Advances in Nanochemistry
ISSN: 2676-5462

Research

Incorporating $ZnFe_2O_4$ nanoparticles and β-cyclodextrin into carbon paste electrode as a sensitive methyldopa electrochemical sensor

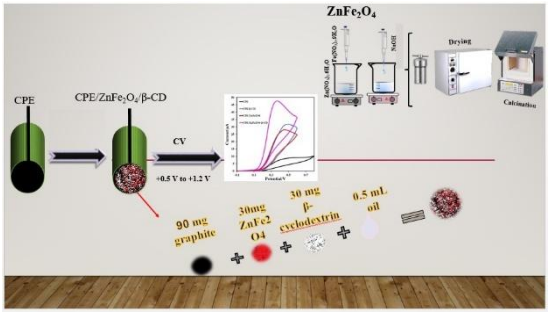
Bahman Mohammadian Asiabar *[,1], Mohammad Ali Karimi *[,1], Hossein Tavallali [1], Mahdi Gholampour [2], Seied Isa Karanian [2], Hasan Tavakoli [2]

Received 1st June 2021,
Accepted 29th July 2021,
DOI: 10.22126/anc.2021.6533.1025

[1] Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran.
[2] Department of Physics and Chemistry, Faculty of Basic Sciences, Imam Ali Military University, Tehran, Iran.

Abstract

A new electrochemical sensor for antihypertensive drug methyldopa (MDop) was prepared from a carbon paste electrode modified by hydrothermally synthesized $ZnFe_2O_4$ nanoparticles and β-cyclodextrin as a supermolecule. $ZnFe_2O_4$ nanoparticles were charectrized using scanning electron microscopy (SEM) and infrared spectroscopy. Comparison of unmodified electrode with electrodes modified by $ZnFe_2O_4$ and β-cyclodextrin and their nanocomposite showed that MDop had a higher oxidation current at the modified electrode by composite than each other electrodes at pH = 7. Moreover, the oxidation potential is lower than other electrodes at this pH. The modified electrode can measure MDop in the concentration range of 1-100 µM with a detection limit of 0.3 µM. The proposed sensor shows good repeatability and selectivity. It is also able to measure MDop in the blood serum sample.



Keywords: *Methyldopa, $ZnFe_2O_4$ nanoparticles, β- cyclodextrin, Electrochemical sensor.*

Introduction

Methyldopa [α-methyl-β-(3,4-dihydroxyphenylalanine)] (MDop) from catechol derivatives is an old antihypertensive agent medication used for treatment of gestational hypertension, pre-eclampsia and renal impairment.[1] High blood pressure is relieved through the relaxation of blood vessels originated from the effect MDop on nerve centers.[2] The mechanism of action is conversion of MDop to α-methyl norepinephrine with dopamine beta-hydroxylase (DBH) in central adrenergic neurons and release and stimulation of central α-2-adrenoceptor agonist which results in blood pressure reduction and inhibition of sympathetic nervous system output.[3,4] The adverse side effects of MDop are depression, impotence, anxiety, nausea, fever and decreased heart rate.[5] According to the literature, various analytical methods based on spectrofluorimetry,[6,7] chemiluminescence,[8] high-performance liquid chromatography,[9] mass spectrometry,[10] NMR spectroscopy,[11] and voltammetry[12] have been used for the determination of MDop.

Among the mentioned methods, the electrochemical approach is preferred for pharmaceutical and biological compound analyses due to some advantages including low cost, rapidity, high dynamic range, less time consumption, low ohmic resistance, no need for an internal solution, stable response and simple instrumentation without requiring some pretreatments.[13-18] In this respect, carbon-paste electrodes (CPEs) are extensively applied for electrochemical determination of a variety of biological species owning to their low residual noise and current, simple fabrication, rapid surface recovery, low cost and wide anodic/cathodic potential ranges.[19-24] However, direct electrochemical oxidation of many materials at the surface of bare electrodes is irreversible and therefore a high overpotential is required for their oxidation.[25-27] To address these problems, electrode surface modification must be performed by addition of different substances to the bulk of electrodes.[28-30] A good modifier substance must facilitate the electron transfer between the electroactive species and electrodes.[31-34]

To this end, nanostructured materials offer numerous unique aspects such as faster responses and higher sensitivity than planar sensor designing. Introducing the metal nanoparticles (MNPs) as modifiers create electrodes with some advantageous such as,

*Corresponding authors: Bahman Mohammadian Asiabar, Email: asiabar61@yahoo.com and Mohammad Ali Karimi, Email: ma_karimi43@yahoo.com

