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# Electrochemical Behavior of Mixed Self-Assembled Monolayers of Azobenzene and Alkanethiol

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The self-assembly and electrochemical properties of mixed self-assembled monolayer (SAMs) of 4-methoxy-4′-(N-(2″-mercaptoethyl)amino)carbonyl)azobenzene ($C_1AzoC_2SH$) and 1-butanethiol ($C_4SH$) were studied on the gold electrode by cyclic voltammetry. Usually the azobenzene groups exhibit very sluggish electron-transfer kinetics in the densely packed films. The alkanethiol as the spacer molecule was introduced to the azobenzene monolayer system to weaken the intermolecular interaction in order to enhance the electrochemical activity of the azobenzene group. Under the different molar ratios of $C_1AzoC_2SH$ and $C_4SH$ we obtain a different electrochemical response and an apparent surface electrochemical rate constant. The experimental results suggested that the azobenzene groups exhibit a higher electrochemical activity in the mixed SAMs systems.

**Key words:** self-assembled monolayers (SAMs), azobenzene, electrochemical activity, voltammetry, kinetics

Chemical modified electrodes have been the subjects of considerable interest for more than a decade [1]. The electrochemical behavior of surface-modified electrodes continues to be of interest for both fundamental and practical perspectives [2,3]. Among them, monolayer self-assembly chemistry is a most promising strategy for constructing stable, well-defined monolayers on electrode surface. It provides a way of immobilizing redox-active groups onto electrode surface at a desired distance and a controlled microenvironment. Up to now, redox couples such as ferrocene [4,5], viologen [6,7] and ruthenium polypyridyl complexes [8,9] within self-assembled monolayers (SAMs) have been widely investigated.

Azobenzene chromophore is photochemically reactive, originating from its reversible *trans*-*cis* photoisomerization and is also electrochemically reactive, owing to its red-oxidation [10]. Recently, efforts have been made to introducing azobenzene group into SAMs [11,12]. Usually, the azobenzene groups exhibit very sluggish electron-transfer kinetics in the densely packed films. Many researchers have indicated that the main reason for the low electrochemically activity of the azobenzene SAMs is the spatial inhibition of monolayer structure on the reactions of azobenzene, which involve conformation change and protonations [13,14]. Basing on this sense, we prepared mixed monolayers, introducing the alkanethiols with the similar carbon chain

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into the azobenzene SAMs in order to enhance the electrochemical activity of the azobenzene groups.

In this paper, the 1-butanethiol ($C_4SH$) acts as the spacer component, which has the same length of alkyl chain as the $–C(O)N(H)(CH_2)_2$- of azobenzene component. We describe the preparation of mixed self-assembled monolayers on gold electrode with a novel thiol-functionalized azobenzene, 4-methoxy-4′-(N-(2″-mercaptoethyl)amino)carbonyl)azobenzene ($C_1AzoC_2SH$) and alkanethiols, 1-butanethiol ($C_4SH$), and the investigation of their electrochemical behavior by cyclic voltammetry.

## EXPERIMENTAL

**Chemicals:** The azobenzene functionality was introduced into the thiol according to Figure 1(A). Thionyl chloride (CP), pyridine (CP) was purchased from Beijing Chemicals. 2-Aminoethanethiol hydrochloride was obtained from Aldrich. Pyridine was dried over potassium hydroxide and distilled before using. All other chemicals were used without further purification. The 4-methoxy-4′-carboxylic azobenzene was prepared following a standard literature procedure [15].

