J. Electrochem. Sci. Eng. **14(1)** (2024) 93-105; http://dx.doi.org/10.5599/jese.2038

Open Access : : ISSN 1847-9286
www.jESE-online.org

Original scientific paper

Facile preparation of a sensitive electrochemical sensor with good performance for determination of methionine

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Received: August 23, 2023; Accepted: November 10, 2023; Published: November 29, 2023

Abstract

In this work, a novel voltammetric sensor for the detection of methionine was designed and prepared by using a carbon paste electrode (CPE) modified with ZnO hollow quasi-spheres (ZnO hollow QSs) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM.PF_6). The results by cyclic voltammetry showed that the prepared electrode (ZnO-BMIM.PF_6/CPE) effectively increased the oxidation peak current and reduced the oxidation peak potential of methionine and had a suitable electrocatalytic activity for the oxidation of methionine. Notably, the ZnO-BMIM.PF_6/CPE exhibited high detection capability towards the quantification of methionine in 0.1 M PBS (pH 7.0) over a concentration range from 0.04 to 330.0 µM with a limit of detection of 0.02 µM. More importantly, the effectiveness of the ZnO-BMIM.PF_6/CPE sensor was also confirmed in real samples (urine detection with acceptable recoveries (98.0 to 102.7 %) and relative standard deviation values ≤ 3.3 %.

Keywords

Voltammetric sensor; carbon paste electrode; ZnO hollow quasi-spheres; 1-butyl-3-methylimidazolium hexafluorophosphate

Introduction

Methionine is classified as a sulfur-containing amino acid because it contains a sulfur atom in this chemical structure. Methionine is a primary source of sulfur in the diet, playing a vital role in maintaining the health and integrity of various tissues, including the hair, skin, and nails [1]. Also, methionine plays a crucial role in various biological processes, including protein synthesis, synthesis of amino acids, such as cysteine, taurine, homocysteine, and glycine, transmethylation reaction, and other physiological processes [2]. By increasing lecithin production in the liver, methionine can indirectly reduce cholesterol levels [3]. In addition, methionine acts as a chelator for heavy metals and functions as a powerful antioxidant for free radicals scavenging [3]. Methionine deficiency has been studied in relation to various diseases, including toxaemia, Parkinson's disease, and acquired

immune deficiency syndrome (AIDS) [4]. In addition to this, methionine deficiencies can lead to hair loss, weight loss, liver deterioration, impaired growth, depression, and muscle paralysis [5]. Therefore, developing an accurate and reliable analytical method for detecting methionine is crucial due to its clinical and physiological significance. At present, several methods, such as capillary electrophoresis [6], chromatography [7], colorimetry [8], fluorescence [9], chemiluminescence [10], and so on, have been extensively used for the analysis of methionine. Although some of these methods can be reliable, it is important to consider that they may require expensive and sophisticated equipment as well as time-consuming procedures.

Electrochemical methods are still widely used and popular due to their distinct characteristics, including fast response, low cost, versatility, simple operation, ease of miniaturization, and so on [11-19]. Modified electrodes play a crucial role in enhancing the performance, sensitivity, and selectivity of electrochemical sensors, allowing for more accurate and reliable detection of target analytes [20-26]. Nanotechnology is a closely related field that deals with the study and manipulation of materials and phenomena at the nanometer scale to create new materials, structures, and functionalities. Nanotechnology opened up new possibilities for innovation in various fields, including electronics, medicine, energy, materials science and more [27-36]. The application of nanostructures for the modification of electrodes has gained significant attention in recent years [37-41]. Nanostructured materials can offer enhanced properties such as high specific surface area and high conductivity, making them ideal candidates for electrode modifications in sensing applications. By providing higher sensitivity and selectivity, nanostructures improve the performance of electrochemical sensors in detecting and measuring different species [42-44].

