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A New Negative Charged Self-Assembled Monolayer for Selective Electroanalytical Determination of Dopamine in the Presence of Ascorbic Acid

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Voltammetric behavior of dopamine and ascorbic acid on a gold electrode modified with the self-assembled monolayer of 2-mercaptoethanesulfunate has been investigated. This negatively charged layer could act as a discriminating layer against ascorbic acid and dopamine based on the electrostatic interactions. Thus modified electrode enabled selective determination of dopamine in an excess of ascorbic acid. The oxidation peak current increases linearly with the concentration of dopamine in the range of 1.0×10^{-5} to 3.5×10^{-4} M. The detection limit is 1.1×10^{-6} M. This method will be applicable to the determination of dopamine in injection of dopamine hydrochloride, and the good recovery of dopamine is obtained.

Keywords: Self assembled monolayers, ascorbic acid, dopamine, 2-mercaptoethanesulfunate

1. INTRODUCTION

Dopamine (DA) plays an important physiological role as an extracellular chemical messenger (neurotransmitter). Because the loss of neurotransmitter may result in some serious diseases, e.g., Parkinson's disease and schizophrenia, the determination of such a component in real biological samples is an obvious target in neurochemical studies [1]. Apart from the need to reach low detection limits, determination of DA is complicated by the coexistence of many interfering compounds. Among them, ascorbic acid (AA) is of particular importance [2]. Both dopamine and ascorbic acid are

electrochemically active compounds and therefore, can be determined by electroanalytical methods. However, it is usually difficult to separate the response of ascorbic acid and dopamine at bare electrodes [3]. In order to solve this problem, some modified electrodes such as various self-assembled monolayers (SAMs) [1-13], Nafion films [14], multi-walled carbon nanotube [15], nanoprous gold [16], p-nitrobenzo resorcinol polymer film [17], poly(Eriochrom black-T) modified carbon paste [18], electropolymerized Ni(II) complex [19], over-oxidized poly(N-acetylaniline) film [20], poly(neutral red) film [21], Poly(N,N-dimethylaniline) film [22], poly(phenosafranine) film [23] and etc were applied to determine DA in the presence of AA. Peak separation of DA from AA was based on difference in electrocatalytic or electrostatic effects of modified electrode surface to the DA and AA.

SAM modified electrodes have received much interest due to their simple preparation method and nicer stability [1-13]. By far there is no report about the electroanalytical application of electrode modified with 2-mercaptoethanesulfunate (MES). In this work, a SAM of MES has been used for modification of gold electrode surface to the electroanalysis of DA in the presence of AA.

2. EXPERIMENTAL

2.1. Apparatus

Electrochemical measurements were carried out on a Metrohm electroanalyzer (Model 757 VA computrace). A three-electrode system is used in the measurements, with a bare gold electrode (d =2 mm) or MES/SAM-Au electrode as the working electrode, a Ag/AgCl/3M KCl electrode as the reference electrode and Pt wire as the counter electrode. All potentials given are referred to the reference electrode. The pH values were measured with a Metrohm 710 pH meter.

2.2. Reagents

AA and DA were purchased from Sigma Chemical Co. (USA). MES also was prepared from Merck (Germany). Other reagents were of analytical grade. All solutions were prepared with twice-distilled water. The experimental results are obtained at room temperature.

2.3. Preparation of MES/SAM-Au electrode

The bare gold electrode was polished to a mirror-like surface with 0.5μm, 0.05μm Al_2O_3, and then rinsed ultrasonically with water and absolute ethanol and sonicated in twice-distilled water. This electrode was voltammetrically cycled and characterized in 1.0 M H_2SO_4 until a stable cyclic voltammogram was obtained. The cleaned gold electrode was immersed in 10 mM MES methanol solution for 4 h at room temperature, and then washed thoroughly with methanol to remove the physically adsorbed MES, and then a MES/SAM-Au electrode was obtained.

3. RESULTS AND DISCUSSION

3.1. Electrochemical characterization of monolayer with electroactive probe

The redox behavior of a reversible couple can be used to probe the packing structure of the monolayer [24]. The characterization of the MES-SAM modified gold electrode was conducted using the hydrophilic redox probe $[Fe(CN)_6]^{3-/4-}$. Figure 1 shows the cyclic voltammograms of the bare Au electrode (Fig. 1a) and the MES/SAM-Au electrode (Fig. 1b) in 1 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl. For a bare gold electrode, a couple of well-defined waves of $[Fe(CN)_6]^{3-/4-}$ should appear with a peak-to-peak separation (ΔE_p) should be 70 mV. However, it can be seen that the peak current decreased and ΔE_p increased for the MES/SAM-Au electrode (216 mV). These results indicate the modifications induced by SAM deposition on the gold surface.

