Electrochemical Characteristic of 2-Mercaptobenzothiazole Self-Assembled Monolayer on Gold

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A monolayer membrane of 2-mercaptobenzothiazole (MBT) was prepared on a gold electrode through a self-assembly procedure. The monolayer structure and the electrochemical properties were investigated by various electrochemical techniques, like cyclic voltammetry and an impedance measurement with external redox. Experiments show that MBT can form a closely packed monolayer that can be charged due to the active N atom. The amount of charge on the membrane surface varies with the solution pH, and the monolayer shows "opening and closing" which depends on the solution pH. The electrostatic interaction of the monolayer with other ions is also related to the pH in solution. An impedance analysis shows that the heterogeneous electron-transfer rate of a fast redox like $\text{Fe}(\text{CN})_6^{3-/4-}$ decreases from 1.2×10^{-2} to $4.7 \times 10^{-5} \text{ cm s}^{-1}$ in neutral solution due to blockage of the self-assembled monolayer membrane.

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The preparation and study of various well-organized two-dimensional system on a solid electrode have attracted much interest within the last decade.¹ Among them, thiol self-assembled monolayers are of special interest, since Nuzzo and Allara² reported that self-assembled monolayers (SAMs) of alkanethiolates on gold could be prepared by a simple one-step adsorption from a dilute solution. These sulfide organic SAMs on gold exhibit high stability, are well-ordered structure and have extensive potential applications.³⁻⁵ Alkanethiols on gold represent the most studied group. The structure and properties of these SAMs have been investigated by means of spectroscopy,^{6,7} microscopy,⁸ electrochemistry and almost every possible surface technique. These monolayers have been used to study electron transfer,^{9,10} proteins and other bio-molecules,^{11,12} and to fabricate biosensor.¹³

Interest in the properties of thin-film organic materials, especially coherently organized monolayer assemblies, has grown enormously in recent years, primarily due to the easiness of fabrication, characterization, and manipulation. Some thioaromatic SAMs and heterocyclic thiols SAMs have been investigated.¹⁴⁻¹⁷ In contrast, studies on heteroaromatic thiols self-assembled monolayers are still rare. MBT SAM has been characterized by X-ray photoelectron spectroscopy (XPS)¹⁸ and the properties of potential-dependent "opening and closing" of the monolayer on gold have been investigated before.¹⁹ Recently, an impedance measurement has been successfully applied to investigate thin monolayer assemblies and electron transfer through them.^{20,21} This technique has some advantages because the effect of the solution resistance, double-layer charge and current due to diffusion or the other processes occurring in the SAM are observed explicitly. Therefore, impedance spectroscopy provides a new method to understand the structure of a thin monolayer, the dielectric constant and the apparent electron-transfer rate constant of the redox probes in

solution.

We have investigated the electron transfer in the MBT self-assembled monolayer on a polycrystalline gold surface in different solution pH using cyclic voltammetry and electrochemical impedance spectroscopy.

Experimental

2-Mercaptobenzothiazole (MBT) was purchased from Sigma; other chemicals were from Chemicals Co. of China. Twice-distilled water was used. A gold disk electrode (0.03 cm²) was employed as a working electrode. Before use, the gold electrodes were exposed to sulfochromic acid (saturated $\text{K}_2\text{Cr}_2\text{O}_7$ in concentrated H_2SO_4) for 1.0 min, and rinsed with twice-distilled water. They were then polished with a 0.3 μm alumina slurry on a polishing cloth, and ultrasonicated in water, ethanol, and water for 1.0 min, respectively. A CV of a Au electrode in 0.5 M H_2SO_4 between -1.5 and 1.8 V (SCE) was obtained and compared with the CV of Au reported by Angerstein-Kozłowska *et al.*²² in order to determine that a clean Au surface was being used each time. After the clean gold electrodes were immersed in a 1.0 mM MBT solution for the required time, an MBT self-assembled monolayer on gold was obtained.

Impedance and cyclic voltammetric measurements were performed with a three-electrode cell comprising a gold-disk working electrode, a large-area platinum flag counter electrode, and a saturated calomel reference electrode (SCE). Cyclic voltammetry was carried out on a Model RDE4 bipotentiostat (USA) in connection with a Model MC X-Y recorder (China). Impedance measurements were carried out with a Model 378/388 Electrochemical Impedance Systems (EG & G, Parc, USA). A 5.0 mV rms perturbation at a formal potential of the redox couple was used, and readings were taken at five discrete frequencies per decade. The measurement was conducted over a wide frequency range of 100 kHz - 0.1 Hz. All experiments

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Fig. 1 Cyclic voltammogram in 2.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ + 0.5 M KCl (pH 7.0) at: (—) bare gold; (---) gold modified with MBT for 1.0 h; (····) gold modified with MBT for 2.0 h. Scan rate: 0.1 V s^{-1} .

were carried out at room temperature ($25 \pm 0.1^\circ\text{C}$).

