

Full Paper

NiFe₂O₄ Nanoparticles-modified Screen Printed Electrode for Electrochemical Detection for Sudan I

Hadi Beitollahi,^{1,*} Somayeh Tajik,² Shohreh Jahani² and Fariba Gargani Najed¹

¹*Environment Department, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran*

²*NanoBioElectrochemistry Research, Center, Bam University of Medical Sciences, Bam, Iran*

*Corresponding Author, Tel.: +98 3426226613; Fax: +98 3426226617

E-Mail: h.beitollahi@yahoo.com

Received: 23 August 2017 / Received in revised form: 25 December 2017 /

Accepted: 26 December 2017 / Published online: 31 October 2018

Abstract- In this work, a sensitive Sudan I electrochemical sensor was assembled using NiFe₂O₄ nanoparticles modified screen printed electrode. Due to the synergetic effect of NiFe₂O₄ nanoparticles displayed high electrochemical activity with well-defined voltammetric peaks of Sudan I oxidation and lower overpotential compared with unmodified electrode. According to the results of differential pulse voltammetry (DPV), under optimized conditions, a good linear response was observed for the concentration of Sudan I in the range of 0.1–100.0 μM with a detection limit of 0.05 μM. The developed electrochemical sensor was successfully applied to determine Sudan I in water samples. This study indicated that NiFe₂O₄ nanoparticles based electrochemical sensor can be a promising and reliable tool for rapid analysis of Sudan I.

Keywords- Sudan I, Voltammetric Sensor, Screen Printed Electrode, Real Samples

1. INTRODUCTION

Food safety has attracted increasing public concerns in recent years because illicit chemicals are sometimes added to food products as colourants by some food and beverage manufacturers [1]. Sudan I (1-(Phenyldiazenyl)naphthalen-2-ol) is a synthetic azo-colorant which has been commonly used as a coloring agent in chemical industries and an additive in foods in daily life, particularly in those containing chilli powders, curry powders, ketchup,

olive oil, because of their intense red–orange color [2,3]. Its carcinogenic action was found in 1970s [4]. Sudan I was classified as a category 3 carcinogen by the international agency for research on cancer (IARC) [5,6]. Although, the use of Sudan I in foods is now banned in many countries, it was still found in foodstuffs as additive due to its low cost, bright color and stability, such as, poultry feed, paprika, ketchup, sausage, pie, etc. [7]. According to the above points, it is substantial to develop a sensitive, rapid and convenient method for detection and determination of Sudan I in foodstuffs.

Till date, various analytical methods have been reported for accurate determination of Sudan I, such as high performance liquid chromatography [8], gas chromatography-mass spectrometry [9], high performance liquid chromatography combined mass spectrometry [10], and capillary electrophoresis [11]. The determination of Sudan I using these techniques shows high sensitivity, but they also requires expensive instruments, time-consuming pre-treatment steps, skilled operators, large quantity of organic solvents. Moreover, these techniques cannot be used for in situ assay [12]. But, electrochemical based sensors have attracted more and more attentions on the determination of Sudan I due to the advantage of reliability, fast response, cheap instrument, low cost, simple operation, timesaving, high sensitivity, good selectivity and real-time detection in situ condition [13-24].

Screen-printed electrodes are favorable since they provide a low cost, single-shot disposable yet highly reproducible and reliable platform for electrochemical measurement of the target analyte [25-28]. Modification of electrodes is good and powerful strategy for overcoming of unmodified electrodes limitation such as poor sensitivity, low selectivity, low stability and the blockage of electron transfer [29-49]. Further, the fabrication and modification of the working electrode with nanoparticles enhances peak current, sensitivity, reproducibility [50-54].

NiFe₂O₄ nanoparticles (NiFe₂O₄ NPs) have attracted an increasing interest in construction of sensors and biosensors because of their good biocompatibility, strong super paramagnetic property, low toxicity, easy preparation and high adsorption ability. NiFe₂O₄ with an inverse spinel structure shows ferrimagnetism that originates from magnetic moment of anti-parallel spins between Fe³⁺ ions at tetrahedral sites and Ni²⁺ ions at octahedral sites. The quantitative cytotoxicity test verified that NiFe₂O₄ nanoparticles had noncytotoxicity. Moreover, NiFe₂O₄ NPs exhibit high surface area and low mass transfer resistance [55,56].

