



Short communication

The permselective layer prepared onto carbon and gold surfaces by electropolymerization of phenolic cyclopentenedione-nostotrebin 6

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ARTICLE INFO

Article history:

Received 2 August 2013

Received in revised form 18 October 2013

Accepted 29 October 2013

Available online 7 November 2013

Keywords:

Carbon and gold

Polymerization

Bioactives sensing

Dopamine

Microelectrode

ABSTRACT

In this study, we report that electrooxidation of phenolic cyclopentenedione, 2,2'-bis[4,5-bis(4-hydroxybenzyl)-2-(4-hydroxyphenyl)-cyclopent-4-ene-1,3-dione] results in the formation of nonconducting films which make uniform, defect-free and stable layers with permselective properties on gold and carbon surfaces. The electropolymerization process proceeds in neutral aqueous medium at potentials higher than +0.6 V (vs. Ag/AgCl, 3 M KCl). The polymer prepared was characterized by electrochemical methods, quartz crystal microbalance, Fourier transform Raman and infrared spectroscopies, and scanning electron microscopy. The polymeric film can be used for electrode coating and thus preparation of an anti-interference barrier, for example, in dopamine microelectrode sensor construction. The results presented here are the first evidence for the preparation of phenolic cyclopentenedione-based functional film.

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1. Introduction

Functional barriers and development of permselective layers (films) are important goals for many applications in chemistry today, e.g. analytical chemistry, energy conversion, biochemistry and industrial chemistry in general. Compact permselective layers, directly fabricated onto the electrode surface are used to suppress the access of the interfering species. The selectivity is mainly provided on the basis of molecular weight, charge and hydrophobicity or hydrophilicity differences among the analyte and several interfering molecules which pass or do not pass through the layer [1–5].

To prepare anti-interference barriers two basic experimental approaches are used [5], the first one being “solvent casting”, i.e. application of the solution of a film-making compound onto the electrode surface and subsequent evaporation of the solvent. Typical examples of films prepared in this way are Nafion, cellulose acetate, polyvinylchloride and polysiloxane films. The second approach is electrosynthesis, i.e. the electrochemically initiated formation of the film on the electrode surface. In this way, it is possible to influence the properties of the fabricated layer such as thickness and/or pore size by the concentration of the deposited compound, potential program during the synthesis and application of additives [6].

In the view of analytical chemistry, electrodes equipped with permselective films are used for the electrochemical analysis of biologically active compounds and metabolites. Examples of electro-synthesized permselective layers include overoxidized polypyrrole, polyethylenimine, polyphenylenediamine and phenol derivatives [2,6–10]. Among the most noteworthy applications of permselective layers is the elimination of interferences during the determination of glucose [11] and nitric oxide [1]. Owing to the broad spectrum of applications of these compact layers, new compounds for their preparation are being designed.

Here, we focus on preparation of novel phenolic cyclopentenedione (PCD) based permselective layer using carbon and gold as solid support. This study was aimed at (i) developing a procedure for the preparation of PCD layer by electropolymerization, (ii) characterization of PCD layer prepared using electrochemistry, quartz crystal microbalance, scanning electron microscopy and Fourier transform Raman and infrared spectroscopies, and (iii) evaluation of the stability and application of PCD permselective layer for dopamine amperometric sensing using microelectrodes.

2. Experimental section

2.1. Chemicals

The PCD used in this study (2,2'-bis[4,5-bis(4-hydroxybenzyl)-2-(4-hydroxyphenyl)-cyclopent-4-ene-1,3-dione]), also known as nostotrebin

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6 (Fig. 1A), was isolated and purified according to a previously published protocol [12].

Ascorbic acid (AA) and paracetamol (PA) were purchased from Sigma Aldrich (USA). Sodium nitrite was obtained from Lachema (Czech Republic). Dopamine (DA) and uric acid (UA) were obtained from Fluka (Germany). PBS solution (0.05 M NaCl and 0.05 M Na_2HPO_4 and NaH_2PO_4) at pH 7.4 was used as supporting electrolyte.

2.2. Instruments

Voltammetric analysis was performed using the CH-Instruments Model 660C electrochemical workstation in three-electrode configuration. Ag/AgCl, 3 M KCl was used as a reference electrode, and Pt-wire served as an auxiliary electrode. The range of working electrodes used in this study included CHI101 gold, CHI102 platinum and CHI104 glassy carbon electrode. A custom-made carbon fiber microelectrode (CFE) was prepared as described in ref. [7].

EQCM measurements were performed on CH-Instruments 440C apparatus using gold coated quartz crystals. The signal is expressed as $\Delta f = f - f(\text{ref})$, i.e. frequency change relative to reference crystal.

Scanning electron microscopy (SEM) images were obtained on Hitachi SU-6600. The pictures were collected with a high voltage of 10 kV at a working distance ranging from 10 mm to 22 mm. Sample material was fixed on carbon conductive discs. No coating method was used [7].