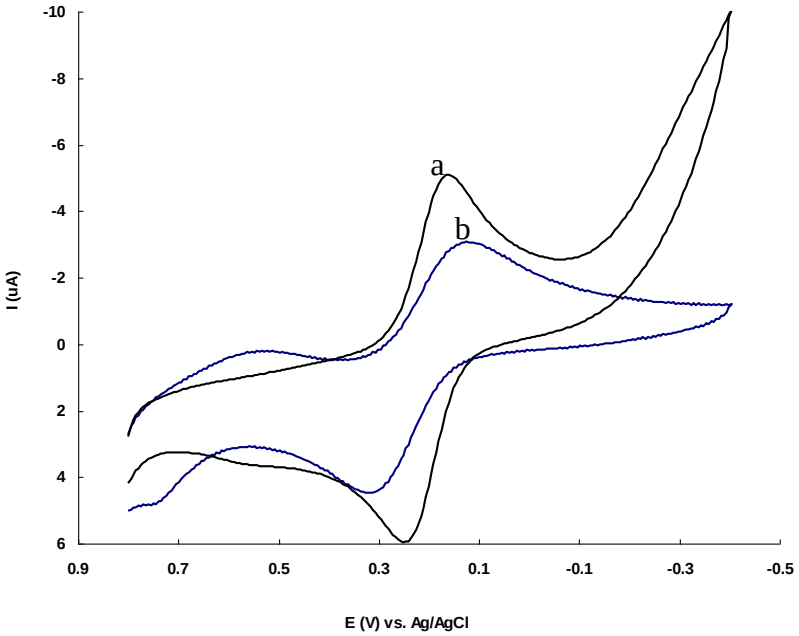


Figure 1. CVs (100 mV s^{-1}) of 1.0 mM $Fe(CN)_6^{3-/4-}$ in 0.1 M KCl at a bare Au (a) and at a MES/SAM-Au (b) electrode.

3.2. Voltammetric response of DA and AA

The cyclic voltammograms of 0.6 mM DA in 0.1 M PBS (pH 5.0) on bare and MES/SAM modified gold electrode were shown in Fig. 2. There is a pair of weak redox peaks observed on the bare gold electrode (see Fig. 2a). The difference between the anodic peak (E_{pa}) and the cathodic peak potential (E_{pc}) is 160 mV. However, a well-defined redox wave of DA was obtained on the MES/SAM-Au electrode at E_{pa}=410 mV and E_{pc}=315 mV (as Fig. 2b), respectively. The E_{pa} shifts 110 mV negatively and also the E_{pc} shifts 45 mV negatively. The difference (ΔE_p) between E_{pa} and E_{pc} is 95 mV. The anodic peak current is higher than to the bare electrode. The above results suggest that there is an electrocatalytic response to dopamine on the MES/SAM-Au electrode.

The AA oxidation at a bare Au and a MES/SAM-Au electrode was examined (Fig. 3). AA is irreversibly oxidized at a bare Au with E_{pa} at ca. 370 mV (curve a). However, no redox peaks are observed at a MES/SAM-Au (curve b). This is because AA has pKa ~ 4 and is in anionic form (ascorbate) in applied pH (5.0). Thus it is effectively repulsed by the similarly charged MES film of electrode surface. Scheme 1 shows electrostatic effects of negatively charged MES/SAM layer on DA and AA in their cathionic and anionic forms, respectively.

