Electrooxidation of DL-norvaline at Glassy Carbon Electrode; Approaching the Modified Electrode for Voltammetric Studies of Hydroquinone and Catechol

Mahmoud M. Kamel

Chemistry department, Faculty of science (Assiut), Al-Azhar University, Egypt.

ABSTRACT:

The DL-norvaline was electrochemically oxidized and deposited on the glassy carbon electrode surface using cyclic voltammetry (CV). The modified electrode was examined for electrochemical oxidation of hydroquinone (HQ) and catechol (CC). It exhibited good electrocatalytic ability towards their oxidation and simultaneous determination in a binary mixture using differential pulse voltammetry (DPV). The peak currents were linear to the concentration of HQ and CC, in the range from 5 μM to 100 μM , and 40 μM to 140 μM , respectively. The determination limits ($S/N = 3$) for HQ and CC were 1 μM and 0.8 μM , respectively. The obtained modified electrode was applied to simultaneous detection of HQ and CC in water sample.

Keywords: DL-norvaline glassy carbon electrode, Hydroquinone, Catechol, Cyclic voltammetry, Differential pulse voltammetry

Received September 30, 2013 : Accepted October 30, 2013

1. Introduction

The electrooxidation of amino acids has been a potential area for intensive investigation. Their uses as a monomer or a polymer for modification of several electrodes have been increasingly used in analytical applications. Among several electrode materials, glassy carbon electrodes (GCEs) have been widely used. The biocompatibility, the low residual current over a wide range and the minimal chances to show deteriorated response¹⁻³⁾ of GCE are some advantages of other electrodes. Several reported studies have involved electrochemical oxidation of L-cysteine,^{4,5)} valine,⁶⁾ glycine,⁷⁾ glutamic acid,⁸⁾ phenylalanine,⁹⁾ and L-aspartic.^{10,11)} Most of these studies have modified the GCE surface and therefore have been used to reduce the overvoltage, overcome the slow kinetics of

many electrode processes and determination of one species as an analytical application. Norvaline an amino acid $\text{C}_5\text{H}_{11}\text{NO}_2$ isomeric with valine and usually made synthetically. It is not found in proteins but has several significant applications in biological systems.¹²⁾ However; no report is available concerning the oxidation of DL-norvaline or its uses as electrode modifying material for electroanalytical applications so far. Thus, the oxidation of DL-norvaline and its single deposition or polymerization on the GCE is concerned in this study. The modified electrode was investigated towards the electrochemical oxidation of hydroquinone (HQ) and catechol (CC). These two isomers of dihydroxybenzene have been extensively studied due to their biological and environmental importance.¹³⁻¹⁵⁾ They are high toxic and low degradable materials in the ecological environment.¹⁶⁾ Their human uptake can induce some diseases such as renal tube degeneration and liver function decrease.¹⁷⁾ Moreover, HQ and CC have similar structures and properties and they usually coexist in products. Hence,

*Corresponding author. Tel.: 0201113033830

E-mail address: mmk.electro@yahoo.com

their determination using several methods has been widely investigated.¹⁸⁻²¹⁾ Chemically modified electrodes (CMEs) as one of the exciting developments in the field of electroanalysis have been exploited for the simultaneous determination of such isomers without previous separations.²²⁻²⁴⁾ Recently, using of amino acids as a modifier for GCE has been applied for the directly simultaneous determination of HQ and CC.⁷⁻⁹⁾ Hence, an attempt for simultaneous determination of HQ and CC using the DL-norvaline GCE will be performed and the electrode response will be compared with other modified electrodes.

2. Experimental

2.1. Materials and reagents

DL-norvaline, hydroquinone, catechol, di-potassium hydrogen orthophosphate anhydrous, and potassium di-hydrogen orthophosphate monohydrate were of analytical grade and obtained from Aldrich. Phosphate buffer solutions of different pH values were prepared using anhydrous di-potassium hydrogen phosphate and potassium di-hydrogen phosphate monohydrate.

DL-norvaline, hydroquinone, and catechol solutions were prepared by dissolving the appropriate amount at the desired phosphate buffer solution according to experimental conditions.

