

Full Paper

CdTe Quantum Dots Modified Carbon Paste Electrode for Voltammetric Determination of Ascorbic Acid

Somayeh Tajik,^{1,*} Mohammad Ali Taher,¹ Shohreh Jahani² and Maryam Shanehsaz³

¹*Department of Chemistry, Shahid Bahonar University of Kerman, P.O. Box 76175-133, Kerman, Iran*

²*Environment Department, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran*

³*Analytical Chemistry Research Laboratory, Mobin Shimi Azma Company, Tehran, Iran*

*Corresponding Author, Tel.: +98 341 3220041; Fax: +98 341 3643853

E-Mail: Tajik.s2012@yahoo.com

Received: 27 August 2016 / Received in revised form: 12 September 2016 /

Accepted: 20 September 2016 / Published online: 15 November 2016

Abstract- A novel CdTe quantum dots is synthesized and used for modification of carbon paste electrode (QDMCPE). This modified electrode was used to study the electrooxidation of ascorbic acid using cyclic voltammetry (CV), square wave voltammetry (SWV) and chronoamperometry (CHA) as diagnostic techniques. SWV peak currents of ascorbic acid increased linearly with its concentrations in the range of 5.0×10^{-7} - 8.0×10^{-4} M with a detection limit of 3.0×10^{-7} M. The main objectives of QDMCPE for determination of ascorbic acid are: wide linear dynamic range, short time of the procedure and no use of electron transfer mediator. Finally this new sensor was used for determination of ascorbic acid in some real samples.

Keywords- Ascorbic acid, Carbon paste electrode, CdTe quantum dots, Chemically modified electrodes

1. INTRODUCTION

The interest in developing sensing devices for use in environmental monitoring, clinical assays or process control is a rapidly growing field of research. Electrochemical sensors

satisfy many of the requirements for such tasks, particularly owing to their simplicity of preparation, high selectivity and sensitivity, and fast response. The utility of sensors based on solid (bare) electrodes is often hampered by their low selectivity arising from high overpotentials [1]. In particular, complexity of real biological systems may result in overlapping voltammetric signals. Moreover, the limited number of electrode materials makes only a restricted number of analytes suitable for electrochemical detection with high sensitivity and selectivity. Therefore, efforts have been made to modify the electrode surfaces for the purpose of lowering the overpotential, improving the mass transfer velocity for effective enrichment of the desired substance and/or restraining the effect of interferences [1–13].

Among all the carbon electrodes, the carbon paste electrode (CPE) is an appealing and widely used electrode material in the fields of electrochemistry, electroanalysis, etc. due to its attractive advantages, such as simple preparation, low-cost implementation, renewability, low background current, and wide potential window [14–18]. The preparation of CPE usually involves the dispersion of graphite powder in a hydrophobic binder to form a homogeneous paste, followed by filling a tube with the resulting paste [18–21]. Sometimes, the modifiers including various biomolecules, organic compounds and nanoparticles are also doped into the carbon paste, which makes CPE quite suitable for bioanalysis [22–29].

Quantum dots (QDs), a kind of semiconductor nanocrystal with average diameter of 2–20 nm, has been placed on significant emphasis in recent years because of its high fluorescence efficiency and significantly quantum size effect [30]. The application of QDs mainly involved fields such as solar cell, laser, photoelectric diode, bio-targeting, drug delivery, protein tracking, cancer diagnoses, cell imaging, light-emitting diode, bio-labeling, modified electrodes and optical biomarkers [31]. However, the application of QDs in electrochemical sensor is still limited. It can predict that QDs showed immense and promising prospects in electrochemical as electrode modified materials due to their very small size, large specific surface area and excellent biocompatibility [32]. Nowadays the design and fabrication of electrochemical quantum dots modified electrodes showed a good effort in acting as a sensor toward the determination of biomolecules [33].

Ascorbic acid (AA) is known for its reductive properties and for its use on a wide scale as an antioxidant agent in food and drinks; it is also important for therapeutic purposes and biological metabolism. Therefore, recent advances in the food and pharmaceutical industries and a need for nutritional assessment have necessitated the development of a selective, simple, and accurate method to determine AA. Due to its selectivity and sensitivity, an electrochemical method to determine AA has been a subject of considerable interest [34–39].

