Electrochimica Acta 53 (2008) 7261–7265

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Fabrication of a stable, switchable An/SAM-Au electrode with tunable electron transfer and excellent electrochemical properties

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ARTICLE INFO

Article history:
Received 11 January 2008
Received in revised form 22 March 2008
Accepted 29 March 2008
Available online 8 April 2008

Keywords:
Switchable electrode
Anthracene (An)
Self-assembled monolayers (SAMs)
Electrochemical impedance spectroscopy
Gold electrode
1-Dodecanthiol

ABSTRACT

This paper describes the electrochemical properties, such as electrode reactivity, and interfacial capacitance of an anthracene/self-assembled monolayer (An/SAM) Au electrode prepared through controllable immersion of the dodecanethiol ($C_{12}SH$) SAM-Au electrode in a THF solution of anthracene (An). The $C_{12}SH$ SAM almost totally blocks heterogeneous electron transfer between the bare Au electrode and $Fe(CN)_6{}^{3-/4-}$ in solution, but adsorption of the An molecules onto the SAM-Au electrode restores electron transfer. The prepared An/SAM-Au electrode possesses good reactivity without a remarkable barrier to heterogeneous electron transfer. On the other hand, the electroactive form of the An/SAM-Au electrode can be converted back to the non-electroactive form by immersing the electrode into pure THF.

1. Introduction

Electron transfer through nanometer-thick organic films is of fundamental importance in the development of nanometer-scale electronic materials [1–5]. Knowledge of how chemical compositions and chemical structures affect electron transfer between a solid substrate and a redox-active molecule is central to the study of molecular-level electron transfer. In particular, the concept of "molecular switching" is relevant to the design and development of new electro-nano-devices [6,7].

Self-assembled monolayers (SAMs) are commonly employed to study the influence of molecular-level modifications on the switching of molecular properties [8–10]. Most of these modifications are based on either photoinduced or electro-induced processes, and are often associated with isomerization, proton transfer, or redox reactions that change nanomolecular structure.

This study addresses the issue of electron transfer across SAMs of 1-dodecanthiol at the surface of a gold electrode before and after treatment with anthracene in THF. The SAMs isolate the gold substrate from the solution, and redox reactions require tunneling through the monolayer. Electrochemical reactions can occur on such modified electrodes, with the monolayer "switched" to a conductance state by immersing the SAM-modified gold electrode in a THF solution of An. The aromatic structure of An makes it an efficient conductor, so the An molecules act as intermediate electron acceptors between the $Fe(CN)_6{}^{3-/4-}$ in solution and the metal electrode.

To the best of our knowledge, the present study has not been reported to date and may offer a new route for fabrication of a stable, switchable An/SAM-Au electrode with tunable electron transfer and excellent electrochemical properties. Such an electrode could be useful in electrochemical studies and electroanalytical applications.

2. Experimental

Electrochemical measurements were performed using a potentiostat and galvanostat (model Autolab, PGSTAT30, Eco Chemie, Netherlands) connected to a Pentium IV personal computer (FRA software for impedance spectroscopy and GPES software for cyclic voltammetry were used). All measurements were carried out at ambient temperature (25 ± 2 °C) in a conventional electrochemical cell consisting of an Au disc working electrode (0.0078 cm^2 area, Metrohm), a Pt wire auxiliary electrode, and an Ag|AgCl reference electrode filled with 3 M KCl. All potentials are reported with respect to this reference electrode. KCl solution (0.1 M) was used as a background electrolyte.

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doi:10.1016/j.electacta.2008.03.074

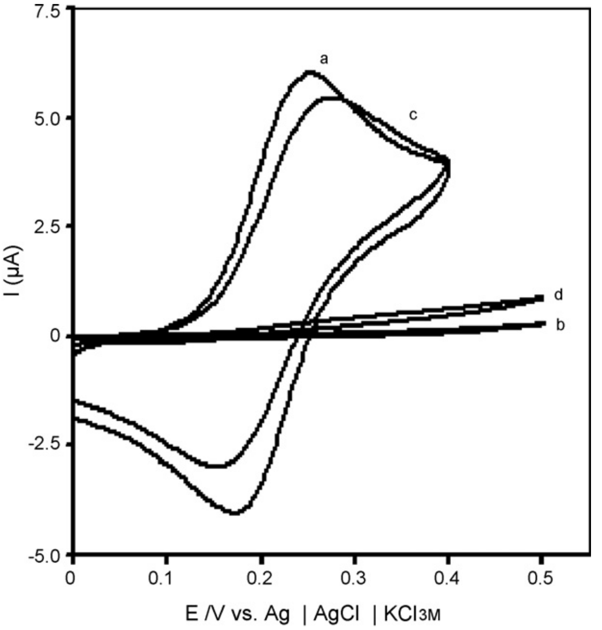

Fig. 1. Cyclic voltammetric response of $K_4Fe(CN)_6$ (1.0 mM) at the surface of (a) bare gold, (b) SAM-Au electrode, (c) SAM-Au electrode after being immersed in THF solution of An for 6 h and (d) An/SAM-Au electrode after being immersed in pure THF for 6 h. The supporting electrolyte was KCl solution (0.1 mol l^{-1}), and scan rate was 100 mV s^{-1}.