Results and Discussion

The influence of MBT SAM on electron transfer

Monolayer films on an electrode surface are usually designed to fulfill two specific tasks: to provide an effective coupling of the sensing component to the electrode surface and to insulate the electrode surface from the bulk of the solution. It is therefore essential to test the integrity and properties of such layered structures on the electrode surfaces. The redox behavior of a reversible couple is usually used to probe the compactness and sensitivity of the monolayer.²⁴ It was shown that the diffusion-limited current, measured during CV experiments at the monolayer-covered electrode, depends on the presence of pinholes in the monolayer.²⁵ The efficiency of the monolayer in blocking redox reactions can be estimated by the kinetics of the redox probe, as expressed by the peak-to-peak separation (ΔE_p).²⁶

Figure 1 shows the CVs of an MBT-modified gold electrode in 2.0 mM aqueous $\text{K}_3[\text{Fe}(\text{CN})_6]$ (pH 7.0) with different coating times. A progressive increase in ΔE_p values can be observed from bare gold to an electrode modified by MBT for longer times. The electrode modified by an 1-h coating almost showed no clear redox response, which indicates that MBT almost forms a closely packed monolayer. A voltammogram taken with an electrode modified for 2 h showed no redox response, except for the nonfaradic background current. There was no further change in the ΔE_p values for an electrode immersed for more than 2 h, the typical time required for the formation of a monolayer. This clearly indicates that, within 2 h, the electrode surface was covered with a compact monolayer, creating a barrier to electron transfer. However, on the MBT monolayer, there were some defect sites (pinholes) through which probe molecules could penetrate completely or partially, and the background current observed was mostly due to the pinholes present in the monolayer. With the progress of monolayer formation, the peaks caused by the redox probe became broader, which is due to a decrease in the rate of electron

Fig. 2 Cyclic voltammogram of an MBT-modified gold electrode in 2.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ + 0.5 M KCl: (—) pH 3.6, (---) pH 5.5, and (····) pH 7.0. Scan rate: 0.1 V s^{-1} .

transfer of $\text{Fe}(\text{CN})_6^{3-/4-}$ on the MBT-modified electrode. With the complete formation of the monolayer, the electron transfer was totally blocked, which could be attributed to the formation of a closely packed monolayer. It can be deduced that the electron transfer of electroactive species depends on the density of MBT SAM on gold.

It is well known that long alkanethiols can form dense, well-ordered and stable monolayers on gold, while short chain thiols are just contrary. Although short-chain thiol monolayer on gold is too thin to effectively block electron transfer on a gold surface,²⁷ our results have proved that MBT SAM could form a dense monolayer within a short time, which can effectively passivate the surface of an electrode and inhibit electron transfer on the gold surface.

The CV of the Au-MBT SAM in 2.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ + 0.5 M KCl solution at different pH is shown in Fig. 2. As can be seen, the peak current increase greatly and ΔE_p becomes small with a decrease of the solution pH. This indicates that the electrode reaction becomes more reversible at a lower solution pH. For example, ΔE_p is 120 mV at pH 3.6, and the reaction is quasi-reversible on MBT SAM/Au electrode. This indicates that the heterogeneous electron transfer of the redox on the MBT modified gold electrode is very easy in a lower pH solution, while it is difficult for the same gold electrode in a neutral solution. Previous studies have showed that this was caused by monolayer tunneling.²⁸ The MBT SAM shows an "opening" in an acidic solution and a "closing" in a neutral solution. This indicates that the structure of the monolayer on gold is greatly changed in different pH. First, the MBT can be protonized in an acidic solution due to a pair of free electrons at the N atom, and the monolayer can carry positive charges. The amount of charge depends on the solution pH. The protonized process for the MBT molecule in an acidic solution is shown in Fig. 3. Second, a structure reorientation of MBT on gold may

Fig. 3 Schematic illustration of the formation of a charged MBT monolayer in an acidic solution (the structure of MBT molecule on gold surface was proposed by Bharathi *et al.*¹⁹).