In this work, a screen printed electrode modified with the NiFe₂O₄ nanoparticles was used for sensitive voltammetric determination of Sudan I and the modified electrode exhibited excellent electrocatalytic activity to Sudan I.

2. EXPERIMENTAL

2.1. 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. Surface analysis was done using a low vacuum JSM, 6380 LV scanning electron microscope (SEM) after coating the samples with a thin layer of gold by magnetron sputtering.

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

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

2.2. Synthesis of NiFe₂O₄ nanoparticles

NiFe₂O₄ nanoparticles were synthesized in the presence of urea using a hydro/solvothermal method. Solution of urea were dissolved in 60 ml of deionized water and then 20 ml polyethylene glycol (PEG) was added to solution to form brown homogeneous solutions. Then 10 mL FeCl₃.6H₂O (16 mmol) and 10 mL NiCl₂.6H₂O (8 mmol) were added into the above solution, respectively.

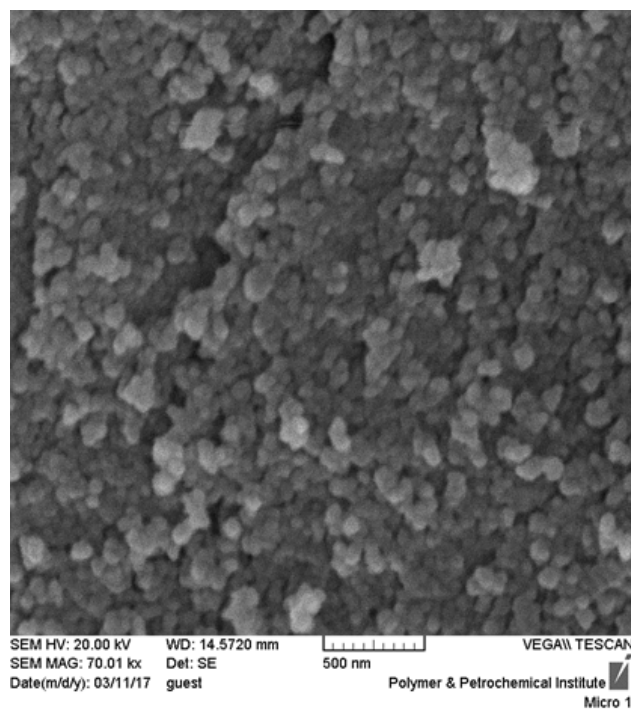


Fig. 1. SEM image of NiFe₂O₄ nanoparticles

The mixed solutions, with stoichiometric 30 molar ratio of urea/ Fe^{3+} (with excess urea that form sufficient precipitating ions for metal oxides formation), were magnetically stirred until all the starting materials were totally dissolved at 25 °C. These solutions were further homogenized in an ultrasonic water bath for 15 min and then respectively transferred into Teflon-lined stainless steel autoclave with a capacity of 200 ml in order to keep them at 200 °C for 24 h in an oven. Subsequently, the autoclaves were air cooled to room temperature. The as-obtained precipitates were centrifuged, and then washed with deionized. water and absolute ethanol for several times to remove the impurities in the products. The resulting products were dried in a vacuum oven at 100 °C for 12 h. A typical SEM of synthesized NiFe_2O_4 nanoparticles is shown in Fig. 1.

2.3. Preparation of the electrode

The bare screen-printed electrode was coated with NiFe_2O_4 according to the following simple procedure. 1 mg NiFe_2O_4 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 electrodes. It remains at room temperature until becomes dry.

