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Asymmetrical Conductivity of TCNQ Modified Au/Thiol-Lipid Bilayers in $Fe(CN)_6^{3-/4-}$ solution

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Abstract: In this work, electron transfer across Au supported octadecanethiolphosphatidylcholine (Au/ODT-PC) bilayers, which were modified with 7,7,8,8-tetracyanoquinodimethane (TCNQ), were investigated using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Results of EIS experiments show that the TCNQ molecules act as electron conductors in the bilayer. Cyclic voltammetry indicates that the TCNQ modified Au/thiol-lipid bilayers display strong asymmetrical conductivity in $Fe(CN)_6^{3-/4-}$ solution.

Keywords: Electrochemistry, supported bilayer, electrochemical impedance spectroscopy, cyclic voltammetry, asymmetrical conductivity.

Due to its similarity to biomembrane in microenvironment and its high mechanical stability, the supported lipid bilayer assembly has provided a good model not only to study biomembranes[1-5], but also to develop biomolecular electronic devices[6,7]. Because the alkanethiol monolayers on gold are characteristic of their high structure order, compactness and stability[8], recent interests in supported bilayers focus on those composed of a self-assembled thiol monolayer and a lipid monolayer[4,5,9-12]. In this work, we report the asymmetrical conductivity of Au/ODT-PC bilayer modified with TCNQ in $Fe(CN)_6^{3-/4-}$ solution.

Experimental

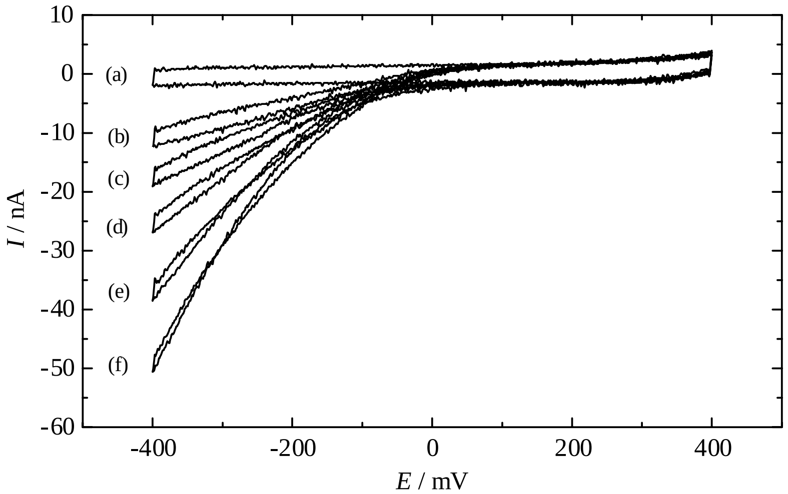
The gold substrates were fabricated by sputtering Au (99.99%) onto single crystalline Si (111). A 10 nm Ti layer was deposited prior to Au deposition to improve adhesion to the Si wafer. TCNQ and phosphatidylcholine (PC) were purchased from Sigma and octadecanethiol (ODT) from Aldrich. Other chemicals were of analytical grade and used as received. All aqueous solutions were prepared with redistilled water. Pinhole-free Au/ODT monolayers were obtained by immersing Au substrates into 10^{-4} mol/L ODT solution of absolute ethanol for 24 hours[13]. Au/ODT-PC bilayers were prepared by painting a drop of PC solution onto the alkylated gold surface and transferring the Au electrode immediately into 0.1 mol/L KCl solution[4]. EIS and CV experiments were performed with an ac impedance system (EG&G, Princeton Applied Research, Model 388) that included a potentiostat/galvanostat (Model 273), a two-phase lock-in analyzer (model 5208), and a personal computer. For EIS measurements, a

5-mV-amplitude sine wave was applied to the electrode at open circuit potential. For CV experiments M270 software was used. All electrochemical experiments were carried out in a conventional three-electrode system at room temperature. Saturated calomel electrode (SCE) and large area Pt was used as reference and counter electrode, respectively. All potentials are reported with respect to SCE.