Cite this article: Mohammadian Asiabar, B., Karimi, M.A., Tavallali, H., Gholampour, M., Karanian, S.A., & Tavakoli, H. (2021). Incorporating ZnFe2O4 nanoparticles and β-cyclodextrin into carbon paste electrode as a sensitive methyldopa electrochemical sensor. *Advances in Nanochemistry*, 3(1), 10-15. DOI: 10.22126/anc.2021.6533.1025

Publisher: Razi University

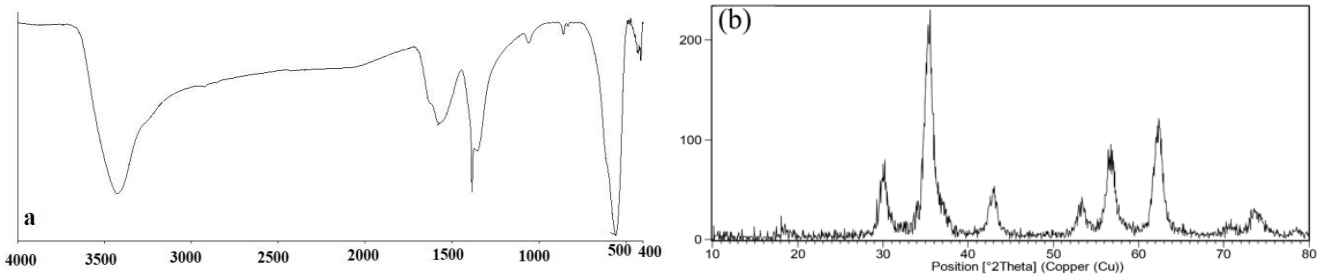


Figure 1. (a) FT-IR spectra of $ZnFe_2O_4$ and (b) XRD pattern of $ZnFe_2O_4$.

improvement in electron kinetics as a result of high surface area, increased mass transport rates, improved control of nanoparticles surface, and tunable functionalization of desired groups.[35-38] In this work, a novel electrochemical sensor based on carbon paste electrode modified with zinc ferrite ($ZnFe_2O_4$), as well as β-cyclodextrin was prepared and used for determination of MDop.

$ZnFe_2O_4$ has long been considered owing to its unique properties such as chemical and thermal stability,[39] lower toxicity relative to other metals,[40] cost-effectiveness, non-toxicity,[41,42] and so on. The most special and important property of $ZnFe_2O_4$ for electrochemical applications is its good conductivity which originates from charge hopping of carriers between cations occupying the octahedral sites.[43] Moreover, there is a significant difference between bulk and nanosized spinel zinc ferrite. The bulk spinel zinc ferrite shows antiferromagnetic order,[44] while the nanosized counterparts present magnetic properties. β-Cyclodextrins (β-CDs) are cyclic oligosaccharides and have the ability to form inclusion complexes with a large range of substrate molecules.[45] Inclusion complexes are formed through the host-guest noncovalent interaction and β-CD (host) can change the redox activity of electroactive guest.[46] In recent years, β-CD coated nanoparticles are interesting supramolecular because of their electronic, conductivity, and catalytic properties are improved.[47,48]

The literature review shows that the electrochemical methods were successfully used for determination of MDop. To quantitative analysis of MDop, many electrochemical sensors have been prepared based on modified carbon paste electrodes with the modifiers of graphene quantum dots (GQD) and 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIPF_6$),[4] $Cu(OH)_2$ nanoparticles,[49] Fe:Co nano-alloy, graphene and ethyl 2-(4-ferrocenyl[1,2,3]triazol-1-yl)acetate,[50] 5-amino-20-ethyl-biphenyl-2-ol (5AEB) and carbon nanotubes (CNTs),[51] TiO_2 nanoparticles and ferrocene monocarboxylic acid (FM),[52] carbon nanotube (CNT) and ferrocene (FC),[53] NiO nanoparticle (NiO/NPs) and 2-(3,4-dihydroxyphenethyl)isoindoline-1,3-dione (DHPID).[54] In the present work, the performance of a carbon paste electrode triply modified by zinc ferrite nanoparticle and β-cyclodextrin was investigated. The prepared modified electrode was successfully used for the cyclic voltammetric determination of MDop in biological samples.

Experimental

Chemicals

$Fe(NO_3)_3.9H_2O$, NaOH, $Zn(NO_3)_2.6H_2O$, glucose, L-cysteine, H_2O_2, citric acid, uric acid, acetaminophen, C_2H_5OH, MDop, and β-Cyclodextrins in analytical grade were purchased from Merck Company. The phosphate buffer solution (0.1 M) was used as the electrolyte. The mix of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ (1.0 mM) containing KCl (0.1 M) was used as the redox probe.

