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A COMPARATIVE STUDY OF GOLD ELECTRODES MODIFICATION METHODS WITH AROMATIC COMPOUNDS BASED ON DIAZONIUM AND THIOL CHEMISTRY

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Acest articol prezintă modificarea electrozilor de aur prin două metode: chemisorbția compuşilor tiolici şi respectiv electrodepunerea a 4-clorobenzidiazoniu. De suprafața electrozilor modificați au fost legate grupări organice care pot fi folosite la imobilizarea ulterioară de enzime sau mediatori pentru dezvoltarea de biosenzori. Stabilitatea electrozilor modificați a fost investigată pentru diferite domenii de potențial în pH acid sau neutru. Suprafața electrozilor poate fi pasivată de un timp de reacție lung cu compuşi tiolici sau prin depunearea diazoniului prin cicluri numeroase. Metoda de diazotare a fost investigată şi pentru suprafețe din carbune sticlos şi platină iar cea mai bună stabilitate a fost obținută pentru electrozii din cărbune sticlos.

This paper presents the modification of gold electrodes by two methods: chemisorption of thiolic compounds and respectively electrodeposition of 4-chlorobenzyldiazonium. On the surface of modified electrodes were bounded organic groups that may be used for further immobilization of enzymes or mediators for biosensors development. The stability of the modified electrodes was investigated for different intervals of potential in acidic or neutral pH. The electrode surface may be passivated by a long reaction time with thiolic compounds or by diazonium deposition by multiple cycles. The diazotation method was investigated also on glassy carbon and platinum surfaces and the best stability was obtained for glassy carbon electrodes.

Keywords: Gold electrodes, diazotation modification, 4-nitrobenzyl chloride, thiol compounds

List of Abbreviations:

4-PhSH - 4-clorothiophenol
4-ABC - 4-aminobenzyl chloride
MUD - 11-mercapto-1-undecanol

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SAM - self assembled monolayer
GCE - glassy-carbon electrode
EIS - electrochemical impedance spectroscopy
RMS - root mean square

1. Introduction

Modified electrodes are widely used in the present and they fulfill a lot of tasks in modern electrochemistry. Over the past two decades, they have been applied on a large scale in electrocatalytic reactions and as electrochemical sensors. The electrodes may be modified with different compounds [1, 2] to achieve the desired chemical, electrochemical, catalytic, photochemical or optical properties [3]. Usually, metallic electrodes (Pt, Ag or Au) or carbon materials such as glassy carbon are used as supports [1, 4].

Gold electrodes are useful to construct electrochemical sensors because they can be utilized in a large potential interval and they are chemically inert. The well established strategy of a self-assembled monolayer formation for immobilization of compounds onto gold surfaces are based on the attachment of thiol (SH) or disulfide (-S-S-) functional groups to Au [5]. In the last years, chemical modified electrodes by self-assembled monolayer of alkanothiols have been extensively used because of their simplicity and efficiency [6, 7]. The functionalization of different self-assembled monolayer leads to new surface properties [7]. During the adsorption of organothiol molecules on gold, the hydrogen is eliminated from the thiol group and a S-Au bond is formed [8, 9]. The S–Au affinity is very high; therefore the chemosorptions of thiolated organic species on gold surfaces are an ideal way to design electrochemical sensors [4]. The attractiveness of Au-thiol chemistry consists in the possibility to obtain a homogeneous monolayer with a relatively strong bond between the immobilized molecule and the electrode, and furthermore, the moieties linked to the molecule may be very diversified in order to attach subsequently other compounds [10].

