



Electrochemical kinetic analysis of a 1,4-hydroxynaphthoquinone self-assembled monolayer

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ARTICLE INFO

Article history:

Received 12 December 2007

Received in revised form 17 April 2008

Accepted 25 April 2008

Available online 16 May 2008

Keywords:

Juglone

1,4 hydroxynaphthoquinone

Self-assembled monolayer

Proton coupled electron transfer

Electron transfer kinetics

ABSTRACT

Electroactive 5-hydroxy-3-hexanedithiol-1,4-naphthoquinone (JUG_{thio}) has been self-assembled on gold. Electrochemical results show the surface coverage is 2.2×10^{-10} mol cm⁻², which is consistent with a dense monolayer. The JUG_{thio} shows one quasi-reversible and stable voltametric wave in aqueous buffered solution. A kinetic analysis of the redox reactions involving both electron and proton transfer has revealed an unusual behaviour of this molecule due to the presence of the hydroxyl function in the vicinity of the quinone group. The apparent kinetic rate constant and the anodic coefficient transfer of this reaction depend on the pH. In acid medium, a classical concerted $2e^-/2H^+$ mechanism is obtained. In basic medium (pH > 7), strong intramolecular hydrogen interactions between the quinone and the hydroxyl function have a strong influence on the redox kinetics. These results show that JUG_{thio} electroactivity is very sensitive to hydrogen interactions in neutral and basic pH solution and is able to act as sensitive layer for electrochemical biosensing.

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1. Introduction

In the development of biosensors, label-free transduction methods, i.e. with no additional label added to the medium to facilitate transduction, have advantages over labeled devices because of the simplicity to operate and their ability to perform in-situ (*in vivo*) measurements. Current methods for nucleic acid sequence detections are mostly based on surface plasmon resonance [1–3] but electrochemical transducers now emerge as powerful tools because they provide simple, rapid and low cost devices. Electrochemical sensors based on the electroactivity of nucleobases (guanine in general) [4–7] or impedance measurements [8–9] allow direct detection.

During the last two decades, electrode modification strategies that employ porous conducting organic membranes have been developed to enable the electrochemical detection of biomolecular interactions involving DNA, enzymes, antibodies and analytes of biological interest [10]. Indeed following adequate functionalization, conducting polymers can act at the same time as immobilization and transduction agent. Transduction can be performed using the intrinsic electroactivity of the polymer backbone [11–13]. Our group is currently concerned with devices based on functionalized conducting polymers modified electrodes, in view of applications in enzymes [14–16] and DNA electrochemical sensors [17–19].

More recently the development of electroactive organic monolayers brings another approach to fabricate a sensitive interface for direct electrochemical biodetection [20]. Indeed, the different monolayer building methods, especially self-assembling alkanethiol derivatives, allow well defined interfaces to be developed where the local environment can be precisely tuned [21–23].

The precise tuning of the local environment, and the perturbation of this environment, provides opportunity for the transduction of biological affinity reactions which involve huge structural reorganization in the vicinity of the interfaces that can disrupt the interfacial physical properties (dielectric constant and interfacial ionic distribution). Hence both the redox activation enthalpy and the standard Gibbs free energy of immobilized species may be modified.

The purpose of the present article is to present results from the study of the mechanism of a multistep charge transfer reaction of quinone derivatives used in bioelectrochemistry with a view to develop modified electrodes for label-free transduction of bioaffinity reactions. We have first characterized a pure SAM composed of 1,4-hydroxynaphthoquinone and then developed an approach to investigate the rate limiting step of the electronic transfer reaction.

2. Experimental

2.1. Reagents

Juglone (Aldrich), was used as received. Absolute ethanol was purchased from Merck. Aqueous solutions were made with bi-dis-

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tilled water. Phosphate buffer saline (137 mM NaCl, 10 mM phosphate, 2.7 mM KCl, pH 7.4), H_3CO_3 , H_2CO_3 , H_3PO_4 , H_2PO_4^- , HPO_4^{2-} (Aldrich), were used as received to prepare various buffer solutions ranging from pH 1 to 13.