Apparatus

The nanocomposite and other nanoparticles morphology was explored by X-ray diffraction (XRD) with a source of the Cu K_α radiation, impedance electrochemical spectroscopy (EIS), Fourier transform infrared spectroscopy (FT-IR), and field emission scanning electron microscopy (FE-SEM) coupled with energy dispersive X-ray (EDX). The μ-Autolab with Nova software and FRA using a three-electrode system equipped with silver/silver chloride (as the reference electrode) and platinum wire (as the counter

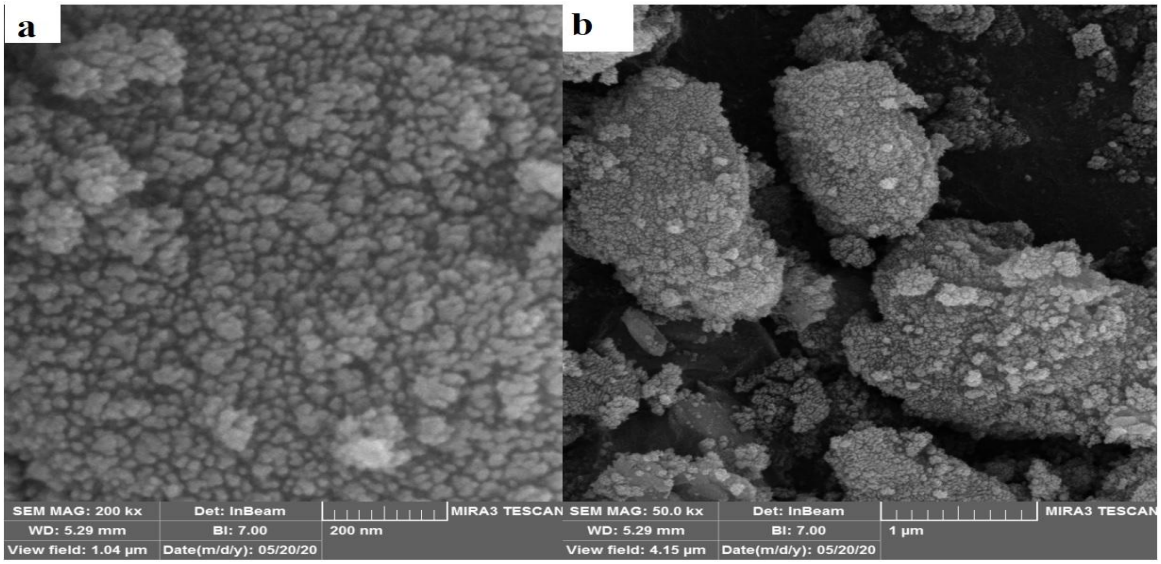


Figure 2. *FE-SEM image of $ZnFe_2O_4$.*

electrode) was used for all electrochemical tests. The bare and modified CPE was used as the working electrode. XRD (X-ray diffraction) pattern was recorded on a Rigaku X-ray diffractometer (D/Max 2500 V, USA). Also, a pH-meter (Metrohm-691, Switzerland) was used for adjusting the pH of the solutions.

Synthesis of $ZnFe_2O_4$

To synthesize $ZnFe_2O_4$, iron nitrate nonahydrate and zinc nitrate hexahydrate were used. 6 g of iron nitrate and 3 g of zinc nitrate were poured into 45 ml of distilled water, and 25 ml of 6 M sodium hydroxide solution was added to reach pH 13 after 30 minutes of ultrasonication. After stirring for 2 hours at room temperature, the solution was transferred to an autoclave and placed at 180 ° C for 3 hours. The resulting precipitates were then washed with water and ethanol, dried at 60 ° C, and finally calcined for 2 hours in an oven at 400 °C.

Electrode preparation

The CPE was prepared from a homogeneous mixture of graphite (0.14 g) and Nujol oil. The CPE was placed in a small Teflon tube with an inner diameter of 2 mm, and a copper wire was used to connect the power and electrochemical device. After drying the prepared electrode in an oven at 50 °C, it was used for electrochemical measurements. The electrode modified with β-cyclodextrins, $ZnFe_2O_4$ nanoparticles, and $ZnFe_2O_4$/β-CD nanocomposite was prepared similar to the unmodified electrode except that 0.01 g of these modifiers were mixed in the presence of graphite and oil.

Preparing of the real sample

Human serum samples were employed to prepare real sample. For this means, 3 ml of methanol was added to the collected serum sample, and the precipitated proteins were separated using a centrifuge at 1000 rpm (10 minutes). The top layer was filtered again with 0.45-µm Millipore filter paper so that the resulting solution was free of protein.

