Int. J. Electrochem. Sci., 7 **(2012)** 11550 - 11557

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Voltammetric Determination of UricAcid on Poly(*p*-Aminobenzene Sulfonic Acid)-Modified Glassy Carbon Electrode

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Received: 20 September 2012 / *Accepted:* 18 October 2012 / *Published:* 1 November 2012

A stable modified glassy carbon electrode based on poly (*p*-aminobenzene sulfonic acid) (*p*-ABSA) film was prepared by electrochemical polymerization technique in phosphate buffer solution (PBS) (pH 7.0) and its electrochemical behavior were studied by cyclic voltammetry (CV). The polymer film-modified electrode has been used for investigation of the dermination of uric acid (UA). The peak potential values for the oxidation processes of $5x10^{-5}$ M UA on a bare glassy carbon electrode and the *p*-ABSA modified glassy carbon electrode surfaces has been obtained at about 509 mV and 309 mV by differential pulse voltammetry (DPV) technique, respectively. The modified glassy carbon electrode had an excellent response and specificity for the electrocatalytic oxidation of UA in PBS (pH 7.0). A linear calibration curve for DPV analysis was constructed in the uric acid concentration range $1x10^{-5}$-$1x10^{-4}$ M. Limit of detection (LOD) and limit of quantification (LOQ) at *p*-ABSA modified electrode were obtained as $1.125x10^{-6}$ M and $3.750x10^{-6}$ M, respectively. This electrode was used for UA determinations in human urine samples satisfactorily.

Keywords: electrocatalytic oxidation; modified glassy carbon; poly(4-aminobenzene sulfonic acid); uric acid; differential pulse voltammetry

1. INTRODUCTION

Uric acid is a metabolism product of purine in human body [1]. The uric acid concentrations in urine and serum are in certain ranges for healthy persons. Therefore, the determination of UA concentration is helpful for the diagnosis of the some diseases such as gout, hyperuricaemia and

Lesch-Nyhan syndrome. Consequently, the methods like chromatography [2], spectrophotometric [3] and electroanalytical [4] development for the detection of UA are usually employed. Electroanalytical methods, which are simple, sensitive, reliable, repeatability and low costs, are more convenient. Chemically modified electrodes have been used to determine the concentration of UA [5, 11]. These electrodes were used to be developed sensitive and selective methods for the detection. Polyaniline nano-networks on *p*-aminobenzene sulfonic acid functionalized glassy carbon electrode were used for the simultaneous determination of ascorbic acid and uric acid [12]. Poly(4-aminobenzene sulfonic acid) modified glassy carbon electrode was used determination of phenylephrine and chlorprothixene. In addition, this electrode was used also for selective determination of hydroquinone in the presence of catechol and resorcinol [13]. However, the determination of UA at the *p*-ABSA modified glassy carbon electrode has not yet been reported up to date.

In this work, we have reported the use of glassy carbon electrodes modified with *p*-ABSA for UA detection.

2. EXPERIMENTAL

2.1. Apparatus

A potentiostat meter (VersaSTAT^3, Princeton Applied Research, USA) was used for the voltammetric measurements. All experiments were carried out in a three electrode system. Glassy carbon (GC) electrodes (3.0 mm diameter) were purchased from BAS and used as a working electrode. A platinum wire auxiliary electrode and a Ag/AgCl (NaCl 3 mol L^{-1}, BAS) reference electrode were used.

The firstly, the deoxygenation process of the supporting electrolyte solutions were carried out with argon gas for 5 min before all experiments. Then, the argon gas was also passed from the solutions for 60 s after the addition of each sample solution in the experiments. In each new experiment, a new bare GC electrode surface was used. A Molspin Titration System was used to pH measurements. All experiments were carried out at ambient temperature of the laboratory (15-20 °C). The parameters for differential pulse voltammetric experiments were employed as pulse height 50 mV, pulse width 0.08 s, step height 10 mV, step width 0.1 s.

2.2. Polishing and Cleaning of GC Electrodes

GC electrodes were polished successively in 1 μm, 0.3 μm, 0.05 μm alumina slurries made from dry Buehler alumina and ultra pure deionize water on Buehler polishing microcloth. Polished GC electrodes were sonicated in Nanopure water, in a mixture of 1:1 (v/v) nitric acid / water (HNO_3+H_2O) (Fluka) and then, in acetonitrile (aldrich) for 10 min each. Before the derivatization, the cleaned electrodes were rinsed with water and dried under a stream of argon.

