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Homogenized redox behavior of electroactive self-assembled monolayers on gold in the organic phase

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ABSTRACT

The redox properties of electroactive self-assembled monolayers (SAMs) on gold in the organic phase were investigated by using the thin-film voltammetry approach, i.e., imposing a thin layer of nitrobenzene between the electrode and the bulk aqueous electrolyte. It was discovered that the structures of binary $Fc(CH_2)_{11}S$-/$CH_3(CH_2)_{10}S$-Au SAMs became more homogeneous than in aqueous medium, as indicated by the appearance of a single pair of redox peaks even at high ferrocenylalkanethiolate surface densities. Intermolecular interactions became much weaker and eventually negligible (at low Fc surface density) as confirmed by simulating the experimental cyclic voltammograms (CVs) based on theoretical *i*-E relationship upon considering a Frumkin isotherm. The formation constant of $iFc^+ \cdot ClO_4^-$ on pairs in the organic phase was found to be much larger than that in aqueous medium, which reaffirms the predominant influence of the microenvironment around the redox centers (organic medium vs. aqueous electrolyte).

1. Introduction

Redox center-tethered self-assembled monolayers have been investigated extensively in the past two decades as model systems for the long-range charge transport in donor-bridge-acceptor configurations [1–6]. These pioneering studies focused mainly on how the electron transfer rate constants depend on the distance and nature of the "bridge" between donor (redox center) and acceptor (the electrode) [5–6]. In order to investigate the long-range electron transfer kinetics of the attached redox couples, the SAMs should be well organized and the redox centers uniformly distributed (without significant intermolecular interactions), which is typically realized by forming binary SAMs terminated with electroactive groups (e.g., ferrocene) and diluted by alkanethiols [6–7]. It has been shown that at low surface density, the ferrocene groups in the binary SAMs on gold show ideal redox behavior, i.e., with the potential separation of anodic and cathodic peaks close to zero and the peak half-width ranging from 90 mV to 100 mV in the cyclic voltammogram (CV) [7–13]. The redox behavior becomes complicated as the surface coverage of the redox moieties in the binary monolayer increases, i.e., the peak broadens and splits [8–9,14–15].

The voltammetric properties of redox-active groups incorporated in SAMs are strongly affected by the nature of the medium in which the redox process occurs [14–18]. Creager et al. discovered that changing the length of co-adsorbed alkanethiols or of the electrolyte leads to interfacial solvation and double-layer effects and results in variations of the formal potential and the peak shape [12–13,16]. Finklea and co-workers studied $py[Ru(NH_3)_5]^{2+}$-terminated SAMs in a range of organic electrolytes; they observed a greater variation of electron transfer rate constants and a smaller reorganization energy in nonpolar solvents than in the aqueous phase [19]. Bard and coworkers applied scanning electrochemical microscopy (SECM) to measure electron transfer rates between the gold electrode and the redox species either covalently attached to the SAMs or diffusing in solution [20]. While a large number of studies have been carried out in aqueous electrolytes, the effect of organic media on their structure and redox behavior is not yet fully understood [11–16].

Shi and Anson reported in 1998 a simple method for examining the voltammetric properties of redox complexes in the organic phase by imposing an immiscible organic thin film between graphite electrodes and the aqueous electrolyte [21]. With this approach, the analytes inclined to dissolve in the organic solvent can be concentrated to produce enhanced redox signals. This method has also been applied to study the electron transfer and mass transport rates across liquid/liquid interfaces [22–25]. We

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have recently investigated the redox behavior of a series of novel ferrocene derivatives with this thin-film method [26–29]. In particular, we chose 1, 3-diferrocenyl-2-buten-1-one, which has two non-equivalent redox centers (two pairs of well-defined CV peaks which correspond to two consecutive electron transfer steps) to study the driving force-dependence of the liquid-liquid interfacial electron transfer kinetics [28]. We also investigated the ion-pairing properties of ferrocene and its derivatives in the organic phase and quantitatively evaluated the correlation between molecular structure and the formation constant of $iFc^+ \cdot ClO_4^-$on pairs [30].

In this work, the thin-film method is explored to examine the redox properties of electroactive SAMs on gold in the organic phase. Particularly, a thin film of immiscible organic solvent (nitrobenzene) is interposed between the gold working electrode (modified with a binary 11-ferrocene-1-undecanethiolate / undecanethiolate SAM, FcC11S-/C11S-Au) and the aqueous electrolyte solution (perchloric acid). Such a simple configuration enabled us to compare the redox behavior of electroactive SAMs on gold in aqueous and organic phase directly, i.e., by first carrying out the electrochemical measurements in an aqueous electrolyte, and then in the organic phase with the same electrode. Ion-pairing properties in these binary FcC11S-/C11S-Au SAMs in the nitrobenzene phase were also studied, and the formation constants at different Fc surface densities were determined.

2. Experimental

2.1. Chemicals

11-Ferrocenyl-1-undecanethiol was purchased from Dojindo Laboratories Inc. 1-undecanethiol from Aldrich. Perchloric acid (96%) was from Fisher Scientific. Nitrobenzene (NB) was from Allied Chemical Co. and purified by consecutive washings with 0.1 M HCl, 0.1 M NaOH, and deionized water. Nitrobenzene for electrochemical measurements was saturated with deionized water (>18.3 MΩ cm), which was produced with a Barnstead Easy Pure UV/UF compact water system.

