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Electrochemical fabrication of polyproline modified graphite electrode decorated with Pd–Au bimetallic nanoparticles: Application for determination of carminic acid

Emine Arslan [a,b], Semiha Çakır [a,*]

[a] Department of Chemistry, Faculty of Science, Gazi University, 06500 Teknikokullar, Ankara, Turkey
[b] Ministry of Health of Turkey, Turkey Pharmaceuticals and Medical Devices Agency, 06520 Çankaya, Ankara, Turkey

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ABSTRACT

A novel modified electrode has been developed, by electrodeposition of Pd–Au bimetallic nanoparticles (Pd–AuNps) on a polypyroline coated (Poly(Pr)) graphite electrode (GE). The structure and morphologies of Pd–AuNps/Poly(Pr)/GE were characterized by cyclic voltammetry (CV), square wave voltammetry (SWV), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray photon spectroscopy (XPS) techniques. The electrocatalytic activities and morphologies of the new electrode were compared with individual monometallic AuNps/Poly(Pr)/GE and PdNps/Poly(Pr)/GE. This new bimetallic nanoparticle modified electrode (Pd–AuNps/Poly(Pr)/GE) was evaluated for determination of carminic acid. The oxidation peak (0.750 V) of carminic acid was found to be linearly related to carminic acid concentration in the range of 1.0×10^{-8} to 1.0×10^{-6} M with a detection limit of 5.90×10^{-9} M. The proposed method was simple, less time consuming and showed a high sensitivity.

1. Introduction

The modification of electrode surfaces with metal nanoparticles provides opportunities to develop various electrochemical sensors. Especially, bimetallic nanoparticles have been an intensive research subject for the design of electrodes. Due to the interaction between two components in bimetallic nanoparticles, they generally show many favorable properties compared with corresponding monometallic counterparts, which include high catalytic activity, catalytic selectivity, and better resistance to deactivation [1–4].

The palladium–gold alloys (Pd–Au) are very attractive because of their high catalytic performance in hydrogenation reactions [5–7], degradation reactions [8–10], oxidation reactions [11–13] and hydrogenation of hydrocarbon [14]. Development of the new Pd–Au bimetallic nanoparticle modified electrodes for application in electrochemical sensors with appropriate characteristics such as high sensitivity, fast response time, wide linear range, better selectivity, and reproducibility becomes significant. There are few reports about using the Pd–Au bimetallic nanoparticle modified electrodes as an electrochemical sensor for the determination of ethanol [15], formic acid [16], and arsenic [17] or as a biosensor for glucose [18,19], DNA [20], dopamine and ascorbic acid [21].

Conducting polymers offer great advantages over electrode materials since they are permeable to electroactive species. The polymers possess high electronic conductivity and a porous structure. The porous structure of modified electrodes with conducting polymers provides opportunities for a large surface area that is necessary for efficient electrocatalysis [22]. The electrodes containing bimetallic nanoparticles and conducting polymers have attracted attention increasingly [22–24].

The biocompounds as amino acids are of interest as metal nanoparticle support for the development of new modified electrodes. Among modified electrodes, amino acid modified electrodes received considerable attention owing to the easily available materials, easiness of preparation and their good biocompatibility [25,26]. Therefore, polyproline is suitable as a nanoparticle support. To the best of our knowledge, the Pd–Au bimetallic nanoparticles dispersed on a polyproline coated graphite electrode have not been reported up to now.

Carminic acid is a hydroxyanthraquinone with a lateral chain of C-glycosyl and only one position free on the aromatic nucleus. Carminic acid is a very common pigment, widely used in foods, beverages, textiles, pharmaceuticals and cosmetic products as a red coloring agent (E120) because of its relatively high chemical and biological stability [27]. The use of colorants as food additives is absolutely controlled by laws and regulations. Their maximum permissible amounts in food are rigidly specified in order to safeguard the interests of consumers. The ingestion of carmine may cause food anaphylaxis and food allergy [28,29]. This necessitates the measurement and control of the amount of carminic acid in food. There are many studies about the quantitative analysis of carminic acid such as HPLC [30,31], capillary electrophoresis [32], and UV–vis spectroscopy [33]. A few voltammetric studies were

* Corresponding author.
E-mail address: scakir@gazi.edu.tr (S. Çakır).

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Table 1
The optimum experimental conditions used modification process.

Optimum experimental conditions for preparing of Poly(Pr)/GE	
Method	Multi cyclic voltammetry
Electrolyte	Phosphate buffer
pH	8.0
Number of cycles	10
Range of potential of cycle	−0.5 V to 1.75 V
Scan rate	100 mV/s
Concentration of proline	0.1 M
Optimum experimental conditions for preparing of Pd–AuNps/Poly(Pr)/GE	
Method	Electrodeposition
Electrolyte	Kcl
pH	3.0
Electrodeposition potential	−0.2 V
Electrodeposition time	200 s
Concentration of $PdCl_2$ and $HAuCl_4$	1.5×10^{-4} M $PdCl_2$; 0.5×10^{-4} M $HAuCl_4$ (3:1)

found in literature about the determination and voltammetric behavior of carminic acid at GCE [34], paraffin-impregnated graphite electrode [35], and mercury drop electrode [36,37]. There is also no study about the determination of carminic acid at a modified electrode.

In this study, a graphite electrode (GE) was modified by electropolymerization of L-proline (Poly(Pr)/GE). Pd–Au bimetallic nanoparticles in various proportions (Pd:Au 1:1, 1:3 and 3:1) loaded on Poly(Pr)/GE were prepared by co-reduction of mixed salts with electrodeposition (Pd–AuNps/Poly(Pr)/GE). The modified electrode Pd–AuNps/Poly(Pr)/GE was successfully applied for the electrochemical determination of carminic acid by square wave voltammetry (SWV) technique in pure form and in popping candy. The developed electrode Pd–AuNps/Poly(Pr)/GE will be particularly useful for electrochemical biosensor studies.

