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The Intermolecular Interaction in Self-Assembled Monolayers on Gold Electrode

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Abstract: The intermolecular interaction in an azobenzene self-assembled monolayers (SAMs) on gold electrode was investigated by controlling the assembling time and using mixed self-assembled techniques, and the variation of apparent electron transfer rate constant (k_s) of azobenzene SAMs with different molecular packing density is reported.

Keywords: Self-assembled monolayers; intermolecular interaction; electron transfer rate constant.

The understanding of the interaction among molecules is of fundamental interest. Self-assembled monolayers (SAMs) have been used as a powerful method to anchor redox active species onto electrodes with a desired distance and a controlled microenvironment, which presents an ideal model for the study of intermolecular interaction and long range electron transfer (ET) kinetics[1]. The azobenzenealkanethiol ($HS-CH_2CH_2NHC(O)-\phi-N=N-\phi$, denoted as AzoC2SH) we studied, contains a large π-conjugated system (azobenzene) and an amide group, which can form strong intermolecular π-π interaction and hydrogen bond network. Therefore, the interactions between the adsorbate molecules, as well as secondary interactions between them, are very important factors to further investigate the properties of azobenzene SAM, especially the ET kinetics in these SAMs. In this work, by controlling the assembling time and using mixed self-assembled technique (solution containing AzoC2SH and $HS-CH_2CH_2NHC(O)C_6H_{13}$, denoted as C8SH, 1.0×10^{-3} mol/L total thiol concentration), AzoC2SH SAMs with different surface packing density were prepared, and the intermolecular interaction in the SAMs on gold surface was studied.

In **Figure 1a** a very stable pair of anodic and cathodic peaks attributable to the reduction/oxidation of the azobenzene group was observed in all cyclic voltammetric (CV)[2]. The peak separation increases with increasing the potential scan rate for all the azobenzene SAMs, suggest that the surface reaction was controlled by ET kinetics. In **Figure 1b** the peak current decreased and the peak potential nearly unshifted with decreasing mole fraction of the AzoC2SH in the adsorption solution, suggest that the microenvironment of azobenzene molecules with adding mixed C8SH is not changed.

The apparent electron transfer rate constant (k_g) can be extracted using Laviron's treatment[4]. We noted that, k_g value shows a gradual decrease with increasing assembling time and surface concentration, and reaches a constant finally (not shown). For mixed

SAMs the k_S value kept nearly constant with different mole fraction of AzoC2SH in the adsorption solution (not shown). ET distance and intermolecular interaction are two important factors affecting the ET kinetics of a redox center in the SAMs. For a through-bond tunneling ET[3], the electron traveling distance is roughly the same as the alkyl chain length between the electroactive site and the underlying electrode due to the perpendicular molecular orientation in AzoC2SH SAMs. As mentioned above, with increasing the SAM formation time, the molecular packing density increases, which results in an increase of intermolecular interaction involving hydrophobic interactions between alkyl chains, aromatic interactions between azobenzene chromophores and hydrogen bonding between the amide groups. Such kinds of interactions make it difficult to undergo structural change for azobenzene molecules which is essential for carrying out the electrochemical reduction. As a result, the k_S rapidly decreases and becomes nearly constant with increasing assembling time. On the other hand, the strong intermolecular interaction can not be destroyed by coadsorption molecules of C8SH, in other words, the electrochemical environment of AzoC2SH does not change. Therefor, the strong π-π interaction and hydrogen bonding network are important factors affecting the ET kinetics.

Figure 1a Typical CVs of AzoC2SH SAM on gold prepared with different adsorption time: (···) 4 s; (—) 32 s; (- - -) 600 s (Scan rate 100 mV/s, Phosphate buffer solution, pH=5.5)

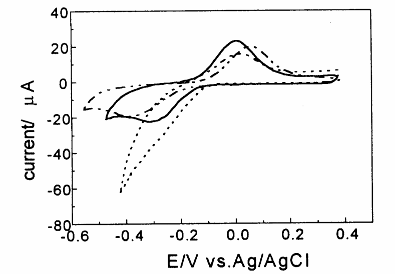
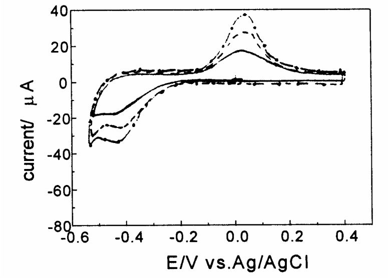


Figure 1b Typical CVs of mixed SAMs of AzoC2SH and C8SH formed from ethanol solutions containing various fractions of AzoC2SH thiol (x_{Azo}=0.9 (-•-), 0.7 (---), 0.5 (—)). Scan rate 100 mV/s.



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