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Electrochemical Studies on a Self-Assembled Viologen Monolayer Using Quartz Crystal Microbalance

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1. Introduction

Molecular self-assemblies of surfactant viologen are of recent interest because they can form functional electrodes as well as micellar assemblies, which can be profirably utilized for display devices, photo electrochemical studies and electrocatalysis as electron acceptor or electron mediator [1-3]. Fromherz et al studied the self-assembly of thiol and disulfide derivatives of viologens are bearing long n-alkyl chains on Au electrode surface [4]. In this study, the electrochemical behavior of self-assembled viologen monolayer has been investigated with QCM, which is known as nano-gram order mass detector. The self-assembly process of viologen was monitored using resonant frequency (ΔF) and resonant resistance (R). The redox process of viologen was observed with resonant frequency (ΔF).

2. Experimentals

Figure 1 shows the chemical structure of viologen incorporated with thiol group. All other reagents are used in this experiments were of analytical grade and used without any purification. All solutions were prepared by using Milli-Q water. The 9MHz AT-cut gold coated QCM was cleaned in a piranha solution ($H_2SO_4/H_2O_2;3:1$), was exposed to a solution of viologen mixture in ethanol-acetonitrile(1:1, v/v) purged with Ar gas. The concentration was 2mmol/l. Figure 2 shows the experimental setup for measuring electrochemical and physical data, simultaneously. The resonant frequency (ΔF) and resonant resistance (R) have been measured using QCA 922(Seiko EG&G, Japan) and the cyclic voltametry(CV) using Versastat II(Seiko EG&G Instrument, Japan). The QCM electrode modified with self-assembled viologen and Pt plate were used as the working and counter electrode, respectively. A KCl saturated Ag/AgCl was a reference electrode.
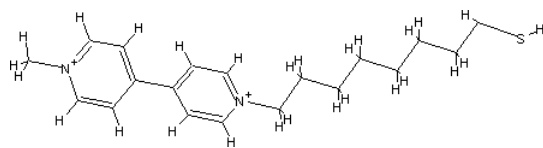

Fig. 1. The chemical structure of viologen used in this study

The 0.1 M NaCl, KCl, LiCl are used as the electrolyte solution. The cyclic scans from -0.2 V to -0.8 V were performed for 10 cycles and CV curve shown in the present work were 10th cycle.
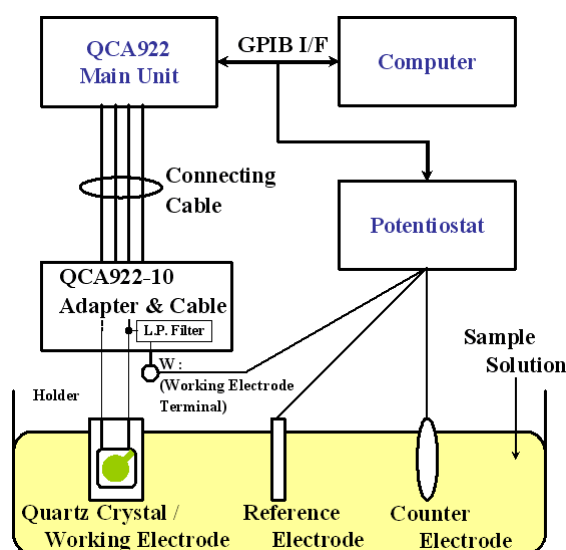

Fig. 2. The electrochemical 3-electrode setup using QCA 922

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) during self-assembly process of viologen. The resonant frequency was dramatically decreased and saturated. The ΔF was 300 Hz and the mass absorbed can be calculated to be 320 ng, according to the equation (1) [5].

$$\Delta F = \frac{-2F_0^2 \Delta m}{A \cdot \rho_q^{1/2} \cdot \mu_q^{1/2}} \qquad (1)$$

