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Electrochemical Impedance Study of Schiff Base by Means of Self-assembled Monolayer

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Abstract: In this work, the self-assembled monolayer of Schiff base was first investigated using electrochemical impedance spectroscopy (EIS). The complexation of Cu^{2+} with the Schiff base was also detected with EIS method. The approximate linear relationship between Cu^{2+} and the reaction resistance (R_r) was observed. All the results suggest that the electrochemical property of Schiff base could be studied conveniently by means of forming self-assembled monolayer.

Keywords: Schiff base, self-assembled monolayer, electrochemical impedance spectroscopy, complexation.

Schiff base and its metal complex have attracted much attention because of their wide applications in biomedicine and their specific character in photochromic field[1]. Up to now, reports about Schiff base mainly covered its synthesis and structure[2,3]. To the best of our knowledge, there is no paper dealing with Schiff base using electrochemical impedance spectroscopy technique by forming self-assembled monolayer. The complexation of Schiff base with the transition metal ions has been confirmed by the report[4], so we considered that Cu^{2+} might complex with the Schiff base. It also reported that EIS method could be employed to probe the complexation of transition metal ion with its ligands[5].

The results of our work has not only proved the formation of self-assembled by Schiff base, but also confirmed the complexation of the Schiff base with Cu^{2+}. We calculated that the monolayer is somewhat loose comparing with thiol alkyl monolayer. The most interesting thing of this work is that, when Cu^{2+} is in the range of 10^{-5} - 5×10^{-4} mol/L, approximate linear relationship between the reaction resistance (R_r) and the logarithmic concentration of Cu^{2+}, was observed, which could be used to titrate Cu^{2+} quantitatively. The purpose of this work is to offer a new way to probe Schiff base, so as to reveal the functional mechanism of Schiff base or its complexes in biological systems.

The Schiff base tailored with -SH group (Φ-CH = N-Φ-$CONHCH_2CH_2SH$) is offered by Capital Normal University. All other reagents were analytical grade. The Schiff base monolayer was accomplished basing on the previous report[6]. The whole

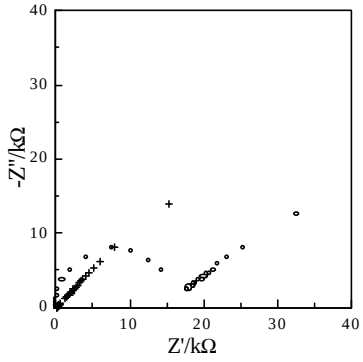
process must be carried out at 45°C, because the Schiff base could dissolve in ethanol only at this temperature. The electrochemical experiments were performed in the traditional three-electrode cell. A large Pt foil and SCE electrode were used as the counter and reference electrode, respectively. One redox couple of 1 mmol/L $Fe(CN)_6^{3-/4-}$ served as the probing-pin, 0.1 mol/L KCl as the supporting electrolyte. The complexation of Cu^{2+} with Schiff base was performed in 0.1 mol/L KCl solution containing $CuCl_2$.

Results and Discussion

The formation of self-assembled monolayer by Schiff base

Figure 1 is the complex resistance plot recorded at the open circuit potential using EIS technique. The dramatic variation has confirmed the formation of Schiff base monolayer on Au substrate. According to the formula reported before[7], the apparent rate constant k_{app} for the electrode modified with Schiff base was calculated to be 8×10^{-4} $cm\cdot s^{-1}$, while for the bare Au electrode, k_s is equal to 0.026 $cm\cdot s^{-1}$ [8]. Hence, the coverage of Schiff base monolayer on Au substrate could be estimated to be 99.2%. Though the coverage has exceeded 99%, the 45° line in the low frequency range proves the existing of diffusion process, *i.e.*, this monolayer self-assembled is still loose comparing with alkyl thiol monolayer[9]. Whereas, the phenomena observed strongly indicate that the monolayer of Schiff base has come into being. Some electrochemical properties of Schiff base could be studied by this means conveniently.

Figure 1 The complex resistance plots for two different electrodes



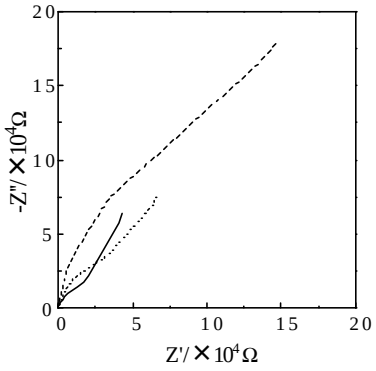
(++) bare Au electrode, (oo) Au electrode modified with Schiff base

The complexation of Cu^{2+} with Schiff base

The typical response of the complex resistance plots when the monolayer of Schiff base complexing with Cu^{2+} was shown in **Figure 2**. The main trend of these plots is that the thicker the concentration of Cu^{2+} was, the smaller R_t was presented, which could be represented by the diameter of the semicircle in the higher frequency range. Though the complexity of the real system could not be entirely reflected by some electric

elements or their group, but the value of R_r could really embody the feature of the monolayer partly. Commonly, the smaller value of R_r corresponds to the looser structure. The result showed that introduction of Cu^{2+} could lead to the looser structure of the monolayer.

Figure 2 The typical complex resistance plots for Schiff base-modified Au electrode in 0.1 mol/L KCl solution containing Cu^{2+} with different concentration



(---) 10^{-5} mol/L, (▪▪▪) 10^{-4} mol/L, (—) 10^{-3} mol/L

Figure 3 The relationship between the logarithmic concentration of Cu^{2+} and reaction resistance R_r

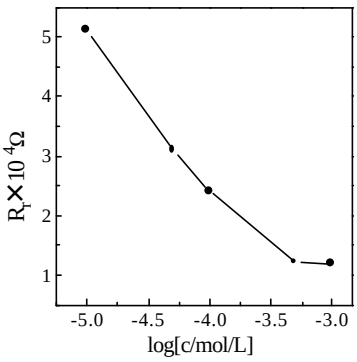


Figure 3 is the plot of R_r *vs* the logarithmic concentration of Cu^{2+}, where the concentration range of Cu^{2+} is from 10^{-5} to 10^{-3} mol/L. The value of R_r decreases with the addition of Cu^{2+} into the solution, but when the concentration of Cu^{2+} comes to 10^{-3} mol/L, one approximate plateau of R_r appeared. When the concentration of Cu^{2+} exceeds 10^{-3} mol/L, there is no effect of concentration of Cu^{2+} on the value of R_r any more. The encouraging thing is that the natural logarithmic concentration of Cu^{2+} relates with the value of R_r in a approximate linear way in the range of $10^{-5} - 5\times10^{-4}$ mol/L, suggesting that the Schiff base could complex with Cu^{2+} quasi-quantitatively. Hence, the amount of Cu^{2+} could be titrated by EIS method in the above Cu^{2+} concentration range.

The formation of packed well-ordered monolayer is the first step to investigate the electron-transferring mechanism of Schiff base and its other electrochemical character as well. The aim of our work is to testify the possibility of fabricating Schiff base monolayer using SAM technique and to find out if the R_r can reflect the complexation of Cu^{2+} with Schiff base. The approximate linear relationship of Cu^{2+} with the reaction resistance (R_r) was observed, suggesting that this method could be used to titrate Cu^{2+}. The detailed research is in progress.

Acknowledgments

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