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Electrochemical Properties of Self-Assembled Monolayers Composed of TTF Derivative

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Electrochemical Properties of Self-Assembled Monolayers Composed of TTF Derivative

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We prepared self-assembled monolayers (SAMs) composed of tetrathiafulvalene (TTF) derivative modified on gold substrate and investigate their electrochemical properties by cyclic voltammogram (CV). The first and second oxidation peaks were observed at $E_1^{1/2} = 0.40$ V and $E_2^{1/2} = 0.81$ V, respectively. The peak current was observed to be proportional to the scan rate, suggesting the feature of modified SAMs molecules. The result indicates that TTF-thiolate SAMs on gold electrode have electronic structure similar to bulk TTF molecules.

Keywords: Self-assembled monolayers; TTF; Cyclic voltammogram; Electrochemistry.

INTRODUCTION

Self-assembled monolayers (SAMs) on metal surface are the focus of intensive investigation, because of usefulness in the development of electronic devices and electrochemical applications. The major studies have concerned self-assembled organosulfur monolayers consisting of functionalized adsorbate, which contains an alkyl chain with a

surface-active sulfur group. In this study, we investigate electrochemical properties of SAMs with TTF-type molecules whose structure is shown in FIGURE 1.

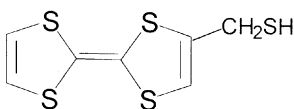


FIGURE 1. The molecular structure of TTF-CH₂SH

EXPERIMENTAL

The sample was prepared by 24 h immersion of the Au substrate into 0.1 mM TTFCH₂SH acetonitrile solution. The prepared samples were removed from the solution, rinsed with pure solvent, and dried by N₂ gas. Cyclic voltammograms were obtained using a voltammetric analyzer (model 100W, BAS Co., Ltd., Japan) at room temperature. A homemade three-electrode configuration was used with a gold-coated glass substrate as the working electrode, Ag/Ag⁺ as reference electrode, and a platinum wire as the counter electrode in a glass vessel. The gold substrate for the CV measurement was prepared by 100 nm of gold deposition on the slide glass. All of the electric potentials reported in this paper were measured with respect to the reference electrode. The area of working electrode exposed to the electrolyte solution was about 0.3 cm².

RESULTS AND DISCUSSION

The cyclic voltammetry measurements were carried out for investigating electron-transfer at the electrochemical interface of TTF-CH₂SH SAMs on the surface. FIGURE 2 shows a comparison of the cyclic voltammetric responses of the SAMs at the different scan

rates. The values are 100 (lowest current), 150, and 200 mVs^{-1} (highest current), respectively. In

dichloromethane with tetra-n-butylammonium perchlorate (TBAP) as the supporting

electrolyte, the first and second oxidation peaks were observed at $E_1^{1/2} =$

0.40 V and $E_2^{1/2} = 0.81$ V, respectively. The peak current was observed to be proportional to the scan rate, indicating a "surface wave" response, and the peak potentials and peak-to-peak separations were independent of the scan rate at the least up to 200 mV/s , indicating that kinetic effects at the surface-confined redox centers were insignificant on the voltammetric time scale. The determination of surface coverage was carried out by electrochemical experiments. The integration of redox waves associated with surface-confined species has been used extensively as a method to determine the surface coverage of redox active monolayer films.¹⁻² Surface coverage, calculated by integration of the current during the first scan, yielded an average value of 2.1×10^{-10} mol/cm^2 , compared to the theoretical value 3.56×10^{-10} mol/cm^2 based on an idealized close-packed monolayer of TTF-CH₂SH/Au SAMs.³ It is thought that the value of the surface coverage might be reasonable considering the defect or ununiformity on the gold substrate. Moreover, as TTF-CH₂SH/Au SAMs have the very short thiol chain, the coverage for this compound may be critically dependent on the pretreatment or the roughness of the electrode surface.

Repeated electrochemical cycling makes response of TTF-CH₂SH

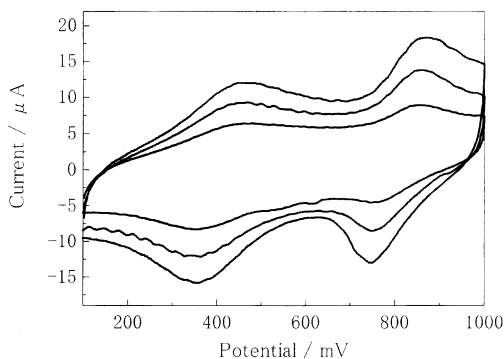


FIGURE 2. CV data for SAMs of TTF-CH₂SH on Au electrode vs Ag/Ag⁺ reference, 0.1 M TBAP/CH₂Cl₂, at scan rates of 100 (lowest current), 150, and 200 mVs^{-1} (highest current).

SAMs gradually decreased when the potential was scanned beyond the first oxidation, which suggests chemical instability of the oxidized form of the monolayers. This behavior is similar to that reported by Yip *et al.*³ As is shown in FIGURE 2, it is obvious that the surface charge transfer for the second immobilized TTF-CH₂SH SAMs reaction leads to a sharper cyclic voltammetric peak than that for the first step. This is an interesting effect not expected in the electrochemistry of the solution analogue, which is normally shaped. Similar result has been obtained for TTF-silane derivative on Ru or Pt electrodes.⁴

CONCLUSION

We made clear electrochemical properties of two-dimensionally arranged TTFCH₂SH SAMs. This result may mean the control of the charge was possible by the potential operation for having the properties of bulk TTF on Au substrate.

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