The formation of self assembled monolayer (SAM) when a clean gold support is kept in contact with a diluted solution of alkylthiols has been studied and reported by a variety of techniques. If a long chain alkylthiol is used for gold modification, the adsorption may lead to high density films formation due to the lateral chain stabilization [11].

$$\mathrm{Au} + \mathrm{HS(CH_2)_nX} \longrightarrow \mathrm{Au\text{-}S(CH_2)_nX}$$

Electrochemical reduction of diazonium salts of different aryl derivatives and the addition of radicals produced to the surface is another path to construct modified electrodes with catalytic, analytical or biotechnological applications [12]. Electrochemical deposition of different diazonium aromatic derivatives, presented in Fig. 1, was characterized and used for surface modification of different carbon (glassy carbon, graphite, carbon fiber, carbon paste, carbon nanotubes, *etc.*) or metallic electrodes with various practical applications [13]. Aromatic diazonium salts ($R\text{-}N^{+}\equiv N\,X^{-}$) are a class of organic compounds, usually unstable, that can be prepared *in situ* by the treatment of aromatic amines with sodium nitrite in the presence of a mineral acid (HCl) [14]. Aminophenyl groups were electrochemically grafted at the surface of a gold electrode by reduction of *in situ* generated aminobenzyl chloride monodiazonium cations.

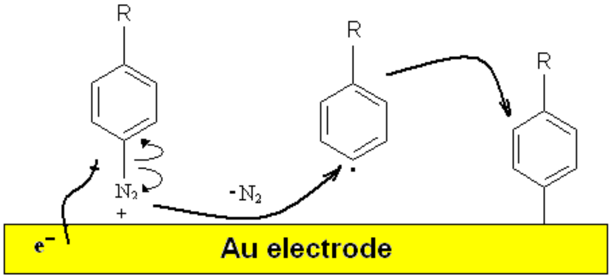

Fig. 1. Mechanism of diazonium salt electrografting on gold surfaces

The versatility of the method is based on the possibility of grafting a large variety of functionalized aryl groups, hence allowing the attachment of a broad spectrum of substances. The main disadvantage of diazonium approach is the multilayer formation that may induce surface passivation [15]. The surface coverage can be controlled by optimization of diazonium concentration and electrografting conditions [16].

In this work our purpose was to compare two methods of aromatic compounds deposition on gold electrodes based on thiol and diazonium links.

2. Experimental

1.1.Reagents and materials

4-aminobenzyl chloride was obtained by reduction of 4-nitrobenzyl chloride catalyzed with hydrogen chloride in water-acetonitrile solution and with Zn ACS reagent. All other reagents: acetonitrile, 4-nitrobenzyl chloride, Zn ACS reagent, potassium ferrocyanide, 11-mercapto-1-undecanol, potassium phosphate monobasic, sodium phosphate dibasic, potassium chloride, sodium acetate, acetic acid, nitric acid and hydrogen peroxide 30% were purchased from Sigma–Aldrich (www.sigmaaldrich.com). 4,4’-Dipyridyl, 98% and 4-chlorothiophenol were obtained from Acros Organics (www.acros.be). Methanol was purchased from Merck (www.merck-chemicals.com). Aqueous solutions were prepared with purified water (18 MΩ cm−1, Millipore, USA, www.millipore.com). The buffer solutions used were: acetate (0.1 molL^{-1} sodium acetate, 0.1 molL^{-1} acetic acid, pH 5.5, 0.1 molL^{-1} KCl) for analysis and phosphate buffer saline PBS (0.06 molL^{-1} Na_2HPO_4, 0.04 molL^{-1} KH_2PO_4 and 0.1 molL^{-1} KCl, pH 7.0) for electrode characterization by cyclic voltammetry and impedance spectroscopy.

1.2. Apparatus

All electrochemical measurements were performed using a PGSTAT302N potentiostat/galvanostat (Metrohm-Autolab, The Netherlands, www.metrohm-autolab.com) equipped with three-electrode cell (Metrohm) and controlled using Nova 1.5 software. The working electrodes were 3 mm diameter GCE, Au, Pt from Metrohm, reference electrode was an Ag/AgCl//3 molL^{-1} KCl (Metrohm) and counter electrode was a Pt wire. An Autolab pX1000 module was used for pH corrections.