Nitrogen purge was used to remove oxygen from the solutions in the electrochemical cell. The Faradaic impedance measurements were performed in the presence of a 1.0 mM $K_3[Fe(CN)]_6$ + 1.0 mM $K_4[Fe(CN)_6]$ mixture as a redox probe. The Faradaic impedance spectra were recorded upon application of a bias potential equal to the open circuit voltage (OCV) of 0.2 V while applying an AC voltage of 5 mV amplitude in the frequency range from 100 mHz to 10 kHz. The Faradaic impedance spectra are plotted in the form of complex plane diagrams (Nyquist plots). The experimental impedance spectra were simulated using equivalent electronic circuits. For this purpose, the fit option in the frequency response analyzer (FRA) software (Eco Chemie B.V. Utrecht, The Netherlands) was employed.

The preparation of the monolayer-modified electrode was carried out as follows: Au electrodes were polished with alumina slurry (0.3 μm) and sonicated in water for 5–10 min. The polished electrodes were then electrochemically cleaned by cycling the potential between −0.3 and 1.5 V in 0.5 M H_2SO_4 at a scan rate of 0.1 V s^{-1}. The cyclic voltammogram characteristics for a clean Au electrode were obtained after 30–40 cycles. After rinsing with deionized water and ethanol then drying with nitrogen gas, the gold electrode was immersed in a 5.0 mM ethanol solution of $C_{12}SH$ for 24 h. The electrode was then rinsed with fresh ethanol and deionized water, and used for voltammetric and electrochemical impedance spectroscopy (EIS) studies.

3. Results and discussion

3.1. Cyclic voltammetry studies

The choice of $C_{12}SH$ in this study for preparation of the An/SAM-Au electrode is due to its ability to form a stable monolayer on an Au substrate through the formation of an Au–S bond [11]. On the other hand, the monolayer can hydrophobically interact with the An molecules.

The cyclic voltammogram (CV) of the $K_4Fe(CN)_6$ solution at the surface of the bare gold electrode gave anodic and corresponding

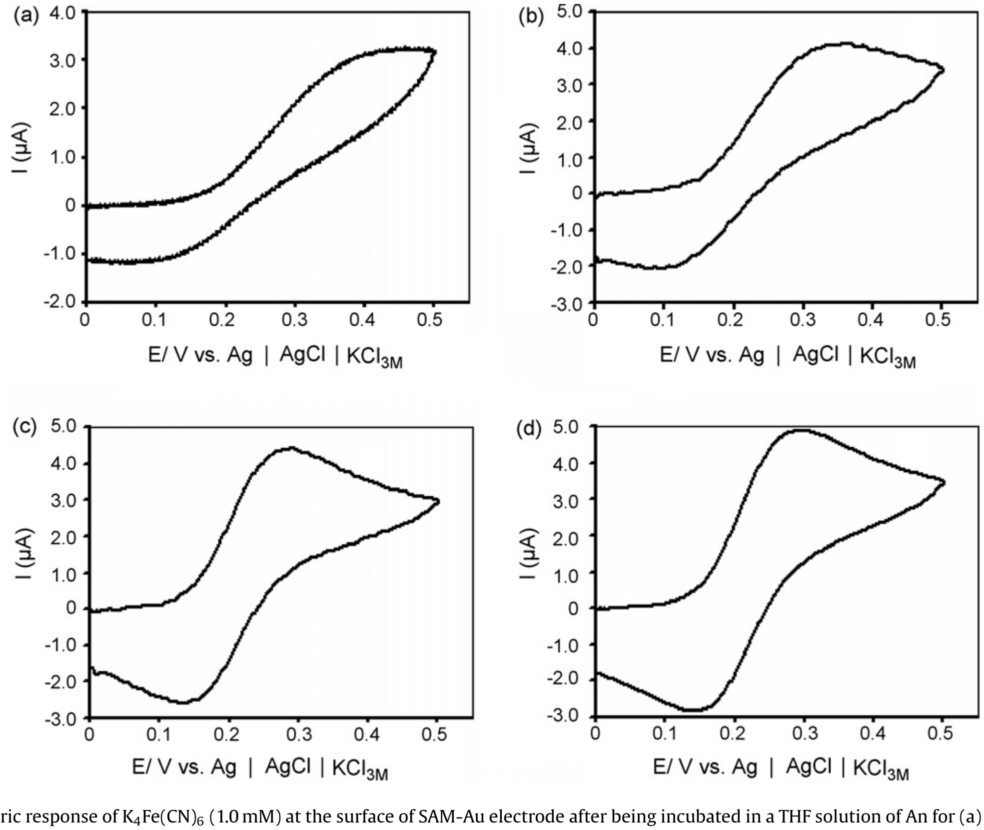

Fig. 2. Cyclic voltammetric response of $K_4Fe(CN)_6$ (1.0 mM) at the surface of SAM-Au electrode after being incubated in a THF solution of An for (a) 0.5 h, (b) 1.0 h, (c) 6 h and (d) 24 h. The solution conditions were the same as in Fig. 1.