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SELF-ASSEMBLING KINETICS OF AN AZOBENZENEALKANETHIOL MONOLAYER ON GOLD

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Abstract The self-assembling kinetics of a new azobenzenealkanethiol (C8AzoC3) on gold surface was studied by means of contact angle measurements and electrochemical techniques. A two-step adsorption kinetics was observed: the fast adsorption step and the following long-term rearrangement process. The first step is consistent with a first order adsorption kinetics with a rate constant of 1.2×10^3 $mol^{-1}\cdot dm^3\cdot s^{-1}$. The unique variation of the electrochemical behavior of the C8AzoC3 SAMs on gold formed with different assembling time was investigated, which was well explained by a dynamic model we suggested.

INTRODUCTION

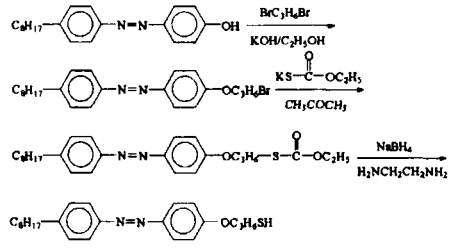
The electrochemical and photochromic properties of azobenzene species have been paid great attention for decades. The incorporation of azobenzene groups into organized molecular assemblies opens a new avenue in the field of electrochemistry and interface science.[1-10] The electrochemical behavior and related properties of azobenzene groups have been thoroughly studied both in Langmuir-Blodgett (LB) films[2-4] and self-assembled monolayers (SAMs).[5-8] Since the self-assembly technique is the most promising method to prepare the stable and highly oriented monolayer systems, it became one of our most interested research subjects. We have fabricated a new class of azobenzene self-assembled monolayers which showed clear-cut faradic response in an aqueous medium,[5] and extensively investigated the pH effects on the apparent electron-transfer kinetics,[6] the molecular structural dependence,[7] the effect of functional group by comparing with ferrocene.[8] In this paper, we will describe the assembling kinetics of a long-chain azobenzenealkanethiol and the unique electrochemical behavior of its monolayer on gold with different surface coverage.

The kinetics of the formation of alkanethiol monolayers on gold was firstly studied by Bain et al [12]. The concentration of adsorbate, the alkyl chain length, and the attached bulky group (e.g. phenyl ring), all play crucial roles in the assembling kinetics. Following studies we could find in literature were carried out by Ulman,[13] Uosaki[14] etc.

For the azobenzenethiol assembles into monolayer on gold surface, its kinetic behavior is still an unprocessed area, although this kind of information is of undoubtedly importance in evaluating the unique electrochemical behavior of azobenzene functionalized self-assembled monolayers.

EXPERIMENTAL

The preparation of the azobenzene-functionalized thiol compound C8AzoC3 was according to the procedure shown in Scheme I:



Scheme I

The characterization was based on: MS(FAB) m/e: 385 (M+1); ^{1}H NMR ($CDCl_3$): d: 0.88 (t, 3H, CH_3, J=6.86 Hz); 1.30 (m, 10H, CH_2). 1.64 (m, 2H, CH_2CH_2-ph, J=6.86Hz); 2.74-2.90 (m, 2H, CH_2-ph, J=7.04Hz); 4.14 (m, 2H, OCH_2, J=6.00Hz); 2.20-2.25 (m, 2H, CH_2-CH_2-S); 2.66(t, 2H, CH_2S, J=7.48Hz); 6.99 (m, 2H, -ph); 7.28 (two double, 2H, -ph, J_1=8.36Hz, J_2=2.24Hz); 7.80 (two double, 2H, J_1=8.36Hz, J_2=2.12Hz); 7.89(m, 2H, ph). Anal. calcd for $C_{23}H_{32}N_2OS$: C, 71.8; H, 8.39; N, 7.28. found:C, 71.56; H, 8.16; N, 7.21.

The gold substrate was prepared by vacuum evaporating 150 nm of high-purity Au (99.999%) onto 15nm-Cr-precoated glass microscope slides. Before the self-assembly, it was cleaned by immersing into *"piranha solution (H_2SO_4: H_2O_2 7:3 v/v)"* for about 5 min at 90°C, followed by extensive ringing with pure water and ethanol.

