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Electrochemical conversion of poly-aniline into a redox polymer in the presence of nordihydroguaiaretic acid

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ABSTRACT

Thin films of poly-aniline (PANI) undergo electrochemical restructuring when subjected to potential cycling in the presence of nordihydroguaiaretic acid (NDGA). As a consequence, the properties of PANI change from those of a conducting polymer to those of a redox polymer. Thus formed composite PANI–NDGA films show redox activity characterized by two new electrochemical couples observed at mid-peak potentials of 0.32 and 0.52 V (vs. Ag/AgCl, 0.5 M H_2SO_4). The peak currents exhibit a linear dependence on the potential scan rate as expected for surface-confined redox species and the peak potentials shift toward lower potentials with increasing solution pH at a rate of ca. 60 mV/pH unit. The PANI–NDGA composite film was found to electrocatalyze the oxidation of NADH in a nearly neutral (pH 7.4) phosphate buffer.

1. Introduction

Poly-aniline (PANI) has been attracting the attention of electrochemists for many years because of its easy preparation, high electroconductivity as well as attractive electrochemical and optical properties [1,2]. The main drawback of PANI is however the limited pH range in which PANI retains its electrochemical activity. It usually becomes insulating and electrochemically inactive at pH above 4 [3], which limits its use as a sensing platform for applications requiring neutral or alkaline electrolytes. Many approaches have been used to overcome this problem. These are based on (i) post-polymerization grafting of sulfonic groups on PANI chains by fuming sulfuric acid treatment [4], copolymerization of parent aniline with –COOH or $–SO_3H$ functionalized aniline derivatives [5–8], or performing (electro)polymerization in the presence of various organic acids [9–14]. All these approaches by introducing an ionogenic acidic group to the PANI structure hinder the deprotonation of the conducting form of PANI (emeraldine salt) and thus extend its electroactivity toward less acidic pHs.

PANIs when deposited on common electrodic materials as thin films exhibit valuable electrocatalytic properties and have been used as transducers for electrochemical sensing of different organic (bio)molecules. Electrochemical detections of ascorbic acid (AA) and reduced nicotinamide adenine dinucleotide (NADH) are the most representative examples of such applications [9,10,12,14–18]. PANI was also found to enhance the reversibility of electrochemical oxidation/reduction of reversible systems such as Fe^{2+}/Fe^{3+} and hydroquinone/quinone [19]. However, researchers overlooked one important reaction that may take place along with this redox cycling, namely the covalent attachment of electrogenerated quinone (Q) to the PANI chain, which generates new redox active groups. This process was observed both for parent catechol and electrogenerated catechol-sulfonic acid, leading in the latter case to the generation of self-doped PANI showing a new voltammetric couple in cyclic voltammograms, electroactivity in a wide pH range and electrocatalytic properties toward the oxidation of AA [20].

It seems likely that the above mentioned reaction due to the commercial availability of a large number of catechol derivatives may become a simple and effective entry point for post-polymerization modification of PANI, giving new materials with attractive (electro)chemical properties.

In this paper a method of converting ultrathin PANI films to a redox active material by an electrochemical reaction with nordihydroguaiaretic acid (1,4-bis-(3,4-dihydroxybenzene)-2,3-dimethylbutane, NDGA) is presented and discussed in detail.

2. Experimental

2.1. Chemicals

Nordihydroguaiaretic acid (NDGA) was obtained from Sigma, aniline from POCH (Gliwice, Poland). Aniline was distilled under reduced pressure before use. Doubly distilled water was used to

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prepare all solutions. All buffer materials were reagent grade and used without further purification.

2.2. Apparatus

The electrochemical experiments were carried out using a μAutolab electrochemical analyzer (EcoChemie, Utrecht – Netherlands) connected to a PC for control, data acquisition and storage. An Au electrode (BAS MF2014, 1.6 mm diameter) was used as the substrate electrode for all experiments. The counter electrode was a platinum wire. All potentials reported in this paper are referenced to an Ag/AgCl electrode with no regard for the liquid junction potential. A rotating disc electrode (EcoChemie) with an Au active disc (3.0 mm diameter) was used for electrochemical measurement under hydrodynamic conditions.

2.3. Electrode preparation

Before its modification, the working surface was polished with alumina slurries of 1 and 0.05 μm on Buehler polishing cloth with water as a lubricant, rinsed with doubly distilled water, and sonicated in a water bath for 3 min. PANI electrodeposition was performed using commonly applied conditions. Briefly 0.05 mM aniline in 0.5 M HCl was used as the plating solution and the potential of the working electrode was scanned between -0.2 and 0.9 V at 100 mV s^{-1} for 2 scans to initiate the electropolymerization, which was followed by scanning between –0.2 and 0.78 V for a desired number of cycles. After the modification procedure, the PANI-modified electrode was thoroughly rinsed with water and cycled between –0.2 and 0.8 V in 0.5 M H_2SO_4/acetonitril (1:1 v/v) containing 0.2 mM NDGA until a steady cyclic voltammogram was obtained, i.e. typically for 50 scans. Thus obtained PANI–NDGA electrode was characterized electrochemically as described in the next section.

