Original scientific paper

A novel dopamine electrochemical sensor based on La^{3+}/ZnO nanoflower modified graphite screen printed electrode

Somayeh Tajik[1,2,✉], Hadi Beitollahi[3], Mohammad Reza Aflatoonian[2,4]

^{1}Bam University of Medical Sciences, Bam, Iran
^{2}Research Center for Tropical and Infectious Diseases, Kerman University of Medical Sciences, Kerman, Iran
^{3}Environment Department, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran
^{4}Leishmaniasis Research Center, Kerman University of Medical Sciences, Kerman, Iran

Corresponding author: ✉mmtajik_s1365@yahoo.com

Abstract

Flower-like La^{3+}/ZnO nanocomposite was facile synthesized. A simple and ultrasensitive sensor based on graphite screen printed electrode (SPE) modified by La^{3+}/ZnO nanoflower was developed for the electrochemical determination of dopamine. The electrochemical behavior of dopamine was studied in 0.1 M phosphate buffer solution (PBS) using cyclic voltammetry (CV), chronoamperometry (CA) and differential pulse voltammetry (DPV). Compared with the unmodified graphite screen printed electrode, the modified electrode facilitates the electron transfer of dopamine, since it notably increases the oxidation peak current of dopamine. Also, according to CV results the maximum oxidation of dopamine on La^{3+}/ZnO/SPE occurs at 150 mV which is about 140 mV more negative compared with unmodified SPE. Under optimized conditions, the modified electrode exhibited a linear response over the concentration range from 0.15 to 300.0 μM, with a detection limit of 0.08 μM (S/N = 3). The proposed sensor exhibited a high sensitivity, good stability and was successfully applied for dopamine determination in dopamine ampoule, with high recovery.

Keywords

Dopamine; sensor; graphite screen printed electrode; La^{3+}/ZnO nanoflower

Introduction

Dopamine (3,4-dihydroxyphenyl ethylamine), as an excitatory neurotransmitter in mammalian central nervous systems [1], plays an important role in several physiological activity such as mood, attitude and movement [2]. Abnormal levels of dopamine may lead to neurological diseases, such

as Parkinson's disease and schizophrenia [3-5]. Hence, sensitive and selective detection of dopamine is of great importance for the understanding and diagnostics of neurological diseases. Significant effort has been applied to develop procedures for detection of dopamine, making use of chemiluminescence [6], fluorimetry [7], electrophoresis [8], colorimetry [9], high performance liquid chromatography [10], and electrochemical techniques [11]. As compared to other analytical methods, the electrochemical techniques employing a three electrode system have drawn a considerable attention because of the electroactive nature of dopamine, high selectivity, high sensitivity, low cost, reproducibility, simplicity and short operational duration [12-16].

Screen-printed electrodes (SPEs), which are fabricated by printing several types of inks on a specific substrate have been considered superior. Such SPEs have been recently employed as diagnostic tools for food poisoning, diseases, and environmental pollutants [17-21].

Nowadays, the nanomaterials have been attracted much attention to modify the surface of electrodes for electrochemical detection of target analytes. Thus, modified electrode surfaces offer high effective surface-to-volume ratio, possess a unique ability to enhance the electron transfer between redox centres in the analyte and electrode surfaces, provide a decrease of the overpotential of many analytes with respect to unmodified electrodes and show high catalytic efficiency [22-39]. ZnO is considered as one of the most important and functional metal oxide semiconductor material, due to its various fascinating properties and high technological applications. Because of several interesting properties such as wide band gap (3.37 eV), large exciton binding energy (60 MeV) at room-temperature (larger than several other important semiconductors such as GaN and ZnSe), thermal and mechanical stabilities, piezoelectric and pyroelectric properties, electrochemical and optoelectronic properties, biocompatibility, *etc.* [40-44]. Due to various interesting properties, ZnO is widely used for variety of applications. Therefore, the excellent properties and wide applications variety of ZnO nanomaterials such as nanorods, nanowires, nanobelts, nanoflowers, nanodisks, nanosheets, nanospirals, nanotubes and so on were prepared via several techniques and reported in the literature [40,45].

