Int. J. Electrochem. Sci., 13 **(2018)** 4309 – 4318, doi: 10.20964/2018.05.53

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Electrocatalytic Determination of L-cysteine in the Presence of Tryptophan Using Carbon Paste Electrode Modified with MgO Nanoparticles and Acetylferrocene

Vinod Kumar Gupta[1,*], *Zahra Shamsadin-Azad*[2], *Somaye Cheraghi*[2,3], *Shilpi Agarwai*[1], *Mohammad A. Taher*[2,*]*Fatemeh Karimi*

[1] Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa
[2] Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran
[3] Department of Chemistry, Graduate University of Advanced Technology, Kerman, Iran
[4] Department of Chemical Engineering, Laboratory of Nanotechnology, Quchan University of Technology, Quchan, Iran
[*]E-mail: vinodfcy@gmail.com; ma-taher@uk.ac.ir

Received: 27 January 2018 / *Accepted:* 10 March 2018 / *Published:* 10 April 2018

The electrical conductivity effect of MgO nanoparticle (MgO-NPs) and electro-catalytic effect of acetylferrocene (AF) was studied for modification of carbon paste electrode (CPE) as a highly sensitive electrochemical sensor for electro-catalytic determination of L-cysteine in the aqueous solution. The AF/MgO-NPs/CPE showed good electro-catalytic activity for analysis of L-cysteine in the concentration range 0.1-700.0 μM with limit of detection 30.0 nM using differential pulse voltammetric method (DPV). In addition, the AF/MgO-NPs/CPE showed two separated oxidation signals with ΔE~170 mV in the solution containing L-cysteine and tryptophan that is sufficient for simulations determination of these amino acids with same oxidation potential at a surface of unmodified electrode.

Keywords: Acetylferrocene; MgO nanoparticle; L-cysteine, Tryptophan, Electrocatalysis

1. INTRODUCTION

Modified electro-analytical sensors showed many advantages for analysis of food, drug, biological and environmental electro-active compounds [1-10]. The application of conductive mediators to electrochemical analysis of electro-active compounds can be increased the selectivity of analytical system [11-19]. On the other hand, modification of electro-catalytic sensors (based on EC/ mechanism) with nanomaterials can be useful for increasing sensitivity of electro-active compounds analysis [20-24]. On the other hand, inorganic complexes such as ferrocene derivatives and organic

ligands such as catechol derivatives showed good ability for modification of electrodes surface for electro-catalytic interaction with drugs or other biological and environmental compounds for trace level analysis [25-27]. The variety of voltammetric method for electrochemical investigation and especially for analysis of materials introduced this technique as a powerful method for analysis of food, biological, pharmaceutical and environmental compounds [28-37].

L-cysteine is an important semi-essential amino acid and plays a significant role in making glutathione (an essential antioxidant) in the human body [38]. On the other hand, L-cystine is an important thiolic source in the human body and is essential in protein structure. In addition, tryptophan is one of the essential amino acids in the human body and plays an important role in making serotonin. As we know, serotonin is a vital biological compound in the brain and it is necessary for relaxation, promotes feelings of calm, and sleepiness in the human body [39]. Due to important analysis of these amino acids, some analytical methods were suggested for determination of them [40-43]. In between, electrochemical sensors can be useful for analysis of these amino acids due to L-cysteine and tryptophan are electro-active at a surface of electrodes [44, 45].

According to the above points and important analysis of L-cysteine and tryptophan, we fabricated an electro-catalytic sensor based on carbon paste electrode modified with AF and MgO nanoparticles for analysis of them. The AF at a surface of AF/MgO-NPs/CPE can be attending in an electro-catalytic interaction with L-cysteine.

Therefore, the oxidation potential of this amino acid transfer to mediator oxidation potential and so overlapping signal of L-cysteine and tryptophan resolved at a surface of AF/MgO-NPs/CPE and simultaneously determination of L-cysteine and tryptophan can be occurred at a surface of this electrode. On the other hand, the AF/MgO-NPs/CPE showed high performance ability for determination of L-cysteine in real samples.

2. EXPERIMENTAL

2.1.Chemicals and Apparatus

L-cysteine, tryptophan, magnesium nitrate hydrate, acetylferrocene were purchased from Sigma-Aldrich. Also, graphite powder, sodium hydroxide and nujol oil were purchased from Merck. Metrohm (potentiostat/galvanostat) was used for electrochemical investigation. Pt wire, AF/MgO-NPs/CPE and Ag/AgCl/KCl_{sat} were used as a counter, working and references electrodes, respectively.