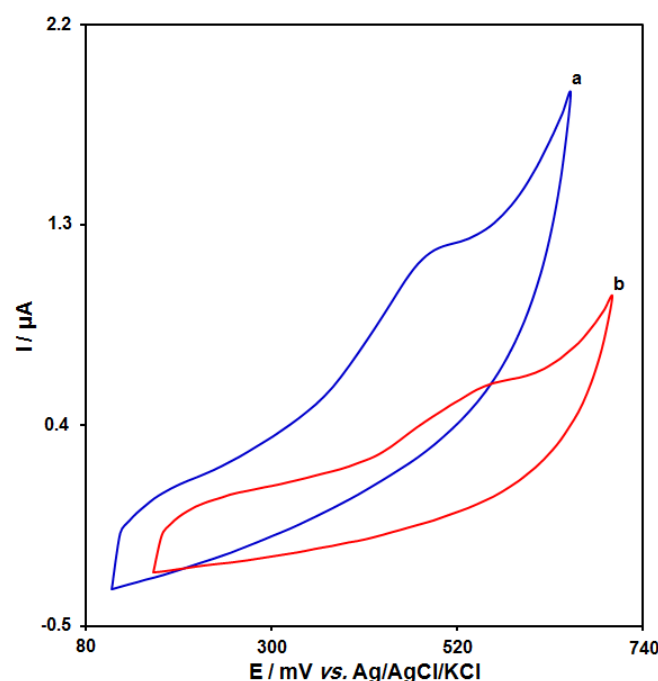


Fig. 2. Cyclic voltammograms of (a) $\text{NiFe}_2\text{O}_4/\text{SPE}$ and (b) bare SPE in 0.1 M PBS (pH 7.0) in the presence of 50.0 μM at the scan rate 50 mVs^{-1}

3. RESULT AND DISCUSSION

3.2. Electrochemical profile of the Sudan I on the NiFe₂O₄/SPE

To study the electrochemical behaviour of Sudan I which is pH-dependent, it is necessary to obtain the optimized pH value in order to achieve the accurate results. By performing the experiments by use of modified electrodes at various pH values ranging from 2.0–9.0, it was revealed that the best results for electro-oxidation of Sudan I occur at pH=7.0. The obtained cyclic voltammograms in the presence of 50.0 μM Sudan I using the NiFe₂O₄/SPE (Curve a) and bare SPE (Curve b) are shown in Fig. 2. According to CV results the maximum oxidation of Sudan I on the NiFe₂O₄/SPE occurs at 500 mV which is about 80 mV more negative compared with unmodified SPE.

3.2. Effect of scan rate on the results

Increasing in scan rate leads to enhanced oxidation peak current according to the obtained results from the study of the effect of potential scan rates on the oxidation currents of Sudan I, Fig. 3. In addition, there is a linear relationship between I_p and the square root of the potential scan rate ($v^{1/2}$) that demonstrates that the oxidation procedure of analyst is in control of diffusion.

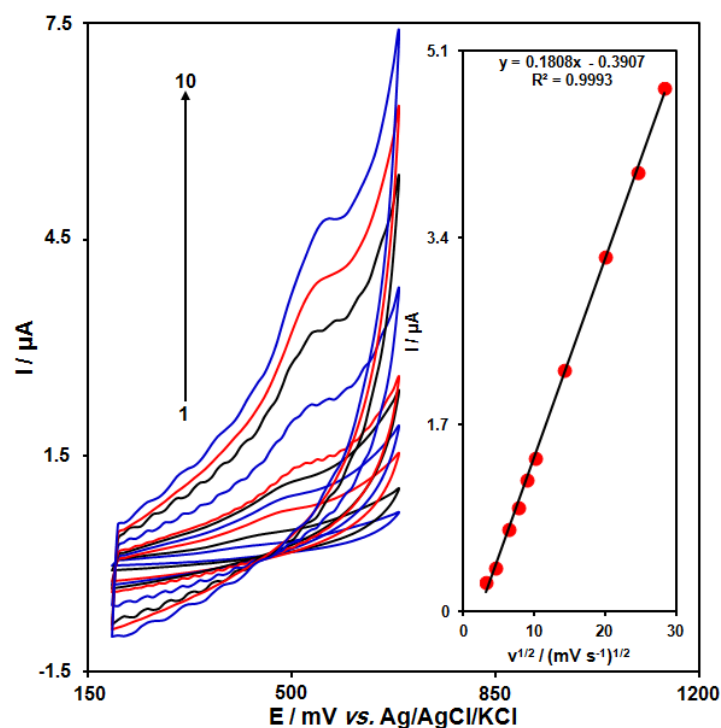


Fig. 3. Cyclic voltammograms of NiFe₂O₄/SPE in 0.1 M PBS (pH 7.0) containing 300.0 μM Sudan I at various scan rates; numbers 1-10 correspond to 10, 20, 40, 60, 80, 100, 200, 400, 600 and 800 mV s^{-1} , respectively. Inset: variation of anodic peak current vs. $v^{1/2}$

