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Electrochemical Behavior and Electronic Characteristics of Self-Assembled Viologen Monolayers using QCM and Au(111) surface

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1. Introduction

Electrochemical properties of a redox molecule incorporated in a phospholipid monolayer, bilayer or membrane have attracted much attention in the past several decades. Viologens are actually a kind of desirable electron mediator [1]. The viologens, which have been widely studied for their redox activity and electrochromic properties, are attractive materials because of their chemical stability, their relatively simple behavior of redox reaction and their possible practical applications due to their electrochemical properties.

We studied the electron transfer properties of a viologen, its use as a redox-active linker on a gold substrate, and a study of electron transfer. The electrochemical quartz crystal microbalance (EQCM) method is used in ex situ experiments to measure mass changes at electrode surfaces after electrochemical deposition of metal[2,3]. We applied scanning tunneling microscopy (STM) to investigate the self-assembly and electron transfer properties of passivated gold clusters onto Au(111) surface.

In this paper, the electrochemical behavior of self-assembled viologen monolayers has been measured with QCM which has been known as a nano-gram order mass detector. The EQCM frequency change was about 7.3 Hz, 16.4 Hz, 7.6 Hz during redox reaction. From these result, we could calculate the total transferred mass and number of shifted ions by Sauerbrey's equation.

We used the scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) for obtaining surface properties of self-assembled Au(111) substrates. The STM has been effective to observe molecular images and also attracted much attention that the current flows. We consider as a kind of the STS to measure the current-voltage curve characteristics through such a self-assembled viologen monolayer which is adsorbed onto the Au(111) substrates. We investigated STM images to allow to the electrochemical behavior of viologen molecules.

2. Experimental

Fig. 1 shows the chemical structure of the viologen bonded 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.

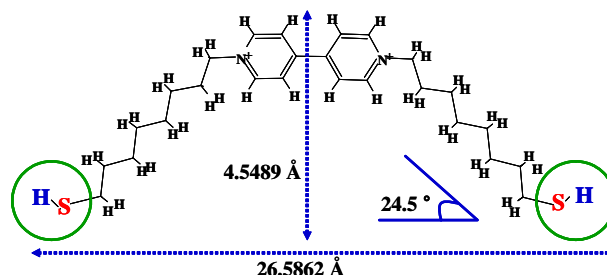
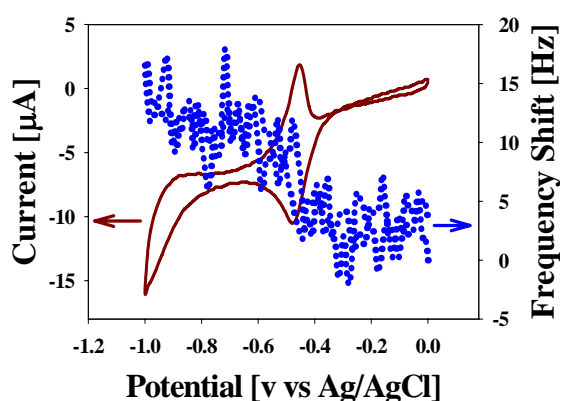


Fig. 1 The Chemical Structure of viologen

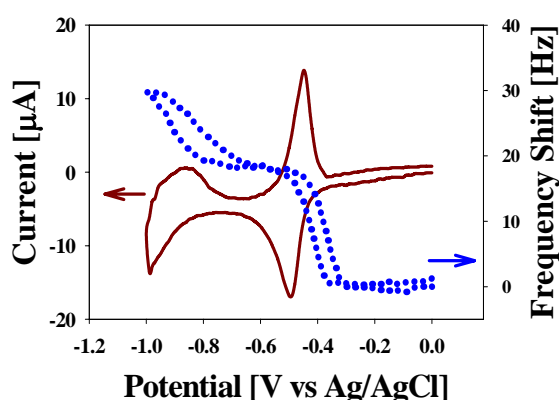
We used the QCM which is AT-cut gold-coated onto quartz crystals with a resonant frequency of 9 MHz (5 mm diameter). A gold electrode of the QCM was cleaned by a piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2=3:1$) and was concentrated 2m mol/l viologolgen in ethanol-acetonitrile (1:1) solution compounding of pure Ar gas. The experimental equipment was measured electrochemical and physical data, simultaneously. The redox reaction and EQCM properties have been measured QCA 922 (Seiko EG&G, Japan) and potentiostat 263A (PerkinElmer, USA). The self-assembled viologen monolayers onto gold substrate of QCM were used as the working electrode. Electropolymerization was performed on 0.6 mm diameter platinum wires conditions (from 0 mV to -1000 mV versus Ag/AgCl, scan rate $\nu = 100 \text{ mV/s}$) for the CV measurements and on 0.196 cm^2 gold layers of quartz crystals with resonance frequency of 9 MHz [3]. Estimation of the peak current was based on the second cycle of cyclic voltammetry curve. The purpose of these investigations was to obtain information about the electron transfer behavior which was carried out under practical conditions in aerated solutions. We also observed the surface images on Au(111) substrate by STM (DI, USA). The experimental setup based on the STM measurement (Nanoscope IV). The STM operation was in constant height mode.