According to the previous points, it is important to create suitable conditions for analysis of dopamine in biological fluids. In this study, La^{3+}/ZnO nanoflowers were used to improve the sensitivity of sensors for voltammetric determination of dopamine. The proposed sensor showed good electrocatalytic and accumulative effect on dopamine. In addition, the analytical performance of the suggested sensor for dopamine determination in real samples was evaluated.

Experimental

Chemicals and apparatus

An Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was employed to perform the electrochemical experiments and the system was controlled using a general purpose electrochemical system software.

The screen-printed electrode (DropSens, DRP-110, Spain) consists of three conventional electrodes: graphite counter electrode, Ag/AgCl/KCl reference electrode and unmodified graphite working electrode. pH was measured by a Metrohm 710 pH meter.

Dopamine and all other reagents were of analytical grade, and purchased from Merck (Darmstadt, Germany). For the preparation of buffers, orthophosphoric acid and its salts were used to provide the pH range of 2.0–9.0.

Preparation of La³⁺-doped ZnO nanoflowers

All the chemicals used for the preparation of nano-powders, namely zinc acetate $(Zn(CH_3COO)_2 \times 2H_2O)$, lanthanum nitrate $(La(NO_3)_3 \times 6H_2O)$, thiourea $((NH_2)_2CS)$ and ammonia $(25\% NH_3)$, were of analytical grade. All the precursors were dissolved in deionized water. During the preparation of nano-powders, ammonia was used as a complexing agent. ZnO nanostructures were prepared by dissolving 0.46 mol of zinc acetate in 80 mL of deionized water, 0.0046 mol of lanthanium nitrate in 80 mL of deionized water, 0.18 mol of thiourea in 80 mL of deionised water and lastly by adding 19.76 mL of ammonia in 80 mL of deionised water. The amount of solutions of zinc acetate, thiourea and ammonia was held constant at a ratio of 1:1:1. Then the zinc acetate solution was added in a beaker in the reaction bath, followed by adding thiourea and lanthanium nitrate solution in the same reaction bath and the mixture was stirred for a few seconds. Lastly ammonia solution was added slowly into the mixture, while continuing stirring for 5 min. The temperature of the bath was then allowed to increase up to 80 °C. After that, the precipitates were formed, left overnight and filtered thereafter. The precipitates were then washed with ethanol. The obtained powders were dried at ambient conditions for several days.

Preparation of the electrode

The bare graphite screen printed electrode was coated with La³⁺/ZnO nanoflower composite according to the following simple procedure: 1 mg La³⁺/ZnO nanoflower was dispersed in 1 mL aqueous solution within 45 min ultrasonication. Then, 5 µl of the prepared suspension was dropped on the surface of carbon working electrode and left to dry at room temperature.

Preparation of real samples

One milliliter of a dopamine ampoule (Caspian Tamin Company, Iran, containing 200 mg in 5 ml of dopamine hydrochloride) was diluted to 10 mL with 0.1 M PBS (pH 7.0) and then, different volumes of the diluted solution were transferred into each of a series of 25 mL volumetric flasks and diluted to the mark with PBS. The dopamine content was analyzed by the proposed method using the standard addition method.

Result and Discussion

Electrochemical profile of dopamine on La³⁺/ZnO/SPE

Since the electrochemical behaviour of dopamine is pH-dependent, it is necessary to obtain the optimized pH value in order to achieve the accurate results. Experiments performed by use of the modified electrode at various pH values ranging from 2.0–9.0, revealed that the best results for electrooxidation of dopamine are obtained at pH 7.0. The cyclic voltammograms measured in 0.1 M PBS (pH 7.0) containing 60.0 µM dopamine, using La³⁺/ZnO/SPE and bare SPE are shown in Figure 1. According to CV results, the maximum oxidation of dopamine on La³⁺/ZnO/SPE occurs at 150 mV which is about 140 mV more negative compared with unmodified SPE.