To the best of our knowledge, no study has been reported so far on the determination of ascorbic acid by using CdTe quantum dots-modified carbon paste electrodes (QDMCPE). Although, there are many reports about the determination of ascorbic acid using electron

transfer mediator, but in this study, we report the preparation and application of a CdTe quantum dots-modified carbon paste electrodes for the determination of ascorbic acid without any additional modification such as addition of electron transfer mediator or specific reagents for the first time.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrode cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode (Azar Electrode Co., Urmia, Iran), a platinum wire (Azar Electrode Co., Urmia, Iran), and QDMCPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. Ascorbic acid and all of the other reagents were of analytical grade and were obtained from Merck (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts (Darmstadt, Germany).

2.2. Synthesis of CdTe quantum dots

CdTe quantum dots in a thiol-capped form were synthesized as reported by Zhang et al. with some modifications, as follows. First, sodium hydrogen telluride (NaHTe) was prepared by reducing Te powder with sodium borohydride (at a mole ratio of 1:2) in doubly distilled water under stirring and N₂ purging.

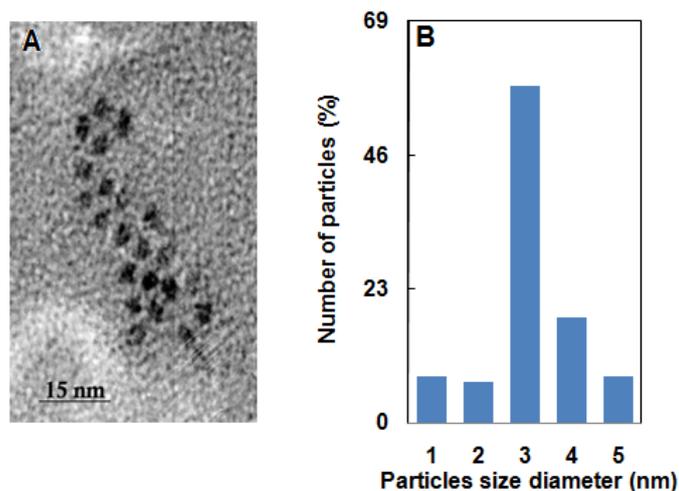


Fig. 1. TEM image (A) and size distribution diagram; (B) of synthesized CdTe quantum dots

After 8 h, the color of the solution changed from violet to white and sodium tetraborate was precipitated out. The resulting NaHTe in the clear supernatant was separated and used in the preparation of CdTe particles. In the next step, the freshly prepared NaHTe was added to a CdCl₂ solution containing thioglycolic acid (TGA) under N₂ atmosphere. The molar ratio of Cd²⁺: Te: TGA was set as 1.0: 0.5: 2.4. The pH of solution was adjusted to 11, and then the mixture was heated and refluxed at 100 ° C for 4 h. The obtained QDs were precipitated with ethanol and then separated using a centrifuge. The resulting precipitate was re-dispersed in 250 mL water and kept at 4 ° C in the dark (mother solution of QD). The morphology of the prepared TGA-capped CdTe was studied by TEM (Fig. 1A). As seen, the QDs possess a spherical morphology and are homogeneously size distributed. The distribution histogram illustrated in Fig. 1B revealed an average particle size of about 3 nm.

2.3. Preparation of the electrode

The QDMCPEs were prepared by mixing 2 ml quantum dots nanoparticles, 1.0 g of graphite powder and ~0.7 mL of paraffin oil with a mortar and pestle until a uniform paste was obtained. The paste was then packed into the end of a glass tube (ca. 3.4 mm i.d. and 10 cm long). The electrical contact was provided by inserting a copper wire into the carbon paste. Prior to each experiment, the surface of the carbon paste was polished with fine paper. The unmodified carbon paste electrode was prepared in the same way without adding quantum dots nanoparticles to the paste.

3. RESULTS AND DISCUSSIONS

3.1. Cyclic voltammetric study of ascorbic acid oxidation

Fig. 2 depicts the cyclic voltammetric responses for the electrochemical oxidation of 50.0 μM ascorbic acid at QDMCPE (curve a) and bare CPE (curve b). As can be seen, the anodic peak potential for the oxidation of ascorbic acid at QDMCPE (curve a) is about 200 mV, while the corresponding peak on the bare CPE peak potential occurs at 520 mV (curve b). Similarly, when we compared the oxidation of ascorbic acid at the QDMCPE (curve a) and bare CPE (curve b); there is a drastic enhancement of the anodic peak current at QDMCPE relative to the value obtained at the bare CPE (curve a). In the other words, the data obtained clearly show that the combination of graphite powder and CdTe quantum dots definitely improve the characteristics of ascorbic acid oxidation.