2.3. Preparation of modified electrode

A bare GC electrode was immersed in 0.10 mol L^{-1} PBS (pH 7.0) containing 2.0×10^{-3} mol L^{-1} *p*-ABSA solution and conditioned by cyclic sweeping between -1.5 to +2.5 V at 100 mV s^{-1} for 5 scans. Finally, the modified electrode was activated by cyclic voltammetry from -1.0 to +1.0 V in 0.10 mol L^{-1} PBS (pH 7.0). Consequently, a bare GC electrode and modified GC electrode was used as a working electrode.

3. RESULTS AND DISCUSSION

3.1. Electropolymarization of p-ABSA at the GCE Surface

Figure 1 shows the voltammograms of *p*-ABSA on the GCE in 0.10 mol L^{-1} PBS (pH 7.0) containing $2.0x10^{-3}$ mol L^{-1} of *p*-ABSA. In the first scan, a weak anodic and cathodic peak were observed with peak potential value at E_{pa} = 0.99 V and E_{pc} = -0.70 V, respectively. From the second cycle on two anodic peaks appeared on voltammograms with potential at +0.13 V and +1.45 V, respectively. The peaks current increased upon continuous scanning, reflecting the continuous growth of the polymerization film, and a blue polymer film was formed on the GCE surface. These results indicated that *p*-ABSA was deposited on the surface of GCE by electropolymerization [14,15]. The poly(p-ABSA) modified electrode was thoroughly washed with double-distilled water and stored in 0.1 mol L^{-1} PBS (pH 7.0) before use.

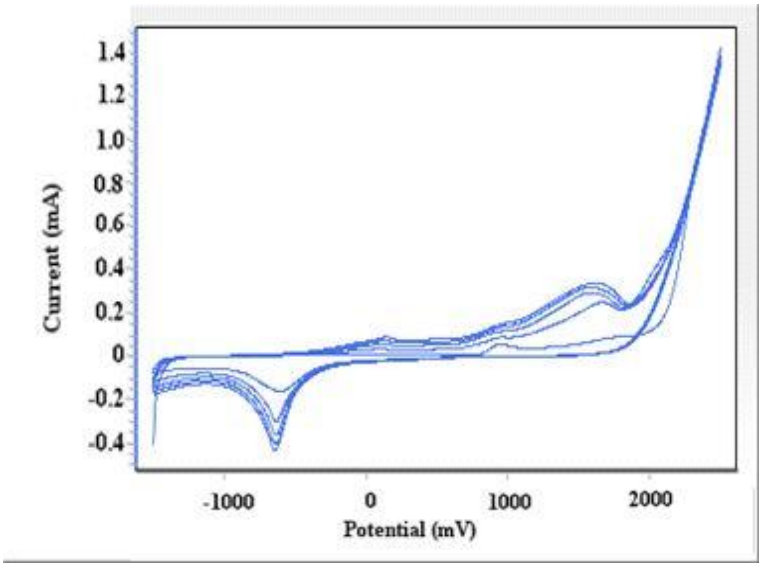

Figure 1. Repetitive cyclic voltammograms of p-ABSA in 0.10 mol L^{-1} PBS (pH 7.0) containing $2.0x10^{-3}$ mol L^{-1} initial potential -1.5 V; terminal potential +2.4 V; scan rate 100 mV s^{-1}.

3.2. Electrochemical oxidation of UA on p-ABSA Modified Glassy Carbon Electrode

The electrochemical responses of UA on the bare GC and *p*-ABSA Modified GC have been studied by using cyclic voltammetry. Fig. 2, which are the cyclic voltammograms of 0.2 M PB solution (pH= 7.0) in the absence of UA, shows only baseline.

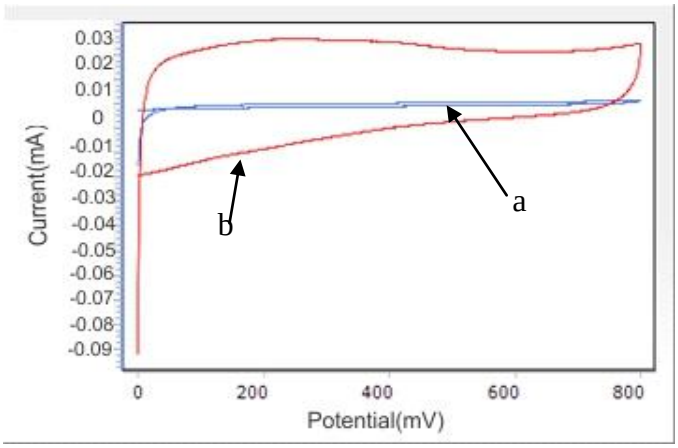

Figure 2. The cyclic voltammograms of 0.2 M PB solution (pH= 7.0) on (a) bare GC and (b) modified GC electrode surface.