2.2. Apparatus and procedure

Electrochemical experiments (Cyclic Voltammetry and differential pulse voltammetry) were carried out with an EG&G PAR 273A potentiostat using 250-270 electrochemical analysis software, manufactured by Princeton Applied Research, NJ, USA. All the experiments were carried out in a conventional electrochemical cell. The electrode system contained a glassy carbon working electrode (2- mm diameter), a platinum wire counter electrode and Ag/AgCl electrode served as the reference electrode. All measurements were carried out at room temperature. Prior to each experiment, the glassy carbon electrode was first polished with 0.05 μm alumina in a water slurry using a

polishing cloth and rinsed with 1:1 HNO_3 , acetone and water, respectively.

2.3 Modification procedure

After rinsing with water, the electrode was placed in a solution containing 0.01 M DL-norvaline in 0.2 M phosphate buffer (pH7.4) which was previously de-aerated with high purity nitrogen for 10 min. The electrode was treated with cyclic scanning between -0.5 and 1.8 V at a scan rate of 100 mV s^{-1} , for ten cycles. The electrode was taken out and rinsed with water to remove any unreacted materials from the electrode surface. Scanning electron microscope (SEM) images were performed by JEOL-TSM 5400LV Scanning electron microscope, Japan.

3. Results and Discussion

3.1. Oxidation of DL- Norvaline at the GCE surface

The chemistry of amino acids consist transformation of functional groups already present in these molecule. Ions of amino acids that only contain hydrocarbon moieties have not been subjected to chemical reaction due to inertness of the hydrocarbon chain comparing to the high reactivity of the functional groups.²⁵⁾ DL-norvaline is one of synthetic α -amino acid which is oxidized through NH_2 group and it is prone to adsorption on the electrode surface. Adsorption phenomena on GCE surface are very common with many organic molecules, in particular, polar organic molecules.²⁶⁻²⁸⁾ According to literature,²⁹⁾ the prospected oxidation mechanism of DL- norvaline and its adsorption occur through one-electron oxidation of the amino group turns into its corresponding cation radical. These obtained cation radicals form carbon-nitrogen links at the carbon electrode surface as indicated below.

Cyclic voltammograms for the consecutive ten cycles of the DL-norvaline oxidation are shown in Fig. 1. At the first cycle; two anodic peaks are observed. The first anodic peak at about 0.2 V is attributed to the background or charging current in the PBS supporting electrolyte. This result is confirmed by recording a cyclic voltamme-

Scheme 1.

try of GCE in 0.2 M phosphate buffer (pH5) supporting electrolyte without DL-norvaline as shown in Fig. 2. A similar oxidation peak at around 0.225 V referring to charging current is observed. The obtained charging current is due to the surface faradic reaction of redox active oxides that forms a pseudo capacitance.^{30,31)} The formation of such carbon-oxides is generally consequent to polishing the electrode surface. McCreery *et al.*³²⁾ have reported that conventional polishing of GCE in Al_2O_3 /Nanopure slurries produced a 8-15% O/C ratio. Results show also that the first peak successively decreases with increase in the number of potential cycles until it disappears. According to Frysz *et al.*³³⁾ high capacitance is often associated with high surface roughness and high concentration of oxygen-containing functional groups. Hence, the sequentially diminution of the first peak is due to the progressively deposition and covering the electrode surface by DL-norvaline as indicated by SEM images (Fig. 3). Another anodic peak current at around

1.65 V is caused by the oxidation of DL-norvaline. This peak completely disappears after the first potential scan which proves the binding of the molecule to GC surface.

The SEM micrographs of the obtained modified GCE that are shown in Fig. 3 confirm the upper mentioned discussion. Separate miniature monoliths of needle nature shapes are observed implying that the polymerization is not obtained and the only DL-norvaline and its oxidation product are deposited.

