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THE ELECTROCHEMICAL STUDIES ON A SELF-ASSEMBLED VIOLOGEN MONOLAYER USING QUARTZ CRYSTAL MICROBALANCE

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The electrochemical behavior of viologen self-assembly monolayer has been investigated with QCM, which has been known as nano-gram order mass detector. The self-assembly process of viologen was monitored using resonant frequency (ΔF) and resonant resistance (R). The QCM measurements indicated a mass adsorption for viologen assembling on the gold surface with a frequency change about 135 Hz and calculated its surface coverage (Γ) to be 3.5273 × 10^{-9} mol/cm^2. Also a reversible redox process was observed and analyzed with an ionic interaction at the viologen/solution interface using △F.

Keywords: cyclic voltamogram (CV); quartz crystal microbalance (QCM); self-assembly; viologen

1. INTRODUCTION

Particularly, Viologens have been extensively investigated in the literature because their well-behaved electrochemistry has led to their use in a variety of studies, including electron transfer mediation to various biological molecules [1–2]. The surface-enhanced Raman studies of the

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adsorption at electrode surfaces [3], the behavior of supramolecular assemblies at electrode surfaces [4], and the applications for the electrochromic display devices [3]. The viologens exist in three main oxidation states, namely, $V^{2+} \leftrightarrow V^{\bullet +} \leftrightarrow V^{0}$. These redox reactions, especially the first one ($V^{2+} \leftrightarrow V^{\bullet +}$), are highly reversible and can be cycled many times without significant side reactions [5]. In this study, the electrochemical behavior of the self-assembled viologen monolayer has been investigated with the QCM, which has been known as a nano-gram order mass detector. The self-assembly process of the viologen was monitored using a resonant frequency (ΔF) and a resonant resistance (R).

2. EXPERIMENTAL

Figure 1 shows the chemical structure of the viologen incorporated with a thiol group. The rest of the reagents used in this experiments were of analytical grade and used without any purification. All solutions were prepared using Milli-Q water. The QCM measurements were carried out using AT-cut gold-coated quartz crystals with a resonant frequency of 9 MHz. (5 mm diameter Seiko EG&G, Japan.) A gold electrode of the QCM was cleaned in a piranha solution (H_2SO_4/H_2O_2;3:1), was exposed to a solution of vilolgen mixture in ethanol-acetonitrile(1:1, v/v) purged with Ar gas. The concentration was 2 mmol/l. Figure 2 shows the experimental setup for measuring electrochemical and physical data, simultaneously. The resonant frequency (ΔF) and the resonant resistance (R) have been measured using QCA 917 (Seiko EG&G, Japan) and the cyclic voltametry (CV) using Versastat II (Seiko EG&G Instrument, Japan). The QCM

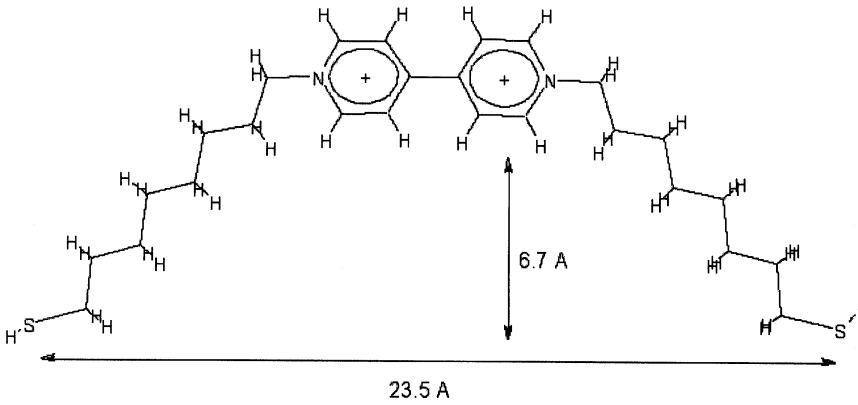

FIGURE 1 The chemical structure of viologen used in this study.

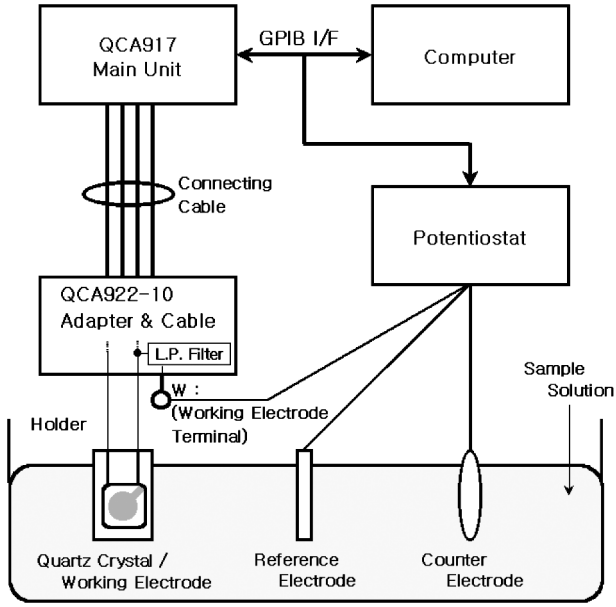

FIGURE 2 The electrochemical 3-electrode setup using QCA.

electrode modified with the self-assembled viologen and Pt plate were used as the working and counter electrode, respectively. A KCl saturated Ag/AgCl was the reference electrode. The 0.1 mol/l $NaClO_4$ was used as the electrolyte solution. The cyclic scans from 400 mV to −800 mV were performed for 10 cycles, also the CV curve shown in the present work were 10th cycle.