2.2. Synthesis of MgO nanoparticle

100 mL magnesium nitrate hydrate dropt wise to 100 mL sodium hydroxide solution under magnetic stirring 2 h. The precipitated sample dried at 120 °C for 12 h and calcined at 500 °C for 1.5 h.

2.3. Preparation of the electrode

AF/MgO-NPs/CPE was prepared by mixing of 0.01 g of acetylferrocene, 0.1 g of MgO-NPs and 0.89 g of graphite powder in mortar and pestle and hand mixed with suitable amount of nujol oil. A portion of the paste was filled firmly into one glass tube as described above to prepare AF/MgO-NPs/CPE.

2.4. Preparation of real samples

The pharmaceutical serum sample was used for real sample analysis without any pretreatment. Urine samples was prepared according to our previous published procedure and using phosphate buffer pH=7.0 [46, 63-75].

3. RESULTS AND DISCUSSION

3.1. MgO nanoparticle characterization

Figure 1 show the SEM image of MgO nanoparticle synthesized by recommended procedure. As can be seen, the MgO nanoparticle synthesized with diameter ~26.89-57.48 nm with spherical shape. This spherical shape with good distribution can be useful for increasing the electrical conductivity of carbon paste electrode after modification with MgO/NPs.

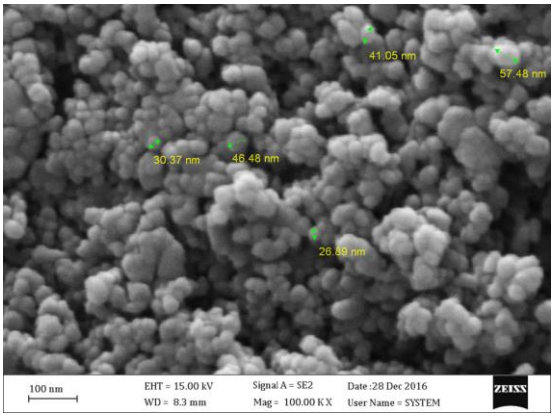

Figure 1. SEM images of MgO-NPs.

3.2. Electrocatalytic investigation

Figure 2 A showed cyclic voltammograms of AF/MgO-NPs/CPE in the absence (curve a) and in the presence of 500.0 μM L-cysteine (curve c) with a scan rate of 10 mV/s (pH=7.0). Also, the cyclic voltammograms of 500.0 μM L-cysteine was recorded at a surface of AF/CPE (curve b), MgO-NPs/CPE (curve d) and CPE (curve e), respectively. A quasi-reversible signal with ΔE=100 mV can be

observed for electro-oxidation of AF at a surface of AF/MgO-NPs/CPE. After addition of 500.0 µM L-cysteine, the oxidation signals of mediator increased and reduction signal of AF reduced simultaneously. This phenomenon confirmed an electro-catalytic interaction between AF and L-cysteine with EC′ mechanism. As can be seen, the oxidation current of 500.0 µM L-cysteine at a surface of AF/MgO-NPs/CPE is more than its signal at a surface of AF/CPE that can be relative to presence of MgO nanoparticle with good electrical conductivity. In addition, we detected a low oxidation signal for 500.0 µM L-cysteine at a surface of MgO-NPs and CPE. The oxidation current at a MgO-NPs/CPE is more than unmodified CPE electrode that can be relative to the presence of Mgo/NPs. According to the previous reported papers, the nano-materials have high surface area with good electrical conductivity that improves electrical conductivity of oxidation/reduction systems [47-56].

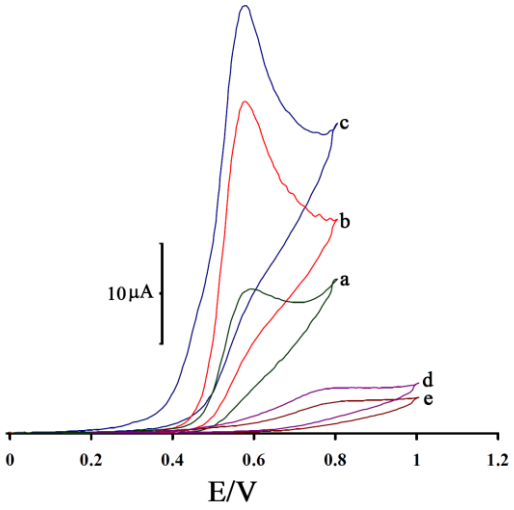

Figure 2. Cyclic voltammograms of 500.0 µM L-cysteine at a surface of AF/CPE (curve b), AF/MgO-NPs/CPE (curve c), MgO-NPs/CPE (curve d) and CPE (curve e) with a scan rate of 10 mV/s (pH=7.0). Curve a) showed cyclic voltammogram of AF/MgO-NPs/CPE with scan rate of 10 mV/s (pH=7.0).