3.2. Voltammetric behavior of HQ at DL-Norvaline modified GCE

Fig. 4 show the cyclic voltammograms of the obtained modified GCE in 0.05 M PBS (pH 5) in the presence (curve b) and absence (curve c) of 0.1 mM HQ, and is compared with the bare electrode in presence of 0.1 mM HQ (curve a). The DL-norvaline modified electrode itself is electro inactive at 0.05 M PBS 5 in the potential range from -0.2 to 0.6 V (curve c). The electrochemistry of HQ is notably enhanced at the modified electrode. The voltammetric response of the

Fig. 1. Cyclic voltammograms of the glassy carbon electrode in 0.2 M PBS (pH 7.4) containing 0.01M DL-norvaline; scan rate, 0.1 V.s^{-1} .

Fig. 2. Cyclic voltammograms of the glassy carbon electrode in 0.2 M PBS (pH 7.4); scan rate, 0.1 V.s^{-1} .

Fig. 3. SEM images of the DL-norvaline modified GCE with 150 times, 350 times, and 750 times magnification.

Fig. 4. CVs of (a) bare GCE, (b) the DL-norvaline modified GCE in 0.05 M PBS(pH5) containing 0.1 mM HQ and (c) the DL-norvaline GCE in 0.05 M PBS(pH5); scan rate, 100 mV s^{-1} .

HQ at the bare electrode is observed as broad and overlapped peaks. On the other hand, on the DL-Norvaline modified GCE, well defined oxidation peak at potential 0.219 V and reduction peak at 0.153 V with $\Delta E_p = 0.066 \text{ V}$ are observed. Note also the enhanced sensitivity in comparison with the bare electrode is observed (e.g., current enhancement of 4). According to these results, the DL-Norvaline modified GCE shows good electrocatalytic ability for oxidation of HQ. Here, this ability is certainly due to the adsorbed DL-norvaline layer on GCE and not related to an electrochemical oxidation of the electrode surface associated during experiment. Such conclusion can be demonstrated by comparing cyclic voltammograms of DL-norvaline modified GCE with the oxidized surface modified GCE electrode³⁴⁾ in phosphate buffer. A couple of well-defined and reversible redox peak has been observed for the oxidized surface modified GCE electrode,³⁴⁾ while the DL-norvaline modified GCE is electro inactive and no redox peak is obtained. The lack of a redox peak in case of the DL-norvaline modified GCE proves that the electrocatalytic effect is particularly due to the adsorbed DL-norvaline layer which performs as a promoter. This conclusion is quite similar to that obtained in cases of the glassy carbon modification by other amino acids.⁷⁻⁹⁾

3.3. Influence of scan number and pH values of phosphate buffer (0.2 M) on electrochemical synthesis of DL-norvaline modified GCE.

The voltammetric response of the HQ oxidation at modified GCE obtained at different scan numbers (2, 4, 8, 10, and 15 cycles) is investigated. Results (not shown) indicate that the magnitude of HQ oxidation

current slightly increases as increasing of the scan number. The maximum oxidation current is obtained at 10 cycles and no significant increase of current with further cycles. It has been reported that the repeated potential application would promote the build-up of deposited layers of compounds and its oxidation products.^{7-9,35,36)} However, obtaining lower current values is probably due to the difficulty of the build-up of adsorbed layers as well as polymerization. This observation is attributed to the fact that the modification of a GC electrode with amine-containing compound suggests that diffusion rates as well as steric effects are most significant factors affecting the immobilization of amine-containing compounds at GC electrode surface.³⁷⁾ The varying of the 0.2 M PBS pH (4-8) shows also a slight increase of the HQ oxidation current value as increasing of pH value up to pH 7.4 which represents the high current value.

3.4. Voltammetric behavior of CC at DL-Norvaline modified GCE

The oxidation of CC at the bare electrode shows a broad oxidation peak at potential of 0.372 V and broad as well overlapped reduction peak (Fig. 5, curve a). While, the redox peaks of CC at the DL-Norvaline modified electrode can be observed clearly (Fig. 5, curve b). The oxidation peak potential negatively shifts to 0.309 V and a single reduction peak is depicted at 0.257 V giving $\Delta E_p = 0.052 \text{ V}$. Note also the enhanced sensitivity in comparison with the bare electrode is observed (e.g., current enhancement of 4). Hence, the DL-Norvaline modified electrode exhibits the similar electrocatalytic effect for the electrochemical oxidation of CC.

