

EQCM법을 이용한 자기조립된 Viologen 유도체의 광학적 특성 및 전기화학적 특성 연구

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Optical and Electrochemical Property of Self-Assembled Monolayers Containing Viologen Derivative by EQCM Study

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Abstract - A monolayer assembly of anthracene-viologen linked thiol (AMVC₆SH) was fabricated on a gold electrode by self-assembly method. Structural property of the self-assembled monolayers (SAMs) was carried out by optical and electrochemical method. Firstly, we investigated PL spectrum and UV/visible absorption for the optical properties in solution state. Secondly, we determined the characteristics of charge transfer in different electrolyte solutions by electrochemical quartz crystal microbalance (EQCM). From the data, the PL spectrum and UV/visible absorption were observed and the well-defined shape peaks were nearly equal charges during redox reactions and existed to an excellent linear relationship between the scan rates and redox peak currents. The mass change was determined during redox reaction. 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 in the electrolyte solution.

1. Introduction

Electrochemistry of self-assembled monolayers (SAMs) having redox-active groups has been getting great interest in recent years [1,2]. Theory on cyclic voltammograms of such surface-confined redox species has been developed with use of the Langmuir adsorption isotherm and the Nernst equation [3]. The self-assembling molecules possess a redox-active site, the adsorption process can be monitored in real time by electrochemical techniques, such as cyclic voltammetry (CV). A number of researchers have also employed various electrochemical techniques to study the stability, permeability, and uniformity of self-assembled films. The electrochemical techniques are very useful in monitoring the adsorption process; however, they can only monitor the amount of the adsorbed species having an electro-active site, as mentioned above [4].

Electrochemical property of the self-assembled viologen derivatives have been investigated with quartz crystal microbalance (QCM), that has been known as a nano-gram order mass detector. The viologen derivatives exist in three redox states, namely, $V^{2+} \leftrightarrow V^{\bullet+} \leftrightarrow V^0$. These redox reactions are highly reversible and can be cycled many times without significant side reactions, respectively [5,6].

The QCM technique is based on the tendency of a piezoelectric crystal to change its resonant frequency when additional mass adsorption or desorption on the crystal electrodes takes place [7]. Since the QCM can detect mass loadings onto the quartz plate with nano-gram resolution, it is a powerful technique for monitoring the self-assembly processes. The analytical technology has been improved or newly developed as to the incremental requirement for electrochemical phenomena at the interface. QCM combined with other techniques, namely electrochemical quartz crystal microbalance (EQCM), is a powerful tool in investigating the interfacial processes that occur on surface and thin films [8]. The electrochemical reactions possibly involved at the surface were evaluated by frequency change. Based on the sensitive mass response of QCM, this technique was also employed for in situ monitoring mass transfer processes between electrode and electrolyte solution interface [9].

The purpose of this study is to investigate the optical and charge transfer characteristics of self-assembled monolayers. We observed optical property of viologen derivative using PL spectrum and UV/visible absorption and determined the charge transfer properties of self-assembled viologen monolayers in different electrolyte solution from cyclic voltammetry and EQCM response.

2. Experimental

A novel material that is 9-(1'-Anthracene-9-ylmethyl-[4,4']bipyridinyl-1-yl)-nonane-1-thiol (AMVC₆SH) was synthesized by B. J. Lee et al (Inje university, Korea). Figure 1 shows the chemical structure of the viologen

incorporated with a thiol group. The rest of the reagents used in this experiment were of analytical grade and were used without any purification. All solutions were prepared using Milli-Q water.

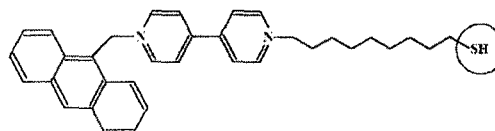


Fig. 1 Molecular structure of viologen derivative.