Effect of scan rate on the results

According to Figure 2, increase of the potential scan rate leads to enhanced oxidation peak current values (I_p). In addition, there is a linear relationship between I_p and the square root of the potential scan rate ($v^{1/2}$) which demonstrates that the oxidation and reduction of dopamine is diffusion controlled.
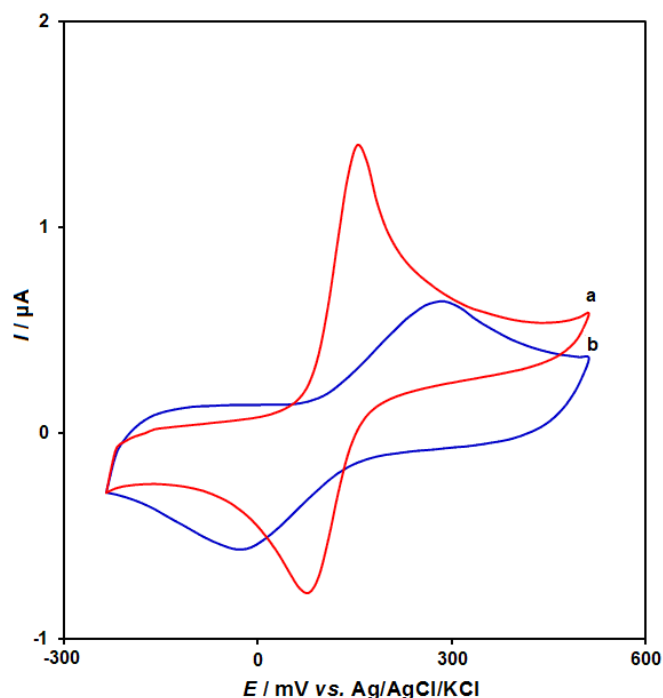
Fig. 1. *Cyclic voltammograms of (a) La³⁺/ZnO/SPE and (b) bare SPE in 0.1 M PBS (pH 7.0) in the presence of 60.0 µM dopamine at the scan rate 50.0 mVs⁻¹.*
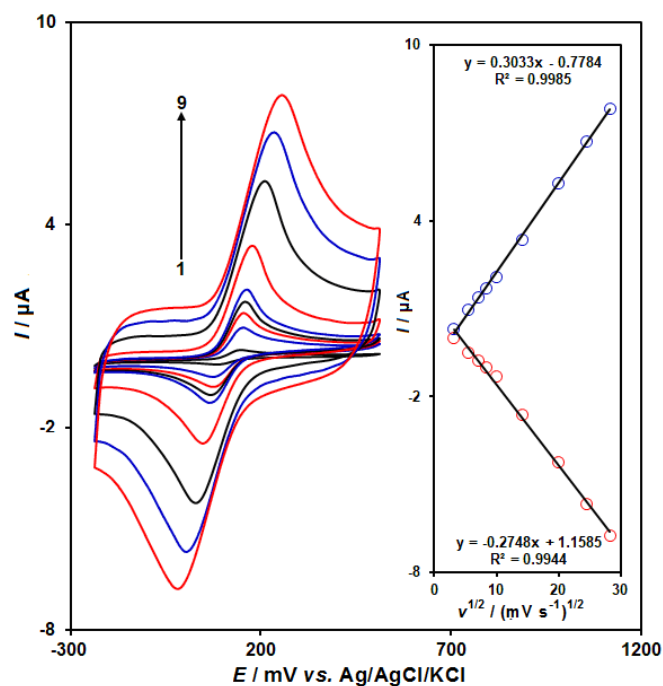
Fig. 2. *Cyclic voltammograms of La³⁺/ZnO/SPE in 0.1 M PBS (pH 7.0) containing 60.0 µM dopamine at various scan rates; numbers 1-9 correspond to 10, 30, 50, 70, 100, 200, 400, 600 and 800 mV s⁻¹. Inset: variation of anodic and cathodic peak currents vs. v¹ᐟ².*

Chronoamperometric (CA) analysis

The analysis of CA for dopamine samples was performed by use of La³⁺/ZnO/SPE vs. Ag/AgCl/KCl (3.0 M) at 0.2 V. CA results for different concentrations of dopamine in PBS (pH 7.0) are demonstrated in Figure 3. The Cottrell equation for CA analysis of electroactive moieties under mass transfer limited conditions is as follow [46]:

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

where D represents the diffusion coefficient, cm^2 s^{-1}, and c_b is the bulk concentration of analyte, mol cm^{-3}. Experimental results of I vs. $t^{-1/2}$ are plotted in Figure 3A, with the best fits for different concentrations of dopamine. The resulted slopes corresponding to straight lines in Fig. 3A were then plotted against the concentration of dopamine (Figure 3B). The mean value of D was determined to be 1.15×10^{-6} cm^2 s^{-1} according to the resulting slope and Cottrell equation.
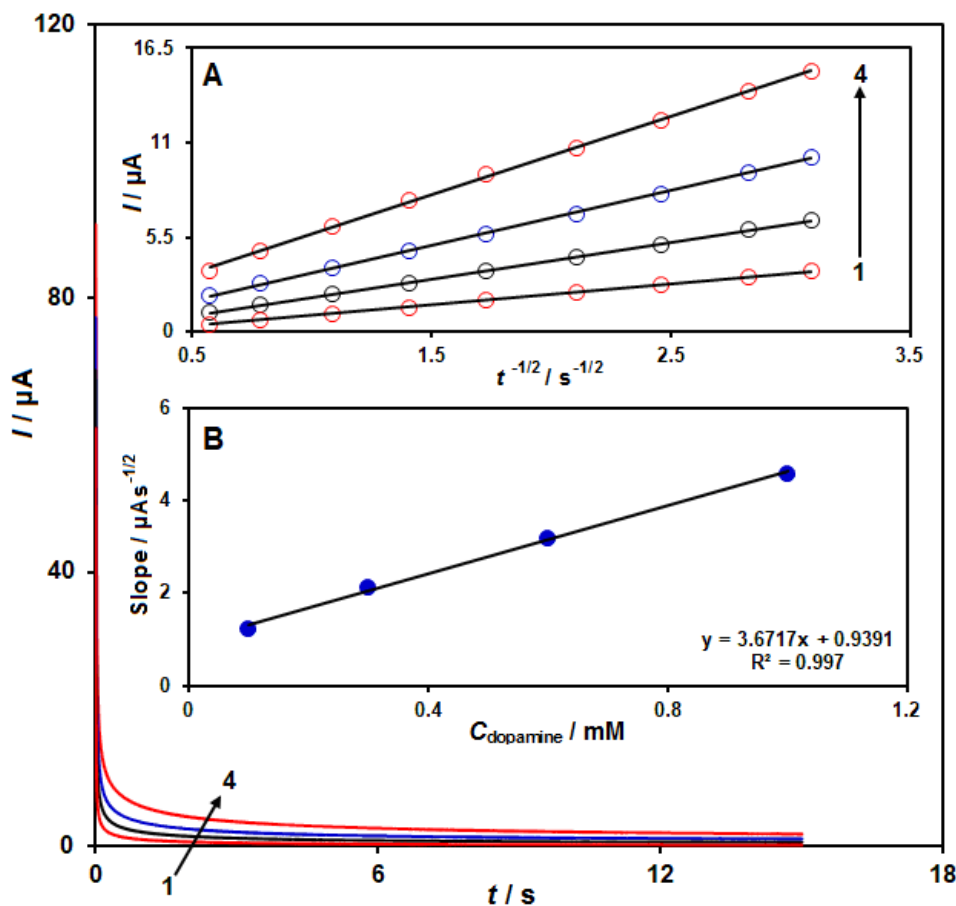

Fig. 3. *Chronoamperograms obtained at La^{3+}/ZnO/SPE in 0.1 M PBS (pH 7.0) for different concentrations of dopamine. The numbers 1–4 correspond to 0.1, 0.3, 0.6, and 1.0 mM of dopamine. Insets:*
(A) Plots of I *vs.* t$^{-1/2}$ *obtained from chronoamperograms 1–4.*
(B) Plot of slopes of-straight lines against dopamine concentration.