3. RESULTS AND DISCUSSION

The self-assembly process of viologen molecules to Au electrode of QCM was monitored. Figure 3 shows the resonant frequency shift (ΔF) and resonant resistance shift (R) during self-assembly process of the viologen. The resonant frequency was dramatically decreased and saturated [5]. The ΔF was 135 Hz and the mass absorbed can be calculated to be 126.6 ng, according to the Eq. (1)[6].

$$\Delta F = \frac{-2F_0^2 \Delta m}{A \cdot \sqrt{\rho_q \cdot \mu_q}} \tag{1}$$

where, F_o is fundamental resonant frequency, Δm is the mass gain, A is the electrode area, ρ_q is the density of the quartz, and μ_q is the shear module.

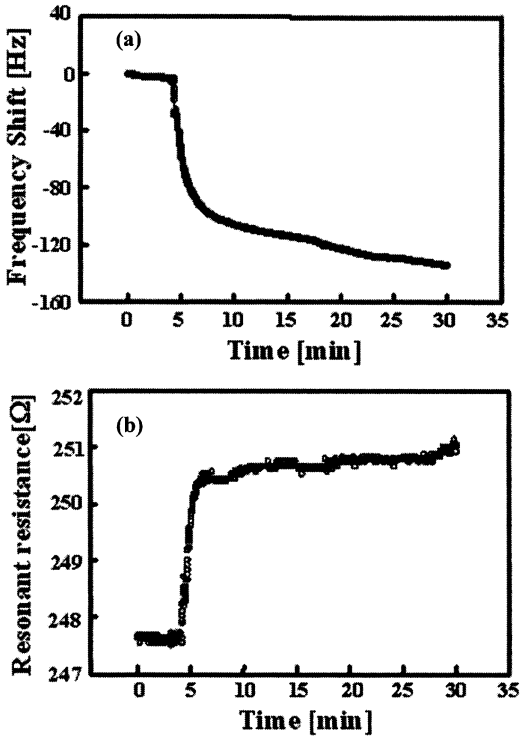

FIGURE 3 The time dependent frequency (a) and resonant resistance (b) shift during self-assembly process of viologen.

By considering the mass gain and the molecular weight, we can calculate the surface coverage (Γ) to be 3.53×10^{-9} mol/cm^2. According to the mass adsorption onto QCM surface, its rheological change can be originated and supported by the resonant resistance (R) change (See Fig. 3(b)). This result was compared with theoretical value which was calculated to be 313.82 ng, according to the Eq. (2). The ratio of the adsorption was calculated 40.34%.

$$\Delta m = \frac{E_{area}}{M_{area}} \times \frac{M_w}{N} \tag{2}$$

Where, E_{area} is the electrode area (0.196×10^{-2} m^2), M_{area} is the molecular area (4.635×10^{-18} m^2), M_w is molecular weight and N is Avogadro's number.

Figure 4 shows that the oxidative cyclic voltametry of a self-assembled monolayer of viologen in 0.1 mol/l $NaClO_4$ electrolyte solution with 100 mV/s of the scan rate. The cyclic voltametry shows two pairs of redox peak such

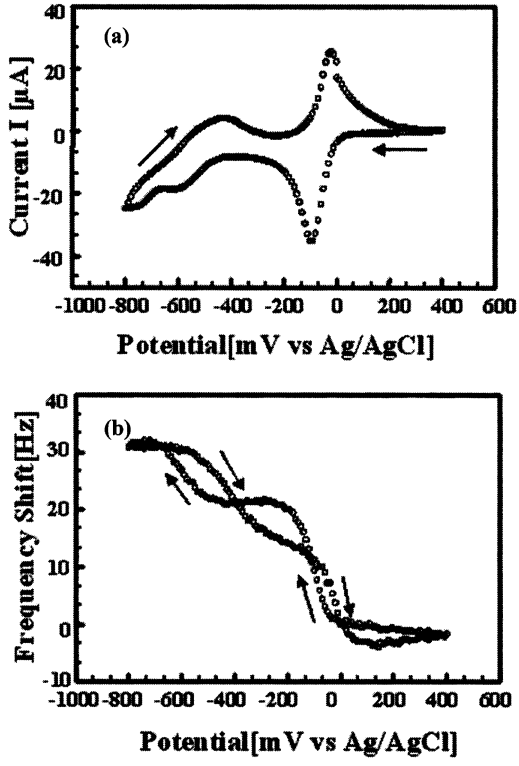

FIGURE 4 Cyclic voltamogram (a) and resonant frequency shift (b) of QCM modified with viologen SA monolayer.

as −100 mV and −620 mV. The resonant frequency and resistance was measured during the cyclic voltametry. At Figure 4(b), the EQCM frequency data reveals that mass is lost during the two reduction processes and that these mass losses are reversed during the reoxidations. These frequency changes have been previously interpreted as indication of anion loss (or gain) from the monolayer which is consequent to the injection (or removal) of electrons [4].

4. CONCLUSIONS

The self-assembly process of the viologen was monitored using resonant frequency (ΔF) and resonant resistance (R). The mass adsorption was calculated to be 126.6 ng and the surface coverage (Γ) was calculated to be 3.53×10^{-9} mol/cm^2. In addition to this, two pairs of the reversible redox

peak were observed. And the electrochemical properties were analyzed using the behavior of resonant frequency (ΔF) simultaneously.

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