

Study on Charge Transfer Characteristics of Self-Assembled Viologen Monolayers

Sang-Hyun Park*, Dong-Yun Lee* and Young-Soo Kwon†

Abstract - Viologen has been extensively investigated in the paper because their well-behaved electrochemistry has led to their use in a variety of theses, including the electron acceptor for the electric charge delivery mediation of the devices. It was formed monolayer in QCM by self-assembly method. We could know the adsorbed mass of viologen molecules from the frequency shift. We calculated that the adsorbed mass was about 196 [ng/cm²]. We studied the electron transfer property of viologen by the cyclic voltammetry among the electrochemical process so we changed an anion like 0.1 M NaClO₄ and Na₃PO₄ electrolyte solution and investigated the interrelationship between scan rate and peak current when scan rates were increased twice.

Keywords: viologen, quartz crystal microbalance(QCM), frequency shift, cyclic voltammetry

1. Introduction

An Oriented monolayer assembly can be created by both the Langmuir-Blodgett and self-assembly methods using various alkane derivatives and substrates. 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 and the S-anchored monolayers thus formed are in well-oriented structure[1, 2].

Particularly, viologens have been widely 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 [3, 4]. The surface-enhanced Raman studies of the adsorption at electrode surfaces, the behavior of supra-molecular assemblies at electrode surfaces, and the applications for the electrochromic display devices[5].

The study of the thiol-functionalized viologen derivatives, SH₈V₈SH, has been achieved to elucidate voltammetric data. Viologen has three oxidation and reduction states, namely, V²⁺ ↔ V⁺ ↔ V⁰. These redox reactions are highly reversible and can be cycled many times without significant side reaction, respectively. Especially, the first reaction is highly reversible among the oxidation and reduction reactions[5].

In this study, the self-assembly process of the viologen was monitored the resonant frequency shift(ΔF). The electrochemical property of the self-assembled viologen

monolayers has been investigated by redox reactions using QCM which has been known as a nano-gram order mass detector.

2. Experimental

SH₈V₈SH was synthesized by D. J. Qian et. al.[6]. Fig. 1 shows the chemical structure of the viologen bonded with thiol group. In this experiment, we used the QCM which is AT-cut gold-coated onto quartz crystals with a resonant frequency of 9 MHz(5mm diameter, Seiko EG&G, Japan). A gold electrode of the QCM was cleaned by a piranha solution (H₂SO₄:H₂O₂ =3:1) and was concentrated 2m mol/l viologen in ethanol-acetonitrile (1:1) compound with pure Ar gas.

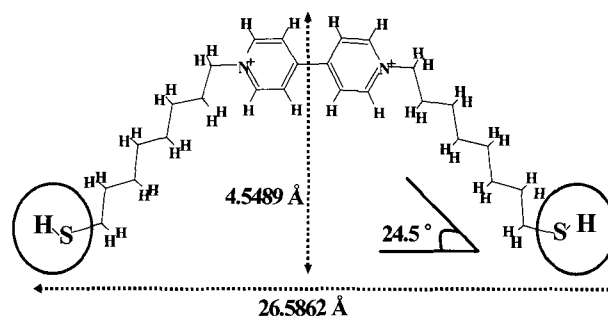


Fig. 1 Chemical structure of viologen

The resonant frequency shift(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 monolayers onto the QCM, was used as working electrode. The

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Pt wire and KCl saturated Ag/AgCl were used as the counter and reference electrode, respectively. The scan range from 0 V to -1.0 V were performed for 5 cycles. We observed the electron transfer property of SA viologen monolayers in 0.1 M NaClO₄ and Na₃PO₄ electrolyte solutions.