ZnO is regarded as a versatile material that has been extensively studied in a wide range of applications in various fields, including catalysis [45], gas sensors [46], energy storage [47], electrochemical sensors and biosensors [48], water treatment [49], biomedicine [50], and *etc*. However, researchers continuously explore innovative ways to synthesize ZnO nanostructures with desired properties to unlock their potential fully. By manipulating the synthesis process, researchers can control the shape, size, and morphology of ZnO nanostructures, leading to significant changes in their physical and chemical characteristics. This control over nanostructure design opens avenues for tailoring ZnO properties to meet specific application requirements. In recent years, ZnO hollow nanostructures have gained significant attention in scientific research and technological applications [51-53]. The unique properties of ZnO hollow nanostructures, including low density, porous structure, and high specific surface area, make them promising candidates for the development of high-performance electrochemical sensors.

Ionic liquids (ILs) are non-molecular ionic compounds composed of oppositely charged ions arranged in a crystal lattice structure, and they exhibit distinct properties different from molecular compounds. The diverse combinations of cations and anions allow for the creation of ILs with tailored properties and functionalities [54]. ILs have gained significant attention in various fields, notably electrochemistry, because of their thermal and chemical stability, high conductivity, wide potential window, and low vapor pressure [55]. The combination of nanomaterials with ILs has shown great potential in the fabrication of electrochemical sensors. By creating the synergistic effects of nanomaterials and ILs, researchers can design and fabricate innovative electrochemical sensors with improved performance, sensitivity, and selectivity. This opens up new possibilities for applications in fields such as environmental monitoring, healthcare diagnostics, and industrial process control [56,57].

Herein, we developed a high-performance modified CPE based on ZnO hollow QSs-BMIM.PF_6 for detection of methionine. The ZnO-BMIM.PF_6 modified CPE reduces the overpotential and enhances the oxidation peak current for the effective electrochemical detection of methionine. Furthermore, the modified CPE provided acceptable results for the detection of methionine in real samples.

Experimental

Instruments and materials

All electrochemical studies and measurements were done using a potentiostat/galvanostat device *(*Metrohm Autolab – PGSTAT302N (Utrecht, The Netherlands)), controlled by the GPES 4.9004 software. The electrochemical tests were performed in a typical three-electrode setup by using reference electrode (RE) (Ag/AgCl/KCl (3 M)), counter electrode (CE) (platinum), and working electrode (modified CPE). All solvents and chemicals were commercially available (Merck and Sigma-Aldrich companies) with analytical grade and used directly without further purification.

The synthesis and characterization of ZnO hollow QSs were reported in our previous work [58]. Figure 1 shows the FE-SEM image of ZnO hollow QSs.