Calibration curves

Based on the resulting peak currents of dopamine by use of La^{3+}/ZnO/SPE, the quantitative analysis of dopamine was done in 0.1 M PBS (pH 7.0) (Figure 4). The modified electrode (La^{3+}/ZnO/SPE) as a working electrode in the range of dopamine concentration in 0.1 M PBS was used in differential pulse voltammetry (DPV) due to the advantages of DPV including the improved sensitivity and better performance in analytical applications. According to the results, a linear relationship exists between the peak currents and concentrations of dopamine within the concentration range of 0.15 to 300.0 μM with the correlation coefficient of 0.9992. The detection limit was obtained as 0.08 μM. Table 1. shows a comparison of the analytical figures of merit of the proposed method with some other modified electrodes for the determination of dopamine.
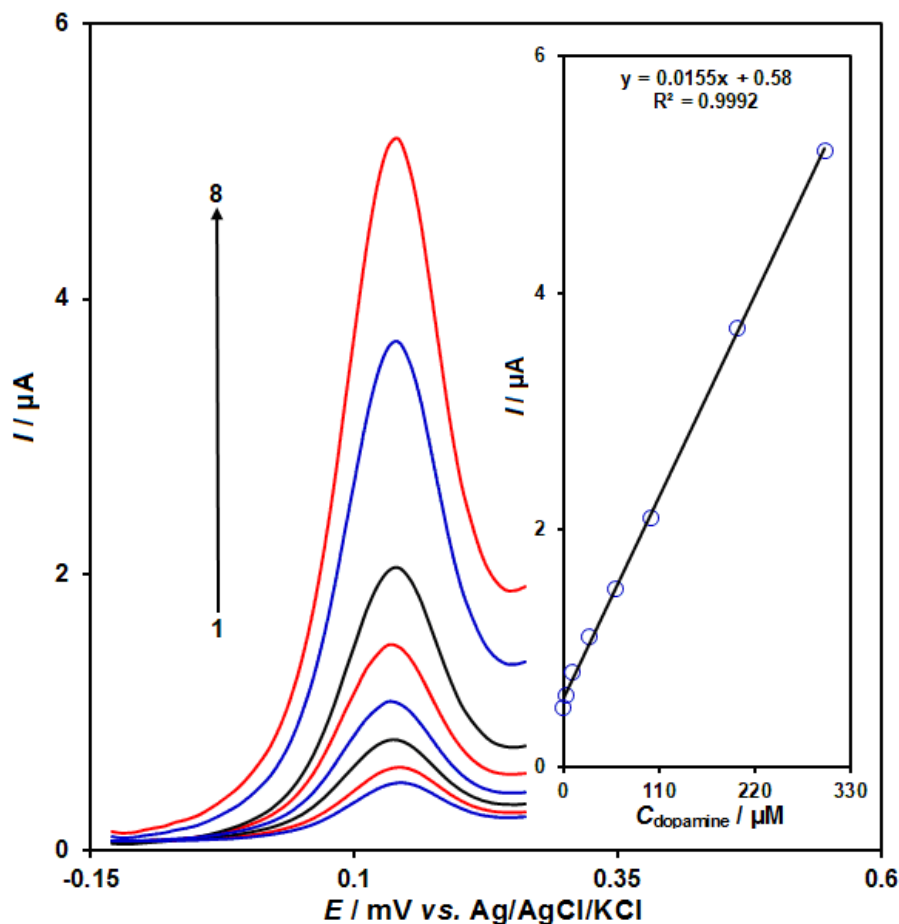
Fig. 4. *DPVs of La^{3+}/ZnO/SPE in 0.1 M (pH 7.0) containing different concentrations of dopamine. Numbers 1–8 correspond to 0.15, 2.5, 10.0, 30.0, 60.0, 100.0, 200.0 and 300.0 µM of dopamine. Inset: Plot of peak current as a function of dopamine concentration in the range of 0.15-300.0 µM.*

Table 1. *Comparison of the efficiency of some modified electrodes used in the electro-oxidation of dopamine*