Fig. 5. CVs of (a) bare GCE, (b) the DL-norvaline modified GCE in 0.05 M PBS(pH5) containing 0.1 mM CC and (c) the DL-norvaline GCE in 0.05 M PBS(pH5); scan rate, 100 mV s^{-1} .

Fig. 6. (a) CVs of the DL-norvaline modified GCE in (A) 0.1 mM HQ, and in (B) 0.1 mM CC at various pH values of PBS (0.05 M); (b and c) The dependences of all peak potentials (b) and redox peak currents (c) on pH.

3.5 Voltammetry of HQ and CC at DL-norvaline modified GCE at different pH value

The effect of pH supporting electrolyte on the electrochemical behaviors of HQ and CC is investigated in the pH value range from 4 to 8. Fig. 6a shows the cyclic voltammograms of 0.1 mM HQ (curve A) and CC (curve B) at the modified electrode, respectively in different 0.05 M PBSs. The relationship between the peak potential and pH is illustrated in Fig. 6b. With increasing pH, both anodic and cathodic peak potentials decrease linearly. The linear regression equations of HQ and CC are listed in Table 1. The slopes of the 4 regression equations are close to the theory value of 58.5 mVpH⁻¹ for the electrode reaction pro-

Table 1. The linear regression equations for peak potentials (E_p) of HQ and CC versus pH.

HQ		CC	
E_{pa}	$E_{pa}(V) = 0.4793 - 0.0519 \text{ pH}$ [R = 0.9955]	$E_{pa}(V) = 0.589 - 0.0538 \text{ pH}$ [R = 0.9825]	
E_{pc}	$E_{pc}(V) = 0.4131 - 0.0500 \text{ pH}$ [R = 0.9803]	$E_{pc}(V) = 0.5204 - 0.0505 \text{ pH}$ [R = 0.984]	

cess of equal electron and proton,³⁸⁻⁴⁰⁾ indicating that the electrode process of HQ and CC at the modified electrode should be a two electrons and two protons process. Fig. 6c shows the dependence of anodic peak currents of HQ and

Fig. 7. (a) Cyclic voltammograms of the DL-norvaline modified GCE in (A) 0.1 mM HQ and in (B) 0.1 mM CC, at different scan rates in 0.05M PBS(pH 5). The scan rates from inside to outer are 20-400 mVs⁻¹; (b) The plots of redox currents vs. square root of scan rate for HQ(A) and CC(B).

Table 2. The linear regression equations for peak currents (I_{pa} or I_{pc}) of HQ and CC versus (scan rate, v)^{1/2}

	HQ	CC
I _{pa}	I _{pa} = -0.5419 + 11.9082 v ^{1/2} [μA, (V.s ⁻¹) ^{1/2} , R = 0.9991]	I _{pa} = -0.3272 + 12.762v ^{1/2} [μA, (V.s ⁻¹) ^{1/2} , R = 0.9942]
I _{pc}	I _{pc} = 0.4252 - 9.5458 v ^{1/2} [μA, (V.s ⁻¹) ^{1/2} , R = 0.9939]	I _{pc} = 0.5286 - 9.743v ^{1/2} [μA, (V.s ⁻¹) ^{1/2} , R = 0.9912]

CC on pH. It can be seen that the peak currents of HQ and CC increase with increasing pH value until pH reaches 5.0, then they decrease when pH increased further.

3.6 Effect of scan rate

Cyclic voltammograms with different scan rates at the DL-norvaline modified GCE in 0.05 M PBS solution (pH 5.0) containing 0.1 mM HQ (curve A), and 0.1 mM CC (curve B) are shown in Fig. 7a. With

increasing scan rate from 0.02 to 0.400 V/s, all the redox peak currents of HQ and CC increase linearly with the square root of the scan rate (v^{1/2}) as shown in Fig. 7b. The linear regression equations of peak currents (I_{pa} or I_{pc}) versus v^{1/2} are listed in Table 2. The good linearity indicates that the electrode process of HQ and CC is a typical diffusion-controlled process.