Fig. 3 demonstrates an irreversible redox process of UA on the bare GC and *p*-ABSA modified GC electrode surface. The anodic peak potential values of UA at the bare GC and modified GC electrode are at about 580 mV and 350 mV, respectively. Chemically modified electrodes used to determine the concentration of UA have also observed to show the similar behaviours [6-8].

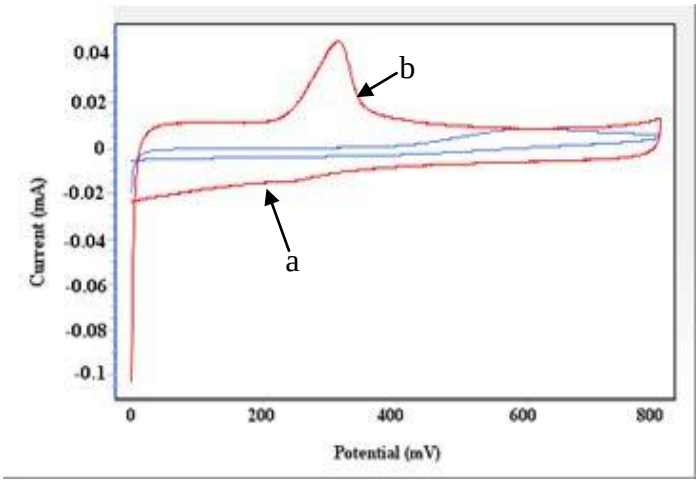

Figure 3. The cyclic voltammograms of $5x10^{-4}$ M UA in 0.2 M PB solution (pH:7.0) (a) on the bare GC and (b) *p*-ABSA modified GC electrodes scan rate 100 mVs^{-1}

The anodic peak current obtained from the electrooxidation of UA at modified electrode increased by more than two-fold than the unmodified electrode. Thus, the modified electrode has improved the electron transfer kinetic. The anodic peak potential is shifted to the negative direction by 220 mV. Therefore, *p*-ABSA modified GC electrode could be beneficial to the determination of UA.

3.3. Effect of scan rate

Fig. 4 reveals the cyclic voltammogram of UA at *p*-ABSA modified GC electrode for scan rates 10 to 100 mV s^{-1}. The effect of scan rate on the anodic peak current (I_{pa}) of UA was studied by cyclic voltammetry with scan rate increasing the anodic peak current increased. As the scan rate is increased, the anodic peak potential, E_{pa}, shifts to more positive values. Also, there is corresponding current response on the reverse scan as being scan rate. This current increased by increasing of scan rate. Consequently, the reversibility, which is reflected by the I_{pc}/I_{pa} ratio, increased as being the scan rate. Therefore, this indicated that the oxidation process of UA at *p*-ABSA modified GC electrode has a reversible nature.

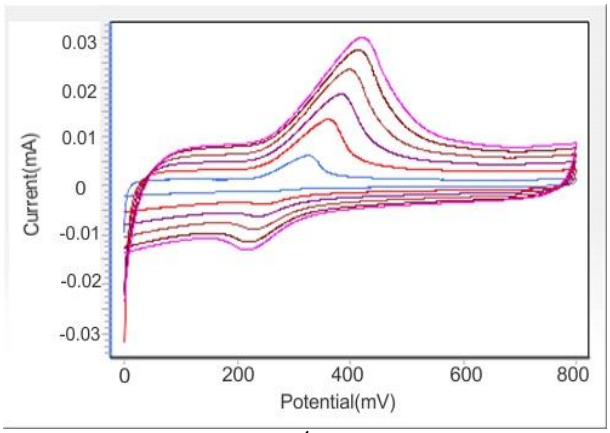

Figure 4. The cyclic voltammograms of 1×10^{-4} M UA in 0.2 M phosphate buffer (pH= 7.0) at *p*-ABSA modified GCE. Scan rates: 100, 300, 500, 700, 900 and1000 mVs^{-1}.