2.2. Electrochemical apparatus

For electrochemical experiments, a conventional one-compartment, three-electrode cell was used with an Autolab PGSTAT 30. The SAM modified electrodes were tested using 1 cm^2 platinum flag auxiliary electrode and an SCE reference electrode.

2.3. Synthesis of 5-hydroxy-3-hexanedithiol-1,4-naphthoquinone

5-Hydroxy-3-hexanedithiol-1,4-naphthoquinone (JUG_{thio} , scheme below) was synthesized in our laboratory. JUG_{thio} was synthesized in a one step reaction from one equivalent of Juglone and one equivalent of hexanedithiol in ethanol at $45\text{ }^\circ\text{C}$, stirred 15 min and cooled. The product was allowed to precipitate 48 h at $0\text{--}5\text{ }^\circ\text{C}$, then filtered and washed with ethanol to obtain orange needles after recrystallisation. The ESP-MS gives the expected mass product (i.e. 294 g mol^{-1}). NMR characterisation was performed with a Brücker 200 MHz apparatus. $^1\text{H NMR}$ (200 MHz, CD_2Cl_2) 11.55 (s, 1H, OH); 7.74 (m, 2H, ph-H); 7.09 (m, 1H, ph-H); 6.46 (s, 1H, ph-H); 2.75 (m, 2H, CH_2); 2.44 (m, 2H, CH_2); 1.72 (m, 4H, CH_2) and 1.42 (m, 1H, SH).

2.4. Electrochemical roughness of the gold supporting electrode

Gold electrodes (radius 1 mm) were sequentially polished on polishing clothes (Struers, Denmark) with diamond pastes of decreasing particle size. Then, the electrodes were ultrasonicated for several minutes in acetone and ethanol. Then, they underwent potential scanning from -0.3 to 1.5 V during 10 cycles at 50 mV s^{-1} in 0.5 M aqueous H_2SO_4 . In order to obtain a control parameter for the washing procedure, the cathodic currents recording during successive potential scans (50 mV s^{-1} , between -0.3 and 1.5 V vs SCE) were integrated giving access to the electrochemical roughness factor [24] ($R_f = 1.46$). Before modification, the washed gold electrode was put inside an UV-ozone cleaner (3 min).

2.5. Monolayer formation

The self-assembled monolayers were obtained by immersing a freshly washed and pre-treated gold electrode in ethylacetate 1 mg/mL JUG_{thio} solution overnight under stirring and argon atmosphere.

3. Results and discussion

3.1. Electrochemical behaviour of the JUG_{thio}

After 5-hydroxy-3-hexanedithiol-1,4-naphthoquinone (JUG_{thio}) was assembled on the gold electrode, cyclic voltammetry experiments were performed in PBS medium. The electroactivity of the quinone end-group, shown in Fig. 1, is stable for several hundred cycles (50 mV s^{-1}). A quasi-reversible signal is observed with only one cathodic and anodic peak at -0.45 V and -0.36 V , respectively (pH 7.4). Integration of the area under the Faradaic peak of the voltammogram gave a charge passed of $3.3 \pm 0.4 \times 10^{-7}\text{ C}$ for both anodic and cathodic waves whatever the pH value. This charge passed corresponds to a surface coverage of JUG_{thio} of $(2.2 \pm 0.3) \times 10^{-10}\text{ mol cm}^{-2}$, close to the coverage of a full monolayer [25]. Indeed Bulova et al. [26] have found a value of $3.4 \times 10^{-10}\text{ mol cm}^{-2}$ for 2-methyl-3(ω -mercaptoalkyl)-1,4-naph-