2. Experimental

2.1. Chemicals

All compounds were of analytical-reagent grade. $PdCl_2$, $HAuCl_4$, L-proline and carminic acid were obtained from Sigma-Aldrich. 0.1 M phosphate buffer solution and 0.1 M KCl solution were used as the supporting electrolyte for voltammetric characterization studies, and 0.1 M $HClO_4$ solution was used as the supporting electrolyte for determination of carminic acid. Triple distilled water was used to prepare solutions.

2.2. Instrumentation

A PAR 507 model micro cell containing a three-electrode system (pencil graphite working electrode, platinum counter electrode and Ag/AgCl (saturated KCl, reference electrode)) along with a PAR VersaSTAT 3 potentiostat was used for voltammetric and impedimetric measurements. Pencil graphite electrodes were Tombo leads with a diameter of 0.5 mm and they were attached to a holder. Electrical contact with the pencil graphite electrode was obtained by soldering a copper wire to the metallic part of the holder. Characterization of the electrode surface was performed using SPECS EA 300 XPS, Quanta 400F FE-SEM and JXA-8230 Electron Probe Microanalysis device for EDX analysis.

Electronic spectra were recorded on P general T80 Double beam UV–vis spectrophotometer in the 800–200 nm range at 1 cm cell length.

2.3. Preparation of Pd–AuNps/Poly(Pr)/GE

The L-proline is polymerized on the activated graphite electrode surface by multicyclic voltammetry from −0.5 V to 1.75 V for 10 cycles at a scan rate of 100 mV/s in PBS (pH 8.0) containing 0.1 M L-proline. This

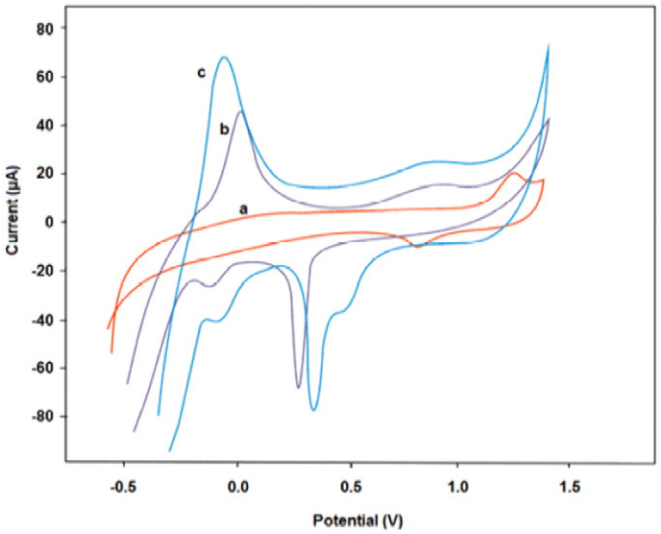

Fig. 1. Cyclic voltammograms of pH 7 PBS at a scan rate of 100 mV/s from −0.5 V to 1.2 V recorded at AuNps/Poly(Pr)/GE (a), PdNps/Poly(Pr)/GE (b), and Pd–AuNps/Poly(Pr)/GE (c).

electrode was modified with Pd–Au bimetallic nanoparticles by electrodeposition of 1.5×10^{-4} M $PdCl_2$ and 0.5×10^{-4} M $HAuCl_4$ (ratio of Pd:Au 3:1) during 200 s at −0.2 V in 0.1 M KCl at pH 3. For comparison, PdNps/Poly(Pr)/GE and AuNps/Poly(Pr)/GE were prepared by electrodeposition of 2×10^{-4} M $PdCl_2$ and 2×10^{-4} M $HAuCl_4$ during 200 s at −0.2 V in 0.1 M KCl at pH 3 on polypyroline coated (Poly(Pr)) graphite electrode. Finally, the resulting electrodes, PdNps/Poly(Pr)/GE, AuNps/Poly(Pr)/GE and Pd–AuNps/Poly(Pr)/GE, were cleaned by several rinses with triple distilled water.

3. Results and discussion

In our previous work, a monometallic nanoparticle modified electrode was developed by electrodeposition of palladium nanoparticles on a polyproline coated graphite electrode (PdNps/Poly(Pr)/GE) [38]. In the present work, a new bimetallic nanoparticle modified electrode was developed by electrodeposition of palladium–gold bimetallic nanoparticles on polyproline coated graphite electrode (Pd–AuNps/Poly(Pr)/GE).

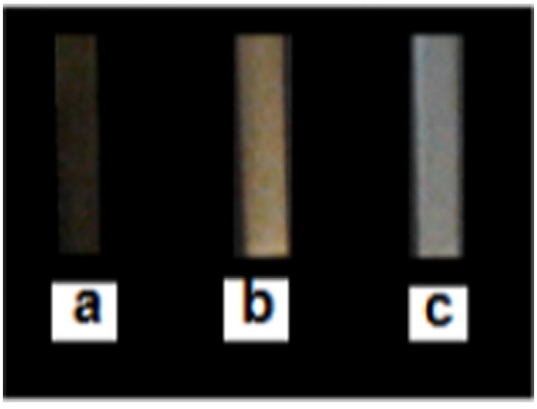

Fig. 2. The colors of PdNps/Poly(Pr)/GE (a), AuNps/Poly(Pr)/GE (b) and Pd–AuNps/Poly(Pr)/GE (c).