2.2. Apparatus and procedure

Electrochemical measurements were performed in a conventional three-electrode, single-chamber glass cell. The working electrode was a gold disk electrode with a diameter of 2 mm sealed with Teflon; a platinum wire was used as counter electrode while an Ag/AgCl/3 M NaCl electrode was used as reference electrode. The gold electrode was polished with 0.3 μm and 0.05 μm alumina successively until a mirror-like surface was obtained. Then the electrode was sonicated in ethanol and deionized water for 7 min, respectively, prior to electrochemical cleaning (cycling between -0.2 V and +1.6 V vs. Ag/AgCl with a scan rate of 50 mV s^{-1} in 1.0 M H_2SO_4 until the CV curve remained stable). Upon washing with deionized water, the cleaned gold electrode was dried under nitrogen, then immersed in a binary solution of 11-ferrocenyl-1-undecanethiol and 1-undecanethiol in ethanol (total thiol concentration was 1.0 mM) overnight. After modification, the electrode was sonicated in ethanol for 2 min and then washed with copious amounts of water.

The electrochemical measurements were performed with a CHI1040A Electrochemical Analyzer in a Faraday cage. The FcC11S-/C11S-Au SAM-modified gold electrode was first tested in the aqueous electrolyte (1.0 M $HClO_4$); it was then removed from the aqueous solution, washed with water and dried under nitrogen carefully. A thin film of nitrobenzene (NB) was applied to the gold electrode by dropping 4.0 μL water-saturated NB atop, and the electrode was subsequently put back into the electrochemical cell for the measurements in the organic phase. No additional electrolyte was added to the organic phase. The electrolyte solutions were deoxygenated by bubbling Ar for at least 15 min before the electrochemical measurements. All experiments were performed at room temperature under ambient conditions.

3. Result and discussion

3.1. Redox behavior of FcC11S-/C11S-Au SAMs: from aqueous to organic phase

The redox behavior of binary FcC11S-/C11S-Au SAMs has been demonstrated to be rather complex; not only the composition but also the microenvironment of the ferrocene groups significantly alter the position and shape of the redox peaks during a CV scan [7,9–18,20]. We have recently investigated the redox properties of single-component 11-ferrocenyl-1-undecanethiolate (FcC11S-Au) and of binary SAMs when mixed with 1-undecanethiol (C11SH), in particular when the surface density of ferrocenylundecanethiolates (Γ_{Fc}) increases or a small amount of less polar solvent was

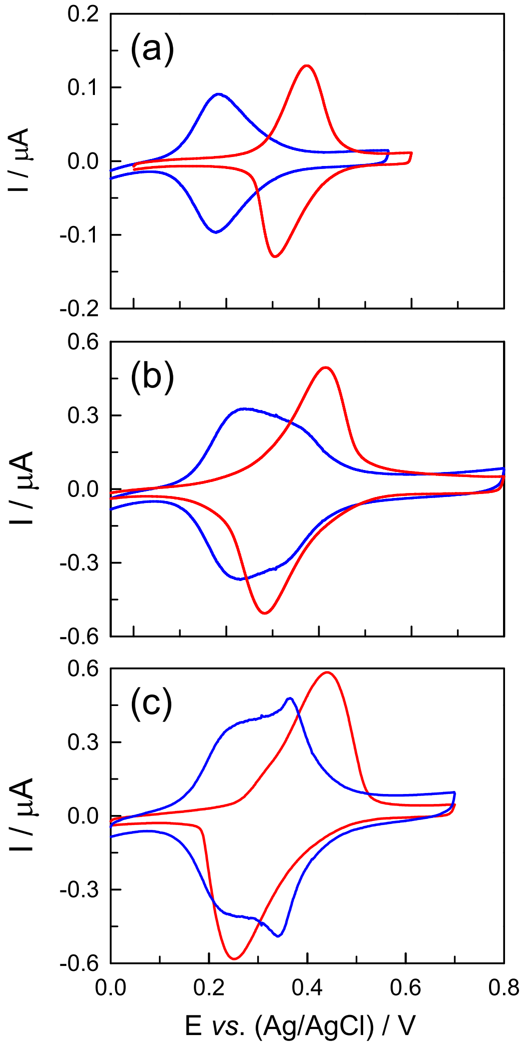

Fig. 1. Cyclic voltammograms of binary FcC11S-/C11S-Au SAMs of different compositions, i.e., different Fc surface densities before (blue curve) and after (red curve) the application of a thin film of nitrobenzene to the electrode surface. The bulk aqueous electrolyte was 1.0 M $HClO_4$, the scan rate was 50 mV s^{-1}. (a) $\Gamma_{Fc} = 0.95 \times 10^{-10}$ mol cm^{-2}; (b) $\Gamma_{Fc} = 2.8 \times 10^{10}$ mol cm^{-2}; (c) $\Gamma_{Fc} = 3.72 \times 10^{-10}$ mol cm^{-2}.