3.4. Effect of concentration of UA

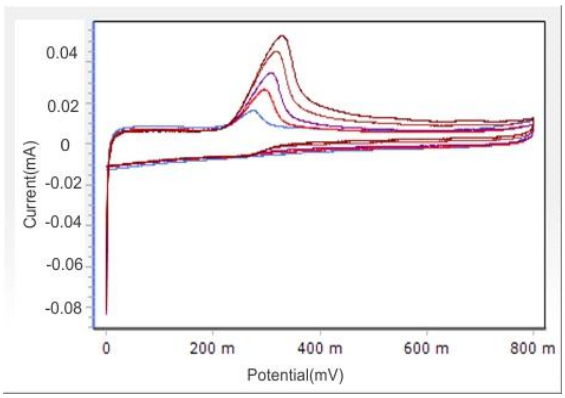

Figure 5. The cyclic voltammograms of $1x10^{-5}$ M, $5x10^{-5}$ M, $9x10^{-5}$ M, $3x10^{-4}$ M and $7x10^{-4}$ M UA in 0.2 M phosphate buffer (pH:7.0) at *p*-ABSA modified GCE. Scan rate: 50 mVs^{-1}.

The electrocatalytic oxidation of UA was carried out by varying its concentration at *p*-ABSA modified GCE. Fig. 5 shows that the concentration of UA increase the electrochemical anodic peak currents by increasing from $3x10^{-5}$ to $9x10^{-4}$ M and shift the more positive values of E_{pa}. Also, the shape of the oxidation peak remains.

3.5. Calibration curve of UA

As differential pulse voltammetry has relatively better current sensitivity and resolution than the cyclic voltammetry it is, then, utilized for preparation of calibration curve in the analysis of UA. Fig. 6A depicts the differential pulse voltammogram (DPV) obtained at different concentrations of UA at *p*-ABSA GCE.

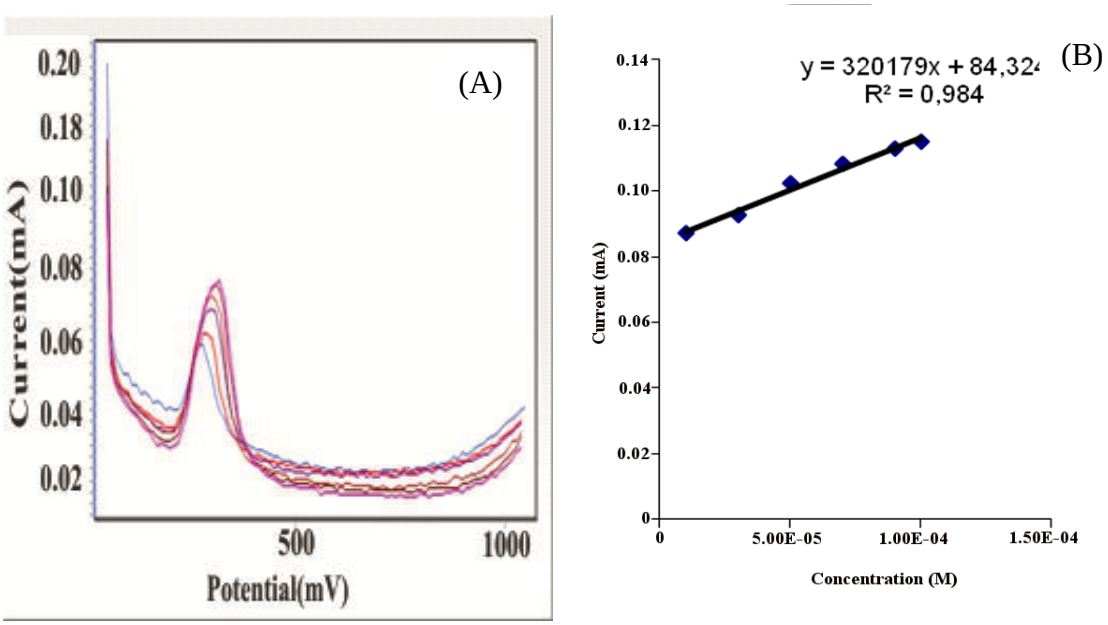

Figure 6 (A). The differential pulse voltammograms of the concentration range of $1x10^{-5}$ M, $3x10^{-5}$ M, $5x10^{-5}$ M, $7x10^{-5}$ M, $9x10^{-4}$ M, $1x10^{-4}$ M in 0.2 M PB solution (pH 7.0) of the UA (B) The corresponding calibration plot.