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. By considering the mass gain and the molecular weight, we can calculate the surface coverage (Γ) to be 5.02×10^{-9} mol/cm^2. After the adsorption of the viologen onto the gold electrode of QCM was

completed, the electrode was rinsed with solvent and transferred to 0.1M NaCl, KCl and LiCl for the electrochemical measurements.
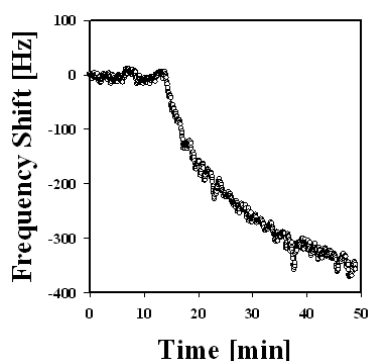

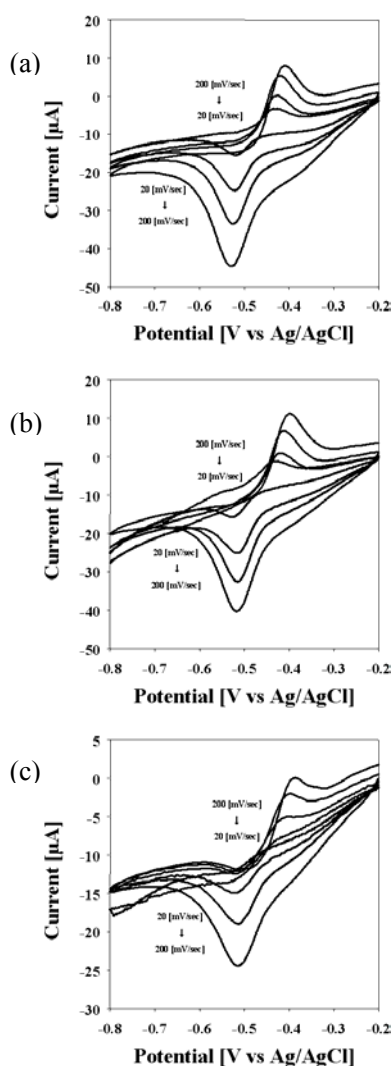Fig. 3. The time dependent frequency shift during self-assembly process of viologen

Fig. 4. Cyclic voltammogram of QCM modified with viologen SA monolayer in the various electrolyte
(a) 0.1M NaCl (b) 0.1M KCl (c) 0.1M LiCl

Figure 4 shows the cyclic voltammograms of a self-assembled monolayer of viologen on a gold electrode surface in various electrolyte. There is a pair of rather well-defined redox peak. The cathodic (E_{pc}) and anodic (E_{pa}) potential peaks are -0.42 V and -0.52 V, respectively.

This is ascribed to the first $1e^-$ reaction of the bipyridinium moieties involving a radical cation intermediate, $V^{2+} + e \Leftrightarrow V^{+\bullet}$. The effective surface coverage calculated from slopes is 5.520×10^{-9}, 5.353×10^{-9}, 3.011×10^{-9} mol/cm^2 according to the equation (2) [6].

$$\Gamma = \frac{4RTi_p}{n^2AF^2\upsilon} = 5.3585 \times 10^{-6} \left(\frac{i_p}{n^2\upsilon} \right) \quad (2)$$

Where n, F, A and υ are the number of electrons, the Faraday constant, the electrode area, and the potential scan rate, respectively. These values are similar with the result from the previous QCM measurement. All electrolyte solution, the peak height of the redox response corresponding to the viologen decation/redical cation (V^{2+}/V^+) couple was proportionally to the scan rate υ in the range from 20 to 200 mV/sec for both anodic and cathodic peaks.

4. Conclusions

The self-assembly process of the viologen was monitored using resonant frequency (ΔF). The mass adsorption was calculated to be 320 ng and the surface coverage (Γ) was calculated to be $5.02 \times 10-9$ mol/cm2. In addition to this, two pairs of the reversible redox peak were observed.

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