Results and discussion

FTIR spectra of $ZnFe_2O_4$ are shown in Figure 1a. In FTIR spectrum of $ZnFe_2O_4$, the peak at 552 cm^{-1} corresponds to stretching vibrations of Zn-O and the absorption bands at 3434 cm^{-1} is attributed to vibrations of -OH groups on the nanoparticles. The XRD patterns of $ZnFe_2O_4$ (Figure 1b) shows diffraction peaks with 2θ = 18.19 (111), 29.92 (220), 35.26 (311), 42.86 (400) 56.63 (511), and 62.21 (440) correspond to the crystal plane of cubic structure $ZnFe_2O_4$ [Space group Fd-3m, JCPDS code 00-022-1012] show the as-synthesized $ZnFe_2O_4$ nanostructures.

To analyze the morphological features of the prepared $ZnFe_2O_4$ the FE-SEM was performed. Figure 2 shows the FE-SEM image of the synthesized $ZnFe_2O_4$ nanoparticle with rock-shaped containing small inhomogeneous spherical nanoparticles.

The measurements of 50 µM MDop were performed on the surface of CPE, CPE/$ZnFe_2O_4$, CPE/β-CD, and CPE/$ZnFe_2O_4$/β-CD in phosphate buffer solution with pH = 7. The results in Figure 3 show that the currents respective to CPE, CPE/$ZnFe_2O_4$, CPE/β-CD, and CPE/$ZnFe_2O_4$/β-CD are 8.64, 28.16, 31.78, and 47.58 µA, respectively. Moreover, the oxidation potential of MDop at the electrode surface of CPE, CPE/$ZnFe_2O_4$, and CPE/β-CD is 450 mV, but at the electrode surface of CPE/$ZnFe_2O_4$/β-CD is 90 mV lower than other electrodes. Such a result is due to the synergistic effect of $ZnFe_2O_4$, and β-cyclodextrin, which increases the electron transfer rate at the surface of CPE/$ZnFe_2O_4$/β-CD and provides higher sensitivity for measuring MDop at the surface of this electrode.

The increased catalytic effect and improved conductivity of CPE/$ZnFe_2O_4$/β-CD may be due to good conductivity of zinc ferrite and improving its electrochemical activity by incorporating β-cyclodextrin. The surface area of the CPE, CPE/$ZnFe_2O_4$, CPE/β-CD, and CPE/$ZnFe_2O_4$/β-CD was obtained using Equation 1. The results show that the CPE/$ZnFe_2O_4$/β-CD (0.075 cm^2) surface area is larger than CPE/β-CD (0.052 cm^2), CPE/$ZnFe_2O_4$ (0.043cm^2), and CPE (0.031 cm^2)[49]:

$$Ipa = 2.69 \times 10^5\, n^{3/2} A C_0 D^{1/2}\, v^{1/2} \quad (1)$$

where *n* refers to the electrons transferred in the oxidation and reduction process of ferrocyanide, *C* points to the ferrocyanide concentration (5×10^{-9} mol cm^{-3}), D denotes diffusion coefficient of 7.5×10^{-6} Cm^2 s^{-1} and *v* implies the scan rate. The surface area of the CPE/$ZnFe_2O_4$/β-CD (0.075cm^2) is greater than the CPE (0.031 cm^2), βCD improved electrode (0.052 cm^2) and CPE/$ZnFe_2O_4$ (0.043 cm^2) which can be lead to exists of more electrochemical reaction sites.

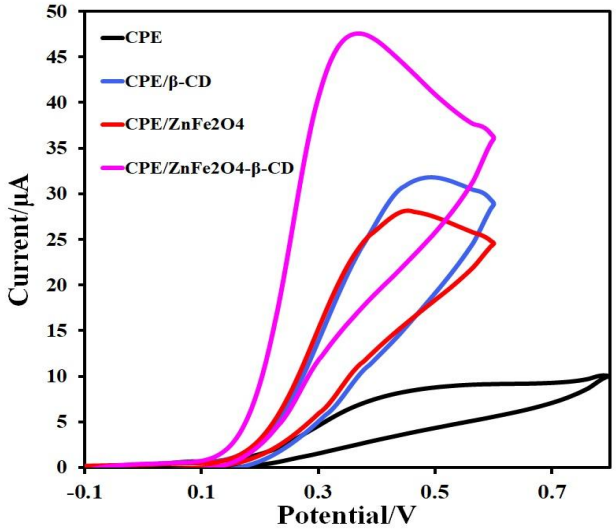


Figure 3. *Cyclic voltammetry of the CPE, CPE/$ZnFe_2O_4$, CPE/β-CD and CPE/$ZnFe_2O_4$/β-CD in 0.1 M phosphate buffer solution (pH = 7) containing 50 µM MDop at the scan rate of 50 mV s^{-1}.*

The effect of different pH on the oxidation of MDop was investigated at CPE/$ZnFe_2O_4$/β-CD. The results in Figure 4 a-c was indicated that the highest maximum current occurred at pH = 7. The relationship between the oxidation potential of MDop and pH has a linear slope of 56 mV, which is due to the proximity to the slope of the Nernst equation. It revelas participation of the equal number of electron and proton during oxidation of MDop at the surface of this electrode.