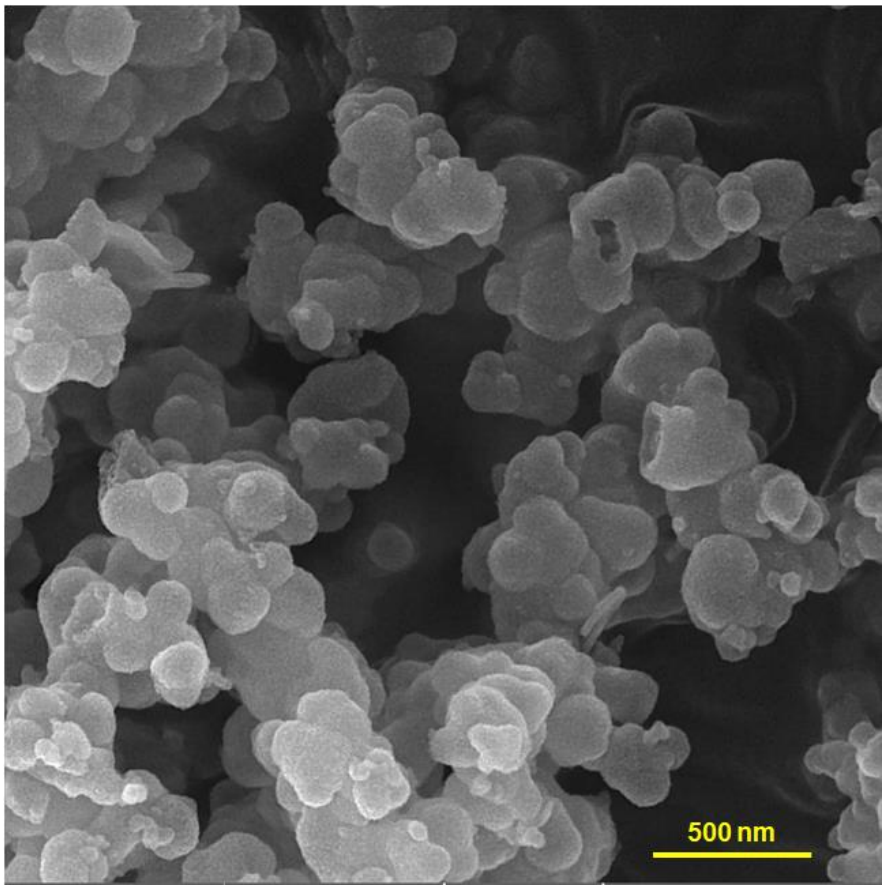

Figure 1. *FE-SEM image of ZnO hollow QSs*

Preparation of ZnO-BMIM.PF_6/CPE

The ZnO-BMIM.PF_6 modified CPE with a mass of 0.5 g was achieved by hand-mixing 0.48 g of graphite powder and 0.02 g of ZnO hollow QSs for 5 min until a homogeneous blend was formed. Then, paraffin oil and BMIM.PF_6 in the ratio 3:1 was added to the blend of graphite and ZnO hollow QSs, which was mixed again for at least 30 min to obtain the ZnO-BMIM.PF_6 modified carbon paste. Finally, the modified paste was packed into the glass tube cavity. The electrical contact was

established through a conductive copper wire. Also, the surface of the prepared electrode (ZnO-BMIM.PF_6/CPE) was polished on a smooth paper to obtain a shiny and smooth appearance.

To calculate the electrochemically active surface area (EASA) of the unmodified CPE and ZnO-BMIM.PF_6/CPE, the CVs were recorded at different scan rates in 0.1 M KCl solution containing 1.0 mM $K_3[Fe(CN)_6]$ as a redox probe. Using the Randles–Ševčik equation, the value of the ESCA for ZnO-BMIM.PF_6/CPE (0.297 cm^2) was found 3.3 times greater than unmodified CPE.

Results and discussion

Electrocatalytic response of ZnO-BMIM.PF_6/CPE towards methionine

The effect of pH values (from 2.0 to 9.0) of the supporting electrolyte (0.1 M PBS) on methionine's electrochemical oxidation was studied using the ZnO-BMIM.PF_6 modified CPE via DPV technique. It was observed that by changing the pH value of PBS, the prepared electrode showed different voltammograms for oxidation of methionine. The peak potential and peak current from the oxidation of methionine showed a strong dependence on pH. By increasing the pH from lower to higher values, the anodic peak potential of methionine was shifted towards the negative potentials. Also, the I_{pa} of methionine gradually increased with the increase of pH from 2.0 to 7.0 and then decreased. The maximum I_{pa} was obtained at pH 7.0. Therefore, pH 7.0 was used for further electrochemical studies.

To assess the electrocatalytic activity of the IL (BMIM.PF_6) and as-prepared ZnO, the electrochemical responses of methionine on unmodified CPE and modified CPE were examined by cyclic voltammetry (CV). Figure 2 shows the cyclic voltammograms from the response of unmodified CPE (voltammogram a) and ZnO-BMIM.PF_6/CPE (voltammogram b) towards the 150.0 µM methionine in 0.1 M PBS (pH 7.0).