Electrode	Modifier	method	LOD, M	LDR, M	Ref.
Glassy carbon	Carbon nanohorns/poly(glycine)	Voltammetry	3.0×10^{-8}	1.0×10^{-6} – 2.8×10^{-4}	47
Carbon fiber	Reduced graphene oxide	Voltammetry	7.7×10^{-7}	1.4×10^{-6} – 2.24×10^{-4}	48
Glassy carbon	l-tyrosine (l-Tyr) covalently functionalized graphene oxide (GO) composite	Voltammetry	2.8×10^{-7}	1.0×10^{-6} – 5.0×10^{-4}	49
Glassy carbon	Graphene quantum dots	Voltammetry	1.15×10^{-7}	1.0×10^{-6} – 1.5×10^{-4}	50
Graphite screen printed	La^{3+}/ZnO nanoflower	Voltammetry	8.0×10^{-8}	1.5×10^{-7} – 3.0×10^{-4}	This work

Interference study

The influence of various substances as compounds potentially interfering with the determination of dopamine was studied in the presence of 75.0 µM dopamine. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than ±5 % in the determination of dopamine. According to the results, uric acid, L-serine, L-phenylalanine, ethanol, benzoic acid, isoproterenol, methanol, serotonin, L-asparagine, acetaminophen, NADH, saccharose, urea, glucose, L-lysine, L-glycine, carbidopa, caffeine, levodopa, fructose, L-threonine, lactose, L-histidine, L-proline, S^{2-}, Mg^{2+}, SO_4^{2-}, NH_4^+, F^- and Al^{3+} did not show interference in the determination of dopamine.

Analysis of real samples

The applicability of this modified electrode in the determination of real samples was assessed through the determination of dopamine in dopamine ampoule using the described method. In order to perform this analysis, standard addition method was employed, and the results are listed in Table 2. Accordingly, the results of dopamine recovery are satisfactory, and the reproducibility of the results is proved by the mean relative standard deviation (R.S.D.).

Table 2. *Application of La^{3+}/ZnO/SPE for determination of dopamine in dopamine ampoule (n=5)*

c / μM (spiked)	c / μM (found)	Recovery, %	RSD, %
0	5.0	-	3.2
2.5	7.4	98.6	1.8
7.5	12.7	101.6	2.5
12.5	17.9	102.3	2.8
17.5	22.3	99.1	3.1

The repeatability and stability of La^{3+}/ZnO/SPE

The long-term stability of the La^{3+}/ZnO/SPE was evaluated over 3-week period. After the modified electrode was stored for 3 weeks in atmosphere at room temperature, the experiments were performed again. According to cyclic voltammograms, the peak potential for dopamine oxidation remained unchanged and a decrement of less than 2.5 % compared with initial response was observed.

The antifouling properties of the modified electrode towards dopamine oxidation and its oxidation products were studied by recording CVs. Voltammograms were recorded in the presence of dopamine after cycling the potential 17 times at a scan rate of 50 mV s^{-1}. Results demonstrated that peak potentials remained unchanged and the currents decreased by less than 2.4 %. According to the results, application of modified La^{3+}/ZnO/SPE provided increased sensitivity and decreased fouling effect of the analyte and its oxidation product.

Conclusions

In this work, we prepared La^{3+}/ZnO nanocomposite-modified graphite screen printed electrode, which can significantly increase the electron transfer rate, electrocatalytic performance and efficiency of dopamine detection. The modified electrode showed the linear range of 0.15 to 300.0 μM with the detection limit of 0.08 μM towards dopamine detection. Furthermore, this modified electrode was further used for detection of dopamine content in dopamine ampoule and good recoveries were found.