1.3. Gold electrodes modification

The procedure for modifying the gold electrodes surface is based on the reduction of diazonium salt or on covalent attachment of thiolic compound. Prior to modification, the gold electrode surface was cleaned by polishing with alumina (0.3 µm, Metrohm, England), immersion in hydrogen peroxide for 30 min, thoroughly rinsing with Milli-Q water and drying with a nitrogen gas stream. The modification with monodiazonium was made by cyclic voltammetry: 3 cycles from –0.6 to +0.4 V at a scan rate of 0.1 V/s. The diazonium reagent was generated *in situ* by reaction of 4-aminobenzyl chloride (4-ABC) with sodium nitrite 5mmolL^{-1} in 0.1molL^{-1} HCL under ice. The electrode modification with thiolic compounds was made by electrode immersion in 1m molL^{-1} solution for different periods of time.

1.4. Electrode characterization

The modified electrodes were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The CV was made using as redox probe a solution of 1mmolL^{-1} potassium ferricyanide in PBS (pH 7.0 in 0.1 molL^{-1} KCl) at 0.1 V/s scan rate in the domain of –0.2 to +0.6 V. The EIS measurements were made in 1mmolL^{-1} potassium ferri/ferrocyanide equimolar solution prepared in PBS at a DC voltage = 0.226 V and an alternative current that had a potential amplitude of 5mV (rms). The measurements were performed at 40 frequencies logarithmically distributed between 9.5 kHz and 0.1 Hz. The results were represented as Nyquist plots and interpolated using Randles equivalent circuit.

3. Results and discussions

1.5. Optimization of deposition methods

The number of cycles performed for the diazotation electrode modification was varied from 1 to 5. The modified electrodes were characterized by CV and EIS (Fig. 2).

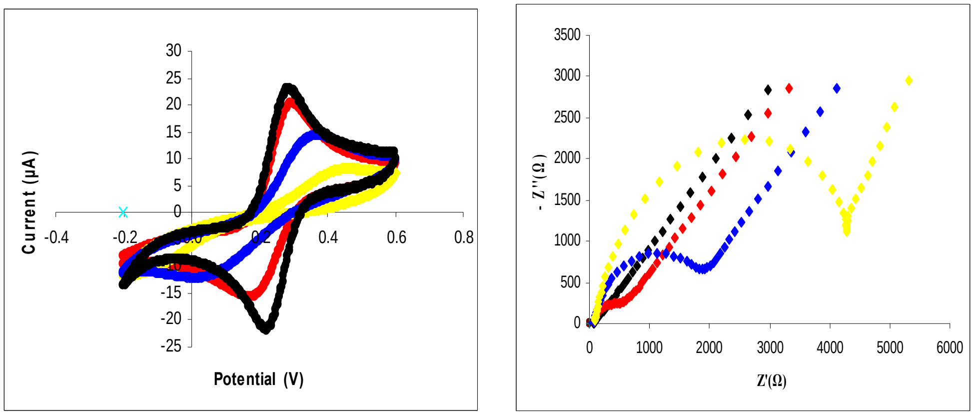

Fig. 2. The cyclic voltammograms and EIS spectra (points are the experimental data and lines are the fitting obtained with the equivalent circuit) of a clean gold electrode (black), after diazotation by recording 1 cycle (red), 3 cycles (blue) and 5 cycles (yellow)

The results indicate that the thickness of the organic layer on the electrode surface depends on the number of cycles. For one cycle, the intensity of the peaks in CV is slightly reduced, for three cycles, the presence of the modifying layer is evident and for five cycles or more, a surface passivation was observed. From the Nyquist representations it may be seen that the resistance of the charge transfer at the electrode surface (R_{ct}) is increasing with the number of cycles. This experiment concludes that optimum deposition was performed by 3 cyclic voltammograms in diazotation media.

The SAM formation on gold electrode was made in a dilute solution of 1 mmolL^{-1} 4-chlorothiophenol (4-PhSH) in ethanol for different periods of time. The CV and EIS data obtained are presented in Fig. 3.