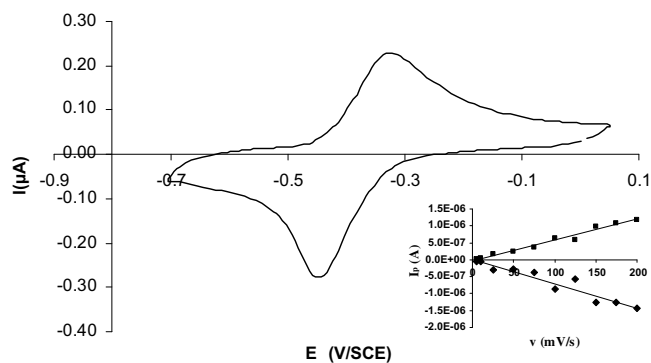


Fig. 1. Cyclic voltammogram of a gold electrode modified by a self-assembled monolayer of JUG_{thio} , scan rate 50 mV s^{-1} , phosphate buffered solution (pH 7.4). Inset: evolution of the (■) cathodic and (◆) anodic peak currents with the scan rate.

thoquinone and Hong et al. [27] have found surface coverage values between 4.5 and $5.6 \times 10^{-10}\text{ mol cm}^{-2}$ for 2,5-dihydroxythiophenol. Our value is consistent with these results considering that Juglone is a bigger molecule. It is also consistent with the theoretical maximum coverage of simple straight chain alkanethiols of $7.6 \times 10^{-10}\text{ mol cm}^{-2}$ [28]. The current peak is a linear function of the scan rate indicating typical thin film behaviour (see insert on Fig. 1). The anodic and cathodic peak potential difference (ΔE_p) at a sweep rate of 50 mV s^{-1} is large compared to usual values expected for immobilized reversible redox species [29] and will be discussed in Section 3.3.

In the potential window where no Faradaic process occurs, the charging current for a linear scan rate is independent of the applied voltage at a constant sweep rate. The difference between anodic and cathodic currents has been measured at a potential specifically chosen for comparative purpose (-100 mV vs SCE) and has been applied to estimate the differential double layer capacitance (C_d) [30–31]. The pure SAM capacitance was $17 \pm 2\text{ }\mu\text{F cm}^{-2}$. This value is comparable to those obtained for monolayers of smaller quinone derivatives (e.g. $15\text{ }\mu\text{F cm}^{-2}$ for 2-(1-mercaptobutyl)hydroquinone)) [32] and so is consistent with a dense monolayer formation.

We have studied the electrochemistry of $\text{Fe}(\text{CN})_6^{3-}$ on a JUG_{thio} modified gold electrode. Ferro/ferricyanide has a redox potential ($E^\circ(\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}) = 0.16\text{ V}$) which is much more positive than that of the JUG_{thio} redox reaction ($E^\circ = -0.40\text{ V}$ at pH 7.4, cf. Fig. 1). Compared with a bare gold electrode the voltammetric currents of the ferro/ferricyanide couple were smaller, and the separation of the potentials for the anodic and cathodic peaks was greater on a JUG_{thio} modified electrode. These differences imply that the standard electron transfer rate constant on a modified electrode is less than that on a bare gold electrode. The electrochemical reaction requires electrons to tunnel across the monolayer, the thickness of which, controls the electron transfer rate. In this case, the distance that the electron must traverse is crucial. For charged redox probes, modification of the monolayer surface charge could modulate the electron rate constant due to a change in the electron hopping distance between the redox probe and the underlying electrode. In the case of an immobilized acido–basic species, the electrode surface charge depends on the solution pH with respect to the pK_a of the species. By following the variation of ΔE_p of a redox probe with pH, the pK_a of the immobilized species could be estimated [33,34]. We have used the same approach to characterize the JUG_{thio} modified gold electrode. $\Delta E_p(\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-})$ is plotted as a function of the pH in the Fig. 2. A sigmoid function ($\Delta E_p = a\text{ pH}/(1 + b\text{ pH})$) is used to fit the experimental data. The function shows a point of inflexion near pH 8.4 (± 0.3). At the redox potential of $(\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-})^-$, the quinone is not reduced and species able to be involved in proton transfer reaction are those

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