Fourier transform Raman spectra were acquired using Equinox 55/S (Bruker, Germany) spectrometer equipped with FRA 106/S Raman module (Bruker). Samples were irradiated by the Nd-YAG laser beam (1064 nm, 50 mW, Coherent, USA). The spectra were collected and processed using the OPUS 4.0 (Bruker) software. The electrodeposition was performed on electrochemically gold coated platinum electrodes (7 mm side, 0.3 mm thickness of Pt, thickness of Au layer ca. 2 μm) [13].

Fourier transform infrared (FTIR) spectra were collected using Nicolet 6700 (Thermo Scientific) spectrometer equipped with single-bounce attenuated total reflection accessory MIRacle based on ZnSe crystal. The spectra were processed using the Omnic 8.2 (Thermo Scientific)

software. The electrodeposition was performed on gold foils (thickness 0.1 mm).

2.3. Stability and reproducibility

Relative standard deviation (RSD) for the preparation of PCD permeselective layer was evaluated which six PCD-modifications of one gold electrode prepared independently and tested to 50 μM DA in the presence of 10 mM AA. For intra-day reproducibility measurement, DA was analyzed after 1 h periods in a mixture of various concentrations of AA (1–10 mM). In case of inter-day reproducibility, DA was measured in the presence of AA for 14 consecutive days.

3. Results and discussion

Cyclic voltammograms of PCD (for chemical structure see Fig. 1A), obtained on glassy carbon electrode (GCE) in PBS at $v = 100 \text{ mV s}^{-1}$, are characterized by a broad peak around +0.6 V (Fig. 1B). The complex irreversible anodic reaction probably proceeds via hydroxyl groups and this is in agreement with previously published results on structurally similar substances [14–16]. In the second and subsequent scans, the current of the oxidation peak sharply decreased, indicating the polymerization process and the film formation. This statement is fully consistent with the fact that formation of typical redox active phenol oxidation products was not observed in the second and subsequent scans [14–16].

In addition to GCE, similar behavior was observed for gold (Fig. 1C) and also platinum electrodes (not shown). For all experiments in the study, PCD film was prepared onto electrode surfaces after bare-electrode immersion into PBS containing 0.1 mM PCD and potential cycling from 0 to +0.9 V at $v = 1000 \text{ mV s}^{-1}$ for 60 s. Then the electrode was washed by distilled water and used for other experiments. The 0.1 mM PCD was used corresponding to fully saturated solution under the conditions used. At higher concentrations, limited solubility of the PCD monomer was observed. The above-described formation of PCD layer can be found only in aqueous environment. No PCD layer was deposited onto electrode surfaces under non-aqueous conditions of

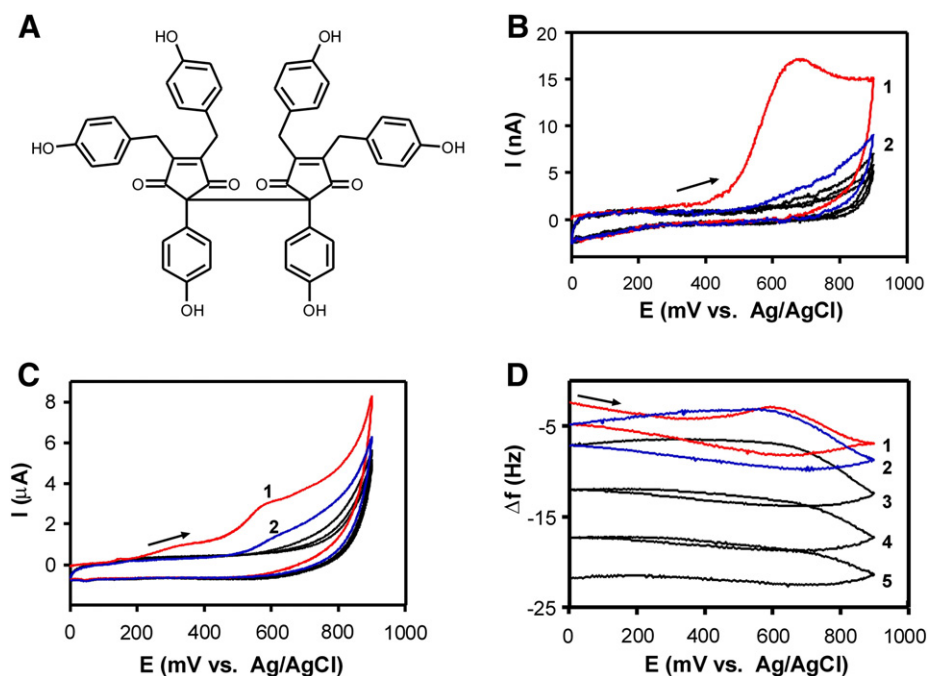


Fig. 1. (A) Structure of the PCD unit used in the study, formerly called nostotrebina 6 [12,22]. Cyclic voltammograms of 0.1 mM PCD in PBS at carbon (B) and gold (C) electrodes. The corresponding EQCM profiles (D) to voltammograms in panel C are shown.

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