The effect of potential scan rate on the electrocatalytic oxidation of ascorbic acid at the QDMCPE was investigated by LSV (Fig. 3). A plot of peak height (I_p) vs. the square root of scan rate ($v^{1/2}$) was found to be linear in the range of 10-700 mV s⁻¹, suggesting that, at sufficient over potential, the process is diffusion rather than surface controlled (Fig. 3 inset).

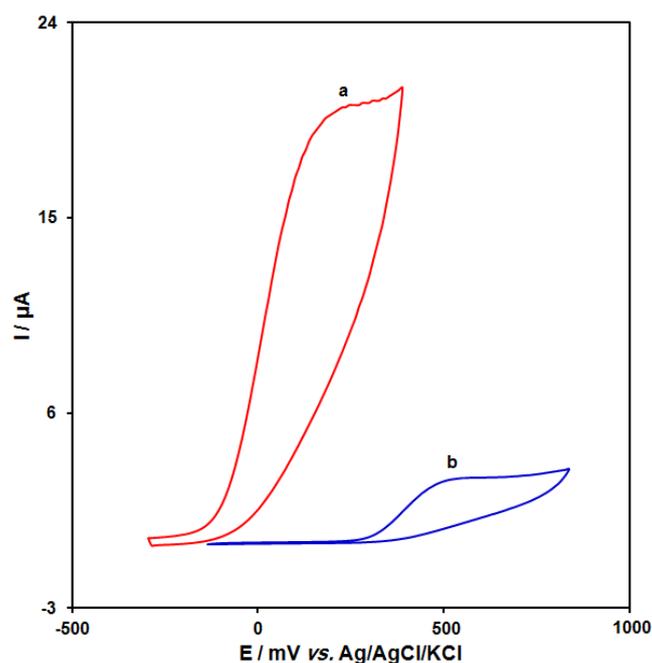


Fig. 2. CVs of 50.0 μM ascorbic acid in 0.1 M PBS (pH 7.0) at the surface of QDMCPE (a) and unmodified carbon paste electrode (b) in scan rate of 50 mVs^{-1}

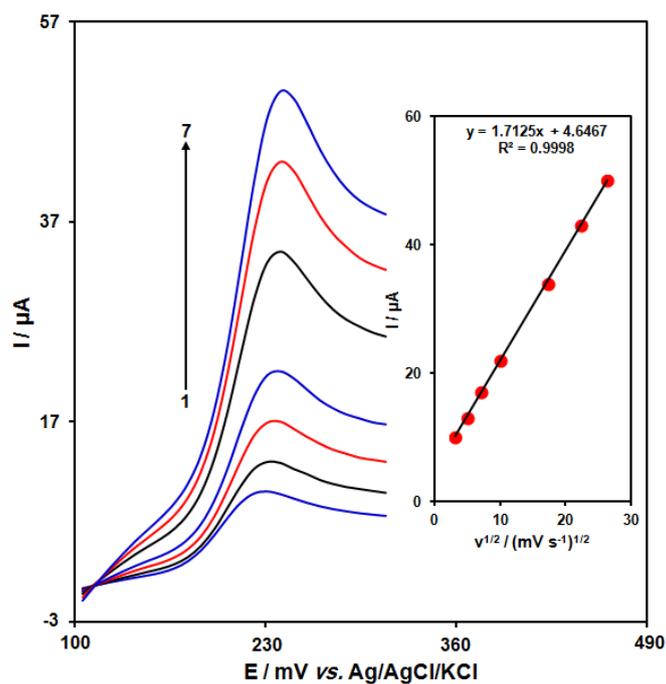


Fig. 3. LSVs of QDMCPE in 0.1 M PBS (pH 7.0) containing 40.0 μM ascorbic acid at various scan rates; numbers 1-7 correspond to 10, 25, 50, 100, 300, 500 and 700 mV s^{-1} , respectively. Inset: Variation of anodic peak current vs. $v^{1/2}$

Fig. 4 shows the Tafel plot for the sharp rising part of the voltammogram at the scan rate of 10 mV s^{-1} . If deprotonation of ascorbic acid is a sufficiently fast step, the Tafel plot can be used to estimate the number of electrons involved in the rate determining step. A Tafel slope of 0.087 V was obtained which agrees well with the involvement of one electron in the rate determining step of the electrode process [40], assuming a charge transfer coefficient, α of 0.32 .