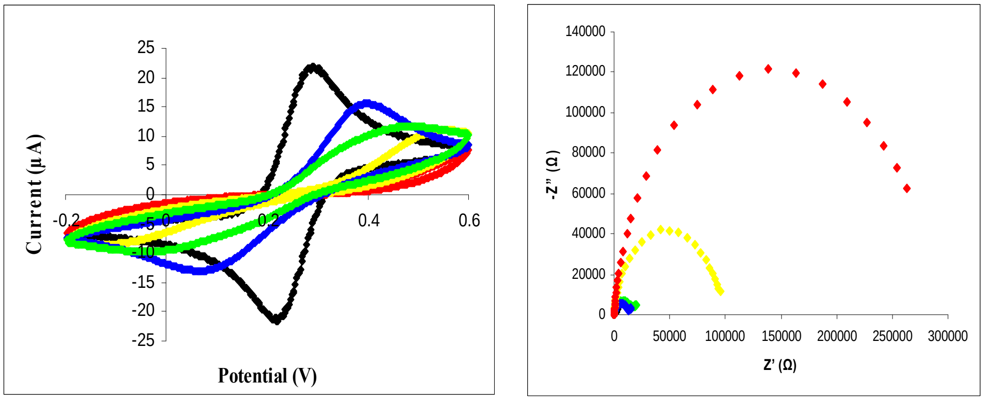

Fig. 3. The cyclic voltammograms and EIS spectra of clean gold electrode (black) and after the immersion in 1mM 4-chlorothiophenol for 1h (blue), 2h (green), 15 h (yellow) and 20 h (red)

In CV it was observed that the peaks intensity was reduced after SAM formation in comparison with clean gold electrodes. For 1h SAM formation, the SAM presence is evident while for 20h, the electrode surface has been passivated. The EIS data also present the increase of the electrode passivation in form of higher R_{ct}. It was considered that the optimum deposition time was 1h in order to have a SAM that will not completely passivate the electrode surface.

The diazonium modification method allows the deposition of benzyl chloride on the electrode surface with variable configurations ranging from submonolayer to multilayer due to the high reactivity of the radicals electrogenerated. The SAM formation is based on the affinity of the sulfur for gold and allows the deposition of 4-chlorothiophenol on the electrode surface in a submonolayer to a compact monolayer configuration.

1.6. The study of modified gold electrodes stability

The modified electrode stability was tested by performing CV at various potential values: two cycles in the ranges –0.5 V ↔ + 0.8 V and respectively –1.0 V ↔ + 1.0 V in different pH/supporting electrolytes. Two solutions were tested: acetate buffer, pH=5.5 and PBS, pH=7. In the case of the larger potential window deoxygenated buffers were used. The CV characterization of the modified electrodes before and after cycling is presented in Fig. 4.

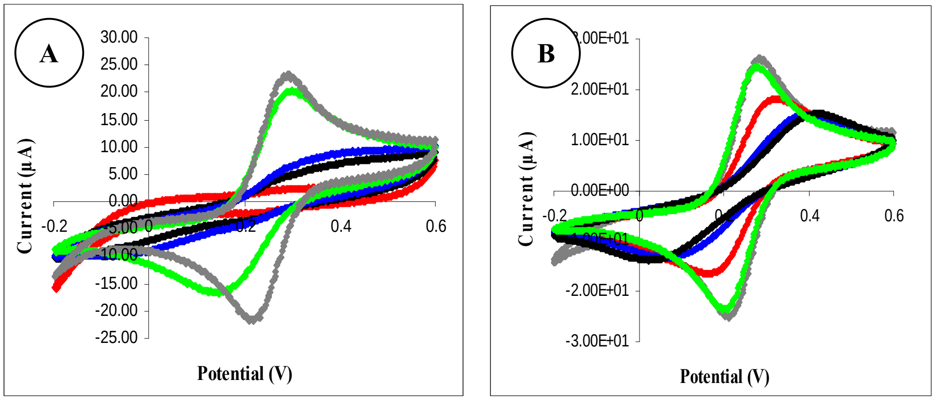

Fig. 4. The cyclic voltammograms of gold electrodes modified with 4-ABC **[A]** or 4-PhSH **[B]**: modified gold electrode (red), after 2 cycling at –0.5V ↔ + 0.8 V in PBS (blue), –0.5V ↔ + 0.8 V in acetate buffer (black), –1.0 ↔ +1.0 V in PBS (green). For comparison is presented the CV of a clean gold electrode (grey).