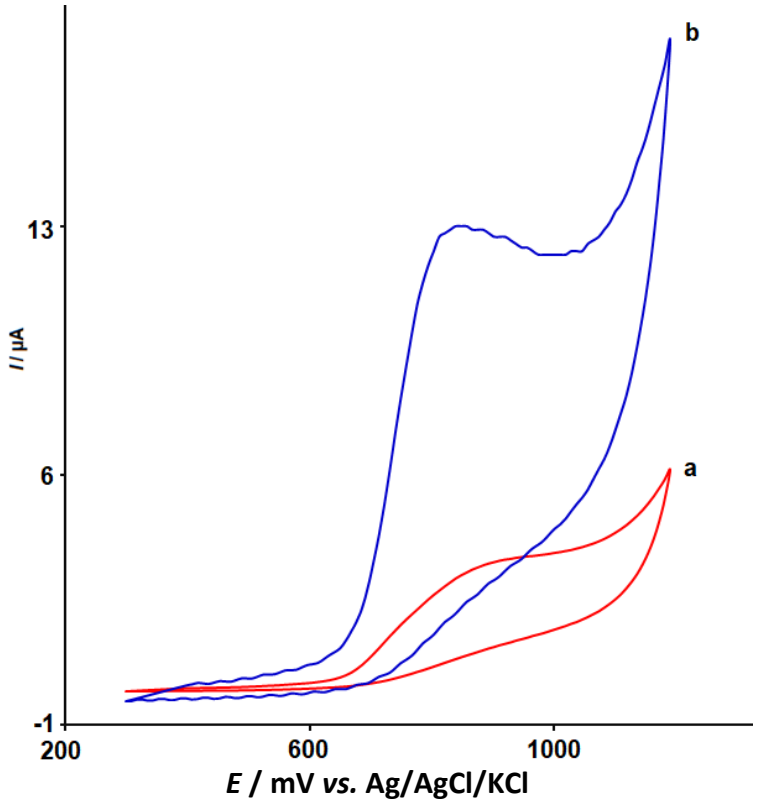

Figure 2. *CVs of unmodified CPE (a) and ZnO-BMIM.PF_6/CPE (b) in 0.1 M PBS (pH 7.0) containing 150.0 µM methionine at a scan rate of 50 mV s^{-1}*

As can be seen, a broad oxidation peak with a low anodic peak current (I_{pa}) was shown for unmodified CPE. The ZnO-BMIM.PF_6/CPE clearly improves the oxidation of methionine, as evident from the increase of the I_{pa} (from 3.5 to 13.0 µA) and decrease of the overpotential (from 950 to 850 mV) when compared with unmodified CPE. This result could be related to the electrocatalytic effect of the IL and ZnO NPs. In addition, the absence of any reduction peak on the reverse scan revealed the irreversible oxidation of methionine over unmodified and modified CPE.

Effect of scan rate on the oxidation reaction of methionine

To investigate the effect of scan rate, CVs of the ZnO-BMIM.PF_6/CPE were recorded at different scan rates (10 to 250 mV/s) in 0.1 M PBS containing 100.0 µM methionine (Figure 3). An increase in the anodic peak current (I_{pa}) with an increase in scan rate can be observed. Also, from the obtained voltammograms, it was possible to observe a linear dependence between I_{pa} of methionine and the square root of scan rate ($\nu^{1/2}$) (I_{pa} = 1.8901 $\nu^{1/2}$ -2.9739) (Figure 3 Inset). This observation suggests that the oxidation reaction is controlled by the diffusion of methionine species from the bulk solution to the surface of ZnO-BMIM.PF_6/CPE.