The QCM measurements were carried out using AT-cut gold coated onto quartz crystals with a resonant frequency of 9 MHz (5 mm diameter, Seiko EG&G, Japan). The gold electrode of the QCM was cleaned with a piranha solution ($H_2SO_4:H_2O_2=3:1$) and exposed to 2 M viologen agitated with pure Ar gas.

The PL spectrum and UV/visible absorption and were measured with LS45 luminescence spectrometer (Perkin Elmer) and Lambda 650 UV/visible spectrometer (Perkin Elmer), respectively. The resonant frequency shift and the cyclic voltammograms were measured with QCA 922 (Seiko EG&G, Japan) and potentiostat 263A (Perkin-Elmer, USA). The gold electrode, which was self-assembled viologen monolayers onto the QCM, was used as the working electrode. The Pt wire and KCl saturated Ag/AgCl electrodes were used as counter and reference electrodes, respectively. The 0.1 M NaCl and NaClO₄ were used as the electrolyte solutions. The cyclic voltammetry curve was shown the second cycle of redox reaction and scan rates.

3. Results and Discussion

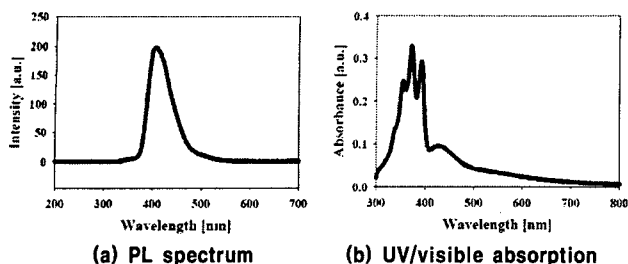
Figure 2 (a) and (b) show the PL spectrum and UV/visible absorption for the optical properties of AMVC₆SH. The PL spectrum and UV/visible absorption of AMVC₆SH were measured from water solution. The PL spectrum peak was observed to be 408 nm which was purple. The maximum UV/visible absorption peak was observed to be 530 nm, which are ascribed to the $\pi > \pi^*$ transition. From the data, the energy bandgap was about 2.34 eV by equation (1).

$$eV = \frac{hc}{\lambda} \quad (1)$$

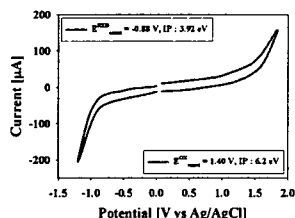
where, h is plank constant (6.626×10^{-34} J·S), and c is light velocity (3×10^8 m/s).

Figure 2 (c) shows the ionization potential (IP) and electron affinity (EA) of AMVC₆SH by cyclic voltammetry. The oxidation onset potential and the reduction onset potential were +1.44 V and -0.88 V, respectively. The HOMO and LUMO level values were calculated by estimating the energy level of ferrocene (FOC). The energy level of FOC was assumed to be 4.8 eV below the vacuum level. The HOMO and LUMO energy level were calculated to be 6.2 eV and 3.92 eV, respectively. So, the energy bandgap was about 2.28 eV.

After the adsorption of AMVC₆SH onto the gold electrode of QCM was completed, it was rinsed out of gold electrode with ethanol: acetonitrile (1/1) solution and performed on electrochemical measurements in electrolyte solutions. Figure 3 shows cyclic voltammetry of the self-assembled viologen monolayers at different scan rates (20, 50, 100, 200 and 400 mV). The SAMs were very stable so that the current does not show detectable decrease after continuously rinsing with the electrolytic solutions or repeated cycling in electrolytic solutions. The formal potential of the redox reaction was corresponding to the successive



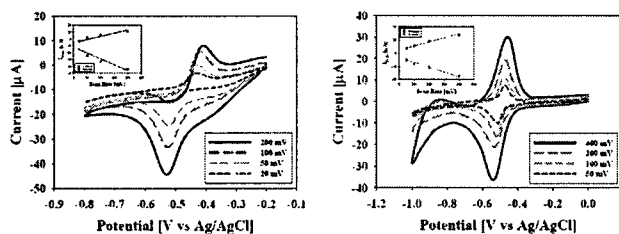
(a) PL spectrum (b) UV/visible absorption