These results indicate that the organic layers from the modified gold electrodes with both 4-ABC and 4-PhSH were completely removed by cycling between –1.0 and +1.0 V. After cycling in the range from –0.5V to + 0.8 V a different behavior for the two modifiers was observed: the intensity of the peaks decreased in the case of PhSH (indicating layer etching) and increased for 4-ABC (indicating layer instability).

Two other functionalized alkylthiol groups: 11-mercapto-1-undecanol, HS-CH$_2$-(CH$_2$)$_9$-CH$_2$-OH (MUD) and 2-mercaptoethanol (HO-CH$_2$-CH$_2$-SH) were tested. It was observed that the stability of SAM made with 2-mercaptoethanol was significantly lower in comparison with MUD. The MUD modified electrodes are very stable for working in different electrolytes and at large potential range. The cyclic voltammograms and EIS spectra are presented in Fig. 5.

In contrast with thiols that have affinity only for gold surfaces, the diazonium bond may be formed with different supports. In order to test the influence of support on the diazonium bond strength, the 4-ABC modification was performed with 3 different electrodes: platinum, gold or glassy carbon electrodes (GCE).

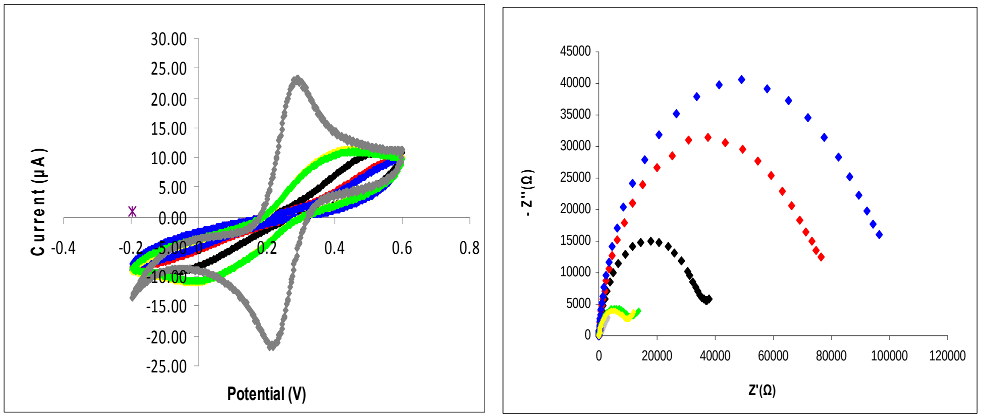

Fig. 5. The cyclic voltammograms and EIS spectra of gold electrode modified with MUD (black) and after 2 cycling –0.5V ↔ + 0.8 V in PBS (red), –0.5V ↔ + 0.8 V in acetate buffer (blue), –1.0 ↔ +1.0V in acetate buffer (yellow), –1.0 ↔ +1.0 V in PBS (green). For comparison is presented a clean electrode (grey)

The results show that the difference between modified surfaces is significant, both in stability and in deposition of interested compound. Glassy-carbon electrode is the most stable for 4-ABC modification. Thus, the modified GCE is stable after several cycles even at –1.0 ↔ +1.0 V potential ranges. In contrast, gold and platinum electrodes are resistant only at –0.5 ↔ +0. 8 V potential ranges, both in PBS (pH=7) and in acetate buffer (pH=5.5).

4. Conclusions

In this work, was presented a comparison between gold electrodes modification with aromatic compounds based on thiol and diazonium. The obtained modified gold electrode is relative stable in the –0.5 ↔ +0.8 V potential ranges. It was observed a higher stability for thiolic SAM in comparision with diazonium. The diazonium modification method allows the formation of multilayers. A comparative study showed that the long chain alkylthiol-compounds are more stable than the used arylthiolated, but they are passivating the electrode surface. The stability of diazonium compound on gold electrodes is weaker that on glassy carbon electrodes.

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