Electrodeposition of Gold Nanoparticles to Modify the Boron-doped Diamond Electrode

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Abstract

This work shows a method of modifying of boron-doped diamond electrode (BDDE) with gold nanoparticles (AuNPs) using electrodeposition. The optimization of the potential and time of electrodeposition of AuNPs was carried out. The obtained modified material of the working electrode was examined using scanning electron microscopy (SEM). The electrochemical properties were investigated using conventional inner sphere and outer sphere redox markers. An example of the use of a modified BDDE and lab-made screen-printed sensor (SPS) with modified BDD working electrode for dopamine neurotransmitter analysis is shown.

Key words: boron-doped diamond electrode, gold nanoparticles, electrodeposition, modification, application, dopamine.

Introduction

The boron-doped diamond electrode (BDDE) was introduced into electroanalytical practice almost 30 years ago and established very well due to its excellent electrochemical properties, such as wide available potential window (up to 3 V), low background currents (low current noise), good chemical resistance (corrosion resistance even at anodic polarization), the resistance to passivation, high hardness, and thermal conductivity [1–4]. BDDE was used in the analysis of various biologically active substances important for the environmental protection and human health [5–6]. In recent years, current electroanalytical chemistry has required miniaturization, acceleration of analysis, and reduction of sample volume. These criteria are met by screen-printed sensors (SPE) which enable rapid and accurate in-situ analyses and the development of portable devices for quantitation of various substances [7]. Combining the technology of printed sensors with their specific advantages and a BDDE with its unique electrochemical properties can lead to a significant improvement or expansion of the possibilities of application of electroanalytical methods in practice [8]. Moreover, the modification of the BDDE surface, e.g., with metals or metal oxides nanoparticles, organic molecules, biomolecules, and carbon materials, can lead to further improvement of SPE properties or application possibilities.

There are many biologically active substances that can be determine at the positive potential values. The modification of BDDE with gold nanoparticles (AuNPs) was chosen because gold has a much more positive oxidation potential (+1.5 V) compared to other metals and thus allows the use of a wider anodic range. It has been shown that modification of carbon-based electrodes with AuNPs leads to an increase in the selectivity of the determination of e.g. dopamine in the presence of various interfering substances [9]. In this work, the procedure of electrodeposition of gold from a solution, that is simple, much faster, and more accessible than other methods, was used to prepare modified sensors which were characterized and applied in dopamine analysis.

Experimental

Britton-Robinson buffer (BRB, pH 5.5) was prepared by mixing the acidic and alkaline components under a pH meter. The acidic component was a 0.04 M solution of H_3PO_4, H_3BO_3

and CH_3COOH (all from Ing. Petr Švec-PENTA s.r.o., Czech Republic). The alkaline component was created by 0.2 M NaOH (from Ing. Petr Švec-PENTA s.r.o., Czech Republic). 1×10^{-3} M solution of dopamine hydrochloride (Sigma-Aldrich) was prepared by dissolving the appropriate batch in water and stored in a refrigerator. The electrolyte for electrodeposition consisted of 1 mmol L^{-1} $HAuCl_4\cdot3H_2O$ (Sigma-Aldrich) in a solution of 0.1 M H_2SO_4 (from Ing. Petr Švec-PENTA s.r.o., Czech Republic).

Voltammetric measurements were performed using Autolab PGSTAT204 (Metrohm Autolab, Netherlands) equipped with software Nova 2.1. Measurements were performed in a three-electrode set up with bulk BDDE (BioLogic, active surface area of 7.07 mm^2, inner diameter of 3 mm, B/C ration during deposition 1000 ppm) as a working electrode (WE), saturated argentchloride electrode (Ag/AgCl (KCl, sat.)) as a reference (RE) and platinum wire as a counter (CE) electrode (both Monokrystaly, CZ). The lab-made (LM) SP/BDDE was the second one consisted of BDD as WE as well as CE and Ag/AgCl RE (active surface area of 7.07 mm^2, inner diameter of3 mm, B/C 312 500 ppm). In all cases, BDDEs were activated at the beginning of the working day by performing 20 cyclic voltammograms in the potential range from initial potential (E_{in}) of −1000 mV to switching potential (E_{switch}) of +2200 mV directly in the supporting electrolyte used. Activation procedure was terminated at the positive potential value, *i.e.*, at the final potential (E_{fin}) +2200 mV. It was found that there was no need to reactivate or regenerate the electrode surfaces in any way between particular measurements.