Fig. 4 Cyclic voltammogram of MBT-modified gold electrode in 1.0 mM CuSO_4 + 0.5 M KCl: (---) pH 3.5 and (—) pH 7.0. Scan rate: 50.0 mV s^{-1} .

take place in an acidic solution due to an electrostatic interaction between two positively charged molecules. The repulsion between the surface charges can result in an open SAM structure on the gold surface. It can be concluded that solution pH can greatly change the properties of the MBT SAM and affect electron transfer on a gold surface.

The MBT SAM can form a closely packed monolayer at a neutral or alkali solution and effectively block the electrode reaction of ferro-ferricyanide redox. While the MBT SAM carries positive charge in an acidic solution, this monolayer can greatly affect the electron transfer at a modified electrode. First, for the MBT monolayer, there exists an interaction between two close positively charged MBT molecules. This interaction can lead to an open channel in the monolayer. It is thus easy for redox to penetrate the monolayer. Second, a positive charge MBT monolayer can attract negatively charged groups such as $\text{Fe}(\text{CN})_6^{3-/4-}$. It is easy for the negatively charged redox to enter the monolayer. On the other hand, the redox having a positive charge will be repelled, and electron transfer at the interface will become difficult. Another probe reaction at the Au/MBT electrode in different pH solutions is shown in Fig. 4. It is clear in this figure that the CVs obtained for the under-potential deposition (UPD) of copper are different in different pH of the solution. At lower pH, UPD Cu was totally blocked due to an electrostatic repulsion between Cu^{2+} and the positively charged monolayer. On the other hand, at neutral solution, Cu^{2+} can penetrate the uncharged monolayer, and is reduced on the gold surface due to pinholes in monolayer and its small radius.

Thus, the electrostatic interaction between the MBT SAM and the redox couples, and among MBT molecules on a gold surface

exists when the self-assembled monolayer takes charge in an acid solution, which causes that electron transfer is to be promoted or inhibited according to the sign of charge of the redox couples. For example, when a self assembled monolayer carries positive charges, the electrochemical reversibility of the $\text{Fe}(\text{CN})_6^{3-/4-}$ couples is observed to increase. Dollhofer has also observed similar trends for a SAM modified electrode in the cyclic voltammogram of the redox of different charges.²⁹ In addition, that the current of the electrochemical reaction has some raise is partially due to the “activation” of electrode at positively charged for negative ions and at negatively charged for positive ions in different pH of solution.

Impedance analysis in the presence of $\text{Fe}(\text{CN})_6^{3-/4-}$

The ac impedance method is based upon a measurement of the response of the electrochemical cell to a small-amplitude alternating potential. The response is often shown in the complex-impedance presentation, and the result can be interpreted in terms of an equivalent electrical circuit.

The surface changes of the electrode must cause a change in the ac response; this change can be understood according to Randles' equivalent circuit,³⁰ and can be used to estimate the electrode coverage and some kinetic parameter, such as the charge-transfer rate constant, and the dielectric constant of the monolayer film.

In terms of the Randles' equivalent circuit, two frequency regions, as at high and low, can be distinguished to understand the change in faradaic impedance. Our attention is focused on the more interesting part of the spectrum at a high frequency where the electrode reaction is purely kinetically controlled, and the heterogeneous charge-transfer resistance is expected to increase due to inhibition of the electron transfer by the monolayer on the electrode surface.³¹ The electrode coverage (θ) is key factor which can be used to estimate the surface state of the electrode, and the charge-transfer resistance is also related to it. Assuming that all the current is passed by pinholes on the electrode, the electrode coverage can be calculated by³²

$$(1 - \theta) = R_{\text{ct}}^0 / R_{\text{ct}}, \quad (1)$$

where R_{ct}^0 is the charge-transfer resistance at bare gold and R_{ct} is the charge-transfer resistance at the monolayer-covered electrode under the same condition.

In the low-frequency region, where mass transfer by diffusion should be taken into account, the Warburg impedance is expected to deviate from a linear dependence upon $\omega^{1/2}$. The defects or pinholes in the monolayer are far apart from each other, which cause a deviation from semi-infinite diffusion in this situation, an overlap of the diffusion layer of neighboring pinholes is not achieved and spherical diffusion seems to be valid.³³ The ac response at the low-frequency region resembles the behavior of a bare electrode.

