The Effect of Packing Density on the Electron-Transfer Kinetics of an Azobenzenethiol Monolayer on Gold

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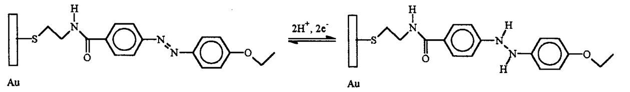
The effect of molecular packing density on the electron transfer kinetics in an azobenzene self-assembled monolayer on gold was investigated for the first time by controlling the assembling time. The apparent electron transfer rate constant (k_s) showed a gradual decrease with increasing the molecular packing density, which can be well understood in terms of a structural inhibition occurred in the closely packed monolayer on the reduction/oxidation of azobenzene.

Self-Assembly (SA) of alkanethiols has been used as a powerful method to anchor redox active species onto gold electrode surface with a desired distance and a controlled microenvironment. Thus prepared self-assembled monolayers (SAMs) present us ideal models for the study of long range electron transfer kinetics.[1] Several research groups have reported electron transfer rates of redox species that either were chemically bonded to the terminus of an alkanethiol monolayer or were freely diffusing in solutions.[2,3] The rate constants were shown to decay exponentially with increasing alkanethiol chain length, which was in accord with theoretical prediction based on through-bond tunneling mechanism.[2] There is also much work concerning the relationship between the monolayer structure and the voltammetric behavior by co-adsorption of both unsubstituted and redox centers (such as ferrocene, quinone, etc.) attached electroactive alkanethiols.[4,5] The electrochemical reaction of azobenzene involves both molecular structural change and protonation reactions in addition to the electron transfer (Scheme 1),[6,7] which may enable us to give further insights into the effect of molecular packing on the long range electron transfer kinetics when we create a series of azobenzene SAMs with different molecular packing densities to investigate their electrochemical kinetic behaviors. In this letter, by controlling the time of the adsorption from solution onto gold electrode (i.e., the assembling time), azobenzene SAMs with different surface coverage (i.e., molecular packing density) were prepared, and further used for electrochemical measurements.



Scheme 1.

The azobenzene alkanethiol we used, CH_3CH_2O-ϕ-N=N-ϕ-C(O)$NHCH_2CH_2SH$ (C2AzoC2SH), was synthesized and purified in our laboratory.[7] The gold substrate was obtained by vacuum deposition of 150 nm high-purity gold (99.999%) onto 10 nm Cr-precoated glass plates (heated to 180°C) at an evaporation rate of 0.1~0.2 nm/s. The C2AzoC2SH SAMs were formed by immersing gold substrates into a 0.1 mM ethanolic solution of C2AzoC2SH for a given time. The details for electrochemical and contact angle measurements have been reported elsewhere.[7]

Contact angle and double layer capacitance measurements are conventional methods for studying the molecular packing density of an organic monolayer on electrode surface. We first followed the variations of these two parameters when changing the assembling time for azobenzene SAMs' formation. The double layer capacitance was obtained by small range potential scan proposed by MacDonald.[8] It was found that the advancing contact angle of water droplet shows an increase initially and reaches a constant value (79±2°) finally, while the double layer capacitance shows a decrease initially and then also reaches a constant (3.1±0.3μF/cm^{-2}). These results demonstrate that azobenzene monolayers with different packing densities have been obtained by simply controlling the assembling time.

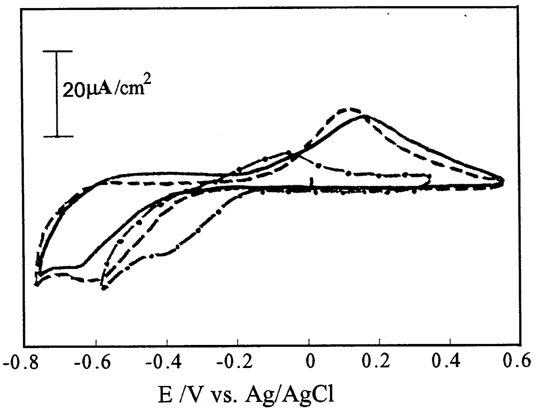


Figure 1. Typical cyclic voltammograms of C2AzoC2SH SAMs on gold prepared with different assembling time: 40 s (–•–); 1h (- - -); 24 h (—); Scan rate: 100 mV/s, Britton-Robinson buffer, pH: 5.5.

