å^{-1}, from the observed $\ln k_{\mathrm{et}}$ slope of -0.36. This value of the electron-tunneling barrier coefficient is somewhat smaller than the majority of the reported values in which β values range from 0.5 to 1.4 Å^{-1}.[13,15,22,25] However, most of these reported values were obtained with alkyl chain monolayers longer than those in the present work. Furthermore, the β value highly depends on the evaluation method of the monolayer thickness. In this connection, Porter et al. reported that the dependence of the monolayer thickness on the alkyl chain length is reduced to ca. 0.56 Å per unit methylene group at the chain lengths not longer than n=7.[1] If we assume this value in the present system, the β value is estimated to be 0.80 Å^{-1}, which is in good agreement with the reported values. As indicated in the above discussion, the evaluation of the β value should be considered with caution, especially in the case of shorter chain monolayers. The uncertainties of the β value caused by evaluation of monolayer thickness were also pointed out by several authors.[3,22,26]

In conclusion, we demonstrated in this paper the applicability of the aminoalkanethiol monolayers to anchor the redox active quinone molecule on a gold electrode surface. From the dependence of the electrochemical response of anchored NQ molecule on the monolayer chain length, we proved that the separation distance between the NQ redox site and electrode surface can be well-controlled by changing the number of the methylene units of the aminoalkanethiol monolayer.

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