2.4. AFM imaging

For surface analysis PANI and PANI–NDGA films were prepared using the same conditions as those for voltammetric electrodes. A gold coated silicon wafer (Aldrich) was used as the substrate. Before deposition of polymeric films the substrate was cleaned by sonication in acetone for 5 min. The AFM imaging was accomplished using a Nanosurf EasyScan 2 AFM microscope.

2.5. FT-IR spectra

RT-IR spectra of thin films of PANI and PANI–NDGA were recorded using a Bruker IFS 113v spectrometer working in an ATR mode. For this characterization the films were deposited electrochemically on a gold plated silicon wafer (Aldrich). Sample size was ca. 1.5 × 2 cm.

3. Results and discussion

3.1. Electrochemistry of NDGA at bare Au and PANI-modified Au electrodes

Fig. 1 shows cyclic voltammograms of NDGA at bare Au (A) and PANI-modified Au electrodes (B) as well as a PANI electrode cycled in an NDGA solution after transferring to pure supporting electrolyte (C). As may be seen in Fig. 1A, at the applied scan rate the cyclic voltammogram of dissolved NDGA exhibited a typical quasi-reversible behavior characterized by the mid-peak potential ($E^{o\prime}$) of 0.52 V and peak separation (ΔE_p) of 70 mV. This may be attributed to the reversible oxidation/reduction of catechol moieties of

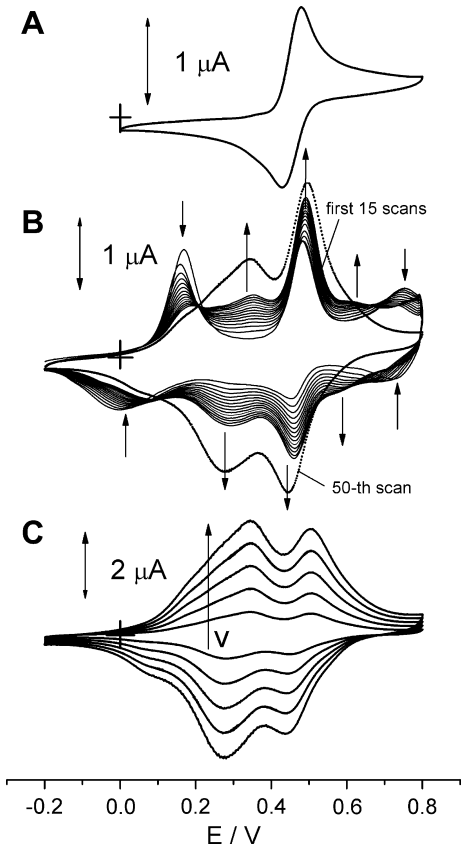

Fig. 1. Cyclic voltammograms of 0.2 mM NDGA at bare gold (A) and PANI-modified electrode (B). Electrolyte; 0.5 M H_2SO_4/acetonitril (1:1 v/v), scan rate; 20 mV s^{-1}. (C) Shows the effect of scan rate on cyclic voltammetry of the electrode obtained in (B) after transferring to pure 0.5 M H_2SO_4. Scan rate are 10, 20, 30, 40 and 50 mV s^{-1} (from inner to outer).

NDGA to corresponding quinones ($QH_2 \Longleftrightarrow Q + 2H^+ + 2e$). Moreover, the anodic-to-cathodic peak ratio is nearly a unity as expected for a fully reversible redox system. The same process at the PANI layer is characterized by smaller ΔE_p (40 mV), which is probably the effect of adsorption of hydrophobic NDGA molecules on organic PANI film, changing the electrochemistry of NDGA from diffusion-controlled to that typical for surface-confined systems. On the other hand, the peak ratio is no longer a unity and significantly increases, which indicates that the Q form of NDGA undergoes a follow-up reaction on this film. Yet the decrease of two couples assignable to PANI, i.e. those corresponding to leucoemeraldine/emeraldine ($E^{o\prime}$ of ca. 0.12 V) and emeraldine/pernigraniline ($E^{o\prime}$ of ca. 75 V) transitions may be seen, along with the development of a new redox system at $E^{o\prime}$ of 0.32 V. All these observations imply a significant restructuring of the PANI film and the formation of new redox active moieties within it. Note also a positive shift of the first PANI couple simultaneous with a negative shift of the second couple, leading finally to their merging with the NDGA peaks. The same shifts were noticed for poly-acrylic acid doped [21] PANI, and substituted PANIs [22], and were attributed to steric and electronic effects provided by bulky organic doping ions. The same effect seems likely for relatively large NDGA molecules incorporated into the PANI film. This assertion can also be supported by literature data showing significant shifts of PANI peaks during post-polymerization cycling in the presence of aminobezonitriles [23] or diamino-methylbenzoate [24], that lead to a covalent modification of the PANI structure. As the cycling continues, a steady-state voltammogram is reached after ca. 50 scans. On washing the modified electrode and transferring it into an NDGA-free electrolyte,