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The self-assembled monolayers of alkane derivatives with sulfur containing head groups on gold substrates have been widely examined recently, since the binding between S atoms and Au surface is strong. We could know it was formed monolayer onto QCM surface by self-assembly from resonant frequency shift using QCA. The measured frequency shift for V_8SH was about 351 Hz. From this value, the adsorption mass was about 375 ng. The EQCM measurements revealed the anions transfer during reduction and oxidation, respectively. From the EQCM data, the well-defined shape peaks were nearly equal charges by cyclic voltammetry.

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

1. INTRODUCTION

The self-assembled monolayers of alkane derivatives with sulfur containing head groups on gold-substrates have been extensively used recently, and the S-anchored monolayers thus formed are in

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well-oriented structure [1,2]. The viologen has been widely investigated their well-behaved electrochemistry including electron transfer mediation, the surface-enhanced of the adsorption and the behavior of supramolecular assemblies at electrode surfaces [3] in theses and various studies. The viologen shows in three main oxidation states, namely, $V^{2+} \leftrightarrow V^{+} \leftrightarrow V^{0}$. The first reaction ($V^{2+} \leftrightarrow V^{+}$) is highly reversible among the redox reactions [4]. In this study, the self-assembly process of the viologen was monitored the resonant frequency shift (ΔF) and the electrochemical behavior of the self-assembled viologen monolayer has been investigated with QCM, which has been known as a nano-gram order mass detector.

2. EXPERIMENT

V_8SH was synthesized by D. J. Qian *et al.* [3]. Figure 1 shows the chemical structure of the viologen bonded with a thiol group. The rest of the reagent was used without any purification. In this experiment, we used the QCM which is AT-cut gold-coated onto quartz crystals with a resonant frequency of 9 MHz (5 mm diameter). A gold electrode of the QCM was cleaned by a piranha solution (H_2SO_4:H_2O_2 = 3:1) and was concentrated 2 m mol/l viololgen in ethanol-acetonitrile (1:1) compound with pure Ar gas.

Figure 2 shows the experimental equipment measured electrochemical and physical data, simultaneously. The resonant frequency (ΔF) and cyclic voltammetry (CV) have been measured QCA 922 (Seiko EG&G, Japan) and potentiostat 263A (PerkinElmer, USA). The gold electrode, which was self-assembled viologen monolayer onto the QCM, was used as working electrode. The Pt wire and KCl saturated Ag/AgCl were the counter and reference electrode, respectively. In this study, we observed the electron transfer property of SA viologen

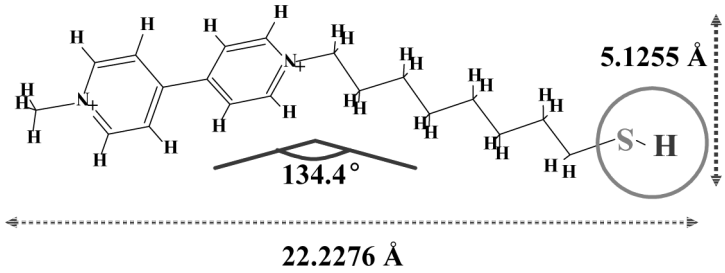

FIGURE 1 Chemical structure of viologen in this study.

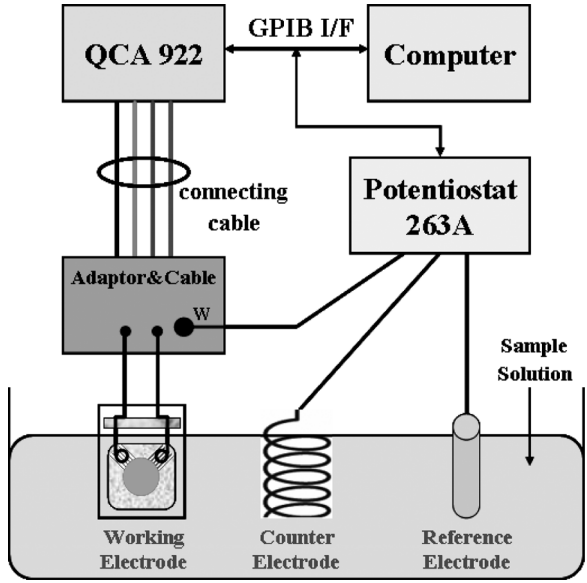

FIGURE 2 Schematic measurement system in this study.

monolayer in 0.1 M $NaClO_4$ electrolytic solution and the interrelation between scan rate and peak current.

3. RESULT AND DISCUSSION

We used the QCM techniques along with electrochemical measurements. The measurements were made on the substrate metal Au while organosulfur molecules adsorbed on the metal. Figure 3 shows the frequency shift (ΔF) as a function of time (t) for the QCM gold resonator in the 2 m mol/l V_8SH ethanol-acetonitrile solution. In this case, the frequency decreased rapidly at first, and then the decrease was getting slow. The assembling process of the V_8SH SAMs can be finished completely in about 80 min. The measured ΔF for V_8SH was about 351 Hz. From this value, we calculated that the adsorption mass of V_8SH was about 375 ng/cm^2, according to the Eq. (1) [5,6].