Contact-angle titrations were performed with a JJC-II contact angle goniometer, while electrochemical experiments were conducted in a single compartment cell with a Hokuto Denko HA-150 Potentiostat, a HB-111 function generator and a Riken Denshi F-35A X-Y recorder. The details of electrochemical and contact angle measurements have been reported previously elsewhere.[6]

RESULTS AND DISCUSSION

Kinetics of Formation of C8AzoC3 Monolayer on Gold:

The azobenzenealkanethiol (C8AzoC3) can form a stable and reproducible monolayer on gold surface from its dilute ethanol solution within 24 hours. The advancing contact angle with pure water on the monolayer surface is 109±1°, much larger than that of bare gold

surface (55±4°), and comparable with that of a long chain n-alkanethiol monolayer on gold (~110°).

Figure 1A shows the variation of the cosine contact angle with increasing the self-assembling time in ethanol. The cosine advancing contact angle of pure water on the monolayer surface, which relates to the surface concentration of C8AzoC3 molecules, initially decreased with increasing the assembling time and then gradually reached a saturated value. The assembling process can be reasonably divided into two consecutive steps: a very fast initial step, which takes a few minutes, and a slow step, which lasts several hours, in agreement with the result of Uosaki [14]. The former may correspond to the "nucleation" process which could be treated as a first order kinetic behavior, and the later correspond to the rearrangement of molecules in the monolayer.

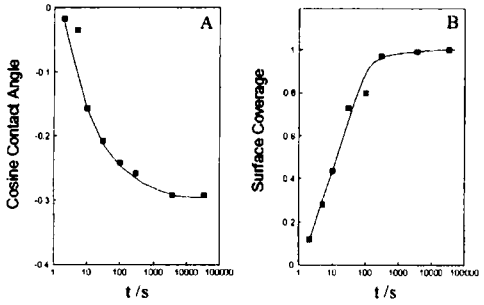


FIGURE 1. The dependence of the cosine contact angle (A), and the surface coverage (B) on self assembling time in ethanol.

During the assembling process, the gold surface was only partially covered by C8AzoC3 monolayer. In this case, both the exposed gold surface and the C8AzoC3 monolayer covered surface contribute to the contact angle values. Assuming that these two different surface states do not interfere with each other, according to the contact angle equation, then we have:

$$\cos\theta = (1-f)\cos\theta_1 + f\cos\theta_2 \quad (1)$$

where, θ, θ_1, θ_2 are the contact angle of mixed surface, bare gold surface and the C8AzoC3 monolayer covered surface, respectively. f is the surface coverage of the C8AzoC3 monolayer, which is the ratio of C8AzoC3 monolayer covered area to the whole surface area. By assuming simple Langmuir adsorption:

$$\ln(1-f) = -k_{ad}\, ct \quad (2)$$

we can derive the rate equation as:

$$\cos\theta = \cos\theta_2 - (\cos\theta_2 - \cos\theta_1)\exp(-k_{ad}\, ct) \quad (3)$$

where the c is the concentration of adsorbate, t is the assembling time and k_{ad} is the rate constant for the self-assembling process. By fitting the experimental results with Eq.3, we obtained the rate constant to be 1.36×10^3 $mol^{-1}\cdot dm^3\cdot s^{-1}$.

An alternative approach used to evaluate the self-assembling kinetic rate constant is based on the blocking effect of the C8AzoC3 monolayer on the oxidation/reduction of gold electrode itself. As we know, the real area of a gold electrode can precisely obtained from the cathodic charge which corresponds to the reduction of gold-oxide. Thus the surface coverage of the C8AzoC3 monolayer on the gold electrode could be deduced form the ratio of the cathodic charge Q (obtained from monolayer covered electrode) and

the saturation value Q_{max} (obtained for the bare gold electrode), which were taken from the CVs of these electrodes in 0.1M H_2SO4 (-0.2~1.5V vs Ag/AgCl):

$$f = 1 - Q/Q_{max} \quad (4)$$

By fitting the data shown in Figure 1B with Eq. 2, we estimated the self-assembling rate constant to be 1.02×103 $mol^{-1} \cdot dm^3 \cdot s^{-1}$. The value is nearly the same as we obtained from the contact angle measurements, indicating that these methods for evaluating the assembling kinetic rate constant are both valid and valuable.