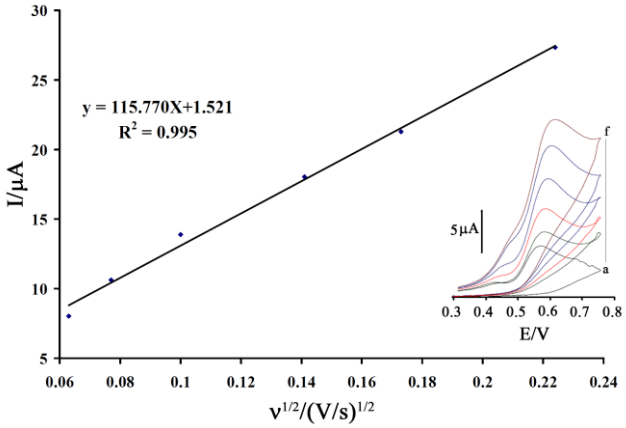

Figure 3. Cyclic voltammograms of AF/MgO-NPs/CPE with scan rates a) 4.0; b) 6.0; c) 10.0; d) 20; e) 30 and f) 50 mV/s.

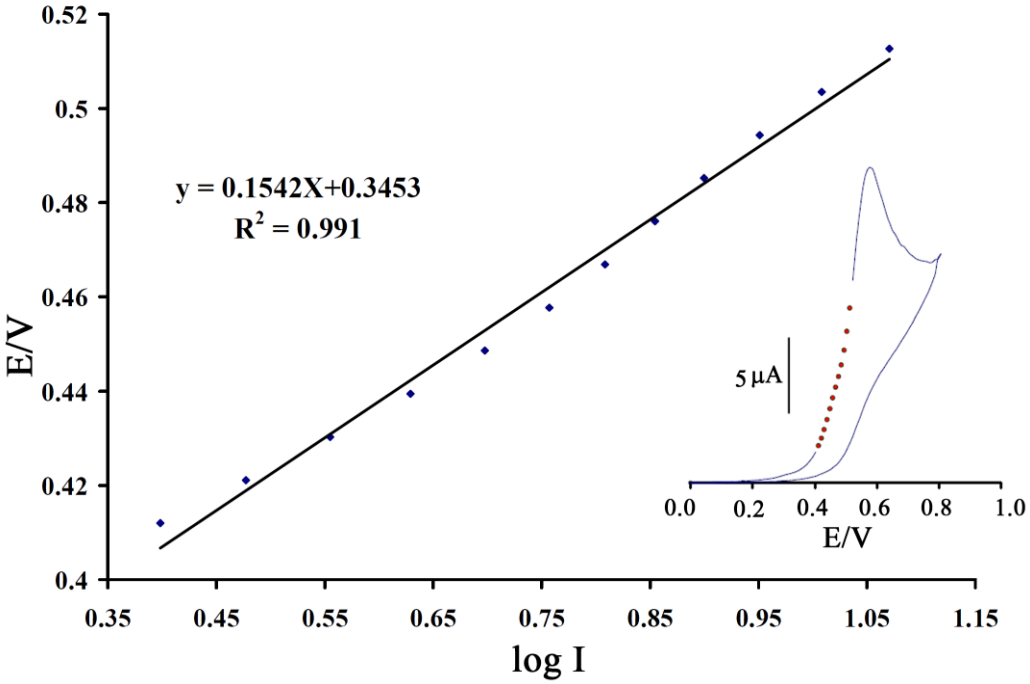

Figure 4. Tafel plot for AF/MgO-NPs/CPE in 0.1 M PBS (pH 7.0) with a scan rate of 10 mV/s in the presence of L-cysteine.