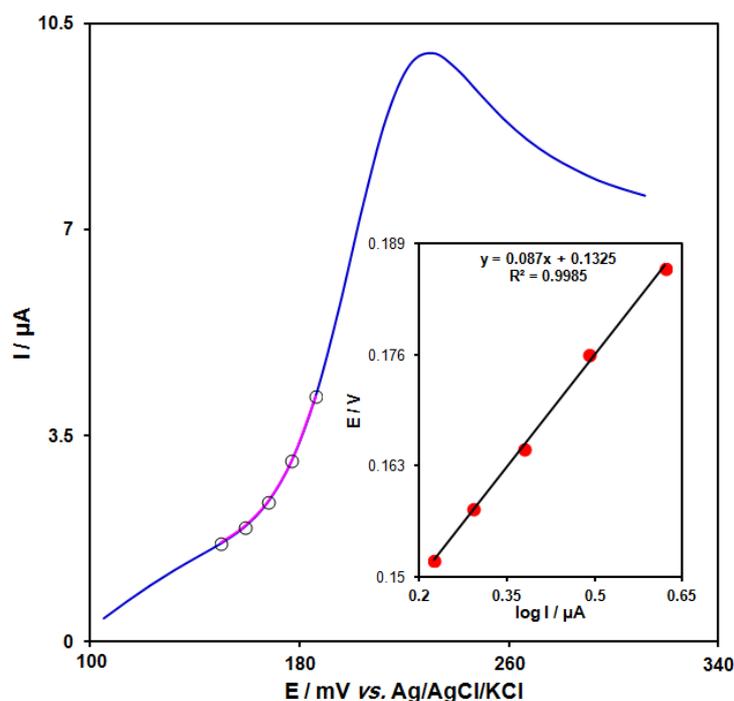


Fig. 4. LSV (at 10 mV s^{-1}) of a QDMCPE in 0.1 M PBS (pH 7.0) containing $40.0 \mu\text{M}$ ascorbic acid. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV

3.2. Chronoamperometric measurements

Chronoamperometric measurements of ascorbic acid at QDMCPE were carried out by setting the working electrode potential at 0.25 V versus Ag/AgCl/KCl (3.0 M) for the various concentration of ascorbic acid in buffered aqueous solutions (pH 7.0) (Fig. 5). For an electroactive material (ascorbic acid in this case) with a diffusion coefficient of D , the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation [40]:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

Where D and C_b are the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$) and the bulk concentration (mol cm^{-3}), respectively. Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of ascorbic acid (Fig. 5A). The slopes of the resulting straight lines

were then plotted vs. ascorbic acid concentration (Fig. 5B). From the resulting slope and Cottrell equation the mean value of the D was found to be $1.3 \times 10^{-5} \text{ cm}^2/\text{s}$.