The assembling rate constant we obtained for the C8AzoC3 monolayer is much larger than that of *n*-alkanethiols [12] and ferrocenealkanethiols on gold [14], demonstrating that the assembling rate is not only determined by the thiol-gold interaction, but also relates to the interaction among the functional groups. It could be concluded that the introducing of azobenzene group into alkanethiols molecule speeds up the self-assembling process compared with the ferrocene group.

The Assembling Time Dependent Electrochemical Behavior of C8AzoC3 Monolayer

Based on the kinetic investigations above, we realized that by controlling the assembling time in ethanol, one can effectively control the packing density or the structure of the C8AzoC3 monolayer on gold. This enable us to give insights into the structure dependence of the electrochemical behavior of C8AzoC3 SAM on gold.

In Figure 2A-E, the cyclic voltammograms (CVs) of C8AzoC3 modified gold electrode with different assembling time in Britton-Robinson (BR) buffer at pH 7.0 are shown. With different assembling time, the electrochemical behavior of these C8AzoC3 monolayers are considerably different. The 2s and 5s assembled monolayers show a pair of reversible redox peaks (see Figure 2A-B, while in the 30s assembled monolayer, a new cathodic peak near to -700 mV appeared. The respective anodic peak is located at -120 mV, the peak separation is up to 580mV, indicating that the surface electrochemical reaction is very "irreversible" or very slow (see Figure 2C-D). However, when the assembling time is rather longer than several hours, the C8AzoC3 monolayers does not show any faradic response (see Figure 2E). It means that the two-electron, two-proton involved azobenzene ⇔ hydrazobenzene reduction/oxidation process could not be conducted in this case. The electrochemical inaccessibility of this

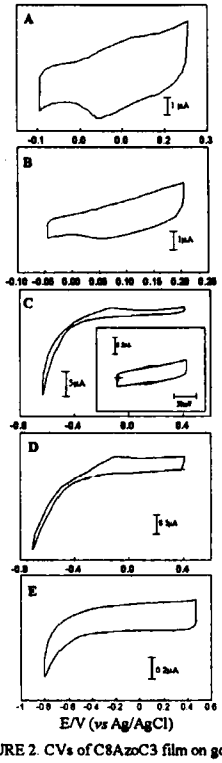


FIGURE 2. CVs of C8AzoC3 film on gold with different assembling time: t/s: A)2 B)5 C)30 D)300 E)86400; B-R buffer, pH=7.0, v=100mV/s

monolayer is quite different from that of azobenzene LB films [2-4] and that of C2AzoC2 SAMs [5,6] we have reported. Based on oxidative peak around -120mV, the surface concentration of electroactive azobenzene groups was calculated and listed in Table I.

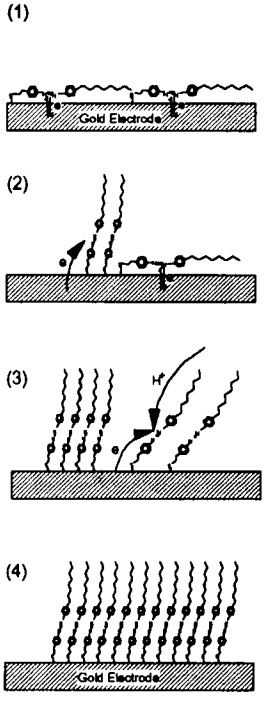
TABLE I The surface concentration of electroactive C8AzoC3 molecules in the SAM on gold electrodes with different assembling time (t).

t/s	2	5	30	300	3600	86400
$10^{12}\times\Gamma$/ mol/cm^2	*	*	5.07	1.72	1.44	0.00

For the cases of 2s and 5s, no clear-cut anodic peak was observed at -120mV, we do not present the values. From Table I, one can see that 30s assembled azobenzene monolayer has the highest surface concentration of active azobenzene groups. However, the value is considerably smaller than that of C2AzoC2 SAM we have reported. As we mentioned before, the surface coverage of C8AzoC3 monolayer gradually increase with the assembling time, as shown in Figure 2B. It is really interesting to note that the surface concentration of electroactive azobenzene group decreased with the increase of surface coverage of the azobenzene monolayer. On this basis, we can conclude that not all of the azobenzene groups within the C8AzoC3 monolayer are electroactive, even when the assembling process has not finished.