3. Results and Discussion

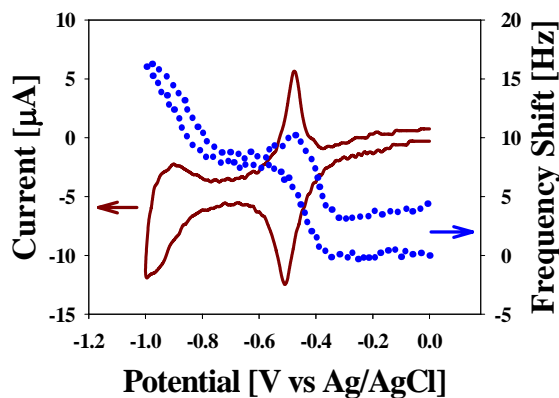
After finishing self-assembly process, the gold electrode on QCM was rinsed with ethanol:acetonitrile (1:1) solvent and determined the EQCM Properties in 0.1 M NaClO_4 , Na_2SO_4 and Na_3PO_4 electrolytic solutions.



(a) 0.1 M NaClO₄



(b) 0.1 M Na₂SO₄



(c) 0.1 M Na₃SO₄

Fig. 2 EQCM response in different electrolytic solutions

Fig. 2 shows the second cyclic voltammograms which display the electrochemical quartz crystal microbalance (EQCM) frequency change and mass variations on quartz crystal during the CV for this same monolayer.

From the data, total frequency changes were 7.3 Hz, 16.4 Hz and 7.6 Hz, which corresponds to a mass transfer of removed electrons from the layer. From the Sauerbrey's equation, the transferred mass was 7.8 ng, 17.5 ng and 8.1 ng, respectively. With multiplying Avogadro's number (6.02×10^{23}), the number of shifted ions were 4.70×10^{11} , 1.06×10^{12} and 4.89×10^{11} [4].

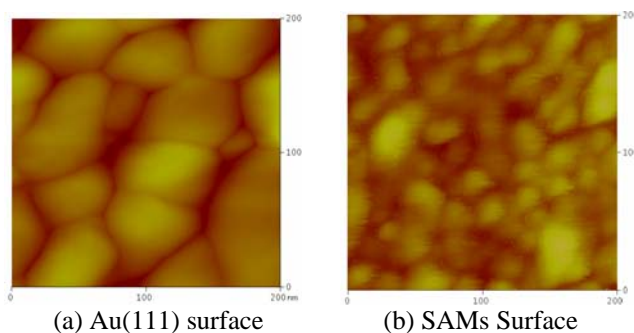


Fig. 3 Surface images of Au(111) and SAMs by STM

Fig. 3 shows the surface images of the SAMs onto gold substrate. The formation of the STM tip Pt-Ir/SAMs/metal(Au). We could observe lighter places which were presumed the self-assembled monolayers. The Current-Voltage (I-V) curves of the SAMs show that the electric resistance in the recorded regions was much lower than that in unrecorded regions[5]. In the STS plot modes, the tip was positioned at a point on the surface and a spectroscopic plot was acquired and displayed in a scope format[6].

4. Conclusion

In this study, we have demonstrated the characteristics of self-assembled viologen monolayers by electrochemical method. The electron transfer properties of self-assembled viologen monolayers were characterized by cyclic voltammetry in electrolytic solutions. We also investigated mass change during redox reaction. The results reveal that the mass change behavior of SAMs was not only governed by the mobility of the ion in the viologen but the valence of the ion and the valences of the ions in the electrolyte solution. As all results, we could know it is possible to gain and control the sensitivity of specific results and furthermore, we will be able to apply to nano devices

Acknowledgement

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