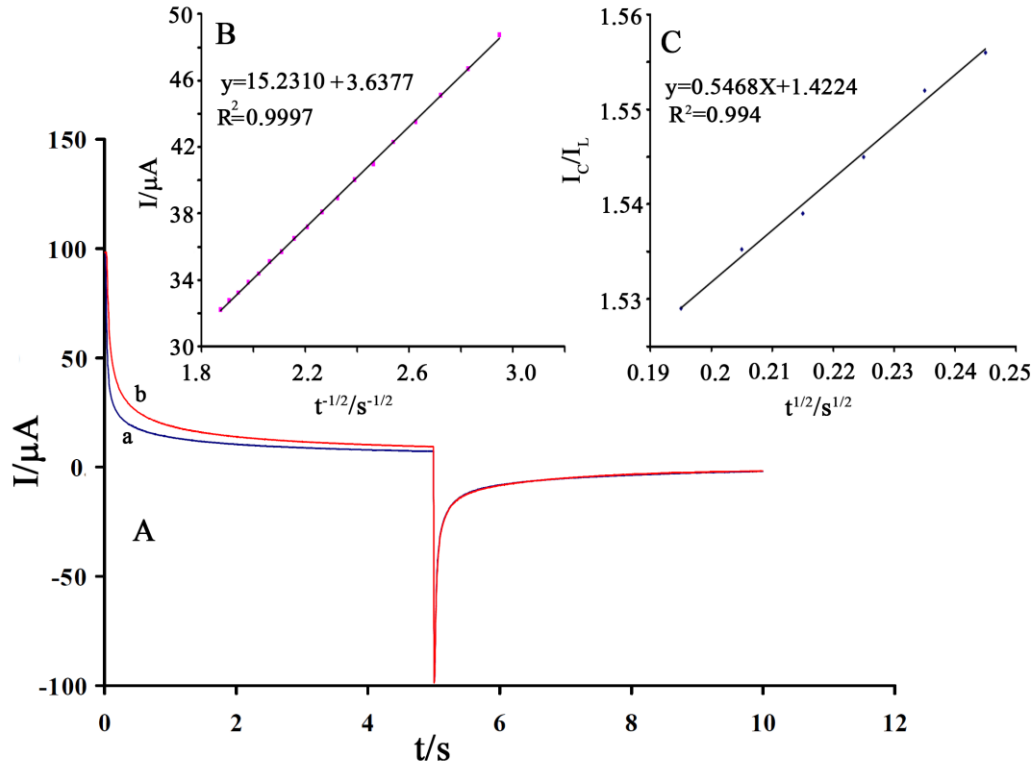

Figure 5. (A) Chronoamperograms obtained at the AF/MgO-NPs/CPE in the absence (a) and in the presence of (b) 200 µM L-cysteine in a buffer solution (pH 7.0). (B) Cottrell's plot for the data from the chronoamperograms. C) dependence of I_C/I_L on the $t^{1/2}$ derived from the chronoamperogram data.

A diffusion-controlled process was detected for electro-catalytic oxidation of 200.0 μM L-cysteine at a surface of AF/MgO-NPs/CPE due to linear relation between current and ($\nu^{1/2}$) (Fig. 3) [57-60]. Using slope of Tafel plot (Figure 4) and Tafel equation (2.3RT/n(1- α)F), we obtained the value of α equal to 0.62 which confirmed that the activation free energy curve is not symmetrical for an irreversible electro-oxidation process.

Chronoamperometric study was used for calculated the diffusion coefficient (D) and rate constant of the catalytic process (k) of L-cysteine at a surface AF/MgO-NPs/CPE at an optimum condition. For the goal, we recorded chronoamperograms of AF/MgO-NPs/CPE in the absence (curve a) and in the presence of 200 μM L-cysteine (Figure 5A). We determine the diffusion coefficient (D) by cottrell equation ($I = nFAD^{1/2} C_b \pi^{-1/2} t^{-1/2}$) equal 2.4×10^{-5} cm^2 s^{-1} by obtained data from figure 5B. The rate constant of the catalytic oxidation between L-cysteine and AF at a surface of AF/MgO-NPs/CPE can be determine by slope of Galus equation ($I_C/I_L = \pi^{1/2}(k_h t)^{1/2}$). Using slope of figure 5 C data and Galus equation, we determine the value of k equal 4.8×10^2 $M^{-1}s^{-1}$.

Differential pulse voltammograms of AF/MgO-NPs/CPE in the presence of different concentration of L-cysteine was recorded in the concentration range of 0.1-700 μM (Fig 6). The detection limit 30.0 nM was obtained for analysis of L-cysteine at a surface of AF/MgO-NPs/CPE. These values of LDR and LOD are comparable and in some cases better than previous electrochemical suggested sensors (see table 2).