Figure 5 is complex-impedance plots of bare gold and MBT-modified gold. A comparison of complex impedance plots of a bare gold electrode and a monolayer-covered gold electrode shows the effect of the absorbed MBT monolayer on the ac response. For a monolayer-covered electrode, R_{ct} , which is the diameter of the semicircle at high frequency, is clearly greater than R_{ct}^0 due to an inhibition of MBT SAM to electron transfer, and R_{ct} increases with the MBT coating time on gold. On the other hand, the Warburg impedance is opposite. It is worth noting that the semicircle measured at bare gold is poorly defined, due to a fast electrode reaction, while it is well defined at the monolayer-coated electrode. From an analysis of the spectrum shown in Fig. 5, the charge-transfer resistance is 303.0

Fig. 5 Complex-impedance plots measured in 5.0 mM $K_4[Fe(CN)_6]$ + 5.0 mM $K_3[Fe(CN)_6]$ + 0.5 M KCl at a bias potential of 0.22 V (vs. SCE) for: (▼) bare gold electrode; (○) gold electrode modified with MBT monolayer for 1.0 h; (●) gold electrode modified with MBT monolayer for 2.0 h. The numbers in the figure are frequency (Hz).

$\Omega \text{ cm}^2$ and $1122.0 \Omega \text{ cm}^2$, respectively. The corresponding electrode coverage value was estimated to be 98.7% and 99.6%, respectively. The charge-transfer resistance for bare gold was measured to be $4.0 \Omega \text{ cm}^2$.

Assuming a parallel combination of a two parallel-plate capacitor, the first is assigned to the double-layer capacitance at the pinholes, and the second is assigned to the build up of charge across the monolayer, itself. The Z-plot can be used to evaluate the total capacitance (C),³²

$$C = C_{dl} + C_m = C_{dl}^0(1 - \theta) + C_m^0\theta, \quad (2)$$

where C_{dl} is the capacitance at the pinholes and C_m is the capacitance across the monolayer itself; C_{dl}^0 is the capacitance of the pure gold and C_m^0 is capacitance of a complete MBT monolayer assuming 100% coverage. C_{dl}^0 can be evaluated from the Z-plot obtained for bare gold, and C can be evaluated from the Z-plot for a MBT-modified gold, respectively. The surface coverage was calculated from Eq.(1). One can evaluate the defect-free monolayer capacitance (C_m^0) by Eq. (2). This C_m^0 can be used to calculate the dielectric constant (ϵ_m) of the monolayer,

$$\epsilon_m = C_m^0 d / \epsilon_0 \quad (3)$$

where d is the monolayer thickness, ($4.5 \text{ \AA}$),¹⁸ and ϵ_0 is the permeability of free space ($= 8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$). The results are given in Table 1.

The charge-transfer rate of the $Fe(CN)_6^{3-/4-}$ couple can be calculated from the Z-Plot of a MBT-modified electrode. Assuming a transfer coefficient (α) of 0.5, for the 1st-order reaction with $c_o = c_r = c$ (c_o , c_r = concentration of oxidized and reduced species at the surface) and for a unit geometric area,

$$R_{ct} = RT/j_0 F \quad (4)$$

$$\text{and } j_0 = Fk_{app}c, \quad (5)$$

Table 1 Different parameters obtained for MBT SAM on a gold electrode from impedance plots in 5.0 mM $Fe(CN)_6^{3-/4-}$ solution

Charge transfer resistance (R_{ct}) $\Omega \text{ cm}^2$	1122
Apparent electrode coverage (θ) %	99.6
Double layer capacitance (C) $\mu\text{F cm}^{-2}$	12.59
Defect-free monolayer capacitance (C_m^0) $\mu\text{F cm}^{-2}$	12.56
Monolayer dielectric constant (ϵ_m)	6.29
Apparent electron transfer rate constant of $Fe(CN)_6^{3-/4-}$ couple (k_{app}) cm s^{-1}	4.7×10^{-5}

$$\text{where } k_{app} = (1 - \theta)k_0. \quad (6)$$

Combining Eq.(4) and Eq.(5) gives

$$k_{app} = RT/F^2 R_{ct} c, \quad (7)$$

where k_0 is the electron-transfer rate constant at bare gold, and k_{app} is the apparent rate constant at the MBT-modified electrode. The k_{app} was calculated to be $4.7 \times 10^{-5} \text{ cm s}^{-1}$ from R_{ct} in Fig.5. With the result, the actual rate constant for the $Fe(CN)_6^{3-/4-}$ couple was estimated to be $1.2 \times 10^{-2} \text{ cm s}^{-1}$ (from Eq.(6)), which is in agreement with the literature value.²⁴

An MBT self-assembled monolayer can be prepared on a gold surface. This monolayer, though being thin, can form a closely packed and stable monolayer that inhibits charge transfer effectively on a gold surface. MBT SAM can carry a surface charge due to an active N atom on the MBT molecule; thus, an electrostatic interaction arises between the charged monolayer and the charged group in solution, which depends on the solution pH. Solution pH can change the structure of the MBT SAM and further affect the electron transfer on the modified gold electrode. This monolayer can be used to avoid the interference of some ions.