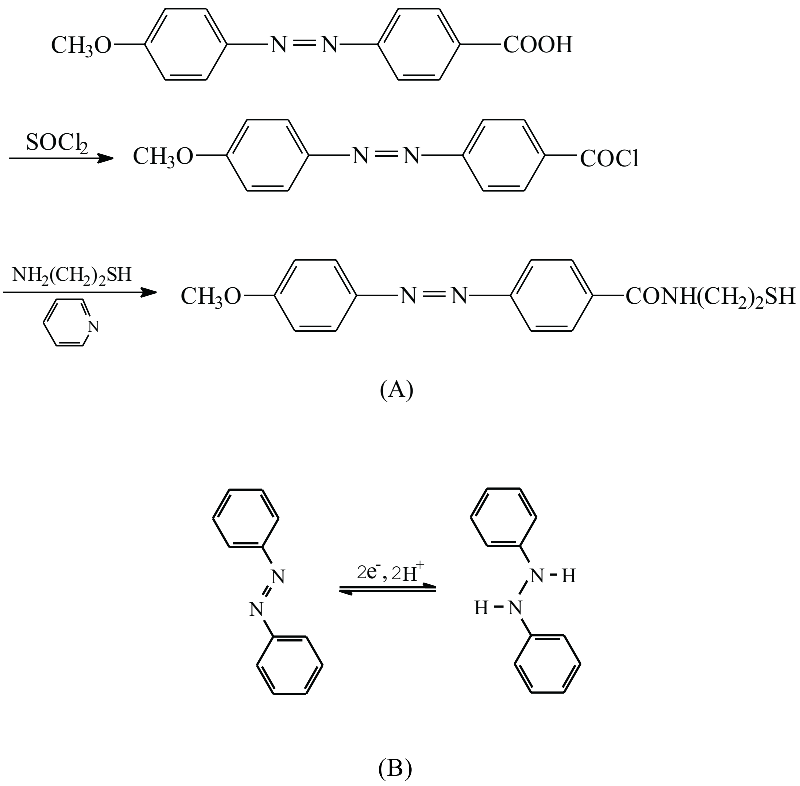


**Figure 1.** (A) Synthesis route for alkanethiol derivatives having both amide and azobenzene groups. (B) Redox process occurs between azobenzene and hydroazobenzene in the monolayer.

**Substrate preparation:** Monolayers were formed by the self-assembling technique on gold electrodes. The electrodes were first polished with 0.5 μm alumina slurry, followed by extensive rinsing with water and sonication. The Au electrode was then electrochemically cleaned and polished by cycling the electrode potentially between –0.20 and +1.40V *vs* Ag/AgCl in 0.5 M $H_2SO_4$ for several minutes until a stable and standard voltammetry was obtained. Self-assembled monolayers (SAMs) were prepared by immersing clean gold substrate into a series of 1.0 mmol/L ethanol solution containing 4-methoxy-4′-(N-(2″-mercaptoethyl)amino)carbonyl)azobenzene ($C_1AzoC_2SH$) and 1-butanethiol ($C_4SH$) with different component ratios over 24 h to reach a saturated and steady coverage. Afterwards, the substrates were washed with ethanol and dried in $N_2$ prior to characterization.

**Apparatus:** Electrochemical measurement was performed by using BAS-100B electrochemical analyzer. A personal computer was used for data storage and processing. The conventional three-electrode system was used. An Ag/AgCl saturated KCl electrode and a Pt plate were used as the reference electrode and counter electrode, respectively. All experiments were carried out in 0.067 mol $L^{-1}$ phosphate buffer (pH: 5.4), which was free from oxygen by bubbling through it with high-purity nitrogen.

## RESULTS AND DISCUSSION

**Electrochemical behavior of $C_1AzoC_2SH$ and mixed SAMs:** Azobenzene group is electrochemically active in aqueous solution owing to its redox (see Fig. 1). The typical cyclic voltammogram of $C_1AzoC_2SH$ SAMs at pH 5.4 in 0.067 mol $L^{-1}$ sodium phosphate buffer is shown in Fig. 2. Under the experiment condition, repetitively cycling over hundreds of scans does not alter the voltammogram, demonstrating that the SAMs are stable to electrochemical cycling. The shapes of voltammetric waves deviate from that predicted for an immobilized quasi-reversible redox couple. In particular, remarkably large separation between anodic peak and cathodic peak was found in a CV plots. Such a peak separation has also been observed by Laviron [16] when azobenzene