References

[1]   M. Cheng, X. Zhang, M. Wang, H. Huang, J. Ma, *Journal of Electroanalytical Chemistry* **786** (2017) 1-7.
[2]   H. R. Zare-Mehrjardi, *Iranian Chemical Communication* **6** (2018) 56-70.
[3]   E. Molaakbari, A. Mostafavi, H. Beitollahi, *Sensors and Actuators: B* **208** (2015) 195-203.
[4]   D. Chen, C. Tian, X. Li, Z. Li, Z. Han, C. Zhai, Y. Quan, R. Cui, G. Zhang, *Microchimica Acta* **185** (2018) 98-104.
[5]   Z. Wang, H. Guo, R. Gui, H. Jin, J. Xia, F. Zhang, *Sensors and Actuators: B* **255** (2018) 2069-2077.
[6]   M. Amjadi, J.L. Manzoori, T. Hallaj, M.H. Sorouraddin, *Microchimica Acta* **181** (2014) 671-677.
[7]   T. Pérez-Ruiz, C. M. Lozano, V. Tomás, E. Ruiz, *Microchimica Acta* **158** (2007) 299-305.
[8]   H. Fang, M. L. Pajski, A. E. Ross, B. J. Venton, *Analytical Methods* **5** (2013) 2704-2711.
[9]   Y. Lin, C. Chen, C. Wang, F. Pu, J. Ren, X. Qu, *Chemical Communications* **47** (2011) 1181-1183.
[10] M. Karimi, J. L. Carl, S. Loftin, J. S. Perlmutter, *Journal of Chromatography B* **836** (2006) 120-123.

[11]   M. R.Ganjali, H. Beitollahi, R. Zaimbashi, S. Tajik, M. Rezapour, B. Larijani, *International Journal of Electrochemical Science*, **13** (2018) 2519-2529.

[12]   S. E. Baghbamidi, H. Beitollahi, S. Tajik, *Analytical and Bioanalytical Electrochemistry 6* (2014) 634-645.

[13]   S. Zeinali, H. Khoshsafar, M. Rezaei, H. Bagheri, *Analytical and Bioanalytical Chemistry Research* **5** (2018) 195-204.

[14]   M. M. Foroughi, H. Beitollahi, S. Tajik, A. Akbari, R. Hosseinzadeh, *International Journal of Electro-chemical Science* **9** (2014) 8407-8421.

[15]   D. Wang, F. Xu, J. Hu, M. Lin, *Materials Science and Engineering:* C **71** (2017) 1086-1089.

[16]   H. Beitollai, F. Garkani-Nejad, S. Tajik, Sh. Jahani, P. Biparva, *International Journal of Nano Dimension* **8** (2017) 197-205.

[17]   S. Ershad, N. Safarzadeh, H. Akhondi-Yamchi, *Iranian Chemical Communication* **4** (2016) 256-264.

[18]   H. Beitollahi, S. Tajik, *Environmental Monitoring and Assessment* **187**(2015) 257.

[19]   M. Baniasadi, Sh. Jahani, H. Maaref, R. Alizadeh, *Analytical and Bioanalytical Electrochemistry* **9** (2017) 718-728.

[20]   S. Rana, S. K. Mittal, N. Singh, J. Singh, C. E. Banks, *Sensors and Actuators B* **239** (2017) 17-27.

[21]   F. Soofiabadi, A. Amiri, Sh. Jahani, *Analytical and Bioanalytical Electrochemistry* **9** (2017) 340-350.

[22]   Z. Lu, J. Zhang, W. Dai, X. Lin, J. Ye, *Microchimica Acta* **184** (2017) 4731-4740.

[23]   S. Tajik, M.A. Taher, Sh. Jahani, M. Shanesaz, *Analytical and Bioanalytical Electrochemistry* **8** (2016) 899-909.

[24]   H. Soltani, H. Beitollahi, A. H. Hatefi-Mehrjardi, S. Tajik, M. Torkzadeh-Mahani, *Analytical and Bioanalytical Electrochemistry* **6** (2014) 67-79.

[25]   B. Habibi, Z. Ayazi, M. Dadkhah, *Analytical and Bioanalytical Chemistry Research* **4** (2017) 155-169.

[26]   A. Jirasirichote, E. Punrat, A. Suea-Ngam, O. Chailapakul, S. Chuanuwatanakul, *Talanta* **175** (2017) 331-337.

[27]   Y. Zhu, W. Choon, A. Koh, Y. B. Shim, *Electroanalysis* **22** (2010) 2908-2914.

[28]   S. E. Baghbamidi, H. Beitollahi, S. Tajik, R. Hosseinzadeh, *International Journal of Electrochemical Science* **11** (2016) 10874-10883.