(c) Cyclic voltammogram of the AMVC₆SH

<Fig. 2> Optical Properties and Cyclic voltammogram of the AMVC₆SH for investigating energy bandgap

one-electron transfer, in 0.1 M NaCl and NaClO₄ electrolyte solutions. In these voltammograms, the cathodic and anodic currents correspond to the reduction and oxidation processes. From the reduction and oxidation potential, the redox reaction was reversible. When the scan rate was increased, the redox peak current will be also increased linearly. This fact was also signified that the redox reaction was reversible [10].



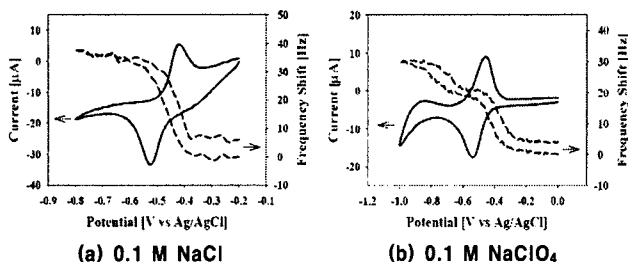
(a) 0.1 M NaCl (b) 0.1 M NaClO₄

<Fig. 3> Redox reaction of self-assembled monolayers in various electrolyte solution

Figure 4 presents the second cyclic voltammograms and mass variations on quartz crystal. The voltammograms display the frequency change which obtains during the CV for this same monolayer. The considerations involved in the use of the EQCM for monolayer systems have been discussed. A total frequency change was about 17.8 Hz and 8.4 Hz, respectively, which corresponds to a mass change of removed electrons from the layer. From the data, we could know that the transferred mass was about 19.0 ng and 9.0 ng by Sauerbrey equation (2)[11]. We also analyzed the number of shifted ions which were 2.30×10^{13} and 1.08×10^{13} by multiplying Avogadro number (6.02×10^{23}).

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

where, F_0 is the fundamental resonant frequency of 9 MHz, Δm is the mass gain, A is the electrode area (0.196 cm^2), ρ_q is the density of the quartz (2.65 g/cm^3), and μ_q is the shear modulus ($2.95 \times 10^{11} \text{ dyn/cm}^2$).



(a) 0.1 M NaCl (b) 0.1 M NaClO₄

<Fig. 4> EQCM response of resonant frequency shift collected simultaneously with voltammogram. Scan rate: 100 mV/s

In figure 4, the reason why the NaClO₄ electrolyte solution was smaller charge transfer than NaCl electrolyte solution by: Cl⁻ ion is smaller than ClO₄⁻ limiting molar conductivity of Cl⁻ is better than ClO₄⁻. We believe that this mass change was caused by the anions present for charge compensation of the viologen and some solvent.

4. Conclusion

We have demonstrated a self-assembled method to prepare well-defined of a viologen derivative. We observed the PL spectrum, UV/visible absorption and cyclic voltammetry property. From the PL data, AMVC₆SH shows purple emission. From the UV/visible and cyclic voltammetry, the energy bandgap was calculated to be 2.34 eV and 2.28 eV which was nearly same. The electrochemical property of viologen derivative was characterized in 0.1 M NaCl and NaClO₄ electrolyte solutions using cyclic voltammetry. The modified electrode showed reversible electrochemical properties and high stability. From the result, the immersed viologen can act as an electron transfer mediator to access to the electrode surface. The EQCM response indicated that charge transfer process was an ordered, closed-packed and ideal model system for studying diffusion. The viologen molecules have their own properties without regard to influence of electrolyte solutions, so we expect to apply to nano-scale devices that the ability to electronically contact metal nanoparticles via redox-active molecules can form basis for a range of nano-scale electronic switches and sensors[12].

[Acknowledgment]

This work was supported by grant No. R01-2006-000-11120-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

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