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Raman spectroelectrochemical study of electrochemical decomposition of poly(neutral red) at a gold electrode

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ABSTRACT

A gold electrode, modified with poly(neutral red), has been studied with surface-enhanced resonance Raman spectroscopy at 676.4 nm excitation. It has been shown that both qualitative and quantitative changes in Raman spectra occur during prolonged holding of the modified electrode in pH 7.0 solution at a controlled electrode potential ranging from −0.6 to −0.2 V vs. Ag/AgCl, indicating that a decomposition of the poly(neutral red) layer proceeds. The decomposition proceeds slower at a more negative electrode potential. From kinetic data obtained, first-order decomposition rate constants have been calculated, ranging from 9.17×10^{-4} to 1.09×10^{-2} min^{-1} for electrode potential ranging from −0.6 to −0.2 V.

1. Introduction

Chemically modified electrodes are finding increasing use in organic electrochemistry and bioelectrochemistry. Among many soft electrode modifiers known, azine-type redox dyes are often used in obtaining modified electrodes for bioelectrochemical and biosensor use. The redox dye neutral red (NR) (3-amino-7-dimethylamino-2-methylphenazine) presents a special interest because of a relatively low formal redox potential of 0.240 V at pH 0.0, and −0.325 V at pH 7.0 [1]. In this respect, NR could be potentially useful for electrochemical reduction processes of selected (bio)organic species, especially of coenzyme NAD. Because of the presence of a primary amino group in its structure, NR can be simply electropolymerized at an inert electrode, yielding redox-active poly(neutral red) (PNR)-modified electrode [2]. Electropolymerization of NR is triggered by the formation of a radical cation at a high electrode potential [3], and can be provided by a simple potential cycling procedure [4] for a variety of electrode materials including glassy carbon, platinum, gold, and transparent ITO glass electrodes [5,6].

Electrocatalytically active PNR-modified electrodes have been used for redox transformations of some solution species, pursuing mainly electroanalytical goals. Simultaneous amperometric determination of ascorbic acid and dopamine [7], electrooxidation and electroreduction of nitric oxide [8], electrocatalytic reduction of bromate, iodate, and oxygen [6] have been reported. Also, composite materials including PNR have been used for electrooxidation of methanol [9], ascorbic acid, dopamine, and uric acid [10], as well as other inorganic and organic species [11,12]. PNR-modified electrodes have been used in bioelectrochemistry and biosensors. Biosensors for determination of glucose and pyruvate based on the corresponding oxidases [13], bienzymatic sensors for glycerol [14], glucose sensors with the use of microencapsulated or cross-linked enzyme [15], acetaldehyde sensors based on bienzyme system [16] have been developed recently with the use of PNR-modified electrodes.

For many applications of PNR-modified electrodes, the stability of PNR layers is of critical importance. When subjected to electrochemical treatment, PNR can undergo depolymerization, hydrolysis, or decomposition processes, leading to the loss of its electrocatalytic properties. Among many factors, the rate of decomposition should depend on the electrode potential, used for operation of modified electrodes. Earlier, we studied the kinetics of decomposition of polyaniline-like polymer-modified electrodes with the use of in situ Raman spectroelectrochemistry [17,18]. The present work was aimed at a Raman spectroelectrochemical study of decomposition kinetics of PNR layers at selected electrode potentials.

2. Experimental

Neutral red (3-amino-7-dimethylamino-2-methylphenazine hydrochloride) (Sigma) and other chemicals of analytical or reagent grade were used as received.

A BASi-Epsilon model potentiostat (Bioanalytical Systems Inc., USA) was used in electrochemical experiments. Electrochemical experiments were done in a conventional one-compartment cell arranged with an Ag/AgCl (saturated KCl) reference electrode. All

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potential values reported below are referred to this reference electrode. A flat circular gold electrode of ca. 5 mm in diameter, press-fitted into a Teflon rod, was used as a working electrode. Before experiments, the working electrode was cleaned for 30 min in a Piranha solution (a mixture of 30% hydrogen peroxide and concentrated sulfuric acid, 3:1 by volume), polished with 0.3 μm alumina powder (Kemet, UK), and ultrasonicated for 2 min in an ethanol and water mixture. Then, the surface of the Au electrode was roughened by cycling for 50 cycles in 0.1 M KCl solution within the potential limits of −0.3 and +1.4 V at a potential scan rate of 200 mV/s. Electropolymerization of NR at electrode has been performed by potential cycling for 4 cycles within the potential range from −0.8 to 1.0 V at a scan rate of 100 mV/s in 0.01 M phosphate buffer solution, pH 7.0, containing 0.1 M sodium sulfate and 1 mM NR. After the electropolymerization, the electrode was rinsed in a supporting electrolyte, and mounted into an electrochemical or spectroelectrochemical cell.