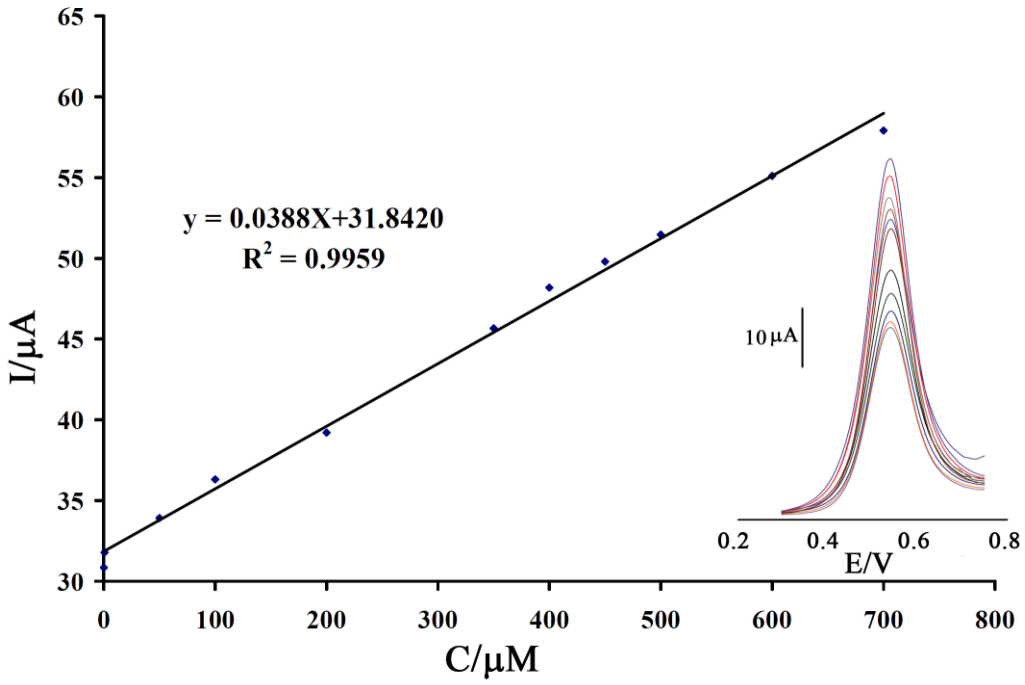

Figure 6. The plots of the electrocatalytic peak current as a function of L-cysteine concentration. Inset shows the DPVs of AF/MgO-NPs/CPE in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of L-cysteine (0.1-700 μM).

Table .1 The comparison of proposed sensors with published electrochemical sensors for determination of L-cysteine

Electrode	pH	LOD (µM)	LDR (µM)	Ref.
Carbon paste	6.0	0.3	0.5-100	[33]
Carbon paste	7.0	0.07	0.2-250	[61]
Carbon paste	5.0	1.0	2-10000	[62]
Carbon paste	5.0	0.2	0.5-100.0	[63]
Carbon paste	7.0	0.03	0.1-700.0	This work

The ability of AF/MgO-NPs/CPE was check for analysis of L-cysteine in the presence of tryptophan as two important amino acids. Figure 7 A show differential pulse voltammograms of L-cysteine in the presence of tryptophan with different concentration of two amino acids. The AF/MgO-NPs/CPE showed two separated oxidation signals with ΔE~170 mV in the solution containing L-cysteine and tryptophan that is sufficient for simulations determination of these amino acids. The sensitivity for L-cysteine in the presence of tryptophan (fig. 7B) (0.0380 µA/µM) is very similar to sensitivity of L-cysteine in the absence of tryptophan (0.0388 µA/µM) that confirm simultaneous determination of two amino acids is possible without any interference.

The stability of AF/MgO-NPs/CPE was investigated by DPV determination of 30.0 µM L-cysteine. When the AF/MgO-NPs/CPE remained in the laboratory, the AF/MgO-NPs/CPE retains 97% of its initial response after 25 days that confirmed good stability of AF/MgO-NPs/CPE.