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References

1. A. Ulman, *Chem. Rev.*, **1996**, 96, 1533.
2. R. G. Nuzzo and D. L. Allara, *J. Am. Chem. Soc.*, **1983**, 105, 4481.
3. M. D. Porter, T. B. Bright, and C. E. D. Chidsey, *J. Am. Chem. Soc.*, **1987**, 109, 3559.
4. E. Sabatani, I. Rubinstein, R. Maoz, and J. Sagiv, *J. Electroanal. Chem.*, **1987**, 219, 365.
5. Y. T. Kim and A. J. Bard, *Langmuir*, **1992**, 8, 1096.
6. C. D. Bain, J. Evall, and G. M. Whitesides, *J. Am. Chem. Soc.*, **1989**, 111, 7155.
7. L. Strong and G. M. Whitesides, *Langmuir*, **1988**, 4, 546.
8. C. A. Widrig, C. A. Alves, and M. D. Porter, *J. Am. Chem. Soc.*, **1991**, 113, 2805.
9. C. E. D. Chidsey, *Science*, **1991**, 251, 919.
10. A. Kumar, N. L. Abbott, E. Kim, H. A. Biebuyck, and G. M. Whitesides, *Acc. Chem. Res.*, **1995**, 28, 219.
11. K. L. Prime and G. M. Whitesides, *Science*, **1991**, 252, 1164.
12. S. Song, P. A. Clark, E. F. Bowden, and M. J. Tarlow, *J. Phys. Chem.*, **1993**, 97, 6564.
13. S.-K. Jung and G. S. Wilson, *Anal. Chem.*, **1996**, 68, 591.
14. E. Sabatani, J. Cohen-Boulakia, M. Bruening, and I. Rubinstein, *Langmuir*, **1995**, 11, 4626.
15. W. A. Hayer and C. Shannon, *Langmuir*, **1996**, 12, 3688.
16. G. Xue, X. Y. Huang, J. Dong, and J. Zhang, *J. Electroanal. Chem.*, **1991**, 310, 139.
17. Y. J. Lee, C. Jeon, W. Paik, and K. Kim, *Langmuir*, **1996**, 12, 5830.
18. C. M. Whelan, M. R. Smyth, and C. J. Barnes, *J. Electroanal. Chem.*, **1998**, 441, 109.
19. S. Bharathi, V. Yegnaraman, and G. P. Rao, *Langmuir*, **1993**, 9, 1614.
20. E. Sabatani, J. Cohen-Boulakia, M. Bruening, and I. Rubinstein, *Langmuir*, **1993**, 9, 2974.
21. T. M. Nahir and E. F. Bowden, *Electrochim. Acta.*, **1994**, 39, 2347.
22. H. Angerstein-Kozłowska, B. E. Conway, B. Barnett, and J. Mozota, *J. Electroanal. Chem.*, **1979**, 100, 417.
23. A. Ulman, *An Introduction to Ultrathin Organic Films From Langmuir-Blodgett to Self-assembly*, **1991**, Academic Press, New York.
24. P. Krysinski and M. Brzostowska-Smolka, *J. Electroanal. Chem.*, **1997**, 42, 61.
25. O. Cailapakul and R. M. Crooks, *Langmuir*, **1995**, 11, 1329.
26. H. O. Finklea, S. Avery, M. Lynch, and T. Furtch, *Langmuir*, **1987**, 3, 409.
27. V. Molinero and E. J. Calvo, *J. Electroanal. Chem.*, **1998**, 445, 17.
28. Li. Tomi. T.-T., and M. J. Weaver, *J. Am. Chem. Soc.*, **1984**, 106, 6107.
29. K. DoBlhofer, J. Figura, and J. H. Fuhrhop, *Langmuir*, **1992**, 8, 1811.
30. M. Sluyters-Rehbach and J. H. Sluyters, "Electroanalytical Chemistry", ed. A. J. Bard, **1970**, Vol. 4, Marcel Dekker, New York.
31. C. Amatore, J. M. Saveant, and D. Tessier, *J. Electroanal. Chem.*, **1983**, 147, 39.
32. E. Sabatani, I. Rubinstein, R. Maoz, and J. Sagiv, *J. Electroanal. Chem.*, **1987**, 219, 365.
33. K. Tokuda, T. Gueshi, and H. Matsuda, *J. Electroanal. Chem.*, **1979**, 102, 41.