Electropolymerization of quinone-polymers onto grafted quinone monolayers: a route towards non-passivating, catalytically active film

Saustin Dongmo, Julia Witt, Gunther Wittstock [*],[1]

Carl von Ossietzky University of Oldenburg, School of Mathematics and Science, Department of Chemistry, D-26111 Oldenburg, Germany

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ABSTRACT

A new preparation of a polymer made from 5-hydoxy-2-methyl-1,4-naphthoquinone (plumbagin) is described. While conventional electropolymerization leads to self-limited growth of an inhibiting film, electropolymerization onto a grafted monolayer of plumbagin on glassy carbon (PLG/GC) yields continuous growth of a polymer film (polyPLG/PLG/GC). The electrochemical properties of polyPLG/PLG/GC have been intensively characterized by cyclic voltammograms (CVs) and showed the preservation of the redox chemistry of the quinone system within the polymer. The concentration of active site was almost five times higher than in the case of direct electropolymerization of plumbagin on GC (polyPLG/GC). The formal potential of the polyPLG/PLG/GC shifted with pH by 57 mV/pH unit up to pH 8 suggesting a two-electron/two-proton process. At higher pH, the slope decreased to 28 mV/pH unit pointing towards a two-electron/one-proton reaction. The pK_a of the redox system was determined as 8.1. The electron-transfer rate constant and the transfer coefficient were determined to be $k_s = 12.5\,s^{-1}$ and $\alpha = 0.5$ for polyPLG/PLG/GC in phosphate buffer solution pH 7. The surface morphology and thickness of polymer films were investigated using scanning electron microscopy (SEM) and atomic force microscopy (AFM). This polyPLG/PLG/GC film showed an electrocatalytic response for oxygen reduction reaction (ORR) similar to a PLG/GC monolayer. This indicates as well as the CVs in oxygen-free solution the preservation of the quinone groups in the first monolayer. Both films were more effective than directly polymerized polyPLG film where the number of accessible quinone groups was much lower.

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1. Introduction

Quinone compounds are considered as some of the oldest organic molecules in the universe and have been observed in the interstellar dust onboard the NASA spacecraft Stardust [1]. In living organism quinone/semiquinone/hydroquinone redox systems are directly involved in the production of reactive oxygen species (ROS), e.g. superoxide radical or hydrogen peroxide, known as a primary cause of oxidative stress [2,3]. Therapeutic effect of quinone compounds have been reported for the treatment of many pathologies like acne, inflammatory diseases, ringworm, fungal, bacterial, or viral infections. Recently, anticarcinogenic or cytotoxic effects have been shown in animals and cancer cells [2,3]. Likewise, quinone compounds were used for electrocatalysis of oxygen reduction reaction (ORR) [3–15]. Due to the good biocompatibility and stable electroactivity, they were also used in preparation of

biosensor [16]. Finally, the quinone moiety was recently used to improve energy storage of battery [17]. All these applications are enabled by the redox chemistry of the quinone group including the ability to produce semiquinone radicals [2,3,6–8,10,16,18–20].

Modification of electrode by electrografting quinone compounds was investigated by several authors. The most widespread approach consists in grafting of anthraquinone, its derivatives and phenanthrenequinone to carbon electrodes using the reduction of their diazonium derivatives as illustrate by the following reactions [7,8,19,21]:

$$RN_2^+ + e^- \rightarrow R^. + N_2 \tag{1}$$

$$R^. + C \rightarrow R\text{-}C \tag{2}$$

The diazonium route can provide thick films because the coupling reaction can also happen to already grafted molecules [21]. The diazonium derivatives have to be synthesized and purified before use. Nevertheless, the goal to find preparation routes for a very stable quinone-containing film encouraged the use of polymer films in which the quinone system was preserved

* Corresponding author. Tel.: +49 441 798 3971; fax: +49 441 798 3979.
E-mail address: gunther.wittstock@uni-oldenburg.de (G. Wittstock).
[1] ISE member.
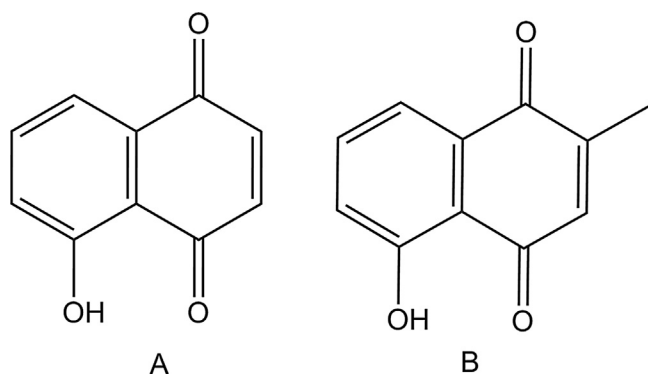
Scheme 1. Juglone (A) and plumbagin (B).

[3,22,23]. This class of polymer films comprises also the films made from naphtoquinone derivatives which possess hydroxyl or an amine group in 5-position (Scheme 1), e.g. natural compounds like juglone (5-hydroxy-1,4-naphtoquinone) and plumbagin (5-hydroxy-2-methyl-1,4-naphtoquinone). Compared to the juglone, it was reported that the plumbagin compound possess a high cytotoxicity property in pig heart due its capacity to produce a superoxide radical [24].