From the CV of 2s or 5s (Figure 2A-B), we can find a pair reversible redox peaks. For the azobenzene monolayer with an assembling time longer than 100s, such as in the case of 300s, only a pair of redox peaks with huge peak separations could be observed (Figure 2D). But for 30s assembled monolayer, both of these two different features could be found in its CV (Figure 2C). Based on the above experimental facts, we proposed a possible assembling kinetic model for C8AzoC3 on gold surface (Scheme II).

The C8AzoC3 molecules adsorb onto gold surface very quickly with a disordered and very loose structure in the first several seconds, and most of the molecules are lying flatly on the gold surface. Thus the electron-transfer occurs directly from the azobenzene group to the gold electrode, leading to a reversible faradic response (Scheme II(1)). With the assembling time being increased, some of the adsorbed molecules tend to stand out of the electrode surface, and assemble into local two-dimensional crystal-like domains



Scheme II

(Scheme II(2)). In this case, the reduction of azobenzene groups can follow two different ways: direct electronic coupling with the electrode as in the case of (1), and through bonding electron-transfer. As a result, two pairs of redox peaks can be observed simultaneously. The further increase of surface coverage makes all the adsorbate molecules standing on the electrode surface. However, some pin-holes or defects are still available in the monolayer, whereby the electrochemical reaction could take place (Scheme II(3)). During these steps, the assembling behavior could be treated as the first "fast assembling process", which can be evaluated as a first order adsorption kinetics. Afterwards, the film undergoes a long-term structural rearrangements, and finally forms a homogenous, stable and highly oriented monolayer (Scheme II(4)). In such a closely packed monolayer, the structural conformational change and proton transportation are both severely inhibited, leading to the electrochemical inaccessibility of the azobenzene moieties.

REFERENCES

1. E. Laviron, and Y. Mungnier, J. Electroanal. Chem., 111, 337(1980).
2. Z.F. Liu, B.H. Loo, K. Hashimoto, and A. Fujishima, J. Electroanal. Chem., 297, 133(1991).
3. Z.F. Liu, B.H. Loo, K. Hashimoto, and A. Fujishima, J. Electroanal. Chem., 324, 259(1992).
4. Z.F. Liu, C.X. Zhao, M. Tang, and S.M. Cai, J. Phys. Chem., 1996, in press.
5. H.Z. Yu, Y.Q. Wang, J. Z. Cheng, J.W. Zhao, S.M. Cai, H. Inokuchi, A. Fujishima, and Z.F. Liu, J. Electroanal. Chem., 395, 327(1996).
6. H.Z. Yu, Y.Q. Wang, J. Z. Cheng, J.W. Zhao, S.M. Cai, H. Inokuchi, A. Fujishima, and Z.F. Liu, Langmuir, 12, 2843(1996).
7. Y.Q. Wang, H.Z. Yu, J.Z. Cheng, J.W. Zhao, S.M. Cai, and Z.F. Liu, Langmuir, 1996, in press.
8. H.Z. Yu, Y.Q. Wang, S.M. Cai and Z.F. Liu, Ber. Bunsenges. Phys. Chem., 1996, in press.
9. W.B. Caldwell, D.J. Campbell, K.M. Chen,B.R. Herr, C.A. Mirkin, A. Malik, M.K. Durbin, P. Dutta, and K.G. Huang, J. Am. Chem. Soc., 117, 6071(1995)
10. M. Jaschke, H. Schonherr, H. Wolf, H.J. Butt, E. Bamberg, M.K. Besocke, and H. Ringsdorf, J. Phys. Chem., 100, 2290(1996).
11. A. Ulman, An Introduction to Ultrathin Organic Films: Academic Press, Boston, MA, 1991, Chapter III.
12. C.D. Bain, E.B. Troughton, Y.T. Tao, J. Evall, G.M. Whitesides, and R.G. Nuzzo, J. Am. Chem. Soc., 111, 321(1989).
13. S.D. Evans, E. Urankar, A. Ulman, N. Ferris, J. Am. Chem. Soc., 113, 4121(1991).
14. T. Kondo, M. Takechi, Y. Sato, and K. Uosaki, J. Electroanal. Chem., 381, 203(1995).