Figure 1 shows the typical cyclic voltammograms (CVs) of C2AzoC2SH SAMs on gold prepared with different assembling time. Linear relation between the potential scan rates and the peak currents in these CV measurements was obtained, indicating that the current arises from the reaction of surface-confined azobenzene species. We noted that there is a significant change in the CVs for C2AzoC2SH SAMs prepared with different assembling time. For a short assembling time less than 40 s, the shape of redox peak was not clear and its peak current was small, indicating that the surface coverage of azobenzenethiol is low in this case. Further, the reproducibility of these CVs is not good, while reversible redox peaks were observed sometimes, probably due to the varied electron transfer mechanisms.[9,10] When the assembling time was longer than 40 s, the CVs become well-developed, and clear-cut cathodic/anodic peaks were observed with large peak separation (see Figure 1). The peak separation ($\Delta Ep = Ep,a - Ep,c$) increases with increasing the potential scan rate for all the azobenzene SAMs prepared with varied assembling times. These observations may suggest that the surface reaction is controlled by electron transfer kinetics and follows the same electron tunneling mechanism. On the other hand, our RA-FTIR data shows that the molecular packing has been highly improved after 40 s assembling, as evidenced by the formation of intermolecular hydrogen bonding, in which case the molecules are believed to possess nearly perpendicular orientation in the monolayer.[11] Therefore, we will focus our discussion of the longer assembling time case in the following section.

Figure 2 shows the assembling time dependent surface concentration (Γ) and electron transfer rate constant (k_s) of C2AzoC2SH SAMs on gold. The Γ value was determined by the cut-and-weigh method, along with a two-electron and two-proton reaction of azobenzene/hydrazobenzene redox couple, as shown in Scheme 1. Obviously, surface concentration rapidly increases, and finally reaches a constant value with increasing the assembling time, which is in good agreement with the contact angle and double layer capacitance measurements.

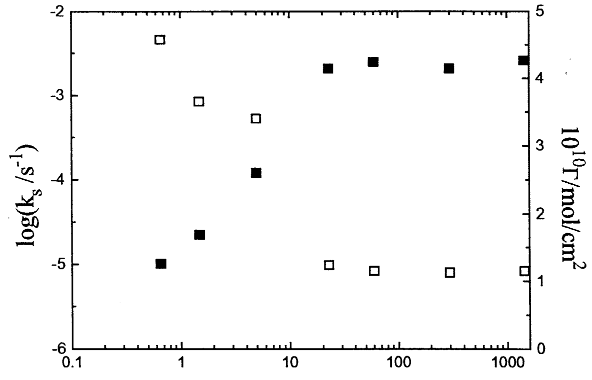


Figure 2. The variations of surface concentration Γ (■) and electron transfer rate constant k_s (□) of C2AzoC2SH SAMs as a function of the assembling time.

The significantly large ΔEp values enable us to evaluate the apparent electron transfer rate constant (k_s) using Laviron's treatment.[12] We noted that, k_s value shows a gradual decrease with increasing the assembling time and reaches a constant finally. Further, the variations of the surface concentration and electron transfer rate constant of these azobenzene SAMs are contrary, i.e., when the Γ value becomes larger, the k_s tends to decrease, but they reach their final values in the same time (see, Figure 2). Since the assembling time dependent surface concentration directly relates to the molecular packing density in the monolayer, the changes of the molecular packing density in these azobenzene SAMs should be considered to further evaluate the origin of the unique variation of k_s when increasing the assembling time.

For highly organized SAMs on electrode surface, the long range electron transfer is believed to follow the through-bond tunneling mechanism rather than the classical space tunneling.[2,3] It should be noted that the molecules in these SAMs are oriented with a certain angle to stand on the electrode surface, the electron transfer distance is determined by the length of the alkyl chain spacer between the redox center and electrode surface. We have shown that the through-bond tunneling also holds true for the electron transfer process in equilibrated azobenzene SAMs.[13] As we have stated above, when the assembling time becomes much longer (>40s), the combined experimental observations by electrochemistry and RA-FTIR suggest that most molecules in the monolayer already oriented vertically to the electrode surface and the electron transfer may follow the through-bond electron tunneling passway. In this sense, we believe that the assembling time dependent kinetic behavior observed in the present study is attributed to the different molecular packing structures. With increasing the assembling time, the molecular packing density becomes increased, making it more difficult to undergo the structural change of the planar azobenzene state to the kinked hydrazobenzene form (Scheme 1), which is essential for the electron transfer in azobenzene SAMs. Such a structural restriction on the redox process is consistent with our forthcoming finding by using a series of azobenzene SAMs (CnAzoC2SH, n=1~4) with different terminal groups: the longer the terminal alkyl chain, the higher molecular packing density, and the slower electron-transfer rates.[14]

In summary, a class of azobenzene SAMs on gold with different molecular packing densities were prepared by controlling the assembling time. There is a unique decrease of the apparent electron transfer rate constants of these azobenzene SAMs, which is explained by considering the spatial inhibition on the molecular structural changes of the closely packed SAM's structure.

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