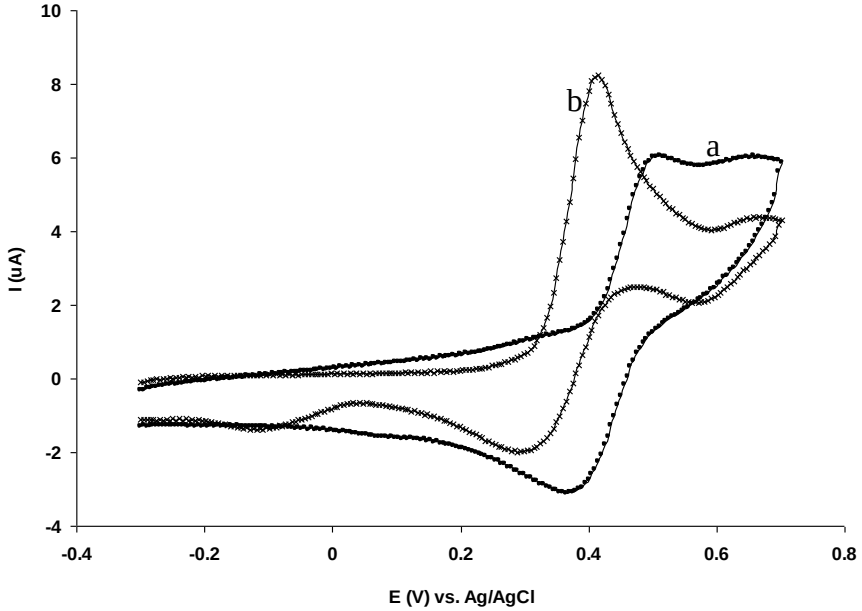


Figure 2. CVs (100 mV s^{-1}) of 0.6 mM DA at a bare Au (a) and at a MES/SAM-Au electrode (b) in pH 5.0 PBS.

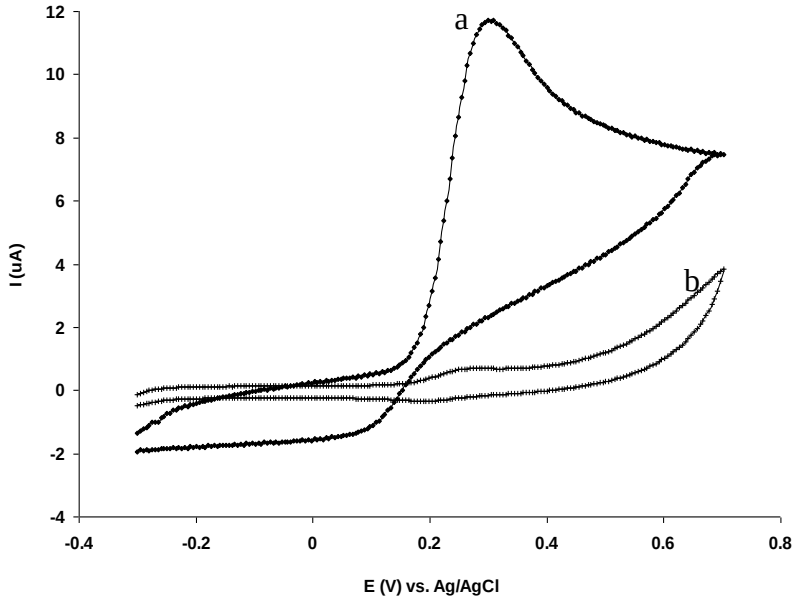
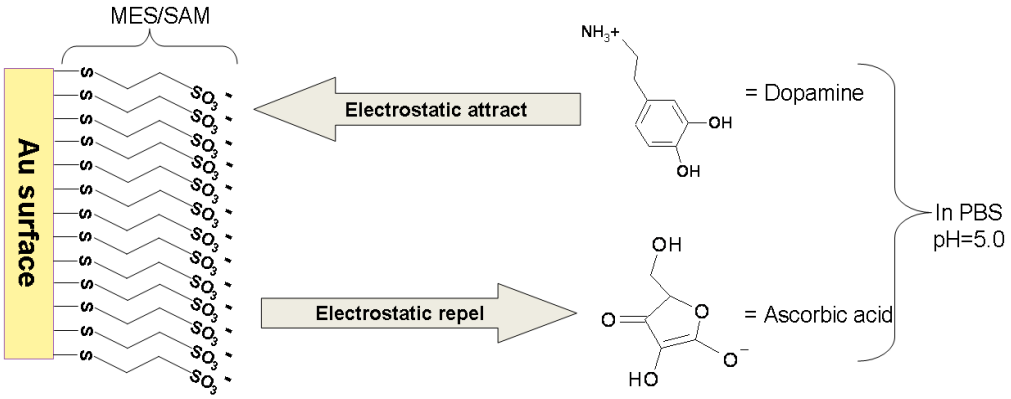


Figure 3. CVs (100 mV s^{-1}) of 1.0 mM AA at a bare Au (a) and at a MES/SAM-Au (b) electrode in pH 5.0 PBS.



Scheme 1. Electrostatic effect of MES/SAM formed on gold surface on the DA and AA in solution.