Results and Discussion

In our previous work[14], we studied the electron transfer across unmodified Au/ODT-PC bilayer and concluded that considerations must be given to the Faradaic reactions occurring at structural defects of bilayer when one studies charge transfer process across supported bilayer in which electroactive proteins or molecular conductors were embedded. We believe that the Faradaic resistance should decrease at least several times after the modification of electroactive proteins or molecular conductors, otherwise one can not conclude that the incorporated molecules take part in the electron transfer across bilayer.

Figure 1 The cyclic voltammograms of TCNQ modified Au/ODT-PC electrode in (a) 0.1 mol/L KCl solution and (b) ~ (c) $Fe(CN)_6^{3-/4-}$ + 0.1 mol/L KCl solutions. The concentration of $Fe(CN)_6^{3-/4-}$ is (b) 0.5 mol/L, (c) 1 mol/L, (d) 2 mol/L, (e) 4 mol/L, (f) 8 mol/L.



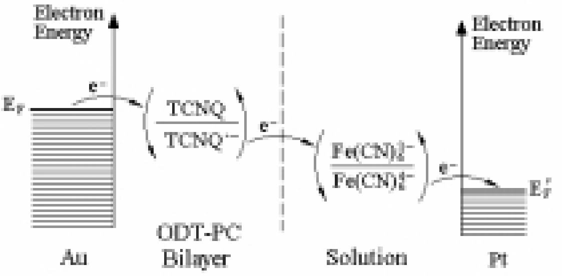
The experimental results of ac impedance indicate that, at open circuit potential, the transmembrane Faradaic resistance of Au/ODT-PC bilayer in 10^{-3} mol/L $Fe(CN)_6^{3-/4-}$ + 0.1 mol/L KCl solution decreased by a factor of > 5 after the modification of TCNQ. According to whether the embedded molecules participate in the transmembrane electron transfer[14], It is reasonable to believe that the TCNQ molecules act as electron conductors in the Au/ODT-PC bilayer.

Figure 1 (a) shows the cyclic voltammogram of TCNQ modified Au/ODT-PC electrode in KCl solution, while **Figure** 1 (b)~(f) show the cyclic voltammograms of the same electrode in $Fe(CN)_6^{3-/4-}$ solutions with different concentrations. From **Figure** 1 we note that , in positive scan from the open circuit potential, no anodic current will be observed regardless of the presence of redox couple. In negative scan, the cathodic current will be seen clearly in the presence of $Fe(CN)_6^{3-/4-}$, however, no cathodic current will be observed if there is no redox couple in the solution.

As TCNQ acts as electron conductor in Au/ODT-PC bilayer, the electron transfer process across bilayer basically consists of two steps. One is the electron transfer between TCNQ and Au electrode, and the other is the electron transfer between TCNQ in bilayer and redox couple in aqueous solution. The asymmetrical conductivity of Au/ODT-PC bilayer incorporated with TCNQ is attributed to the electrochemical properties of TCNQ. In the positive scan, the transmembrane electron transfer cannot occur because it is difficult to oxidize TCNQ. However, in the negative scan, it is easy to reduce TCNQ to $TCNQ^{\cdot -}$ [15]. Because the formal potential for $Fe(CN)_6^{3-/4-}$ (0.22V vs SCE) is a little higher than that for $TCNQ/TCNQ^{\cdot -}$ (0.13V vs SCE[15]), $TCNQ^{\cdot -}$ can transfer the extra electron to $Fe(CN)_6^{3-}$ at the bilayer solution interface and is oxidized back to TCNQ. The electron transfer process across bilayer in the negative scan is shown schematically in **Figure** 2.

Figure 2 The schematic representation of electron transfer process across Au/ODT-PC bilayer in negative scan.

It can also be seen from **Figure** 1 (b)~(f) that the cathodic current increases with the increasing of the concentration of $Fe(CN)_6^{3-/4-}$, which indicates that the electron transfer between $TCNQ/TCNQ^{\cdot -}$ and $Fe(CN)_6^{3-/4-}$ is the rate-determining step.



The asymmetrical conductivity of Au/ODT-PC bilayer modified with TCNQ has great theoretical significance and potential application in developing biomolecular electronic devices. The detailed mechanism of asymmetrical conductivity is under further research.

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