Investigation of the scan rate at the surface of CPE/$ZnFe_2O_4$/β-CD shows that the oxidation of MDOP has a diffusion-controlled behaviour (Equation 2). Voltammograms of MDop at the surface of CPE/$ZnFe_2O_4$/β-CD are shown in Figure 4d and e. As shown, with increase the scan rate, the oxidation current also increases. The relationship between the current and square root of scan rate is:

$$I_p = 2.6989\, \upsilon^{1/2} + 5.1063 \quad (2)$$

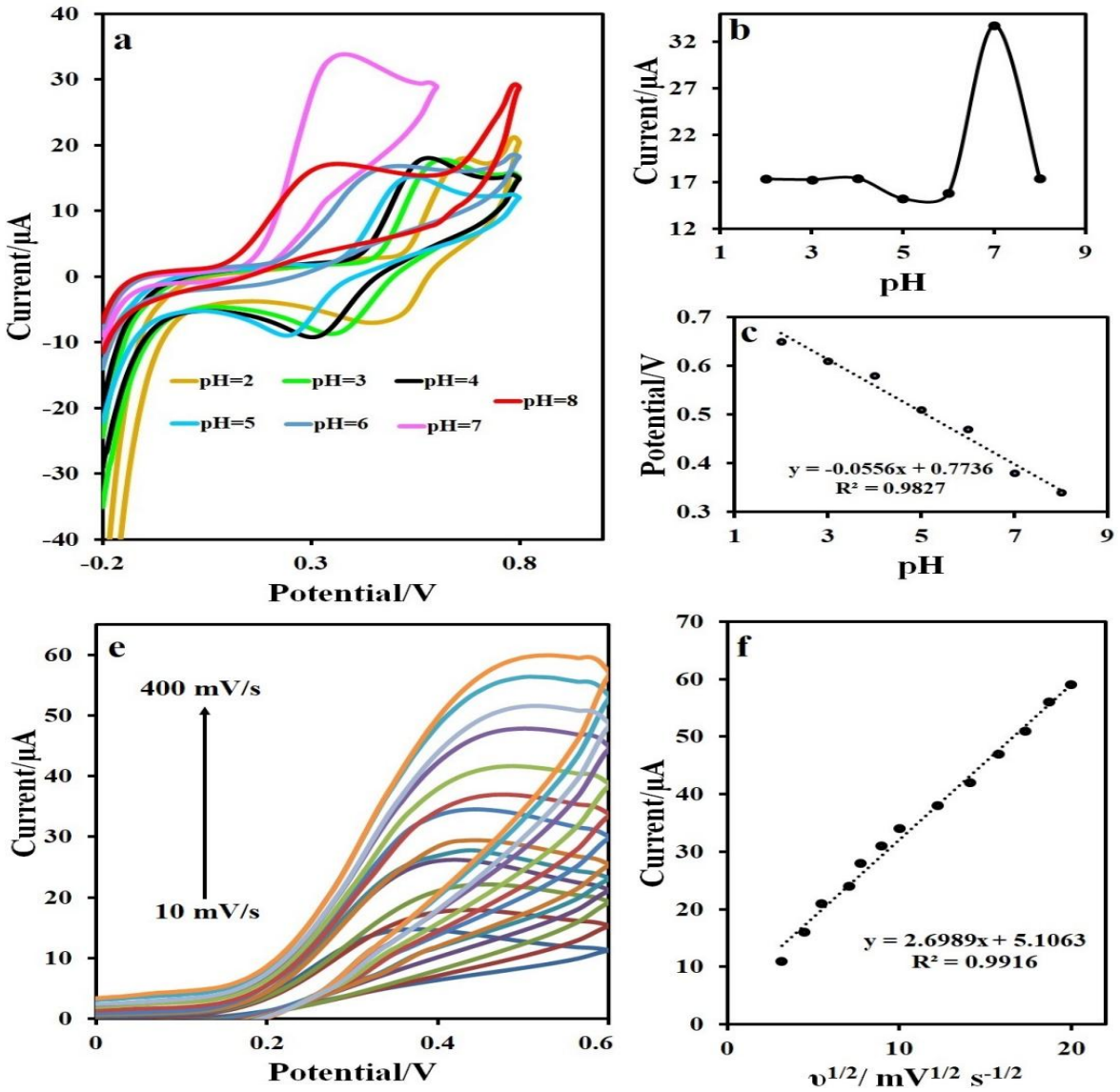


Figure 4. *The pH effect on the oxidation of 50 µM MDop (a to c), (d) Cyclic voltammetry of 50 µM MDOP recorded on the CPE/$ZnFe_2O_4$/β-CD at various scan rates of 10 – 400 mV s^{-1} (e to c).*