3.3. Chronoamperometric analysis

The analysis of chronoamperometry for Sudan I samples was performed by use of NiFe₂O₄/SPE vs. Ag/AgCl/KCl (3.0 M) at 0.6 V. The Chronoamperometric results of different concentration of Sudan I sample in PBS (pH 7.0) are demonstrated in Fig. 4. The Cottrell equation for chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is as follow [57]:

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

Where D represents the diffusion coefficient (cm² s⁻¹), and C_b is the applied bulk concentration (mol cm⁻³). Experimental results of I vs. t^{-1/2} were plotted in Fig. 4A, with the best fits for different concentrations of Sudan I. The resulted slopes corresponding to straight lines in Fig. 4A, were then plotted against the concentration of Sudan I (Fig. 4B). The mean value of D was determined to be 1.14×10⁻⁵ cm²/s according to the resulting slope and Cottrell equation.

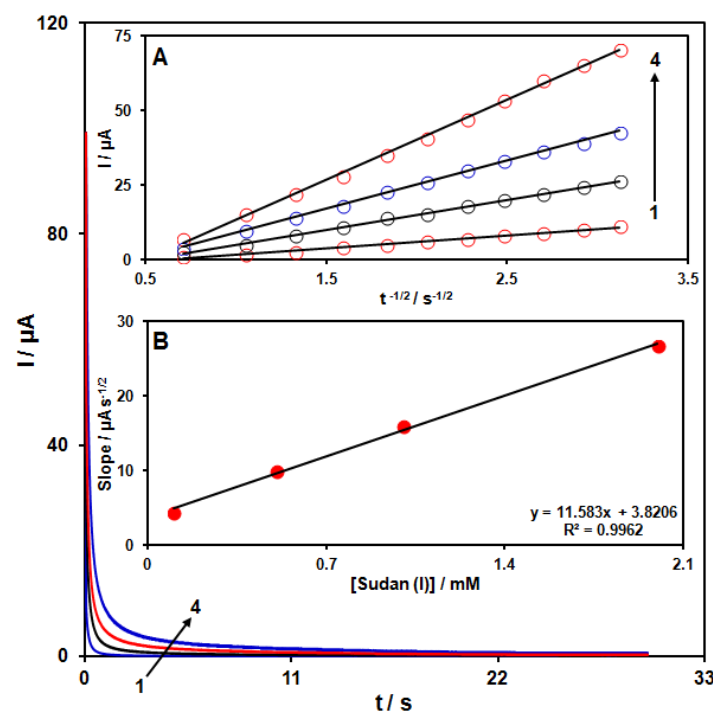


Fig. 4. Chronoamperograms obtained at NiFe₂O₄/SPE in 0.1 M PBS (pH 7.0) for different concentration of Sudan I. The numbers 1–4 correspond to 0.1, 0.5, 1.0, and 2.0 mM of Sudan I. Insets: (A) Plots of I vs. t^{-1/2} obtained from chronoamperograms 1–4. (B) Plot of the slope of the straight lines against Sudan I concentration

3.4. Calibration curves

Based on the resulting peak currents of Sudan I by use of NiFe₂O₄/SPE, the quantitative analysis of Sudan I was done in water solutions. The modified electrode (NiFe₂O₄/SPE) as working electrode in the range of Sudan I 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 (Fig. 5). (Initial potential=0.26 V, End potential=0.61 V, Step potential=0.002 V, Modulation Amplitude=0.02505 V) According to the results, a linear relationship exists between the peak currents and concentrations of Sudan I within the concentration range of 0.1-100.0 μM with the correlation coefficient of 0.9987. The detection limit was obtained 0.05 μM. Table 1. shows a comparison of the analytical figures of merit of the proposed electrochemical method with different reported modifier for the determination of Sudan I.