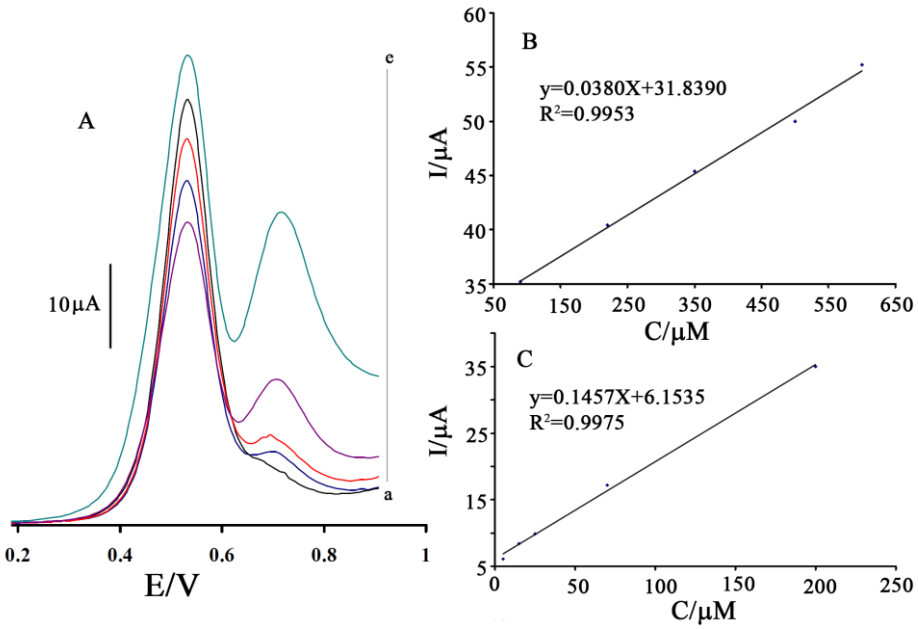

Figure 7. A) Square wave voltammograms of AF/MgO-NPs/CPE at pH 7.0 containing different concentrations of L-cysteine and tryptophan: a) "90.0+ 5.0"; (b): "220.0 +15.0"; (c): "350.0 + 25.0"; (d): "500.0+ 70.0" and e) "600.0+ 200.0" µM L-cysteine and tryptophan, respectively. (B) Plot of the peak currents as a function of L-cysteine concentration and (C) plot of the peak currents as a function of tryptophan concentration.

Table 2. Determination of L-cysteine in pharmaceutical and urine samples (n=3).

Sample	Added (μM)	Expected (μM)	Found (μM)	Recovery (%)
Urine	---	---	<Limit of detection	---
	15.00	15.00	15.67±0.83	104.46
	20.00	20.00	20.73±0.92	103.65
Pharmaceutical Serum	---	---	<Limit of detection	---
	30.00	30.00	29.73±0.68	99.10
	50.00	50.00	51.05±1.33	102.10

In addition, 500 fold of methionine, glycine, valine, leucine and isoleucine did not any interference for analysis of 35.0 μM L-cysteine at a surface of AF/MgO-NPs/CPE. This point confirms good selectivity of AF/MgO-NPs/CPE for analysis of L-cysteine.

Determination of L-cysteine in urine and pharmaceutical serum samples was investigated for indicating the ability of the AF/MgO-NPs/CPE to the determination of L-cysteine in real samples. The results are given in Table 2 indicating that the AF/MgO-NPs/CPE has good ability for determination of L-cysteine in real samples.

4. CONCLUSION

The AF/MgO-NPs/CPE was fabricated a highly selective electrochemical platform for analysis of L-cysteine in the presence of tryptophan in this work. The AF/MgO-NPs/CPE showed good electro-catalytic activity for analysis of L-cysteine in the concentration range 0.1-700.0 μM with limit of detection 30.0 nM. Finally, the AF/MgO-NPs/CPE showed good ability for analysis of L-cysteine in real samples.

References

1. M.R. Ganjali, P. Norouzi, M. Ghorbani, A. Sepehri *Talanta,* 66 (2005) 1225
2. M.L. Yola, N. Atar, *Electrochim. Acta,* 19 (2013) 24
3. T. Alizadeh, M.R. Ganjali, M. Zare, P. Norouzi *Electrochim. Acta,* 55 (2010) 1568
4. A. Taherkhani, H. Karimi-Maleh, A.A. Ensafi, H. Beitollahi, A. Hosseini, M.A. Khalilzad, H. Bagheri, *Chin. Chem. Lett.,* 23 (2012) 237
5. B.J. Sanghavi, A.K. Srivastava, *Analyst,* 138 (2013) 1395.
6. B.J. Sanghavi, A.K. Srivastava, *Electrochim. Acta,* 56 (2011) 4188.
7. N.S. Gadhari, B.J. Sanghavi, A.K. Srivastava, *Anal. Chim. Acta,* 703 (2011) 31
8. F.S. Sabet, M. Hosseini, H. Khabbaz, M. Dadmehr, M.R. Ganjali, *Food Chem.,* 220 (2017) 527.
9. H. Karimi-Maleh, A. Fallah-Shojaei, Kh. Tabatabaeian, F. Karimi, S. Shakeri, R. Moradi, *Biosens. Bioelectron.,* 86 (2016) 879.
10. S.A.R. Alavi-Tabari, M.A. Khalilzadeh, H. Karimi-Maleh, *J. Electroanal. Chem.,* 811 (2018) 84.
11. S. Cheraghi, M.A. Taher, H. Karimi-Maleh, *J. Food Compos. Anal.,* 62 (2017) 254.
12. X.M. Miao, R. Yuan, Y.Q. Chai, Y.T. Shi, Y.Y. Yuan, *J. Electroanal. Chem.,* 612 (2008) 157.