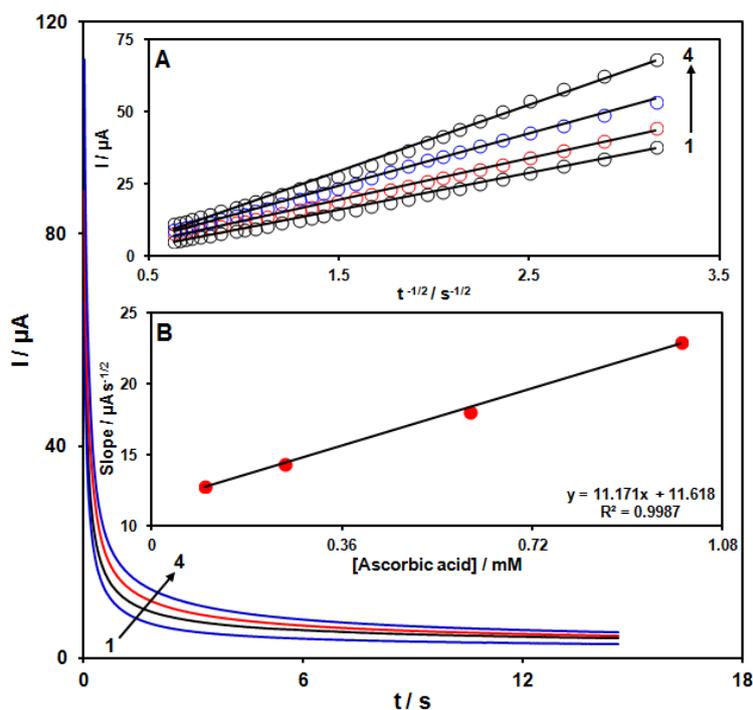


Fig. 5. Chronoamperograms obtained at QDMCPE in 0.1 M PBS (pH 7.0) for different concentration of ascorbic acid. The numbers 1–4 correspond to 0.1, 0.25, 0.6 and 1.0 mM of ascorbic acid. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 1–4. (B) Plot of the slope of the straight lines against ascorbic acid concentration

3.3. Calibration plot and limit of detection

The peak current of ascorbic acid oxidation at the surface of the QDMCPE can be used for determination of ascorbic acid in solution. Therefore, square wave voltammetry (SWV) experiments were performed using modified electrode in 0.1 M PBS (pH 7.0) containing various concentration of ascorbic acid (Fig. 6). The plot of peak current vs. ascorbic acid concentration consisted of a linear segment with a slope of $0.219 \mu\text{A}/\mu\text{M}$ in the concentration range of 5.0×10^{-7} – 8.0×10^{-4} M and the detection limit (3σ) was obtained 3.0×10^{-7} M. These values are comparable with values reported by other research groups for electro-oxidation of ascorbic acid at the surface of chemically modified electrodes (see Table 1).

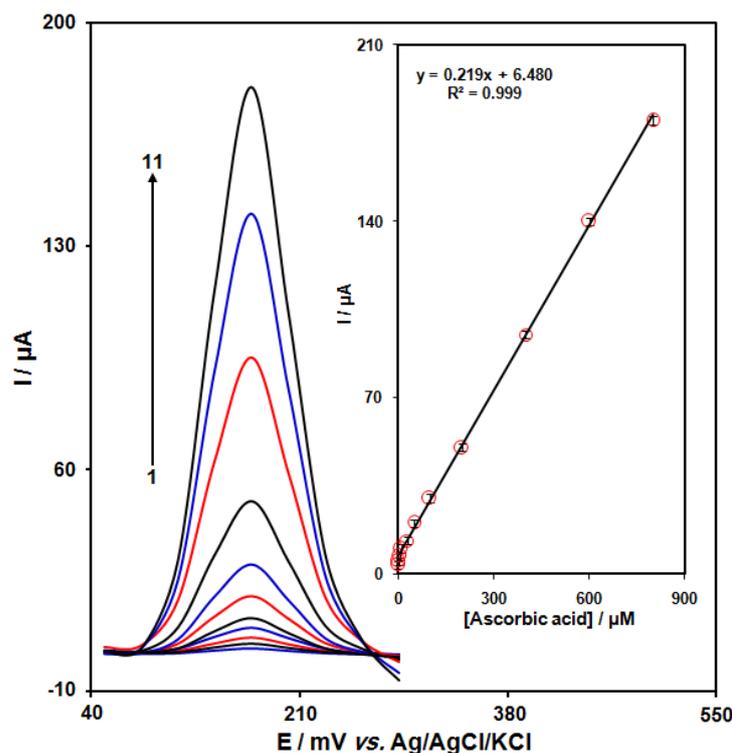


Fig. 6. SWVs of QDMCPE in 0.1 M PBS (pH 7.0) containing different concentrations of ascorbic acid. Numbers 1-11 correspond to 0.5, 2.0, 5.0, 10.0, 30.0, 50.0, 100.0, 200.0, 400.0, 600.0 and 800.0 μM of ascorbic acid. Inset: The plots of the electrocatalytic peak current as a function of ascorbic acid concentration in the range of 0.5-800.0 μM

Table 1. Comparison of the efficiency of some modified electrodes used in the determination of AA

