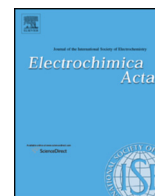




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Research Paper

Basic electrochemical properties of sputtered gold film electrodes

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ABSTRACT

Gold nanolayers made by sputtering of pure gold (physical vapour deposition) are commonly used for many biophysical and material applications. However, the use of sputtering method for fabrication of working electrodes for electroanalytical purposes is less common. This paper focuses on the testing and characterization of sputtered working roughened gold nanostructured film electrodes, which fall into category of upcoming desirable new generation of nanostructured gold working electrodes. Gold nanostructured films (80 nm thin) were sputtered onto 50 μm thin PTFE substrates with three different types of treatment: pristine, plasma treated, and plasma treated and subsequently spontaneously grafted with biphenyl-4,4'-dithiol.

The characterization of gold nanostructured film electrodes was carried out by examination of the electrode reaction of standard redox probes (ferrocyanide/ferricyanide, hydroquinone/benzoquinone) in different types of supporting electrolytes (BR buffers of various pH, KCl, KNO₃, H₂SO₄), by exploration of the electrode surface by scanning electron microscopy, by atomic force microscopy accompanied by elementary analysis and contact angle measurements. The testing of electrodes was complemented by an attempt to calculate their real surface areas from Randles-Sevcik equation. All results were compared to conventional bulk gold electrode. The practical applicability of the nanostructured gold electrodes as sensors for the determination of environmental pollutants was verified by voltammetric determination of hydroquinone as a model electrochemically oxidisable organic environmental pollutant.

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1. Introduction

Nanostructured electrodes are classified according to IUPAC nomenclature as electrodes/structures made of nanoparticles at least one dimension of which falls into the range 1–100 nm [1]. Nanostructured arrangements have received considerable attention and extensive development over the last decade in a broad variety of application including electroanalytical chemistry, physical chemistry etc., where the interfacial nature of measurements favours the fabrication of miniaturized analytical devices. In this context, nano-thin-film technology is intensively explored [2].

The unique chemical and electrical properties of nanostructured layers (films/electrodes) are usually more influenced by their fabrication process and by the size of nanoparticles and their density than by the nature of the used material (type of particles) [3]. The gold nanostructured electrodes from gold nanoparticles

(AuNPs) can be prepared by attachment of AuNPs at the surface of thiol spacer self-assembled at common bulk electrode serving as a conductive substrate [4]. Other possible approaches to the fabrication of gold nanostructured electrode are *in-situ* or *ex-situ* plating of AuNPs from the solution of HAuCl₄ onto selected substrate under controlled potential (electrografting) [5,6]. However, these procedures are very time consuming and labour demanding and require large amounts of chemicals and considerable user experience. The deposition of AuNPs from the concentrated solution of HAuCl₄ can be followed by subsequent deposition of mercury from the concentrated solution of Hg(NO₃)₂ resulting in the gold nanostructured amalgam film electrode (hybrid) [7]. In the case of nanostructured gold film electrodes made by electrografting it is complicated to ensure that the thickness and shape of the gold layer will be completely identical for each thus prepared electrode, especially in nanoscale. To avoid this problem, gold nanostructured screen-printed electrodes can be used. During the preparation of nanostructured gold screen-printed electrodes, the electrode ink is applied on a suitable substrate, mostly made of plastic or ceramic, and it is easier to

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ensure constant film thickness for all electrodes. Another advantage of these film electrodes is very low cost in comparison with common conventional bulk electrodes; thus a new electrode can be used for each single measurement (disposable electrodes). Moreover, traditional three-electrode configuration printed on the same strip is also great advantage of any screen-printed electrodes [8]. Modern approach to fabrication of gold nanostructured film electrodes is physical vapour deposition of Au atoms using sputtering method. This fabrication process can be used in the case of the necessity to use a non-conventional reference electrode or different electrode arrangement impossible to fabricate by common screen printed electrode production technique.

Advantage of sputtering lies in simplicity, reproducibility, and low price of final products. Moreover, it is considered as pollution free (“green”) method. Disadvantage of gold sputtering is that gold is one of the most inert metals and the adhesion between AuNP and a polymer substrate is poor. Film adhesion and electrical contact properties are strongly influenced by the interface structure. Film adhesion can be changed when electrodes are exposed to some types of organic solvents or concentrated acids. Several modification techniques (physical, chemical or their combination) have been suggested for enhancing metal to polymer adhesion, for example treatment by plasma [9,10] or fixing of AuNPs by thiol groups containing spacer [4,9,11].

Universally, nanostructured gold film electrodes offer unique physicochemical properties and advantages such as high surface-to-volume ratio, surface charge, possible change of the hydrophobicity or hydrophilicity, easy miniaturization and change of shape; they can be chemically modified and mechanically or electrochemically pre-treated to further improve their native properties [12]. The electrode material can be modified by addition of another nanoparticle (carbon or metal nanoparticles). Combination of two nanomaterials with different properties can provide a unique hybrid nanoparticle electrode with new properties [13]. Moreover, it is possible to modify the electrode material by inorganic complexes [14], polysaccharides (chitosan) [15], conductive polymers [16], etc., if a special application is required.