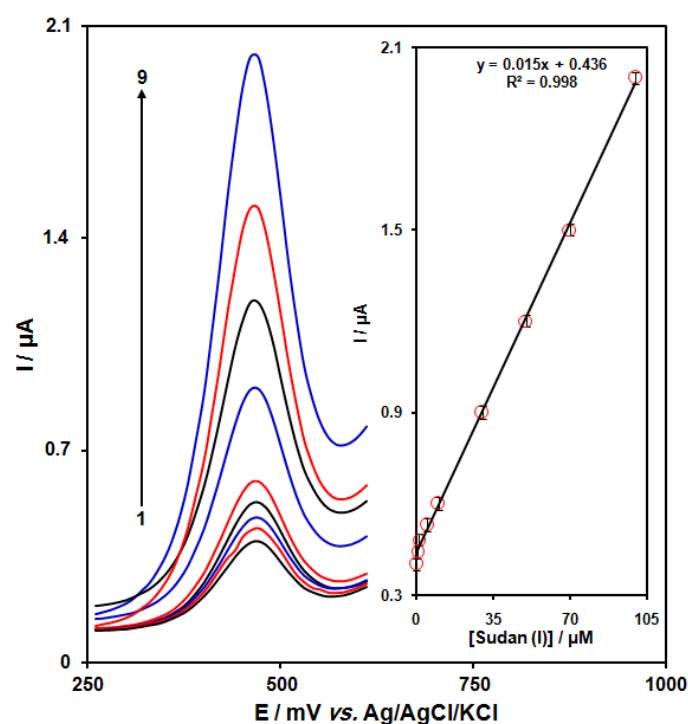


Fig. 5. DPVs of NiFe₂O₄/SPE in 0.1 M (pH 7.0) containing different concentrations of Sudan I. Numbers 1–9 correspond to 0.1, 0.5, 1.0, 5.0, 10.0, 30.0, 50.0, 70.0 and 100.0 μM of Sudan I. Inset: plot of the electrocatalytic peak current as a function of Sudan I concentration in the range of 0.1-100.0 μM

Table 1. Comparison of the efficiency of some methods used in detection of Sudan I

Method	Modifier	LOD	LDR	Ref.
Voltammetry	Graphene	0.04 μM	0.075-7.5 μM	[1]
Voltammetry	Platinum nanoparticles decorated carbon nanotubes	0.003 μM	0.08-600.0 μM	[7]
Voltammetry	Platinum nanoparticles decorated graphene- β -cyclodextrin	1.6 nM	0.005-68.68 μM	[19]
Amperometry	Silver nanoparticles decorated graphene oxide	1.14 μM	3.9-31.9 μM	[58]
Voltammetry	NiFe ₂ O ₄ nanoparticles	0.05 μM	0.1-100.0 μM	This work

3.5. Analysis of real samples

The applicability of this modified electrode in the determination of real samples was assessed through the determination of Sudan I in water samples 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 Sudan I recovery are satisfactory and the reproducibility of the results is proved by the mean relative standard deviation (R.S.D.).

Table 2. The application of NiFe₂O₄/SPE for determination of Sudan I in water samples (n=5). All concentrations are in μM

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Well water	0	-	-	-
	5.0	5.1	102.0	2.4
	10.0	9.8	98.0	1.8
	15.0	15.5	103.3	2.5
	20.0	19.5	97.5	3.7
River water	0	-	-	-
	7.5	7.6	101.3	1.3
	12.5	12.4	99.2	2.8
	17.5	17.9	102.3	3.2
	22.5	23.1	102.7	1.9

4. CONCLUSION

A novel electrochemical sensor for Sudan I based on a NiFe₂O₄ nanoparticles modified screen printed electrode has been developed. Thanks to the excellent electro-catalytic property and high adsorption capacity of NiFe₂O₄ nanoparticles, the oxidation peak current of Sudan I was enhanced significantly compared with the unmodified electrode. The NiFe₂O₄ modified electrodes show some clear advantages, such as a wide dynamic range (0.1-100.0

μM), low detection limit of $0.05 \mu\text{M}$, good stability, repeatability and simple preparation process, with excellent selectivity.

Acknowledgments

The authors acknowledge the financial support provided for this project (No. 96/917) by the Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran.