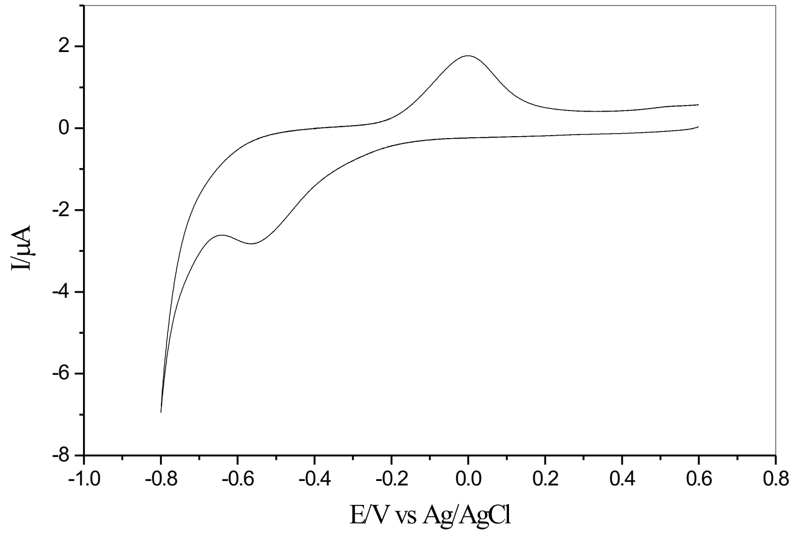
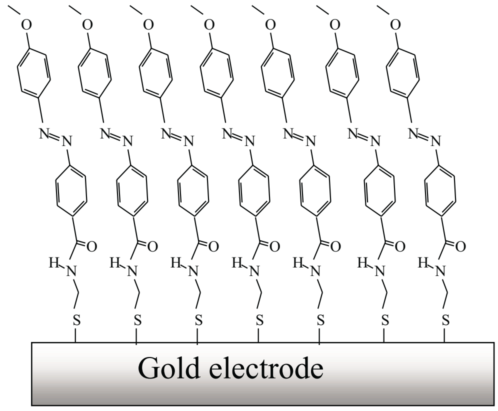


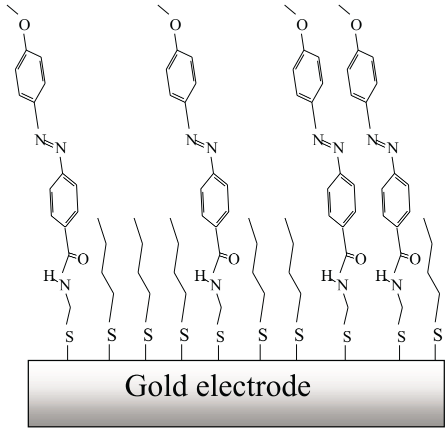
**Figure 2.** Cyclic voltammogram of $C_1AzoC_2SH$ SAMs in pH 5.4 phosphate buffer solution. Scan rate is 100 mV/s.

is reduced on a carbon electrode or a platinum electrode, and is generally attributed to the interaction between the redox active site and electrode surface. The surface concentration of electrochemically active azobenzene groups ($\Gamma_{Azo}$) in $C_1AzoC_2SH$ SAMs was estimated to around $2.035 \times 10^{-10}$ mol cm$^{-2}$, which is obtained by the integration of the current associated with the azobenzene redox wave, assuming a two-electron and two-proton mechanism. In the case of SAMs, $C_1AzoC_2SH$ molecules are highly oriented and closely packed, with the carbon chain (including the amide groups) located between the azobenzene unit and the gold substrate, making it possible to eliminate the specific interaction of the azo group with electrode surface. Therefore, large peak separation observed in this system can mainly be attributed to the sluggish electron transfer kinetics.