Fig. 4 shows the scan rate dependence of the oxidation current of 0.6mM DA on the scan rate in the presence of 1.0 mM AA. Observed redox peaks are due only to DA when compared to Figs. 2 and 3. AA does not affect DA measurement although it is present at higher amount. DA oxidation current is linearly proportional to the square root of scan rate, indicating that DA oxidation process is diffusion controlled (Inset). The diffusion coefficient of DA was calculated using the equation,

$$I_p = 2.95\times10^5 A D_o^{\frac{1}{2}} n^{\frac{3}{2}} \upsilon^{\frac{1}{2}} C_o \qquad (1)$$

where n, A_r (cm^2), D_o ($cm^2\ s^{-1}$), C_o (mol cm^{-3}), and v (V s^{-1}) have their usual meanings. I_p (A) is the peak current. By calculating the slope and putting the necessary values to the equation, we obtained D_o value of 7.5×10^{-6} $cm^2\ s^{-1}$. This value agrees well with the reported ones [19, 24].

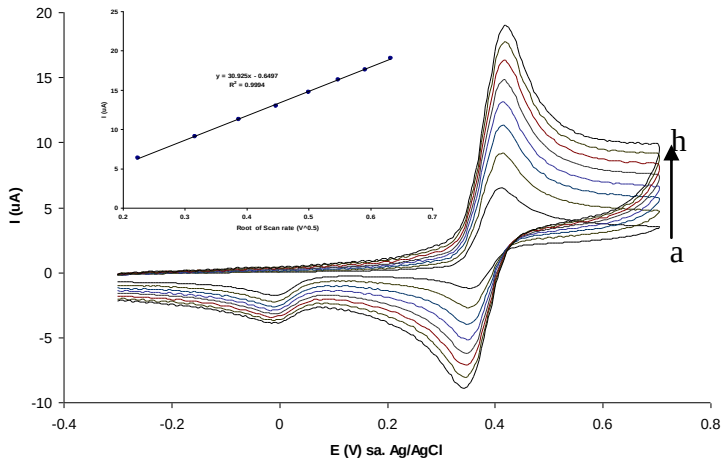


Figure 4. CVs of DA (0.6 mM) in the presence of AA (1.0 mM) at the MES/SAM-Au electrode in pH 5.0 PBS with scan rates of 50 (a), 100 (b), 150 (c), 200 (d), 250 (e), 300 (f), 350 (g) and 400 (h). Inset: plot of scan rate dependency of peak currents.

The peak currents of DA solution on the MES/Sam-Au electrode remained to be unchanged by continuous cyclic scanning. After the MES/Sam-Au being immersed into the solution of 0.6 mM DA for 10 min and then rinsed with distilled water, no response of DA was observed on this modified electrode. Both of the results proved that DA was not adsorbed onto surface of the modified electrode.

3.4. The effect of pH

The effect of solution pH on the response of DA and AA was also examined in the range 2.0–7.0 (shown in Fig. 5). The sulfonate group of MES molecule on electrode surface is in negative (unprotonated) form in applied pH range. More positive DA molecules were attracted to the electrode surface in lower pHs. Thus, the anodic peak current and voltammogram shape of DA oxidation trended to change slowly in the pH range from 2.0 to 5.0 (see Fig. 5A). When solution pH is higher than 5.0, the protonation degree of DA decreased and the statin attraction interaction between DA and MES/SAM monolayer decreased. Therefore, the anodic peak current of DA decreased with the increase of pH in the range 5.0 – 7.0. In addition, we explored the relationship between DA peak potential, E_{pa}, and pH (E_{pa} = -0.052 pH + 0.673). It can be found that peak potential shifted negatively with the increase in solution pH, indicating that protons take part in the redox reaction process of DA on the MES/SAM-Au electrode.