REFERENCES

- [1] X. Ma, M. Chao, and Z. Wang, *Food Chem.* 138 (2013) 739.
- [2] Y. Yao, Y. Liu, and Z. Yang, *Microchim. Acta* 183 (2016) 3275.
- [3] A. Pahlavan, N. Rezanejad, H. Karimi-Maleh, M. R. Jamali, M. Abbasghorbani, H. Beitollahi, and N. Atar, *Int. J. Electrochem. Sci.* 10 (2015) 3644.
- [4] D. M. Marmion, *Handbook of US colorants for food, drugs, and cosmetics* (No. 614.3 M3) (1979).
- [5] M. Du, X. Han, Z. Zhou, and S. Wu, *Food Chem.* 105 (2007) 883.
- [6] H. Lin, G. Li, and K. Wu, *Food Chem.* 107 (2008) 531.
- [7] M. Elyasi, M. A. Khalilzadeh, and H. Karimi-Maleh, *Food Chem.* 141 (2013) 4311.
- [8] C. Long, Z. Mai, X. Yang, B. Zhu, X. Xu, X. Huang, and X. Zou, *Food chem.* 126 (2011) 1324.
- [9] L. He, Y. Su, X. Shen, Z. Zeng, and Y. Liu, *Anal. Chim. Acta* 594 (2007) 139.
- [10] F. Calbiani, M. Careri, L. Elviri, A. Mangia, L. Pistara, and I. Zagoni, *J. Chromatogr. A* 1042 (2004) 123.
- [11] E. Mejia, Y. Ding, M. F. Mora, and C. D. Garcia, *Food Chem.* 102 (2007) 1027.
- [12] H. Yin, Y. Zhou, X. Meng, T. Tang, S. Ai, and L. Zhu, *Food Chem.* 127 (2011) 1348.
- [13] H. Beitollahi, M. A. Taher, M. Ahmadipour, and R. Hosseinzadeh, *Measurement* 47 (2014) 770.
- [14] H. Beitollahi, S. Tajik, M. Malakootian, H. Karimi-Maleh, and R. Hosseinzadeh, *Appl. Organomet. Chem.* 27 (2013) 444.
- [15] L. Wang, R. Yang, J. Li, L. Qu, and P. D. B. Harrington, *Sens. Actuators B* 215 (2015) 181.
- [16] H. Beitollahi, K. Movlaee, M. R. Ganjali, and P. Norouzi, *J. Electroanal. Chem.* 799 (2017) 576.
- [17] T. Alizadeh, M. R. Ganjali, M. Akhoundian, and P. Norouzi, *Microchim. Acta* 183 (2016) 1123.
- [18] Sh. Jahani, and H. Beitollahi, *Anal. Bioanal. Electrochem.* 8 (2016) 158.
- [19] S. Palanisamy, T. Kokulnathan, S. M. Chen, V. Velusamy, and S. K. Ramaraj, *J. Electroanal. Chem.* 794 (2017) 64.

- [20] H. Karimi-Maleh, M. Keyvanfard, K. Alizad, M. Fouladgar, H. Beitollahi, A. Mokhtari, and F. Gholami-Orimi, *Int. J. Electrochem. Sci.* 6 (2011) 6141.
- [21] M. R. Akhgar, H. Beitollahi, M. Salari, H. Karimi-Maleh, and H. Zamani, *Anal. Methods* 4 (2012) 259.
- [22] L. Li, Y. Zhang, T. Shang, H. Guo, X. Liu, and X. Lu, *J. Electroanal. Chem.* 781 (2016) 218.
- [23] H. Beitollahi, J.B. Raoof, H. Karimi-Maleh, and R. Hosseinzadeh, *J. Solid State Electrochem.* 16 (2012) 1701.
- [24] E. Molaakbari, A. Mostafavi, and H. Beitollahi, *Sens. Actuators B* 208 (2015) 195.
- [25] C. W. Foster, J. P. Metters, D. K. Kampouris, C. E. Banks, *Electroanalysis* 26 (2014) 262.
- [26] K. F. Chan, H. N. Lim, N. Shams, S. Jayabal, A. Pandikumar, and N. M. Huang, *Mater. Sci. Eng. C* 58 (2016) 666.
- [27] M. Baniasadi, Sh. Jahani, H. Maaref, and R. Alizadeh, *Anal. Bioanal. Electrochem.* 9 (2017) 718.
- [28] F. Arduini, C. Zanardi, S. Cinti, F. Terzi, D. Moscone, G. Palleschi, and R. Seeber, *Sens. Actuators B* 212 (2015) 536.
- [29] S. Tajik, M. A. Taher, Sh. Jahani, and M. Shanesaz, *Anal. Bioanal. Electrochem.* 8 (2016) 899.
- [30] M. Mazloum-Ardakani, H. Beitollahi, B. Ganjipour, and H. Naeimi, *Int. J. Electrochem. Sci.* 5 (2010) 531.
- [31] H. Beitollahi, S. Tajik, and P. Biparva, *Measurement* 56 (2014) 170.
- [32] N. Atar, M. L. Yola, and T. Eren, *Appl. Surf. Sci.* 362 (2016) 315.
- [33] M.R. Ganjali, F. Garkani Nejad, H. Beitollahi, Sh. Jahani, M. Rezapour, and B. Larijani, *Int. J. Electrochem. Sci.* 12 (2017) 3231.
- [34] H. Mahmoudi Moghaddam, H. Beitollahi, S. Tajik, and H. Soltani, *Electroanalysis* 27 (2015) 2620.
- [35] V. Vikas, B. E. Swamy, C. C. Viswanath, and T. S. Naik, *Anal. Bioanal. Electrochem.* 9 (2017) 164.
- [36] A. Salmanipour, M. A. Taher, and H. Beitollahi, *Anal. Methods* 4 (2012) 2982.
- [37] M. Mazloum-Ardakani, R. Arazi, H. Beitollahi, and H. Naeimi, *Anal. Methods* 2 (2010) 1078.
- [38] S. Jafari, N. Nasirizadeh, and M. Dehghani, *J. Electroanal. Chem.* 802 (2017) 139.
- [39] H. Beitollahi, A. Gholami, and M. R. Ganjali, *Mater. Sci. Eng. C* 57 (2015) 107.
- [40] M. Hasheminejad, and A. Nezamzadeh-Ejhieh, *Food Chem.* 172 (2015) 794.
- [41] H. Beitollahi, H. Karimi-Maleh, and H. Khabazzadeh, *Anal. Chem.* 80 (2008) 9848.
- [42] H. Mahmoudi Moghaddam, H. Beitollahi, S. Tajik, Sh. Jahani, H. Khabazzadeh, and R. Alizadeh, *Russ. J. Electrochem.* 53 (2017) 452.