Oxidative electropolymerization of juglone and plumbagin leads to the passivation of the electrode during deposition of the film [3,25,26]. This behavior was related to the phenolic part of these compounds. Electropolymerization of phenols is a prototypical example for the formation of an insulating film [27–30]. In addition to phenol oxidation, the quinone group can be attacked by nucleophiles in a 1,4-Michael addition [31–34]. This reaction has been used for grafting plumbagin monolayers on electrodes that were pretreated to expose a nucleophilic group such as –OH [31]. This grafting approach avoids the necessity to synthesize a corresponding diazonium derivative before surface functionalization. Here we report the synthesis and characterization of a new class of plumbagin-derived polymers that were obtained when combining the grafted plumbagin layers with subsequent electropolymerization (polyPLG/PLG/GC). Those films show substantially different behavior than films obtained by either grafting (PLG/GC) or electropolymerization (polyPLG/GC) alone.

2. Experimental

2.1. Reagents and apparatus

Plumbagin (5-hydroxy-2-methyl-1,4-naphthoquinone), $NaHCO_3$, NaH_2PO_4, Na_2HPO_4, were purchased from Sigma Aldrich (Steinheim, Germany). Deionized water obtained from a water-purification system (resistance >18.2 MΩ·cm, Seralpur PRO 90 C, Ransbach, Germany) was used for all aqueous solution. Argon was used for deaeration of the solution. Stock solution of plumbagin (10 mM) was prepared in acetone and store at -20 °C.

Electrochemical measurement were performed at room temperature using a potentiostat CHI 660 A and 620A (CH Instruments, Electrochemical Analyser, Austin, TX, USA) in a three-electrode configuration. The working electrode was a glassy carbon (GC) with a diameter of 3 mm (BAS Technicol, UK). For atomic force microscopy (AFM) thickness determination and scanning electron microscopy (SEM) imaging (Figs. 9 and 10, Supporting Information SI-6) GC plates (Alfa Aesar GmbH & Co KG, Germany) were used and pressed against an O-ring (8 mm internal diameter) and a Teflon block with the liquid reservoir. A platinum wire and Ag/AgCl/3 M NaCl electrode served as auxiliary and reference electrodes, respectively.

AFM was performed under ambient conditions with a Nanoscope IIIA controller and an Enviroscope stage (Veeco Instruments Inc., Santa Barbara, CA, USA) operating in contact mode with triangular Au-coated Si_3N_4-cantilever (Bruker, MSCT tip) of a nominal spring constant of 0.6 N/m. Additional information on surface morphology were obtained by SEM using a Helios Nanolab 600i system (FEI Company, Eindhoven, The Netherlands) with an EDAX detector at accelerating voltages of 15 to 25 kV.

2.2. Procedures

2.2.1. Preparation of PLG/GC

PLG/GC electrodes were prepared using the method described by Ardakani et al. [31]. The GC electrode surface was polished with 0.3 and 0.05 μm alumina powder followed by sonicating and rinsing with deionized water after each polishing step for ∼10 min to remove the alumina and abraded particles. Subsequently, pre-cleaned GC electrodes were activated electrochemically in 0.1 M $NaHCO_3$ by performing 40 cycles between -1.1 and 1.8 V at a sweep rate $\nu = 100$ mV s^{-1}. After rinsing with water, grafting of the plumbagin on the electrode surface was done by immersing the activated GC, auxiliary and reference electrodes in 0.1 M phosphate solution pH 4, containing 0.2 mM plumbagin and performing 30 potential cycles between 0.1 and -0.3 V at $\nu = 0.01$ V s^{-1}. The cyclic voltammograms (CVs) are shown in Supporting Information SI-1.

2.2.2. Preparation of polyPLG/PLG/GC

PLG/GC electrode was immersed in phosphate buffer pH 7 containing 0.2 mM plumbagin and the potential was cycled between -0.8 to 1.2 V at 50 mV s^{-1} (25 cycles) causing the formation of phenoxy radicals. After rinsing with water, electrodes were directly characterized or stored in phosphate buffer solution pH 7.

2.2.3. AFM thickness determination

AFM thickness determination was performed similar to established procedures [35,36]. Topographical images of a 5×5 μm^2 area were collected with a scan rate of 0.5–2.0 Hz at a resolution of 256×256 pixel. The set-point was close to 0 V in order to keep the AFM-tip in an appropriate distance to the sample surface allowing higher resolution and non-destructive imaging of soft materials in order to select an area of 1×1 μm^2 without obvious polishing streaks. For the thickness determination of plumbagin polymer, this area was scanned by AFM at a set-point of 10 V. Under those conditions the tip penetrates and abrades the soft polymer film until the typical structure of the GC substrate is visible. Subsequently, a topographic image of the scratched region using low forces (set-points between 0 and 1 V) was recorded at 7 Hz. The thickness was taken as the averaged height difference between the GC substrate and the intact polymer film away from the protruding regions of removed material at the rim of the scratched area (Fig. 7) using the thickness tool of the software Nanoscope Analysis 1.4. The complete documentation of all AFM thickness measurements is given in SI-5. Image flattening was performed with the first order, least-square polynominal function of the software Nanoscope V5.30r3sr3, which removes tilt and the vertical z-offset between lines scans.

3. Results and discussion

3.1. Grafting of plumbagin monolayers to GC and its capability to produce phenoxy radical from 5-hydroxy functionality

Ortho- and para-quinones can undergo a 1,4-Michael addition when attacked by nucleophiles [31]. Such reactions are well documented also for an electrochemical context. The fast attack by