Raman spectroelectrochemical experiments were done in a cylinder-shaped three electrode moving cell, arranged with a gold working electrode as described above, platinum wire as a counter-electrode, and a saturated Ag/AgCl reference electrode. In all experiments, the cell was filled with 0.01 M phosphate buffer solution (pH 7.0) containing 0.1 M sodium sulfate. The flat surface of a working electrode was placed at ≈2 mm distance from the cell window. The 676.4 nm beam of the Kr-ion laser (Coherent, model Innova 90-K) with the power of ca. 20 mW was incident onto the surface at ca. 60° and focused to a spot of ca. 1 mm^2 in area. In order to reduce photo- and thermoeffects, and a possible degradation of a polymer film by the incident light as well, the cell holder was moved periodically with respect to the laser beam at ca. 20 mm/s with the help of custom-built equipment [19]. The experiments were performed in 90° scattering geometry. The Raman scattered light was analyzed by a 500 mm focal length, *f*/6.4 aperture ratio spectrograph (Acton Research Co., Model SpectraPro-2500i) equipped with 600 lines/mm grating, and recorded by the thermoelectrically cooled at −70 °C CCD camera (Princeton Instruments, Model Spec-10:256E). The integration time was 0.1 s. Each spectrum was recorded by accumulation of 600 scans. The cutoff filter (Semrock Inc.) was put in front of the spectrograph to eliminate Rayleigh scattering from the electrode. The Raman frequencies were calibrated using the toluene spectrum. The spectrometer, electrochemical cell, detector, and laser have been mounted onto a massive optical bench. A Model PI-50-1 potentiostat, arranged with PR-8 model programmer and a custom-built A/D converter for data acquisition, was used in Raman spectroelectrochemical experiments.

All calculations were performed using Gaussian for Windows package version G03W [20]. Geometry optimization and frequency calculations were accomplished with the density functional theory (DFT) method using the B3LYP functional. Calculations were done using 6-311+G(2d,p) basis set. Calculated frequencies were scaled as described in previous publications [21,22].

3. Results and discussion

When adsorbed at a roughened gold electrode, neutral red shows a pair of well-defined anodic and cathodic peaks (Fig. 1) with a midpoint potential $(E_{pa} + E_{pc})/2 = -0.56$ V, and a peak separation depending on potential scan rate. After electropolymerization, the resulting PNR-modified electrode is diminished in height of anodic and cathodic peaks, although their position on a potential scale does not change markedly, yielding the midpoint potential $(E_{pa} + E_{pc})/2 = -0.54$ V, i.e., practically coinciding with the corresponding value for adsorbed dye (Fig. 1). For PNR-modified electrode, a new pair of flattened anodic and cathodic peaks appear, characterized by $(E_{pa} + E_{pc})/2 = 0.02$ V (Fig. 1). A similar behavior has been noted recently by other authors [15].

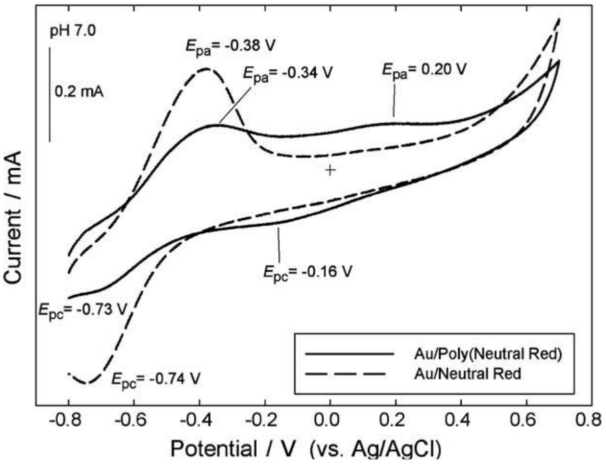

Fig. 1. Cyclic voltammograms of a gold electrode, containing adsorbed or electropolymerized neutral red (as indicated), as obtained in pH 7.0 solution at a potential scan rate of 300 mV/s.

Fig. 2 presents Raman spectra from a PNR-modified electrode, as obtained at a controlled potential of −0.2 V. Following the main redox process around −0.5 V, it could be concluded that at this potential PNR presents presumably in its oxidized form. However, taking into consideration the second redox process observed, centered around 0.0 V, it could be supposed that PNR presents in its intermediate half-oxidized form. A number of well-defined Raman bands are observed. Tentative interpretations of bands observed in resonance Raman spectra of NR using excitation wavelengths of 457.9 and 514.5 nm [23] and spectral assignments for other structurally similar azines—thionine, Nile blue, rhodamine 6G, and methylene blue adsorbed at gold, silver, or copper electrodes or colloidal particles—have been published previously [24–27]. Recently, we have analyzed the Raman spectrum of adsorbed and electropolymerized toluidine blue at gold electrodes [22]. In this work we have conducted theoretical modeling and Raman spec-

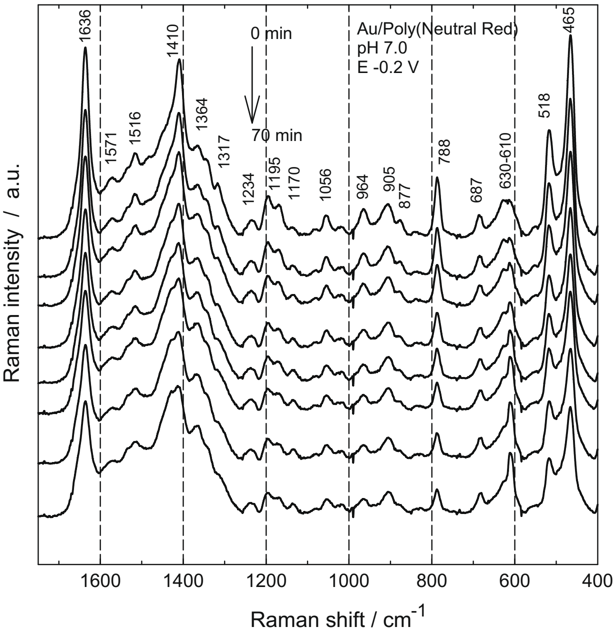

Fig. 2. Raman spectra of poly(neutral red)-modified gold electrode, as obtained in pH 7.0 solution at a controlled electrode potential of −0.2 V at different time intervals ranging from 0 to 70 min.