Parameters of calibration curves and confidence intervals were calculated on the level of significance 0.05. Limit of detection (*LOD*) and limit of quantification (*LOQ*) were calculated from the calibration dependences as three times standard deviation and ten times standard deviation of an intercept divided by a slope.

Results and discussion

As can be seen from Figure 1, three peaks (two reduction and one oxidation) were observed on the cyclic voltammogram measured on the BDDE in the electrolyte ($HAuCl_4\cdot3H_2O$ in H_2SO_4) for electrodeposition of AuNPs. Electrodeposition of gold runs through three stages, the first of which is the chemical conversion of the gold complex in the electrolyte, the other two steps, which belong to peaks 1 and 2, represent the electrochemical reduction of ions to metallic gold. Peak 3 corresponds to the reverse oxidation process of metallic gold [10].

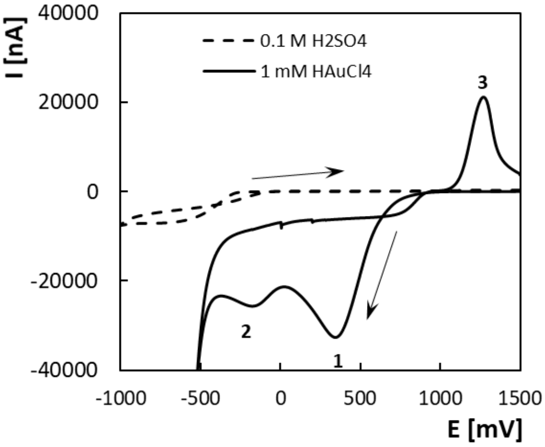

Fig. 1. Cyclic voltammograms of 1 mmol L^{-1} $HAuCl_4\cdot3H_2O$ in 0.1 M H_2SO_4 recorded on the BDDE: Method – CV, $E_{in} = E_{fin} = +1500$ mV, $E_{switch} = -1500$ mV, $\upsilon = 100$ mV s^{-1}; supporting electrolyte – 0.1 M H_2SO_4).

Dopamine was used as a biologically active substance to optimize the electrodeposition process. The first step for optimization was the deposition potential. The values of +100, 0, –100 and –200 mV were tested. For this purpose, the electrodeposition time was constant (t_{dep} = 50 s). As can be seen from the voltammograms (Fig. 2A), there was a significant shift in peak potentials to less positive values and the potential difference between the anodic and cathodic peaks was greatly reduced when using the modified BDDE. Compared with the unmodified BDDE, there is observed also a significant increase in the height of the oxidation as well as reduction peak. The voltammetric curve recorded on the gold electrode (AuE) does not provide significant peaks of dopamine (results are not shown). It can be assumed that the combination of AuNPs and BDDE has significant advantages over a bare BDDE and AuE. The highest and best repeatable signal was obtained at an electrodeposition potential of 0 mV.

The next step was to optimize the deposition time, while keeping the potential constant (E_{dep} = 0 mV). The electrodeposition time varied from 10 to 50 s and the obtained CV curves are shown in Fig. 2B. An increase in the height of the redox peaks of dopamine depending on the deposition time was observed. The deposition duration of 50 s was chosen as optimal. Further prolongation of the time was not appropriate, because the background current increased extenssively.