3.7 Simultaneous Determination HQ and CC

Cyclic voltammetry and differential pulse voltammetry are applied to evaluate the sensitivity and selectivity of the modified electrode for the quantification of HQ and CC. The individual determination of HQ, or CC in their mixtures is carried out when the concentration of one species changes whereas the other species remains constant. Fig. 8A shows the CVs obtained for the binary mixtures of 0.1 mM HQ and 0.1 mM CC at the bare and the DL-Norvaline modi-

fied electrodes. DPVs for 10 μM HQ and 10 μM CC coexisting at bare and DL-Norvaline modified electrodes are illustrated in Fig. 8B. Results show only one broad voltammetric signal for both analytes (curve a)

and hence, the bare electrode can't separate the voltammetric signals of HQ and CC. The fouling of the electrode surface by the oxidation products resulted in a single voltammetric peak for HQ and CC. Therefore

Fig. 8. (A) Cyclic voltammograms at bare GCE (a), and the DL-norvaline modified GCE (b) in presence of 0.1 mM HQ and 0.1 mM CC in 0.05 M PBS (pH 5.0): scan rate, 100 mV s^{-1} ; (B) DPVs of the bare electrode (a), and the DL-norvaline modified GCE (b) in presence of 10 μM HQ and 10 μM CC coexisting in 0.05 M PBS (pH 5.0): scan rate, 4 mV s^{-1} , pulse height: 50 mV.

Fig. 9. (A) DPVs of the DL-norvaline modified GCE in 0.05M PBS(pH 5) containing 50 μM CC and different concentrations of HQ(5,10,20,40,60,80, and100 μM), (C) DPVs of the DL-norvaline modified GCE in 0.05M PBS(pH 5) containing 50 μM HQ and different concentrations of CC(40,60,80,100,120, and 140 μM), (B) and (D) linear plots of I_{pa} versus [HQ] and [CC], respectively.

it is impossible to use the bare electrode for the voltammetric determination of CC in the presence of HQ. Otherwise, voltammograms (curve b) obtained by the DL-Norvaline modified electrode exhibit two well defined voltammetric peaks for the binary mixtures of HQ and CC. Thus, the determination of individual HQ or CC is independent of the other, implying good selectivity and excellent sensitivity of the DL-Norvaline modified electrode in their simultaneous voltammetry. The peaks observed at 0.140 and 0.242 mV in DPV are corresponding to the oxidations of HQ and CC, respectively (Fig. 8B, curve b). The typical DPVs for different concentrations of HQ and CC are shown in Fig. 9(A and C). The good linear relationship between peak currents and the concentration of HQ and CC is obtained under the optimal conditions (Fig. 9 B and D). The linear calibration curves are in the range from 5 μM to 100 μM with a slope of 0.0229 $\mu\text{A}/\mu\text{M}$ for HQ and from 40 μM to 140 μM with a slope of 0.0206 $\mu\text{A}/\mu\text{M}$ for CC. The determination limit ($S/N = 3$) of HQ in presence of 50 μM CC was 1 μM and the determination limit of CC in presence of 50 μM HQ was 0.8 μM . A comparison of the proposed method with other electrochemical methods is listed in Table 3. It can be seen from the

table that the proposed method shows fair linear range and acceptable detection limit comparing with others.

3.8. Reproducibility and stability of DL-Norvaline modified electrode.

The reproducibility for five DL-Norvaline modified electrode is investigated by comparing the DPV peak current of 50 μM HQ, and CC in a mixed solution. The relative standard deviation (RSD) is 2.22% for HQ, and 4.2% for CC, indicating an acceptable reproducibility. Additionally, the stability of the doped electrode is also tested. The results show that the peak currents remain 96% of their initial values after the electrode was kept for 15 days.

3.9. Sample Analysis.

The assessment of the proposed method in direct simultaneous determination of HQ and CC in synthetic sample consisting of HQ and CC in local tap water is tested.

The determination of HQ and CC in the samples is carried out using DPV at the DL-Norvaline modified electrode in 0.05 M PBS (pH 5). The results are listed in Table 4. no obvious oxidation signal is observed for

Table 3. Performance comparison of the fabricated electrode for HQ, and CC detection with other electrodes.