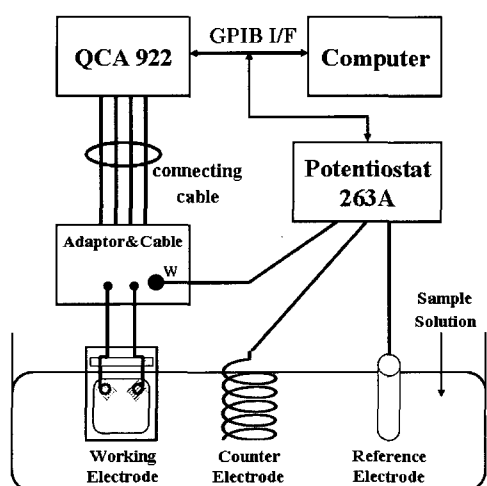


Fig. 2 Schematic measurement system in this study

3. Result and Discussion

Fig. 3 shows the resonant frequency shift (ΔF) as a function of time (t) in the 2m mol/l SH₈V₈SH ethanol-acetonitrile solution. In this case, the frequency decreased rapidly at first, and then the decrease was getting slow. The self-assembly process of the SH₈V₈SH molecules can be finished about 80 min.

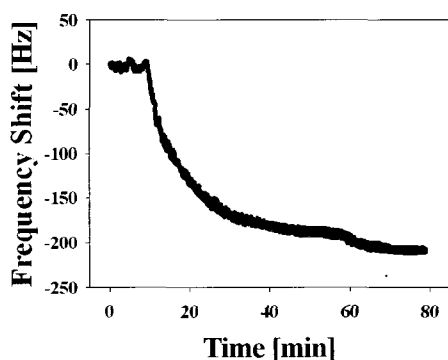


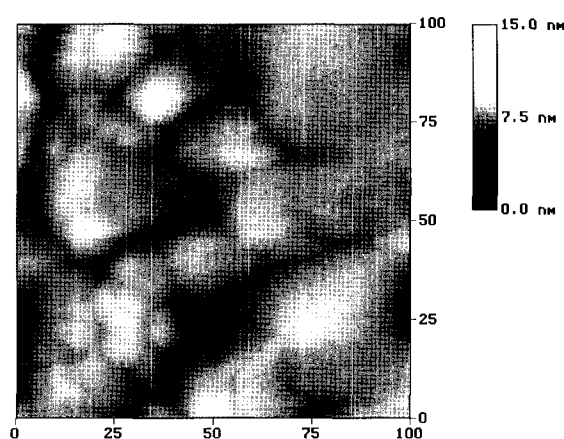
Fig. 3 Time dependence to frequency shift

The measured frequency shift was about 203 Hz. From this value, we calculated that the adsorbed mass was about 217 ng/cm², according to the equation (1)[7, 8].

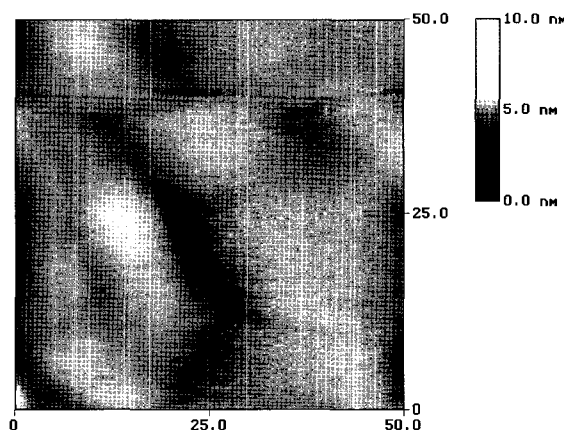
$$\Delta F = -\frac{2F_0^2 \cdot \Delta m}{A \cdot \sqrt{\rho_q \mu_q}} \quad (1)$$

where F_0 is fundamental resonant frequency (9 MHz), Δm is the mass gain, A is the electrode area (0.196 cm²), ρ_q is the density of the quartz (2.65 g/cm³) and μ_q is the shear module of crystal (2.95×10^{11} dyn/cm²). After the adsorption of V₈SH onto the gold electrode of QCM was completed, it was rinsed out of gold electrode with solvent (ethanol: acetonitrile=1:1).

Fig. 4 (a) and (b) show the surface image of self-assembled viologen monolayers by STM. We manipulate the surface on a nanometer scale to form nano-structures. We can presume the bright position to be self-assembled monolayers in places.