Until now, nanostructured gold electrodes made by various techniques have been used as voltammetric sensors for direct determination of metabolites of human body processes [17–19], as well as pharmaceuticals [6,20,21]. Nowadays, nanostructured gold electrodes are applied in a wide range of chemical disciplines such as impedance spectroscopy and chronopotentiometry in analytical chemistry [22], as an electrocatalytic mediators of luminescence in spectroscopy [23], as a platform for the construction of various sensitive electrochemical biosensors in biochemistry, where roughened surface of the electrode is needed for anchoring of enzymes or biomolecules [24–27]. It is necessary to mention the use of these electrodes in supercapacitors, in microelectronics and photovoltaics [28,29], too.

This study is focused on the surface and electrochemical characterization of three types of gold nanostructured film electrodes (GNFE) with roughened surface fabricated by sputtering method which represents further areas of applicability of gold nanomaterials and a promising approach to the use of sputtered electrodes in analytical chemistry. These GNFEs are intended for the large-scale determination of oxidisable environmental pollutants *in-situ* as a final aim of the research.

2. Experimental

2.1. Chemicals

The electrochemical behaviour of three types of nanostructured gold electrodes in different supporting electrolytes was studied using 0.1 molL⁻¹ sulfuric acid, 0.1 molL⁻¹ potassium chloride,

0.1 molL⁻¹ potassium nitrate, and 1 mmolL⁻¹ potassium hexacyanoferrate in 1 molL⁻¹ potassium nitrate (all p.a. grade and obtained from Lach-ner, Czech Republic) as testing solutions.

Britton–Robinson (BR) buffers serving as testing medium and supporting electrolyte were prepared by mixing 0.2 molL⁻¹ solution of sodium hydroxide (Penta, Czech Republic) with a solution of phosphoric acid, boric acid and acetic acid (all Lach-ner, Czech Republic), 0.04 molL⁻¹ each. All chemicals used for buffer preparation were of analytical grade purity and were used without further purification.

The stock solution of 1 mmolL⁻¹ hydroquinone (HQ) (Lach-ner, Czech Republic) was prepared by dissolving the exact amount of the substance in deionized water (Milli-Q-Gradient, Millipore, USA) and it was kept in the refrigerator. This solution was freshly prepared every week to avoid degradation due to spontaneous oxidation to benzoquinone.

2.2. Preparation of gold nanostructured film electrodes

For the fabrication of nanostructured gold film electrodes, 50 μm thick foil of polytetrafluoroethylene (PTFE, density 2.2 g cm⁻³, Goodfellow, United Kingdom) was used as a nonconductive substrate. PTFE substrate was chosen for its thermostability up to 320 °C, for its robustness during measurements in the presence of organic solvents, high hydrophobicity (contact angle > 110°), and for good dielectrical properties. The gold nanolayers were deposited onto substrate from Au target (purity 99.99 %, Safina, Czech Republic) in DC argon atmosphere (Ar, purity ≥99.996%, Siad, Czech Republic). Gold nanolayers were deposited on three types of PTFE: pristine PTFE (GNFE-Pristine), plasma treated (GNFE-Plasma), and plasma treated and subsequently grafted with biphenyl-4,4'-dithiol (GNFE-BPD). The modification by plasma was performed by diode plasma discharge in etching mode on Balzers SCD 050 device (Pfaeffikon Balzers, Liechtenstein) for 240 s. DC Ar plasma treatment was performed under following conditions: discharge power of 8.3 W, Ar flow ~0.3 dm³ s⁻¹, working pressure of 10 Pa, 50 mm distance between the electrode and the sample, area of electrodes 48 cm² and chamber volume about 1.0 dm³. Alternatively, the PTFE was modified by 24 hours spontaneous grafting in methanolic solution of 0.1 mmolL⁻¹ biphenyl-4,4'-dithiol (BPD, Sigma-Aldrich, USA) to improve the adhesion of gold nanolayer.

After BPD grafting, samples were rinsed with p.a. methanol. The deposition of gold was accomplished by sputtering of gold from Au target through contact mask on Balzers SCD 050 device (Pfaeffikon Balzers, Liechtenstein) in sputtering mode. Au nanolayers were prepared under following conditions: discharge power of 15 W (current 40 mA), working pressure of 5 Pa, deposition time 200 s.

Deposition mask parameters were: round shape head with 3 mm in diameter with connected tail 15 mm long and 1 mm thick; the tail was used for connection to potentiostat. The round shape head was isolated from the tail by non-conductive lacquer to ensure uniform electrode area.

2.3. Apparatus

Voltammetric measurements were performed with portable potentiostat PalmSens (Palm Instruments, Netherlands) controlled by PSTrace4.8 software. Voltammetric measurements were carried out with three types of nanostructured gold film electrodes with geometric area 7.1 mm² (Ø = 3 mm) (described in Section 2.2) or gold bulk electrode with the same geometric area (Metrohm, Czech Republic). A gel leakless Ag/AgCl reference electrode (3 M KCl, Cypress Systems, Chelmsword, USA), to which all potentials values are referred, was used to avoid contamination by Cl⁻ ions from

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