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

where F_0 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. After the adsorption of V_8SH onto the gold electrode of

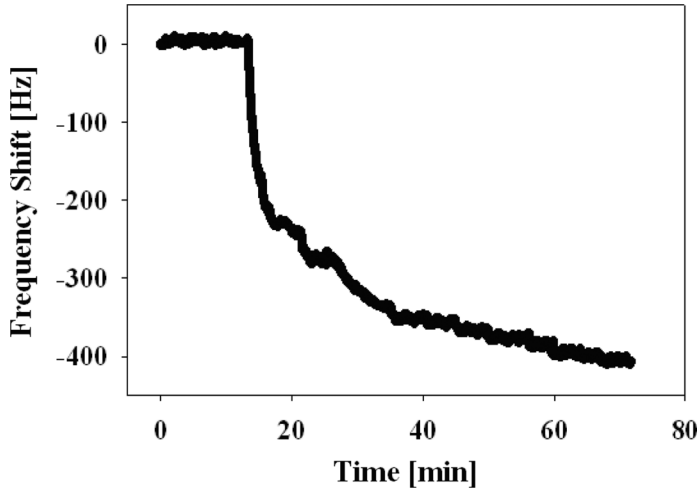

FIGURE 3 Time dependence to frequency shift during self-assembly process of viologen.

QCM was completed, it was rinsed out of gold electrode with solvent (ethanol:acetonitrile = 1:1).

Figure 4(a) shows the cyclic voltammetry (CV) curve for the self-assembled viologen monolayers modified gold electrode surface in 0.1 M $NaClO_4$ electrolyte solution at scan rate of 50–400 mV/s. All curves indicate well reversible broad redox waves, which agree with the electrochemical properties of a lot of viologen-modified electrodes [7]. The cathodic potential (E_{pc}) and anodic potential (E_{pa}) peaks were centered at -0.48 V and -0.44 V, respectively [8]. This is as consequence of the first electron reaction, $V^{2+} + e^- \Leftrightarrow V^+$.

Figure 4(b) shows the interrelation of scan rate and peak current that was verified to increase linearly at different scan rates. According to the Figure 4(b), we could know if the scan rate increases, the peak current will also increase and we will be able to control the specific result [9].

4. CONCLUSION

We have demonstrated a self-assemble method to prepare SAMs of a viologen thiol. The self-assembly process of the viologen was monitored by resonant frequency (ΔF). The adsorption mass was about 375 ng. From this result, the immersed viologen can act as an electron-transfer mediator to access to the electrode surface across the

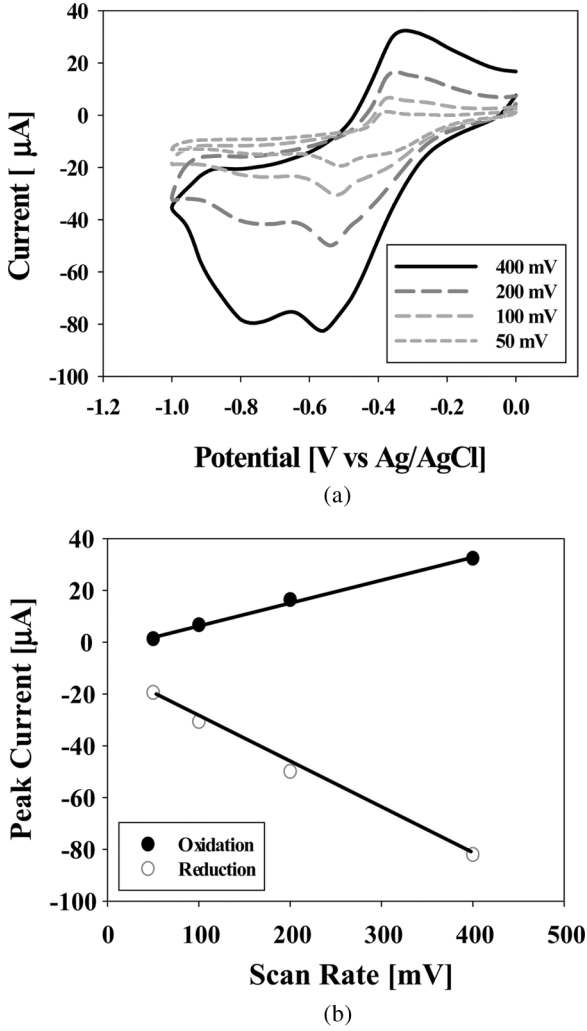

FIGURE 4 Redox reaction (a) and the interrelationship of scan rate and I_{Peak} (b) in 0.1 M $NaClO_4$ electrolytic solution.

phospholipid monolayer. We observed the redox reaction properties of self-assembled viologen monolayer by electron transfer. With increasing scan rates, the redox peak currents also increased linearly. As a result, it is possible to gain and control the sensitivity of specific result. Furthermore, above the result, we will be able to be application of nano devices.

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