Electrode	Method	Dynamic range(M)	Limit of detection (M)	Ref.
Carbon Paste	Voltammetry	3.0×10^{-8} - 7.0×10^{-5}	1.0×10^{-8}	[41]
Carbon Paste	Voltammetry	6.0×10^{-7} - 1.0×10^{-3}	3.0×10^{-7}	[42]
Glassy Carbon	Voltammetry	1.0×10^{-6} - 2.0×10^{-3}	4.0×10^{-7}	[43]
Glassy Carbon	Voltammetry	3.0×10^{-5} - 3.0×10^{-4}	2.01×10^{-6}	[44]
Carbon Paste	Voltammetry	5.0×10^{-7} - 8.0×10^{-4}	3.0×10^{-7}	This work

3.4. Determination of ascorbic acid in ascorbic acid injection and urine samples

In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of ascorbic acid in ascorbic acid injection and urine samples. The results for determination of the ascorbic acid in real samples are given in table 2. Satisfactory recovery of the experimental results was found for ascorbic acid. The reproducibility of the method was demonstrated by the mean relative standard deviation (R.S.D.).

Table 2. The application of QDMCPE for determination of ascorbic acid in some real samples (n=5). All concentrations are in μM

Sample	Spiked	Found	Recovery	R.S.D.
Ascorbic acid injection	0	15.0	-	3.2
	2.5	17.7	101.1	1.7
	5.0	19.5	97.5	2.8
	7.5	23.3	103.6	2.2
	10.0	24.8	99.2	2.9
Urine	0	ND	-	-
	5.0	4.9	98.0	1.7
	10.0	10.3	103.0	2.3
	15.0	14.9	99.3	3.4
	20.0	20.3	101.5	2.9

4. CONCLUSION

In this paper a carbon paste electrode modified with CdTe quantum dots was fabricated and used for the investigation of the electrochemical behaviors of ascorbic acid. Also, the modified electrode was also examined as a selective, simple, and precise new electrochemical sensor for the determination of ascorbic acid in real samples.

REFERENCES

- [1] C. B. Jacobs, M. J. Peairs, and B. J. Venton, *Anal. Chim. Acta* 662 (2010) 105.
- [2] J. Zhao, J. Jin, C. Wu, H. Jiang, Y. Zhou, J. Zuo, and X. Wang, *Analyst* 135 (2010) 2965.
- [3] G. Li, D. Zhang, S. Wang, and Y.Y. Duan, *Sens. Actuators B* 237 (2016) 167.