Electrode	Method	Linear range(μM)		Detection limit(μM)		Ref.
		HQ	CC	HQ	CC	
Graphene/GCE	DPV	1-50	1-50	0.015	0.010	28
PASA/MWNTs/GCE	DPV	6-100	6-180	1.0	1.0	41
Graphene/BMIMPF ₆ /GCE	DPV	0.5-50	0.5-50	0.01	-0.02	-42
PDDA-Graphene/GCE	DPV	1-500	1-400	0.25	0.2	43
Poly-Glycine/GCE	DPV	5-80	1-60	1.0	0.5	7
Poly-Glutamic acid/GCE	DPV	5-80	1-80	1.0	0.8	8
Poly-Phenylalanine/GCE	DPV	5-160	10-140	1.0	0.7	9
DL Norvaline/GCE	DPV	5-100	40-140	1.0	0.8	This work

Table 4. Recovery results for HQ, and CC in water samples.

Sample No.	Tap water Containing CC, (μM)	HQ added (μM)	HQ found (μM)	Recovery (%)	Tap water Containing CC, (μM)	CC added (μM)	HQ found (μM)	Recovery (%)
1	40	40	41.5	103.75	40	40	40.8	102
2	40	50	51.5	103.00	40	50	49.7	99.4
3	40	60	58.2	97.00	40	60	60.08	100.13
4	40	70	67.2	96.00	40	70	70.1	100.14

the water samples without addition of analytes standards. When known amount of HQ are added to the water control samples containing CC, quantitative recoveries of 96% -103.75% are obtained. When known amounts of CC are added to the water control samples containing HQ, quantitative recoveries of 99.4% - 102.0% are obtained.

4. Conclusion

DL-norvaline was oxidized and partially deposited on the surface of GCE. The modified electrode was examined for voltammetric studies of HQ and CC. The modified electrode showed fast electron transfer, excellent sensitivity and good separation for oxidation peaks of HQ and CC, which were indistinguishable at the bare electrode. However, the present modified electrode showed fairly good results for simultaneous determine of HQ and CC, more efforts will be done for enhancing its response in the next studies.