The oxidation peak current increases proportionally with UA in the concentration range $1x10^{-5}$ to $1x10^{-4}$ M. The dependence of the I_{pa} on the concentration of UA is shown in Fig. 6B. The linear calliration plot was obtained in the concentration range of UA from $1x10^{-5}$ to $1x10^{-4}$ M. For the analytical application, the following parameters for DPV were employed: pulse height 50 mV; pulse width 0.08 s, step height 10 mV, step width 0.1 s.

LOD and LOQ were calculated on the electro-oxidation peak current using the following equations: LOD = 3 s/m, LOQ = 10s/m (s is the standard deviation of the peak currents (ten runs), m is the slope of the calibration curve) [16-26].

$$LOD = 3s/m = 3x\ 0.12/3.20x10^{4} = 1.125x10^{-6}\ M$$

LOQ = 10s/m = 10x0.12/3.20x10^{4} =3.750x10^{-6} M

3.6. Working Voltammetric Procedure of Spiked Human Urine

Urine obtained daily from a volunteer was diluted 1:9 with ultrapure-deionized water. Firstly, 8 mL 0.1 M phosphate buffer (pH= 7.0) put into voltammetric cell and take its voltammogram (blank). Then, 2 mL of the diluted urine solution was added to this solution and its voltammogram (urine blank) was also taken. Fig. 7 shows the cyclic voltammograms of 0.2 M PB solution (pH= 7.0) in the absence of UA and the urine sample. Differential puls voltammogram of the UA in the spiked human urine depicts in Fig 8. The UA was determined of the calibration curve plotted by using obtained results. The amount of UA in the spiked urine sample found as 9.32x10^{-4} M. The result shows the modified electrode is suitable for the determination of UA in biological samples.

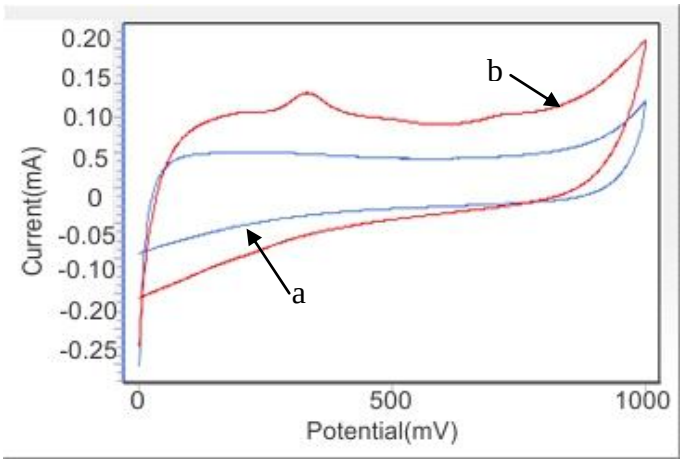

Figure 7. The cyclic voltammograms of (a) 0.2 M PB solution (pH= 7.0) in the absence of UA and (b) the urine sample.

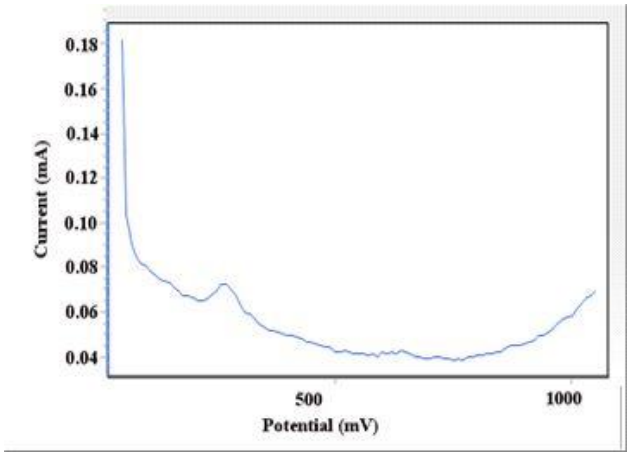

Figure 8. Differential puls voltammogram of the UA in the spiked human urine.

4. CONCLUSIONS

The study demonstrates that the *p*- ABSA modified glassy carbon electrode can be used as a specific electrode. The modified electrode has good sensitivity (LOD) and linear range of UA. A significant negative shift at modified GC electrode is obtained as compared to bare GC on the electrocatalytic oxidation of UA. The electrode is stable for a long time. The modified electrode can be used in phosphate buffer (pH 7.0) at *p*-ABSA modified glassy carbon electrode to determine of UA. Furthermore, the practical analytical utility is illustrated by selective measurements of uric acid in human urine without any preliminary treatment.

ACKNOWLEDGEMENTS
This work was supported by Gaziosmanpasa University Scientific Research Fund with a Grant number 2009/33.

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