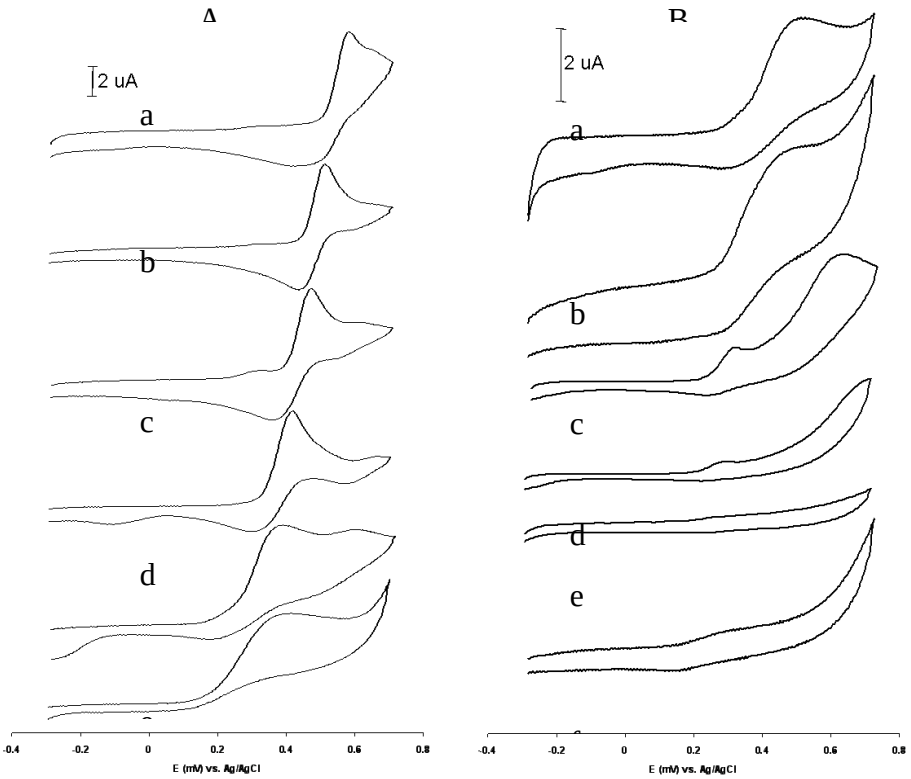


Figure 5. CVs of 0.6 mM DA (A) and 1.0 mM AA (B) at the MES/SAM-Au electrode in 0.1 M PBS with pHs of 2.0 (a), 3.0 (b), 3.0 (c), 4.0 (d), 5.0 (e) and 6.0 (f).

Also, Fig. 5B shows CVs of AA oxidation at the MES/SAM-Au electrodes in different pHs. As shown in this figure, the I_{pa} of AA decreased with increment of pH. In higher pHs AA carrying negative change increased more and repulsion interaction between AA and MES/SAM surface increased. Therefore, the I_{pa} of AA decreased with the increase of pH in the range 3.0 to 7.0.

3.5. Analytical applications

In 0.1 M pH 5.0 PBS, the CVs are measured in different concentrations of DA in the presence of AA (Fig. 6A). In the range of 1.0×10^{-5} to 3.5×10^{-4} M, the dependence of peak currents on the concentration of DA was a linear relationship (Fig. 6B). The detection limit was 1.1×10^{-6} M. For analytical aims, the sample of an injection of DA was determined after suitable dilution. Table 1 shows the results of the sample determination by applying a calibration plot. Recovery was studied for varying amounts of added DA. The acceptable recovery was obtained as shown in Table 1.

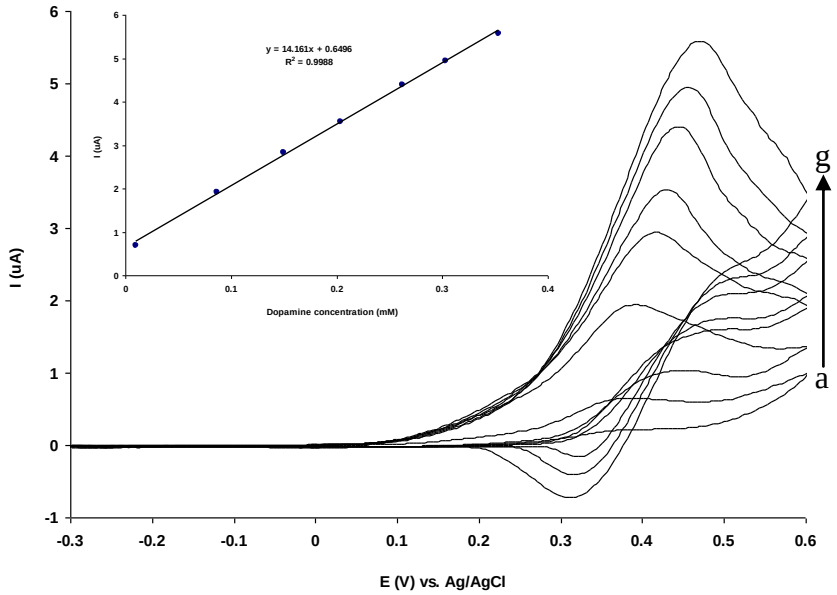


Figure 6. CVs of DA oxidation in the presence of AA (1.0 mM) at MES/SAM-Au electrodes. Curves (a) to (g) correspond, respectively to 0.01, 0.09, 0.15, 0.20, 0.26, 0.30 and 0.35 mM DA concentration. Inset: plot of I_p vs. [DA].