In this work, the mixed SAMs system is introduced into the azobenzene SAMs in order to enhance the electrochemical activity of azobenzene groups. Fig. 3 shows the



Azobenzene SAMs



Mixed SAMs

**Figure 3.** The schematic illustration of $C_1AzoC_2SH$ SAMs and mixed SAMs of $C_1AzoC_2SH$ and $C_4SH$.

schematic illustration of mixed SAMs of $C_1AzoC_2SH$ and $C_4SH$. Since both kinetic and thermodynamic factors may effect the final composition of the monolayers, but the preparation of mixed SAMs is far from trivial [17]. The RA-IR results showed that varying the relative ratio of these two components in the assembling solution could control the ratios of the component in SAMs. The cyclic voltammograms in Figure 4 were obtained from an electrode prepared by soaking gold electrode in ethanol solutions containing various ratios of $C_1AzoC_2SH$ and $C_4SH$. Following modification, the electrode potential was cycled between +600 mV and –800 mV at 100 mV/s in a phosphate buffer solution. The differences in the potentials of the peaks decreased, while the content of $C_4SH$ in the film increased, which indicated that introducing the

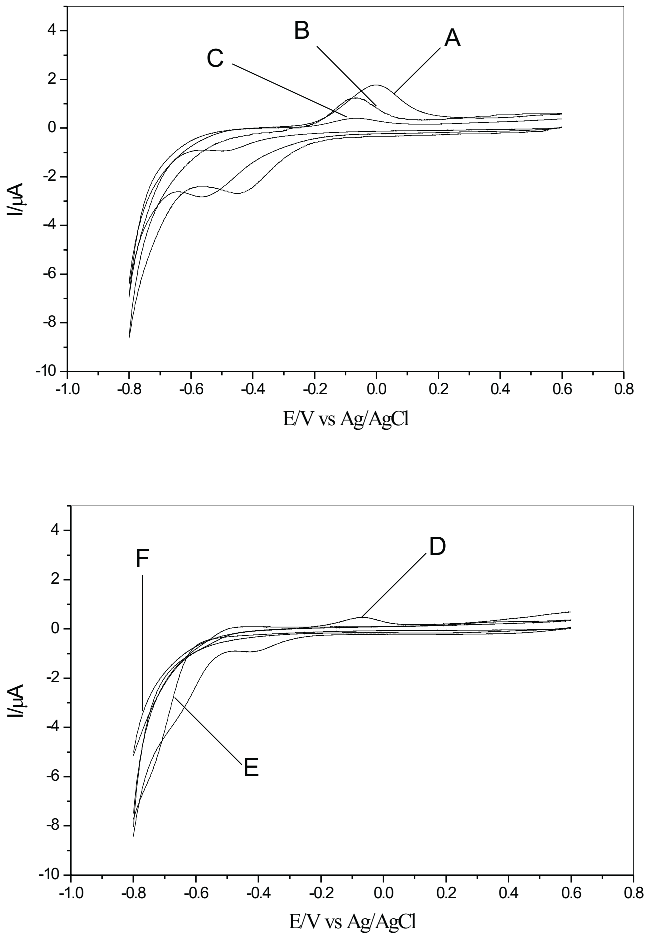


**Figure 4.** Cyclic voltammetry of mixed SAMs of $C_1AzoC_2SH$ and $C_4SH$: (a) pure $C_1AzoC_2SH$, (b) 99.5% $C_1AzoC_2SH$, (c) 99% $C_1AzoC_2SH$, (d) 90% $C_1AzoC_2SH$, (e) 80% $C_1AzoC_2SH$, (f) pure $C_4SH$ (molar percentage in solution). The electrolyte was 0.067 mol/L phosphate solution and scan rate was 100 mV/s.

$C_4SH$ into the SAMs resulted in a change of the microenvironment of azobenzene groups and enhance an electron transfer kinetics. It is clear that $C_4SH$ are preferentially adsorbed relative to $C_1AzoC_2SH$. Thus, when the content of $C_4SH$ is about 20% (molar percentage in the assembling solution), no distinct anodic or cathodic peak appears. The competitive self-assembly of $C_1AzoC_2SH$ and $C_4SH$ results in a decrease of the concentration of azobenzene in the mixed SAMs.