A study of different concentrations of MDop at the CPE/$ZnFe_2O_4$/β-CD showed (Figure 5) that the concentration range in which the relationship between the concentration and oxidation current of MDop is linear follows Equation 3.

$I_p = 0.9072\ C + 12.365 \quad (R^2 = 0.9974)$ (3)

In this regard, two concentration ranges were obtained. The detection limit and the quantitative limit for MDop at the surface of CPE/$ZnFe_2O_4$/β-CD are 0.3 ± 0.03 and 1 ± 0.02 µM, respectively.

Comparison between sensors prepared for oxidation of MDop shows that this electrode has a better concentration range than other sensors. Also, the detection limit obtained from this method is better or comparable to other sensors. Other good features of this sensor include easy preparation of the sensor and its cheapness.

Investigation of the repeatability of the prepared electrode also showed that this electrode, after measuring 5 consecutive

Table 1. *Comparing the electrochemical performance of various electrochemical sensors for MDop determination.*

Electrode	Liner range (µM)	LOD (µM)	Ref.
CPE/GQD/ $BMIPF_6$	0.04-750	0.01	[4]
CPE/$Cu(OH)_2$	2-450	0.61	[49]
CPE/IL/MWCNT	0.4-11	0.1	[55]
CPE/IL/Cellulose acetate	34.8-370.3	5.5	[56]
CPE/TiO_2	10-100	1	[57]
CPE/$ZnFe_2O_4$/β-CD	1-100	0.3	This Work

times of MDop, has a relative standard deviation of 3.12%, which indicates the repeatability of this electrode. Also, the measurement of MDop in the presence of different compounds presented in Table 2 shows that this sensor has good selectivity for measuring MDop in other ionic and organic compounds.

Table 2. *The effect of the interference species in the analysis of MDop at CPE/$ZnFe_2O_4$/β-CD.*

Compounds	Tolerant limits ($C_{Compound}/C_{MDOP}$)
Glucose, L-cysteine, H_2O_2, Citric acid, Acetaminophen, Uric acid	400
Cu^{2+}, Cl^-, Na^+, Fe^{3+},Mg^{2+},Ca^{2+}, Br^-	500

To estimate the efficiency and suitableness of the modified electrode for measuring MDop in blood serum sample at CPE/$ZnFe_2O_4$/β-CD surface, the standard addition method was used (Table 3). For this purpose, different concentrations of MDop in real samplewere analyzed by the sensor. The recovery percentage obtained in the range of 96 to 105% indicates that this electrode can also measure MDop in the real sample.

Table 3. Detection of MDop in human serum samples with CPE/$ZnFe_2O_4$/β-CD.

Added (μM)	Found (μM)	Recovery (%)	RSD % (n=3)
0	-	-	-
10	9.64	96.4	3.41
25	25.83	103.32	3.29
50	48.32	96.64	3.37

Conclusion

Measurement of MDop on the surface of carbon paste electrode modified with zinc ferrite-β-cyclodextrin was performed by differential pulse voltammetry. The improvement of the oxidation current of MDop at the surface of CPE/$ZnFe_2O_4$/β-CD indicates the typical effect of the compounds used as modifiers to measure MDop. The best pH for measuring MDop is 7, in which the detection limit for MDop is 0.3 μM. Reproducibility, selectivity, and measurement in blood samples are unique features of this sensor.