Table 1. Determination and recovery results of DA in injections (n=3)

Sample	Labeled (mg mL^{-1})	Found (mg mL^{-1})	Spiked (mg mL^{-1})	Found (mg mL^{-1})	Recovery (%)
1	40.0	39.5 ± 0.2	50.0	90.4 ± 0.5	101.0

4. CONCLUSION

In the present paper, a stable MES/SAM modified gold electrode was prepared. A $[Fe(CN)_6]^{3-/4-}$ redox probe was used to characterize the MES/SAM-Au modified electrode using cyclic voltammetry and impedance techniques. The modified electrode showed a well-defined electrochemical response for the oxidation of DA in the presence of AA. The results exhibited that AA has no interference with detection of DA, and DA can be detected selectively. The proposed method was successfully applied to the determination of DA in injection solution.

References

1. R.K. Shervedani, M. Bagherzadeh and S.A. Mozaffari, *Sens. Actuators B* 115 (2006) 614–621.
2. K. Kurzatkowska, E. Dolusic, W. Dehaen, K. Stoltny, A. Sieron and H. Radecka, *Anal. Chem.* 81 (2009) 7397–7405.
3. T. Liu, M. Li and Q. Li, *Talanta* 63 (2004) 1053–1059.
4. X. Lin and J. Gong, *Anal. Chim. Acta* 507 (2004) 255–261.
5. M.J. Giz, B. Duong and N.J. Tao, *J. Electroanal. Chem.* 465 (1999) 72–79.
6. H.M. Zhang, N.Q. Li and Z. Zhiwei, *Microchem. J.* 64 (2000) 277–282.
7. G. Zhi Hu, D. Zhang, W. Wu and Z. Yang, *Colloids Surf. B: Biointerf.* 62 (2008) 199–205.
8. G.Z. Hu, Y.C. Liu, J. Zhao, S.Q. Cui, Z.S. Yang and Y.Z. Zhang, *Bioelectrochemistry* 69 (2006) 254-257.
9. C.R. Raj, T. Okajima and T. Ohsaka, *J. Electroanal. Chem.* 543 (2003) 127–133.
10. F. Malem and D. Mandler, *Anal. Chem.* 65 (1993) 37–41.
11. S. Yixin and S.F. Wang, *Microchim. Acta* 154 (2006) 115–121.
12. J. Raoof, A. Kiani, R. Ojani, R. Valiollahi and S. Rashid-Nadimi, *J. Solid State Electrochem.* 13 (2009) 1311-1319.
13. H. Wang, L. Wang, Z. Shi, Y. Guo, X. Cao and H. Zhang, *Electrochem. Commun.* 8 (2006) 1779–1783.
14. L.S. Rocha and H.M. Carapuça, *Bioelectrochemistry* 69 (2006) 258–266.
15. P. Zhang, F.H. Wu, G.C. Zhao and X.W. Wei, *Bioelectrochemistry* 67 (2005) 109–114.
16. H. Qiu, G. Zhou, G. Ji, Y. Zhang, X. Huang and Y. Ding, *Colloids and Surf. B: Biointerf.* 69 (2009) 105–108.
17. X. Lin, Y. Zhang, W. Chen and P. Wu, *Sens. Actuators B* 122 (2007) 309–314.
18. O. Gilbert, B.E.K. Swamy, U. Chandra and B.S. Sherigara, *Int. J. Electrochem. Sci.* 4 (2009) 582-591.
19. G. Xu, M. Xu, J. Zhang, S. Kim and Z. Bae, *Bioelectrochemistry* 72 (2008) 87–93.
20. L.Z. Zheng, S.G. Wu, X.Q. Lin and L. Rui, *Analyst* 126 (2001) 736-738.
21. Y.X. Sun, B.X. Ye, W.M. Zhang and X.Y. Zhou, *Anal. Chim. Acta* 363 (1998) 75–80.
22. P.R. Roy, T. Okajima and T. Ohsaka, *Bioelectrochemistry* 59 (2003) 11–19.
23. T. Selvaraju and R. Ramaraj, *Electrochem. Commun.* 5 (2003) 667–672.
24. K.R. Williams, B. Adhyaru, I. German and T. Russel, *J. Chem. Educ.* 79 (2002) 1475–1476.