**Electrochemical kinetics of $C_1AzoC_2SH$ and mixed SAMs:** The significantly large $\Delta E_p$ values, that we observed for azobenzene SAMs, led us to investigate their possible scan rate dependence. Figure 5 shows the plot, which clearly indicates that $E_c$ and $E_a$ are linearly changed with the logarithmic scan rate, not only for the $C_1AzoC_2SH$ SAMs but also for the mixed SAMs assembled with different ratios solution. According to Laviron's treatment [18], the standard heterogeneous rate constant of electron transfer may be obtained in a straightforward manner from (1, 2 and 3) under totally irreversible conditions

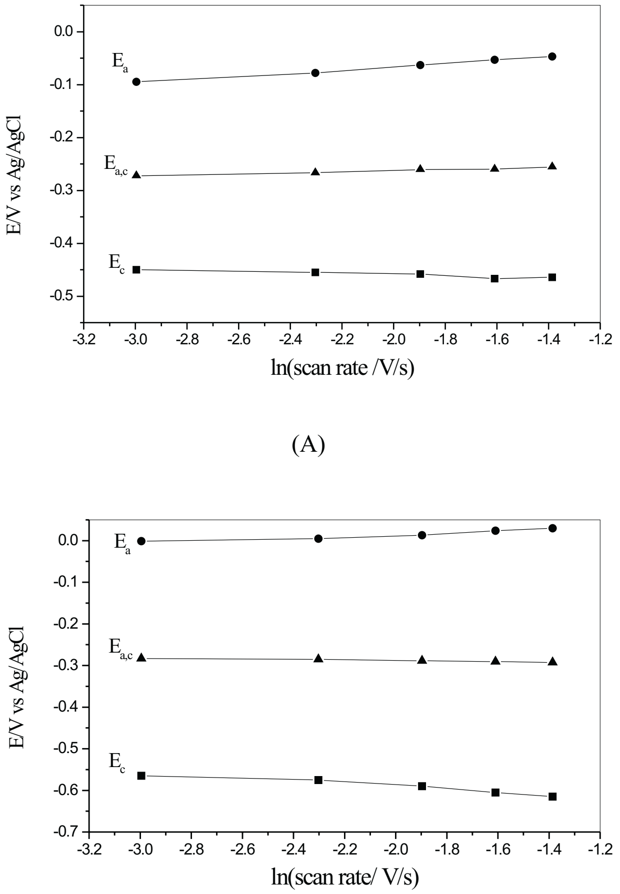
$$E_c = E^{0'} - \frac{RT}{\alpha nF} \ln\left(\frac{\alpha nF\nu}{RTk_{app}}\right) \tag{1}$$

$$E_a = E^{0'} + \frac{RT}{(1-\alpha)nF} \ln\left(\frac{(1-\alpha)nF\nu}{RTk_{app}}\right) \tag{2}$$

$$\log k_{app} = \alpha \log(1-\alpha) + (1-\alpha)\log\alpha - \log(RT/nF\nu) - \alpha(1-\alpha)nF\Delta E_p/2.3RT \tag{3}$$

$$\Delta E_p = E_a - E_c$$

where the notation ν means the potential scan rate and $R$, $T$ and $F$ have their usual meaning. Assuming that the product $\alpha n$ does not vary with potential, the graphs of $E_c$ -ln(ν) and $E_a$ -ln(ν) have been fitted with linear regression lines, as shown in Figure 5. The respective slopes of the lines are $RT/(\alpha nF)$ and $RT/((1-\alpha)nF)$. The values of $\alpha n$ and $(1-\alpha)n$ were thus obtained and substituted back in (1) and (2) to solve for $k_{app}$. The results (see Table 1) demonstrate that the $k_{app}$ of $C_1AzoC_2SH$ SAMs was much smaller than that of mixed SAMs. In the previous study [19], we have shown that in the azobenzene SAMs three kinds of intermolecular interactions exist: aromatic interaction between the azobenzene groups, the hydrogen bonding between the amide groups, and the hydrophobic interactions between the alkyl chains. The existence of these three kinds of interactions attracts the molecules together, forming a closely packed, well-ordered structure in SAMs. Azobenzene groups exhibit very sluggish electron-transfer kinetics in the densely packed films. In this work, we introduced the $C_4SH$ into the azobenzene SAMs to weaken these intermolecular interactions, which allows for required conformational changes of the azobenzene unit. The standard heterogeneous rate constant of the mixed SAMs is two orders of magnitude larger than that of the azobenzene SAMs.