References

1. U. Siddiqi and F. Plaat, *Anaesth. Intensive Care Med.*, 18, **2017**, 106.
2. M. Hochadel, J. Avom, W. Thomas, and K. Greider, The AARP guide to pills, (2005) Sterling, London, 615.
3. C. Manegold, G. Hoffmann, I. Degen, H. Ikonomidou, A. Knust, M. Laass, M. Pritsch, E. Wilichowski, and F. Hörster, *J. Inherited Metab. Dis.*, 32, **2009**, 371.
4. A.L. Sanati and F. Faridbod, *Int. J. Electrochem. Sci.*, 12, **2017**, 7997.
5. M. Imazio, F. Gaita, and M. LeWinter, *Jama*, 314, **2015**, 1498.
6. K. Rona, B. Gachalyi, L. Vereczkey, B. Nadas, and A. Kaldor, *Int. J. Clin. Pharmacol. Ther. Toxicol.,* 25, **1987**, 515.
7. F.B. Salem, *Anal. Lett.*, 26, **1993**, 281.
8. O. Nozaki, T. Iwaeda, H. Moriyama, and Y. Kato, *Luminescence*, 14, **1999**, 123.
9. S. Emara, T. Masujima, W. Zarad, M. Kamal, M. Fouad, and R. El-Bagary, *J. Chromatogr. Sci.*, 53, **2015**, 1353.
10. C.R. Freed, R.J. Weinkam, K.L. Melmon, and N. Castagnoli, *Anal. Biochem.*, 78, **1977**, 319.
11. Z. Talebpour, S. Haghgoo, and M. Shamsipur, *Anal. Chim. Acta*, 506, **2004**, 97.
12. B. Pérez-Mella and A. Álvarez-Lueje, *Electroanalysis*, 25, **2013**, 2193.
13. H. Karimi-Maleh, M.R. Ganjali, P. Norouzi, and A. Bananezhad, *Mater. Sci. Eng. C*, 73, **2017**, 472.
14. T. Alizadeh, M.R. Ganjali, M. Akhoundian, and P. Norouzi, *Microchim. Acta*, 183, **2016**, 1123.
15. A. Rudbaraki and M.A. Khalilzadeh, *Anal. Bioanal. Electrochem*, 8, **2016**, 748.
16. A. Hosseini, E. Sohouli, and M. Gholami, *Anal. Bioanal. Electrochem.*, 11, **2019**, 996.
17. S. Mirsadeghi, H. Zandavar, M. Rahimi, H.F. Tooski, H.R. Rajabi, M. Rahimi-Nasrabadi, E. Sohouli, B. Larijani, and S.M. Pourmortazavi, *Colloids Surf. A*, 586, **2020**, 124254.
18. M.S. Mohammadnia, E.M. Khosrowshahi, E. Naghian, A.H. Keihan, E. Sohouli, M.E. Plonska-Brzezinska, M. Rahimi-Nasrabadi, and F. Ahmadi, *Microchem. J.*, 159, **2020**, 105470.
19. Y. Wang, W. Wei, J. Zeng, X. Liu, and X. Zeng, *Microchim. Acta*, 160, **2008**, 253.
20. M. Javanbakht, M.R. Ganjali, P. Norouzi, A. Badiei, A. Hasheminasab, and M. Abdouss, *Electroanalysis*, 19, **2007**, 1307.
21. M. Javanbakht, A. Badiei, M.R. Ganjali, P. Norouzi, A. Hasheminasab, and M. Abdouss, *Anal. Chim. Acta*, 601, **2007**, 172.
22. T.H. Sanatkar, A. Khorshidi, R. Yaghoubi, E. Sohouli, and J. Shakeri, *RSC Adv.*, 10, **2020**, 27575.
23. B.A.H. Zaidan, E. Sohouli, and S. Mazaheri, *Anal. Bioanal. Electrochem*, 11, **2019**, 108.
24. T.H. Sanatkar, A. Khorshidi, E. Sohouli, and J. Janczak, *Inorganica Chim. Acta*, 506, **2020**, 119537.
25. H. Parham and N. Rahbar, *J. Hazard. Mater.*, 177, **2010**, 1077.
26. W. Liu, H. Yang, C. Ma, Y.-n. Ding, S. Ge, J. Yu, and M. Yan, *Anal. Chim. Acta*, 852, **2014**, 181.
27. N.A. Sobhani, E. Sohouli, N. Gholipour, and M.H. Ghanbari, *Anal. Bioanal. Electrochem.,* 11, **2019**, 546.
28. M.M. Ardakani, Z. Taleat, H. Beitollahi, M. Salavati-Niasari, B. Mirjalili, and N. Taghavinia, *J. Electroanal. Chem.*, 624, **2008**, 73.
29. M. Keyvanfard, V. Khosravi, H. Karimi-Maleh, K. Alizad, and B. Rezaei, *J. Mol. Liq.*, 177, **2013**, 182.
30. S. Chitravathi, B.K. Swamy, G. Mamatha, and B. Sherigara, *J. Electroanal. Chem.*, 667, **2012**, 66.
31. A. Bianco, J. Hoebeke, S. Godefroy, O. Chaloin, D. Pantarotto, J.-P. Briand, S. Muller, M. Prato, and C.D. Partidos, *JACS*, 127, **2005**, 58.
32. E. Naghian, F. Shahdost-fard, E. Sohouli, V. Safarifard, M. Najafi, M. Rahimi-Nasrabadi, and A. Sobhani-Nasab, *Microchem. J.*, **2020**, 104888.
33. E. Sohouli, F. Shahdost-Fard, M. Rahimi-Nasrabadi, M.E. Plonska-Brzezinska, and F. Ahmadi, *J. Electroanal. Chem.*, **2020**, 114309.
34. E. Sohouli, M.S. Karimi, E.M. Khosrowshahi, M. Rahimi-Nasrabadi, and F. Ahmadi, *Measurement*, 165, **2020**, 108140.
35. M. Najafi, E. Sohouli, and F. Mousavi, *J. Anal. Chem.*, 75, **2020**, 1209.
36. S. Mirsadeghi, H. Zandavar, H.F. Tooski, M. Rahimi, E. Sohouli, M. Rahimi-Nasrabadi, M.R. Ganjali, and S.M. Pourmortazavi, *Environ. Sci. Pollut. Res.*, **2020**, 1.
37. E. Sohouli, M. Ghalkhani, M. Rostami, M. Rahimi-Nasrabadi, and F. Ahmadi, *Mater. Sci. Eng. C*, 117, **2020**, 111300.
38. E. Sohouli, E.M. Khosrowshahi, P. Radi, E. Naghian, M. Rahimi-Nasrabadi, and F. Ahmadi, *J. Electroanal. Chem.*, 877, **2020**, 114503.