(a) 100nm × 100nm



(b) 50nm × 50nm

Fig. 4 Images of self-assembled gold surface

Fig. 5 (a) and (b) show the cyclic voltammety (CV) curve for the self-assembled viologen monolayers modified gold electrode surface in 0.1M NaClO₄ and Na₃PO₄ electrolyte solutions at scan rate of 50~400 [mV/s]. The cathodic potential (reduction peak) and anodic potential (oxidation peak) peaks are observed -0.52 V and -0.46 V, respectively[9]. This is as consequence of the first electron reaction, $V^{2+} + e^- \leftrightarrow V^+$.

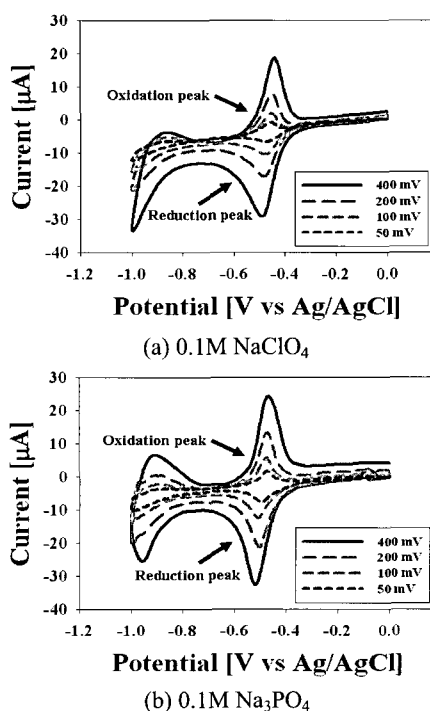


Fig. 5 Redox reactions in different electric solutions

Fig. 6(a), (b) show the interrelationship of scan rate and peak current that was verified to increase linearly at different scan rates. According to the Fig. 6 (a) and (b), we could know if the scan rate increases, the peak current will be also increased. This fact was signified that the redox reaction was reversible. We will be able to control the specific result[10].

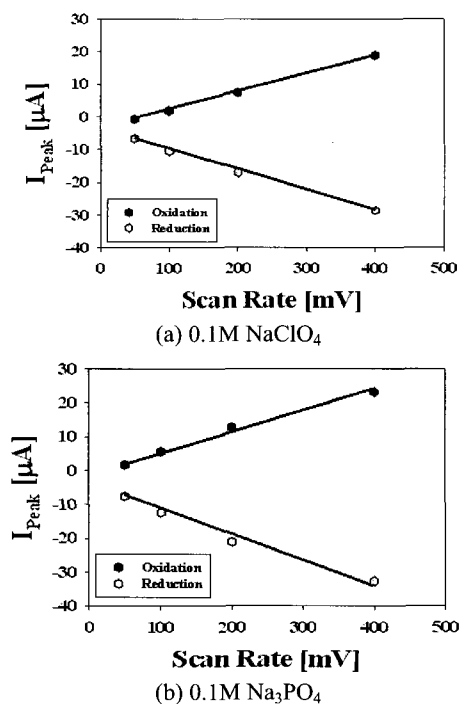


Fig. 6 Interrelationship of scan rate and peak current

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 shift(ΔF). The adsorption mass was about 196 ng/cm². From this result, the immersed viologen can act as an electron-transfer mediator. We observed the electrochemical and interfacial properties of self-assembled viologen monolayers. It was characterized in 0.1 M NaClO₄ and Na₃PO₄ electrolyte solutions by cyclic voltammetry. With increasing scan rate, the redox peak current of the viologen increased linearly. This property was implied the reversible reaction. As all results, we could know it is possible to gain and control the sensitivity of specific results because the viologen molecules have their own property without any relationship where the anions were different in electrolyte solutions. Furthermore, above the result, we will be able to be application of nano-scale switch devices.

Acknowledgements

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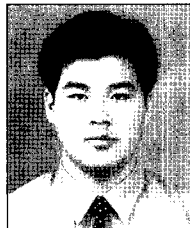
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