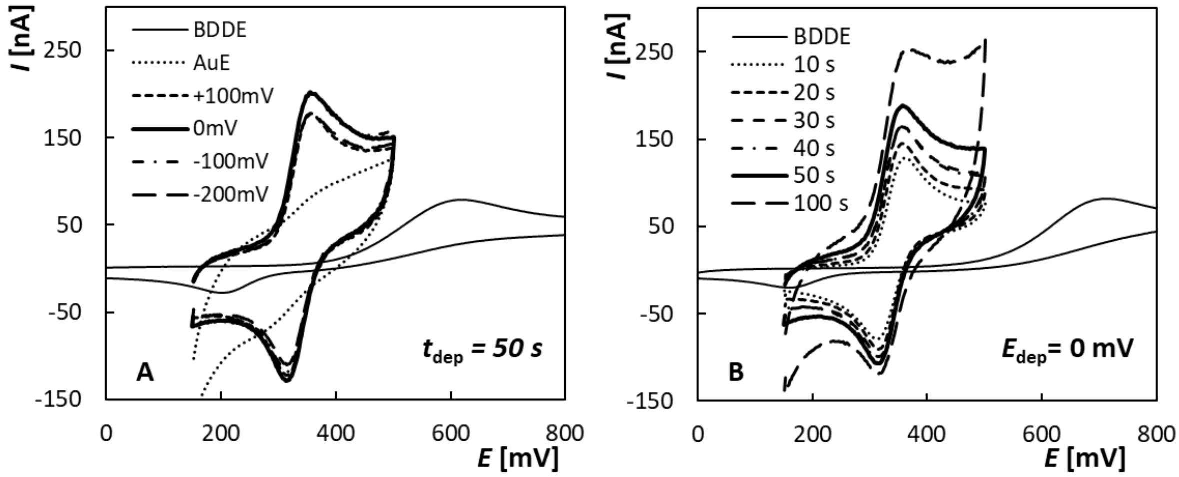

Fig. 2. Cyclic voltammograms of 1.0×10^{-5} mol L^{-1} dopamine recorded on the bulk BDDE and Au_BDDE depending on the potential (A) and time (B) of electrodeposition: Method – CV, $E_{in} = E_{fin}$ = +150 mV, E_{switch} = +500 mV, v = 10 mV s^{-1}; supporting electrolyte – BRB (pH 5.5).

Redox markers $[Fe(CN)_6]^{4-/3-}$ and $[Ru(NH_3)_6]^{2+/3+}$ were used to compare the electrochemical properties of the bare and the modified BDDE. Figure 3A shows cyclic voltammograms of $[Fe(CN)_6]^{4-/3-}$ belonging to an inner sphere redox markers, for which the electrochemical reaction is significantly affected by the electrode surface material and its quality. After modification, the decrease in the separation of the oxidation and reduction peak potentials (ΔE_p) from 339.2 mV to 132.9 mV and the significant increase of peaks height was observed. Similar experiments for the Ru complex are documented in Figure 3B. In contrast to $[Fe(CN)_6]^{4-/3-}$, in the case of $[Ru(NH_3)_6]^{2+/3+}$, ΔE_p values were found approaching the theoretical value of 59 mV which is typical for the one-electron reversible electrode reaction. The lower values of ΔE_p (71.4 mV for BDDE and 73.4 mV for Au_BDDE) for this redox probe could be explained by the nature of the electrode reaction. The outer sphere reaction pathway and the electron transfer as well is in general not influenced by the physicochemical properties of working surface of the electrode [11].