References

1. R.F. Rane and C.D. Blaha, *Langmuir*, **6**, 56 (1990).
2. A.G Ewing, M.A. Dayton and R.M. Wightman, *Anal. Chem.*, **53**, 1842 (1981).
3. J.S. Mattson and T.T. Jones, *Anal. Chem.*, **48**, 2164 (1976).
4. J. Guan, Z. Wang, C. Wang, Q. Qu, G. Yang and X. Hu, *Int. J. Electrochem. Sci.*, **2**, 572 (2007).
5. C.A. Martínez-Huitlea, M. Cerro-Lopez and M.A. Quiroz, *Materials Research*, **12**, 375 (2009).
6. X. Li, M. Chen, X. Ma, and X. Lin, *Int. J. of Chem.*, **2**(1), 206(2010).
7. L. Wang, P. Huang, J. Bai, H. Wang, L. Zhang and Y. Zhao, *Int. J. Electrochem. Sci.*, **2**, 216(2007).
8. L. Wang, P. Huang, J. Bai, H. Wang, L. Zhang and Y. Zhao, *Int. J. Electrochem. Sci.*, **2**, 123(2007).
9. L. Wang, P. Huang, J. Bai, H. Wang, L. Zhang and Y. Zhao, *Int. J. Electrochem. Sci.*, **1**, 403(2006).
10. J. Li and X. Zhang, *Americ. J. of Anal. Chem.*, **3**, 195(2012).
11. Z. YU, X. LI, X. WANG, X. MA, X. LI and K. CAO, *J. Chem. Sci.*, **124**(2), 537(2012).
12. B. B. TEWARI, *J. Chil. Chem. Soc.*, **55**(2), 166 (2010).
13. A. J. Blasco, M. C. Rogerio, M. C. González and A. Escarpa, *Anal. Chim. Acta*, **539**, 237 (2005).
14. H. Notsu and T.J. Tatsuma, *J. Electroanal. Chem.*, **566**, 379(2004).
15. G. Achilli, G. P. Cellerino, G. M. d'Eril and S.J. Bird, *J. Chromatog. A*, **697**, 357 (1995).
16. T.Xie, Q.Liu, Y. Shi and Q. Liu, *J. Chromatog. A*, **1109**, 317 (2006).
17. M. Lv, M. Wei, F. Rong, C. Terashima and A. Fujishima, *Electroanalysis*, **22**, 199 (2010).
18. C. H. Lin, J. Y. Sheu, H. L. Wu and Y. L. Huang, *J. Pharma. and Biomed. Analysis*, **38**, 414 (2005).
19. P. Nagaraja, R. A. Vasantha and K. R. Sunitha, *J. Pharma. and Biomed. Analysis*, **25**, 417 (2001).
20. S. C. Moldoveanu and M. Kiser, *J. Chromatog. A*, **1141**, 90 (2007).
21. J. A. Garcia-Mesa and R. Mateos, *J. Agric. Food Chem.*, **55**, 3863 (2007).
22. H. Du, J. Ye, J. Zhang, X. Huang and C. Yu, *J. Electroanal. Chem.*, **650**, 209 (2011).
23. Y.P. Ding, W.L. Liu, Q.S. Wu and X.G. Wang, *J. Electroanal. Chem.*, **575**, 275 (2005).
24. A. J. Saleh Ahammad, S. Sarker and M. Aminur Rahman, J. J. Lee, *Electroanalysis*, **22**, 694 (2010).
25. A. K. Singh, B. Jain, R. Negi and Y. Katre, S.P. Singh, *Open Catal. J.*, **2**, 12(2009).
26. L. Vracar, *J. of Serb. Chem. Soci.*, **66**, 799 (2001).
27. P. Chen and L. McCreery, *Anal. Chem.*, **68**, 3958 (1996).
28. Z. Wang, D. Liu and S. Dong, *Biophys. Chem.*, **89**, 87 (2001).
29. B. Barbier, J. Pinson, G. Desarmot and M. Sanchez, *J. Electrochem. Soci.*, **137**, 1757 (1990).
30. A. Bachtold, M. Henny, C. Terrier, C. Strunk, C. Schonenberger, J. P. Salvetat, J. M. Bonard, and L. Forro, *Appl. Phys. Lett.*, **73**, 274 (1998).
31. M. M. RAHMAN and I. C. JEON, *CROAT. CHEM. ACTA*, **80**, 67 (2007).
32. S. H. DuVall and R. L. McCreery, *Anal. Chem.*, **71**, 4594 (1999).
33. C.A. Frysz, X. Shui and D.D.L. Chung, *Carbon*, **35**, 893 (1997).
34. S. Thiagarajan, T.H. Tsai and S.M. Chen, *Biosens Bioelectron.*, **24**, 2712 (2009).
35. N. Priyantha and S. Welivegamage, *Int. J. Electrochem. Sci.*, **3**, 125 (2008).
36. J. Li and X. Zhang, *Am. J. Anal. Chem.*, **3**, 195 (2012).
37. C. A. Martinez-Huitlea, M. Cerro-Lopez and M. A. Quiroz, *Materials Research*, **12**, 375 (2009).
38. W. Sun, M. Xi, L. Zhang, T. Zhan, H. Gao and K. Jiao, *Electrochim. Acta*, **56**, 222 (2010).
39. L. Ma and G.C. Zhao, *Int. J. Electrochem.*, **2012**, 1(2012).
40. B. J. Sanghavi and A. K. Srivastava, *Electrochim. Acta*, **55**, 8638 (2010).
41. D.M. Zhao, X.H. Zhang, L.J. Feng, L. Jia and S.F. Wang, *Colloids Surf. B: Biointer.*, **74**, 317 (2009).
42. Z. Liu, Z. Wang, Y. Cao, Y. Jing and Y. Liu, *Sens. Actuators B*, **157**, 540 (2011).
43. L. Wang, Y. Zhang, Y. Du, D. Lu, Y. Zhang and C. Wang, *J. Solid State Electrochem.*, **16**, 1323 (2012).