[29]   A. S. Afonso, C. V. Uliana, D. H. Martucci, R. C. Faria, *Talanta* **146** (2016) 381-387.

[30]   M. M. Motaghi, H. Beitollahi, S. Tajik, R. Hosseinzadeh, *International Journal of Electrochemical Science* **11** (2016)7849-7860.

[31]   M. R. Ganjali, H. Beitollahi, R. Zaimbashi, S. Tajik, M. Rezapour, B. Larijani, *International Journal of Electrochemical Science* **13** (2018) 2519-2529.

[32]   M. Khairy, A. A. Khorshed, F. A. Rashwan, G. A. Salah, H. M. Abdel-Wadood, C. E. Banks, *Sensors and Actuators B* **252** (2017) 1045-1054.

[33]   H. Beitollahi, H. Karimi-Maleh, H. Khabazzadeh, *Analytical Chemistry* **80** (2008) 9848-9851.

[34]   Y. Li, X. Zhai, X. Liu, L. Wang, H. Liu, H. Wang, *Talanta* **148** (2016) 362-369.

[35]   H. Beitollahi, Z. Dourandish, S. Tajik, M. R. Ganjali, P. Norouzi, F. Faridbod, *Journal of Rare Earths*, **36** (2018) 750-757.

[36]   M. R. Ganjali, Z. Dourandish, H. Beitollahi, S. Tajik, L. Hajiaghababaei, B. Larijani, *International Journal of Electrochemical Science* **13** (2018) 2448-2461.

[37]   M. Devaraj, R. Saravanan, R. Deivasigamani, V. K. Gupta, F. Gracia, S. Jayadevan, *Journal of Molecular Liquids* **221** (2016) 930-941.

[38]   S. Tajik, M. A. Taher, H. Beitollahi, *Sensors and Actuators B* **188** (2013) 923-930.

[39]   A. Afkhami, M. Moradi, A. Bahiraei, T. Madrakian, *Analytical and Bioanalytical Chemistry Research*. **5** (2018) 41-53.

[40]   S. S. Low, H. S. Loh, J. S. Boey, P. S. Khiew, W. S. Chiu, M. T. Tan, *Biosensors and Bioelectronics* **94** (2017) 365-373.

[41]   M. Ghobadifard, M. Khelghati, E. Zamani, Q. Maleki, S. Farhadi, A. Aslani, *Iranian Chemical Communication* **3** (2015) 32-49.

[42]   B. Hosseininia, A. Anaraki-Firooz, M. Ghalkhani, J. Beheshtian, *Iranian Chemical Communication* **4** (2016) 483-492.

[43]   Y. Lin, H. Liu, Z. Hu, R. Hu, H. Ruan, L. Zhang, *International Journal of Electrochemical Science* **11** (2016) 7726-7730.

[44]   S. Suresh, P. Saravanan, K. Jayamoorthy, S.A. Kumar, S. Karthikeyan*, Materials Science and Engineering: C* **64** (2016) 286-292.

[45]   G. N. Dar, A. Umar, S. A. Zaidi, S. Baskoutas, S. H. Kim, M. Abaker, A. Al-Hajry, S. A. Al-Sayari, *Science of Advanced Materials* **3** (2011) 901-906.

[46]   A. J. Bard, L. R. Faulkner, Electrochemical Methods Fundamentals and Applications, second ed, *Wiley,* New York, (2001).

[47]   G. Zhang, P. He, W. Feng, S. Ding, J. Chen, L. Li, H. He, S. Zhang, F. Dong, *Journal of Electroanalytical Chemistry* **760** (2016) 24-31.

[48]   B. Yang, H. Wang, J. Du, Y. Fu, P. Yang, Y. Du, *Colloids and Surfaces A* **456** (2014) 146-152.

[49]   X. Wang, F. Zhang, J. Xia, Z. Wang, S. Bi, L. Xia, Y. Li, Y. Xia, L. Xia, *Journal of Electroanalytical Chemistry* **738** (2015) 203-208.

[50]   Y. Li, Y. Jiang, T. Mo, H. Zhou, Y. Li, S. Li, *Journal of Electroanalytical Chemistry* **767** (2016) 84-90.