13. M. Ashjari, H. Karimi-Maleh, F. Ahmadpour, M. Shabani-Nooshabadi, A. Sadrnia, M.A. Khalilzadeh, *Journal of the Taiwan Institute of Chemical Engineers*, 80 (2017) 989.
14. B. Liu, L. Luo, Y. Ding, X. Si, Y. Wei, X. Ouyang, D. Xu, *Electrochim. Acta,* 142 (2014) 336.
15. H. Karimi-Maleh, P. Biparva, H. Karimi-Maleh, *Biosens. Bioelect.,* 48 (2013) 270.
16. H. Karimi-Maleh, M. Hatami, R. Moradi, M.A. Khalilzadeh, A. Amiri, H. Sadeghifar, *Microchim. Acta,* 183 (2016) 2957
17. J.B. Raoof, R. Ojani, A. Kiani, *J. Electroanal. Chem.,* 515 (2001) 45.
18. J.B. Raoof, R. Ojani, S. Rashid-Nadimi, *Electrochim. Acta,* 49 (2004) 271.
19. F. Tahernejad-Javazmi, M. Shabani-Nooshabadi, H. Karimi-Maleh, *Talanta,* 176 (2018) 208.
20. H. Karimi-Maleh, M. Moazampour, A.A. Ensafi, S. Mallakpour, M. Hatami, *Environ. Sci. Poll. Res.* 21 (2015) 5879.
21. Y. Gu, Y. Zhang, F. Zhang, J. Wei, C. Wang, Y. Du, W. Ye, *Electrochim. Acta,* 56 (2010) 953.
22. M. MazloumArdakani, M.A. Karimi, S.M. Mirdehghan, M.M. Zare, R. Mazidi, *Sens. Actuators B,* 132 (2008) 52.
23. A.A. Ensafi, M. Dadkhah, H. Karimi-Maleh, *Coll. Surf. B,* 84 (2011) 148.
24. J.M. Pingarrón, I. Hernández, A. González-Cortés, P. Yáñez-Sedeño, *Anal. Chim. Acta,* 439 (2001) 281.
25. A.A. Ensafi, H. Karimi-Maleh, *Int. J. Electrochem. Sci.,* 5 (2010) 1484
26. Z. Keivani, M. Shabani-Nooshabadi, H. Karimi-Maleh, *J. Coll. Int. Sci.,* 507 (2017) 11.
27. H. Karimi-Maleh, M. Salehi, F. Faghani, *J. Food Drug Anal.,* 25 (2017) 1000.
28. A.A. Ensafi, M. Taei, H.R. Rahmani, T. Khayamian, *Electrochim. Acta,* 56 (2011) 8176.
29. M. Arshadi, M. Ghiaci, A.A. Ensafi, H. Karimi-Maleh, S.L. Suib, *J. Mol. Catal. A: Chem.,* 338 (2011) 71
30. A.A. Ensafi, M. Taei, T. Khayamian, *Int. J. Electrochem. Sci*., 5 (2010) 116.
31. B. Rezaei, O. Rahmanian, A.A. Ensafi, *Sens. Actuator B-Chem.*,196 (2014) 539.
32. H. Karimi-Maleh, A.A. Ensafi, H. Beitollahi, V. Nasiri, M.A. Khalilzadeh, P. Biparva, *Ionics,* 18 (2012) 687.
33. A.A. Ensafi, H. Karimi-Maleh, *Int. J. Electrochem. Sci.,* 5 (2010) 392.
34. A.A. Ensafi, R. Hajian, *Electroanalysis* 18 (2006) 579.
35. B.J. Sanghavi and A.K. Srivastava, *Electrochim. Acta,* 55 (2010) 8638.
36. A.L. Sanati, F. Faridbod, M.R. Ganjali, *J. Mol. Liq.,* 241 (2017) 316.
37. V. Arabali, M. Ebrahimi, S. Gheibi, F. Khaleghi, M. Bijad, A. Rudbaraki, M. Abbasghorbani, M.R. Ganjali, *Food Anal. Method,* 9 (2016) 1763.
38. J. Viña, M. Vento, F. García-Sala, *Am. J. Clin. Nutr.,* 61 (1995) 1067.
39. J.D. Fernstrom, R.J. Wurtman, *Science,* 173 (1971) 149.
40. C. Zhao, J. Zhang, J. Song, *Anal. Biochem.* 297 (2001) 170.
41. H. Edelhoch, *Biochem.,* 6 (1967) 1948.
42. I.N. Mefford, J.D. Barchas, *J. Chromatogr. B,* 181 (1980) 187.
43. A.A. Ensafi, S. Dadkhah-Tehrani, H. Karimi-Maleh, *Anal. Sci.,* 27 (2011) 409
44. M. Mazloum-Ardakani, Z. Taleat, H. Beitollahi, H. Naeimi, *J. Iran Chem. Soc.,* 7 (2010) 251.
45. X. Tang, Y. Liu, H. Hou, T. You, *Talanta,* 80 (2010) 2182.
46. S. Cheraghi, M.A. Taher, H. Karimi-Maleh, E. Faghih-Mirzaei, *New J. Chem*., 41 (2017) 4985.
47. M.S. Ekrami-Kakhki, J. Saffari, N. Farzaneh and S. Abbas, *J. Nanostruct.,* 7 (2017) 292.
48. M. Shaterian, M.A. Rezvani, V. Shahsavandi and K. Qasem, *J. Nanostruct.,* 7 (2017) 97.
49. S. Mathur, M. Arya, R. Jain, S.K. Sharma, *J. Nanostruct.,* 7 (20172) 121.
50. C. Jayakumar, C.M. Magdalane, K. Kanimozhi, K. Kaviyarasu and B. Jeyaraj, *J. Nanostruct.,* 7 (2017) 155.
51. M. Mazloum-Ardakani, F. Farbod, L. Hosseinzadeh, *J. Nanostruct.,* 6 (2016) 293.
52. M. Hasanzadeh, S. Hassanpour, A.S. Nahr, N. Shadjou, A. Mokhtarzadeh, and S. Mahboob, *Anal. Bioanal. Electrochem.,* 10 (2018) 77