- [43] M. Balooei, J. B. Raoof, F. Chekin, and R. Ojani, *Anal. Bioanal. Electrochem.* 9 (2017) 266.
- [44] H. Mahmoudi Moghaddam, H. Beitollahi, S. Tajik, M. Malakootian, and H. Karimi-Maleh, *Environ. Monit. Assess.* 186 (2014) 7431.
- [45] M. Behpour, S. Masoum, and M. Meshki, *Synth. React. Inorg. Met. Org. Nano Met. Chem.* 46 (2016) 1026.
- [46] H. Karimi-Maleh, A. A. Ensafi, H. Beitollahi, V. Nasiri, M. A. Khalilzadeh, and P. Biparva, *Ionics* 18 (2012) 687.
- [47] H. Beitollahi, F. Garkani Nejad, S. Tajik, Sh. Jahani, and P. Biparva, *Int. J. Nano Dimens.* 8 (2017) 197.
- [48] A. O. Idris, J. P. Mafa, N. Mabuba, and O. A. Arotiba, *Russ. J. Electrochem.* 53 (2017) 170.
- [49] S. Esfandiyari Baghbamidi, H. Beitollahi, S. Z. Mohammadi, S. Tajik, S. Soltani-Nejad, and V. Soltani-Nejad, *Chin. J. Catal.* 34 (2013) 1869.
- [50] F. Soofiabadi, A. Amiri, and Sh. Jahani, *Anal. Bioanal. Electrochem.* 9 (2017) 340.
- [51] B. Dinesh, V. Veeramani, S. M. Chen, and R. Saraswathi, *J. Electroanal. Chem.* 786 (2017) 169.
- [52] S. Tajik, M. A. Taher, and H. Beitollahi, *Ionics* 20 (2014) 1155.
- [53] H. Asari-Bami, M. A. Khalilzadeh, and H. Karimi-Maleh, *Anal. Bioanal. Electrochim.* 8 (2016) 1033.
- [54] M. Mazloun-Ardakani, B. Ganjipour, H. Beitollahi, M. K. Amini, F. Mirkhalaf, H. Naeimi, and M. Nejati-Barzoki, *Electrochim. Acta* 56 (2011) 9113.
- [55] H. Chen, J. Yan, H. Wu, Y. Zhang, and S. Z. Liu, *J. Power Sources* 324 (2016) 499.
- [56] U. Kurtan, H. Gungunes, H. Sozeri, and A. Baykal, *Ceramics Int.* 42 (2016) 7987.
- [57] A. J. Bard, and L.R. Faulkner, *Electrochemical Methods Fundamentals and Applications*, second ed, Wiley, New York (2001).
- [58] E. Prabakaran, and K. Pandian, *Food Chem.* 166 (2015) 198.