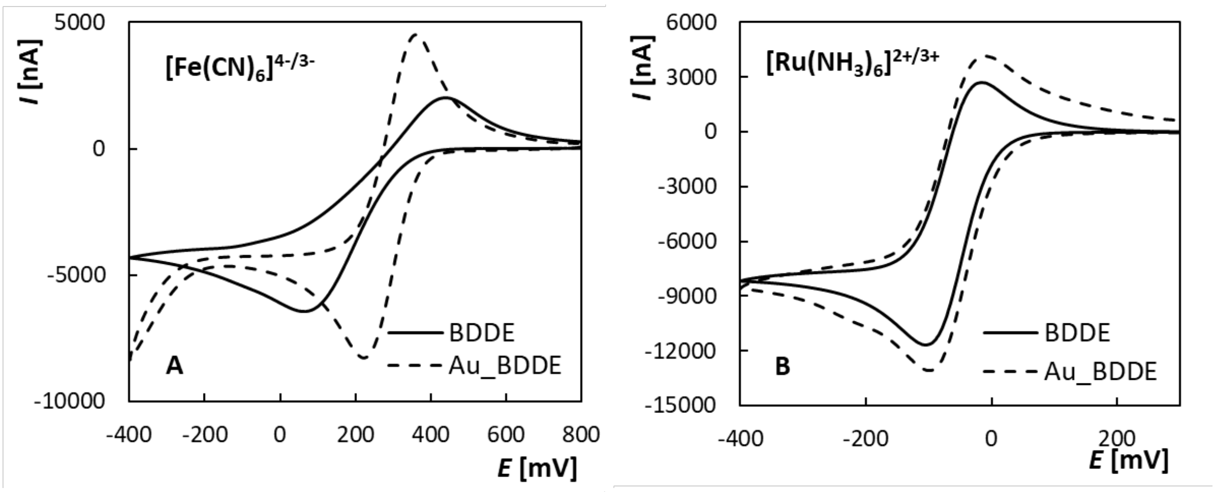

Fig. 3. Cyclic voltammograms of $[Fe(CN)_6]^{4-/3-}$ (A) and $[Ru(NH_3)_6]^{2+/3+}$ (B) recorded on the BDDE before and after modification with AuNPs (electrolyte – 0.1 mol L^{-1} KCl, v = 5 mV s^{-1}, c($[Fe(CN)_6]^{4-/3-}$) = 2.5 mmol L^{-1}, c($[Ru(NH_3)_6]^{2+/3+}$) = 2.5 mmol L^{-1}).

The applicability of the modified BDDE was verified in dopamine analysis. For this purpose, BRB (pH 5.5) was used as the supporting electrolyte and square wave voltammetry (SWV) with the following optimized parameters v = 5 mV s^{-1}, A = +80 mV, f = 10 Hz was applied. In addition to bare and modified BDDE, printed sensors with chemically deposited BDDE modified with gold nanoparticles by electrodeposition (our optimized conditions) or physical deposition (research group of Dr. Vojs, STU Bratislava) were also tested. Concentration dependence was measured in the range from 1 to 10 µM solution of dopamine using all investigated systems. The obtained statistical data of the linear concentration dependence of dopamine are summarized in table 1. The table shows that using sensors with an electrochemically modified surface, a much higher sensitivity was achieved, resulting from a 25 times higher value of the slope than for bare BDDE. The increase in the sensor with physical deposition was not so significant, the directive increased approximately 3 times.

Table 1. Statistical parameters of voltammetric determination of dopamine using SWV in connection with all tested sensors.

Electrode	Slope [nA L µmol^{-1}]	Intercept [nA]	*r*	*LOD* [µM]	*LOQ* [µM]
BDDE	(7.871±0.060)	–(4.43±0.35)	0.9998	0.13	0.44
Au_BDDE	(189.3±1.4)	(25.8±8.9)	0.9998	0.14	0.47
Au_SP/BDDE	(184.8±2.7)	(53±17)	0.9991	0.27	0.91
50nmAu_SP/BDDE	(24.38±0.18)	(0.6±1.1)	0.9998	0.14	0.47

Conclusion

In this work, the electrodeposition of gold nanoparticles was optimized to modify the BDDE. Morphological characteristics were studied applying scanning electron microscopy. The electrochemical properties of the electrode before and after modification was investigated using cyclic voltammetry. The applicability of these modified sensors for voltammetric determination of biologically active substance – dopamine was shown when the modification led to a significant improvement compared to the BDDE bar.

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