53. M. Bijad, H. Karimi‐Maleh, M. Farsi and S.A. Shahidi, *Journal of Food Measurement and Characterization,* 12 (2018) 634
54. H. Mohammadi, M. Khosravi and S.M. Jafari, *Anal. Bioanal. Electrochem.,* 10 (2018) 1
55. S.A.R. Alavi-Tabari, M.A. Khalilzadeh, H. Karimi-Maleh, D. Zareyee, *New J. Chem.*,42 (2018) 3828.
56. P. Norouzi, B. Larijani, M.E. Bidhendi, M. Eshraghi and M. Ebrahimi, *Anal. Bioanal. Electrochem.*, 10 (2018) 18
57. A. Bananezhad, M.R. Ganjali, H. Karimi-Maleh, P. Norouzi, *Int. J. Electrochem. Sci.*, 12 (2017) 8045.
58. A.L. Sanati, F. Faridbod, *Int. J. Electrochem. Sci.*, 12 (2017) 7997
59. S. Cheraghi, M.A. Taher, H. Karimi-Maleh, *Appl. Surf. Sci.*, 420 (2017) 882.
60. H. Karimi-Maleh, A. Bananezhad, M.R. Ganjali, P. Norouzi, *Anal. Methods,* 9 (2017) 6228
61. S. Kazemi, H. Karimi-Maleh, R. Hosseinzadeh, F. Faraji, *Ionics,* 19 (2013) 933
62. M.K. Amini, J.H. Khorasani, S.S. Khaloo, S. Tangestaninejad, *Anal. Biochem.* 320 (2003) 32
63. S. Shahrokhian, M. Karimi, *Electrochim. Acta*, 50 (2004) 77
64. V. K. Gupta, M. R. Ganjali, P. Norouzi, H. Khani, A. Nayak, and Shilpi Agarwal, *Crit. Rev. Anal. Chem.* 41, (2011) 282
65. V. K. Gupta, Tawfik A. Saleh, *J. Colloids Interface Sci.*, 362 (2011) 337
66. I Ali, VK Gupta, TA Khan, M Asim, *Int J Electrochem Sci* 7, (2012). 1898
67. V.K. Gupta, S. Kumar, R. Singh, L.P. Singh, S.K. Shoora and B. Sethi, *J. Mol. Liq*. 195, 2014, 65
68. S. Karthikeyan, V.K. Gupta, R. Boopathy, A. Titus and G. Sekaran, *J. Mol. Liquids* 173, 2012, 153
69. V. K. Gupta, A. K. Singh, L. K. Kumawat, *Sensors & Actuators*: *B. Chemical*, 195 (2014) 98
70. T. A. Saleh, V.K. Gupta, *Sep. Purf. Technol*., 89(2012) 245
71. N. Mohammadi, H. Khani, Shilpi Agarwal, V. K. Gupta, *J. Colloids Interface Sci*., (2011) 457
72. V.K. Gupta, B. Sethi, R.A. Sharma, Shilpi Agarwal and Arvind Bharti, *J. Mol. Liq*. 177, 2013, 114
73. Tawfik A. Saleh, Shilpi Agarwal, V. K. Gupta, *Applied Catalysis B*: *Env*., 106 (2011) 46
74. V. K. Gupta, A. Nayak, S. Agarwal, *Environmental Engineering Research*, 20(1) (2015)001
75. V. K. Gupta, Necip Atar, M. L. Yola, Zafer Üstündağ, Lokman Uzun, *Water Res*., 48 (2014) 210