(A)

(B)

**Figure 5.** The dependence of the anodic peak potential (*E*$_a$), the cathodic peak potential (*E*$_c$) and the mid-point potential ($E_{a,c}$ = ($E_a$ + $E_c$/2)) on the scan rate (ν) for $C_1AzoC_2SH$ SAMs (A) and mixed SAMs (B).

**Table 1.** The electrochemical parameters of $C_1AzoC_2SH$ SAMs and mixed SAMs.

| T = 287.15<br>V = 0.1 V/s | $C_1AzoC_2SH$ | $C_1AzoC_2SH$:$C_4SH$<br>99.5:0.5 | $C_1AzoC_2SH$:$C_4SH$<br>99:1 |
|---|---|---|---|
| E$_c$/mV | –0.575 | –0.455 | –0.499 |
| E$_a$/mV | 0.005 | –0.078 | –0.065 |
| n | 2.000 | 3.275 | 1.778 |
| α | 0.3822 | 0.7525 | 0.5403 |
| $k_{app}$ | 4.1522e-5 | 3.9126e-4 | 1.54078e-3 |
| log$k_{app}$ | –4.3817 | –3.4076 | –2.8123 |

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## REFERENCES

1. Murray R.W., *In Electrochemical Chemistry*; Bard A.J., Ed.; Dekker: NY, **13**, 1191–1368, (1984).
2. Ulman A., *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-assembly*, Academic Press, San Diego, CA. (1991).
3. Murray R.W. (Ed.), *Molecular Design of Electrode Surfaces*, Wiley: NY, (1992).
4. Chidsey C.E.D., *Science*, **251**, 919 (1991).
5. Chidsey C.E.D., Bertozzi C.R., Putvinski T.M. and Mujsce A.M., *J. Am. Chem. Soc*., **112**, 4301(1990).
6. Delong H.C. and Buttry A.D., *Langmuir*, **8**, 2491 (1992).
7. Bunding-Lee K.A., *Langmuir*, **6**, 709 (1990).
8. Finklea H.O. and Hanshew D.D., *J. Am. Chem. Soc*., **114**, 3173 (1992).
9. Ravenscroft M.S. and Finklea H.O., *J. Phys. Chem.*, **98**, 3843 (1994).
10. Liu Z.F., Hashimoto K. and Fujishima A., *Nature*, **347**, 658 (1990).
11. Yu H.Z., Wang Y.Q., Cheng J.Z., *et al.*, *J. Electroanal. Chem*., **395**, 327 (1995).
12. Wang Y.Q., Yu. H.Z., Cheng J.Z., *et al.*, *Langmuir*, **12**, 5466 (1996).
13. Herr B.R. and Mirkin C.A., *J. Am. Chem. Soc*., **116**, 1157 (1994).
14. Yu H.Z., Zhao J.W., Wang Y.Q., *et al*., *Langmuir*, **12**, 2843 (1996).
15. Kawai T., Umemura J. and Takenaka T., *Langmuir*, **5**, 1378 (1989).
16. Roullier E. and Laviron E., *J. Electroanal. Chem.*, **134**, 181 (1982).
17. Bumm L.A., Arnold J.J., Cygan M.T., Dunbar T.D., Burgin T.P., Jones L., Allara D.L., Tour J.M. and Weiss P.S., *Science*, **271**, 1705 (1996).
18. Laviron E., *J. Electroanal. Chem*., **101**, 19 (1979).
19. Zhang J., Zhao J., Zhang H.L., Li H. L. and Liu Z.F., *Thin Solid Film*, **327–329**, 195 (1998).