39. R.R. Shahraki, M. Ebrahimi, S.S. Ebrahimi, and S. Masoudpanah, *J. Magn. Magn. Mater.*, 324, **2012**, 3762.
40. J. Wan, X. Jiang, H. Li, and K. Chen, *J. Mater. Chem.*, 22, **2012**, 13500.
41. J. Shi, X. Zhou, Y. Liu, Q. Su, J. Zhang, and G. Du, *Mater. Res. Bull.*, 65, **2015**, 204.
42. Z. Yang, Y. Wan, G. Xiong, D. Li, Q. Li, C. Ma, R. Guo, and H. Luo, *Mater. Res. Bull.*, 61, **2015**, 292.
43. Z. Shahnavaz, F. Lorestani, Y. Alias, and P.M. Woi, *Appl. Surf. Sci.*, 317, **2014**, 622.
44. M. Mozaffari and H. Masoudi, *J. Supercond. Novel Magn.*, 27, **2014**, 2563.
45. G. Chen and M. Jiang, *Chem. Soc. Rev.*, 40, **2011**, 2254.
46. A.E. Kaifer and M. Gómez-Kaifer, Supramolecular electrochemistry, (2008) John Wiley & Sons, Germany.
47. H. Li, D.-X. Chen, Y.-L. Sun, Y.B. Zheng, L.-L. Tan, P.S. Weiss, and Y.-W. Yang, *JACS*, 135, **2013**, 1570.
48. F. Gandomi, E.M. Khosrowshahi, E. Sohouli, M. Aghaei, M.S. Mohammadnia, E. Naghian, and M. Rahimi-Nasrabadi, *J. Electroanal. Chem.*, 876, **2020**, 114697.
49. S.M. Ghoreishi, F. Saeidinejad, M. Behpour, and S. Masoum, *Sens. Actuators B*, 221, **2015**, 576.
50. H. Beitollahi, K. Movlaee, M.R. Ganjali, P. Norouzi, and R. Hosseinzadeh, *Appl. Organomet. Chem.*, 32, **2018**, e4243.
51. S. Tajik, M.A. Taher, and H. Beitollahi, *J. Electroanal. Chem.*, 704, **2013**, 137.
52. E. Molaakbari, A. Mostafavi, and H. Beitollahi, *Mater. Sci. Eng. C*, 36, **2014**, 168.
53. A. Salmanipour, M.A. Taher, and H. Beitollahi, *Anal. Methods*, 4, **2012**, 2982.
54. M. Keyvanfard, M. Hatami, V.K. Gupta, S. Agarwal, H. Sadeghifar, and M.A. Khalilzadeh*, J. Mol. Liq.*, 230, **2017**, 290.
55. M. Fouladgar and H. Karimi-Maleh, *Ionics*, 19, **2013**, 1163.
56. S.K. Moccelini, A.C. Franzoi, I.C. Vieira, J. Dupont, and C.W. Scheeren, *Biosens. Bioelectron.*, 26, **2011**, 3549.
57. L.F. Garcia, C.E.P.d. Cunha, E.K.G. Moreno, D.V. Thomaz, G. Sanz Lobón, R. Luque, V. Somerset, and E. de Souza Gil, *Pharmaceuticals*, 11, **2018**, 99.