- [4] S. Esfandiari Baghbmidi, H. Beitollahi, and S. Tajik, *Anal. Bioanal. Electrochem.* 6 (2014) 634.
- [5] H. Beitollahi, and F. Garkani Nejad, *Electroanalysis*, DOI: 10.1002/elan.201600143
- [6] Sh. Jahani, and H. Beitollahi, *Electroanalysis*, DOI: 10.1002/elan.201501136.
- [7] M.C. Teixeira, E.F.L. Tavares, A.A. Saczk, L.L. Okumura, M. Graças Cardoso, Z.M. Magriotis, and M.F. Oliveira, *Food Chem.* 154 (2014) 38.
- [8] H. Beitollahi, S. Ghofrani Ivani, and M. Torkzadeh-Mahani, *Mater. Sci. Engin. C* 69 (2016) 128.
- [9] V. V. Tkach, S. C. de Oliveira, F. J. Anaissi, R. Ojani, V. S. Neves, M. O. Galeano Espínola, and P. I. Yagodynets, *Anal. Bioanal. Electrochem.* 8 (2016) 557.
- [10] H. Beitollahi, H. Karimi-Maleh, and H. Khabazzadeh, *Anal. Chem.* 80 (2008) 9848.
- [11] H. Beitollahi, S. Tajik, and Sh. Jahani, *Electroanalysis* 28 (2016) 1093.
- [12] O. Fazlollahzadeh, A. Rouhollahi, and M. Hadi, *Anal. Bioanal. Electrochem.* 8 (2016) 566.
- [13] H. Beitollahi, F. Ebadinejad, F. Shojaie, and M. Torkzadeh-Mahani, *Anal. Methods* (2016).
- [14] S. Tajik, M. A. Taher, and H. Beitollahi, *Sens. Actuators B* 188 (2013) 923.
- [15] F. Faridbod, M. R. Ganjali, B. Larijani, and P. Norouzi, *Electrochim. Acta* 55 (2009) 234.
- [16] H. Beitollahi, and M. Mostafavi, *Electroanalysis* 26 (2014) 1090.
- [17] K. K. Aswini, A. M. Vinu Mohan, and V. M. Biju, *Mater. Sci. Eng. C* 37 (2014) 321.
- [18] H. Beitollahi, and S. Mohammadi, *Mater. Sci. Eng. C* 33 (2013) 3214.
- [19] K. Zhang, G. Song, Y. Li, X. Wu, K. Li, and B. Ye, *Sens. Actuators B* 191 (2014) 673.
- [20] H. Mahmoudi Moghaddam, H. Beitollahi, S. Tajik, and H. Soltani, *Electroanalysis* 27 (2015) 2620.
- [21] H. M. A. Shawish, N. Abu Ghalwa, M. Hamada, and A. H. Basheer, *Mater. Sci. Eng. C* 32 (2012) 140.
- [22] H. Beitollahi, and S. Nekooei, *Electroanalysis* 28 (2016) 645.
- [23] S. Tajik, M. A. Taher, and H. Beitollahi, *Electroanalysis* 26 (2014) 806.
- [24] A. Afkhami, F. Soltani-Felehgari, T. Madrakian, and H. Ghaedi, *Biosens. Bioelectron.* 51 (2014) 379.
- [25] H. Beitollahi, and I. Sheikhshoae, *Mater. Sci. Eng. C* 32 (2012) 375.
- [26] E. Molaakbari, A. Mostafavi, and H. Beitollahi, *Mater. Sci. Eng. C* 36 (2014) 168.
- [27] G. Chen, X. Hao, B. L. Li, H. Q. Luo, and N. B. Li, *Sens. Actuators B* 237 (2016) 570.
- [28] H. Beitollahi, A. Gholami, and M. R. Ganjali, *Mater. Sci. Engin. C* 57 (2015) 107.
- [29] E. Molaakbari, A. Mostafavi, H. Beitollahi and R. Alizadeh, *Analyst*, 139 (2014) 4356.
- [30] H. Beitollahi, M. Hamzavi, M. Torkzadeh-Mahani, M. Shanesaz, and H. Karimi Maleh, *Electroanalysis* 27 (2015) 524.

- [31] H. Zhou, S. Chen, N. Gan, T. Li, Y. Cao, and Q. Jiang, *Electroanalysis* 25 (2013) 2384.
- [32] L. Givalou, M. Antoniadou, D. Perganti, M. Giannouri, C. Karagianni, A. G. Kontos, and P. Falaras, *Electrochim. Acta* 210 (2016) 630.
- [33] B. B. Prasad, A. Prasad, and M. P. Tiwari, *Talanta* 109 (2013) 52.
- [34] G. Burini, *J. Chromatogr.* 1154 (2007) 97.
- [35] H. Beitollahi, M. Mazloun Ardakani, H. Naeimi, and B. Ganjipour, *J. Solid State Electrochem.* 13 (2009) 353.
- [36] C. Guo, Q. Jin, Y. Wang, B. Ding, Y. Li, J. Huo, and X. Zhao, *Sens. Actuators B* 234 (2016) 184.
- [37] H. Beitollahi, A. Mohadesi, M. Mostafavi, H. Karimi-Maleh, M. Baghayeri, and A. Akbari, *Ionics* 20 (2014) 729.
- [38] I. Pandey, and S. S. Jha, *Electrochim. Acta* 182 (2015) 917.
- [39] M. Lavanya, Y. V. M. Reddy, S. Kiranmai, M. Venu and G. Madhavi, *Anal. Bioanal. Electrochem.*, 7 (2015) 555.
- [40] A. J. Bard, and L. R. Faulkner, *Electrochemical Methods Fundamentals and Applications*, second edition, Wiley, New York, (2001).
- [41] A. A. Ensafi, H. Karimi-Maleh, and S. Mallakpour, *Electroanalysis* 24 (2012) 666.
- [42] H. Beitollahi, and S. Mohammadi, *Chin. J. Catal.* 34 (2013) 1098
- [43] A. A. Ensafi, B. Rezaei, S. Z. Mirahmadi Zare, and M. Taei, *Sens. Actuators B* 150 (2010) 321.
- [44] P. Kalimuthu, and S. A. John, *Talanta* 80 (2010) 1686.