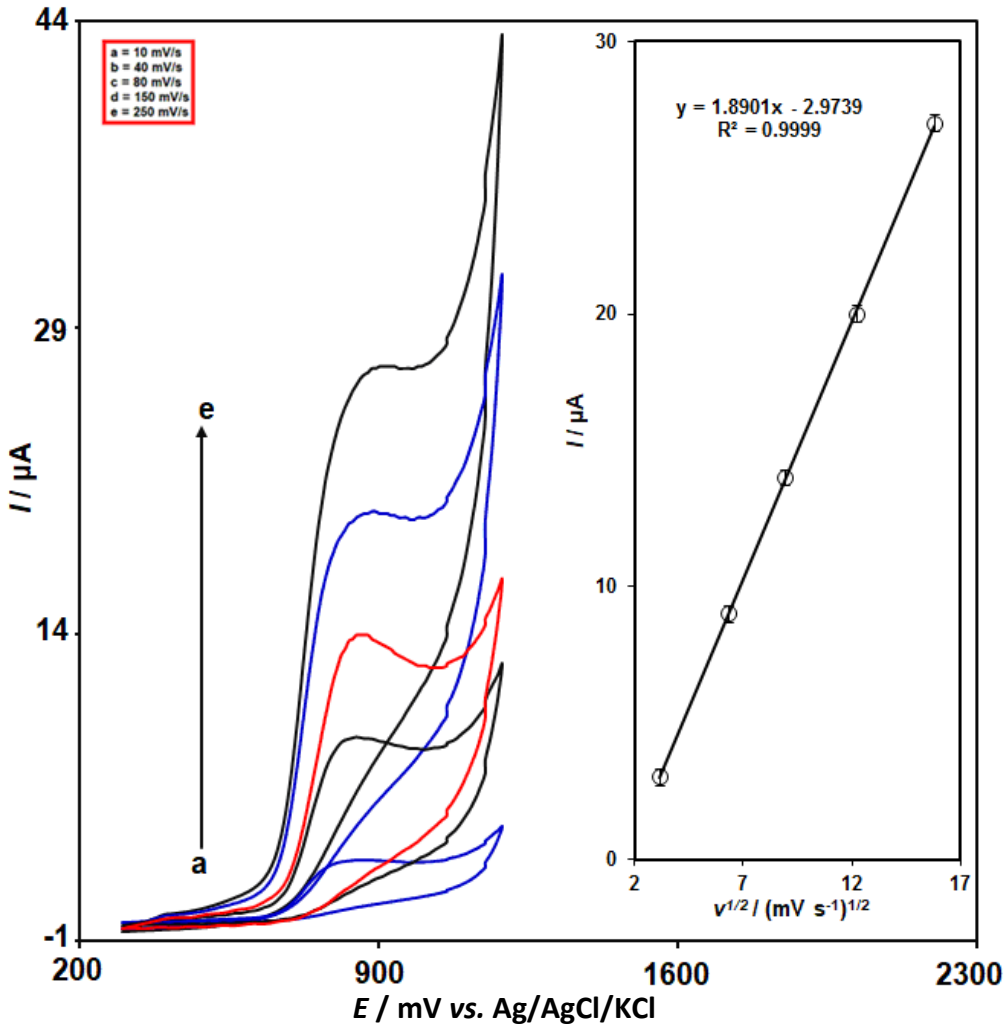

Figure 3. *CVs of ZnO-BMIM.PF_6/CPE performed at different scan rates (from a: 10 to e: 250 mV s^{-1}) in 0.1 M PBS (pH 7.0) containing 100.0 µM methionine. Inset: the linear dependence between* I_{pa} vs. $\nu^{1/2}$

Chronoamperometric measurements of methionine at ZnO-BMIM.PF_6/CPE

To measure the diffusion coefficient (D) of methionine, the chronoamperometric responses of ZnO-BMIM.PF_6/CPE were plotted for different concentrations of methionine from 0.1 to 1.7 mM at the

fixed potential of 0.9 V (Figure 4). The current-time (*I-t*) curves reflect the change in concentration gradient of the electroactive species (methionine) in the vicinity of the electrode surface as time progresses. To determine the *D*, the Cottrell curves (*I* versus $t^{-1/2}$) were plotted over a certain range of time for different concentrations of methionine (Figure 4A). Then, the slope of the obtained Cottrell curves was plotted vs the different concentrations of methionine (Figure 4B) and a straight line with a slope of 19.7 µA $s^{1/2}$ mM^{-1} was obtained. From the slope of the resulting plot and using Cottrell's equation, the *D* of methionine on the surface of ZnO-BMIM.PF_6/CPE was found to be 1.6×10^{-5} cm^2 s^{-1}.

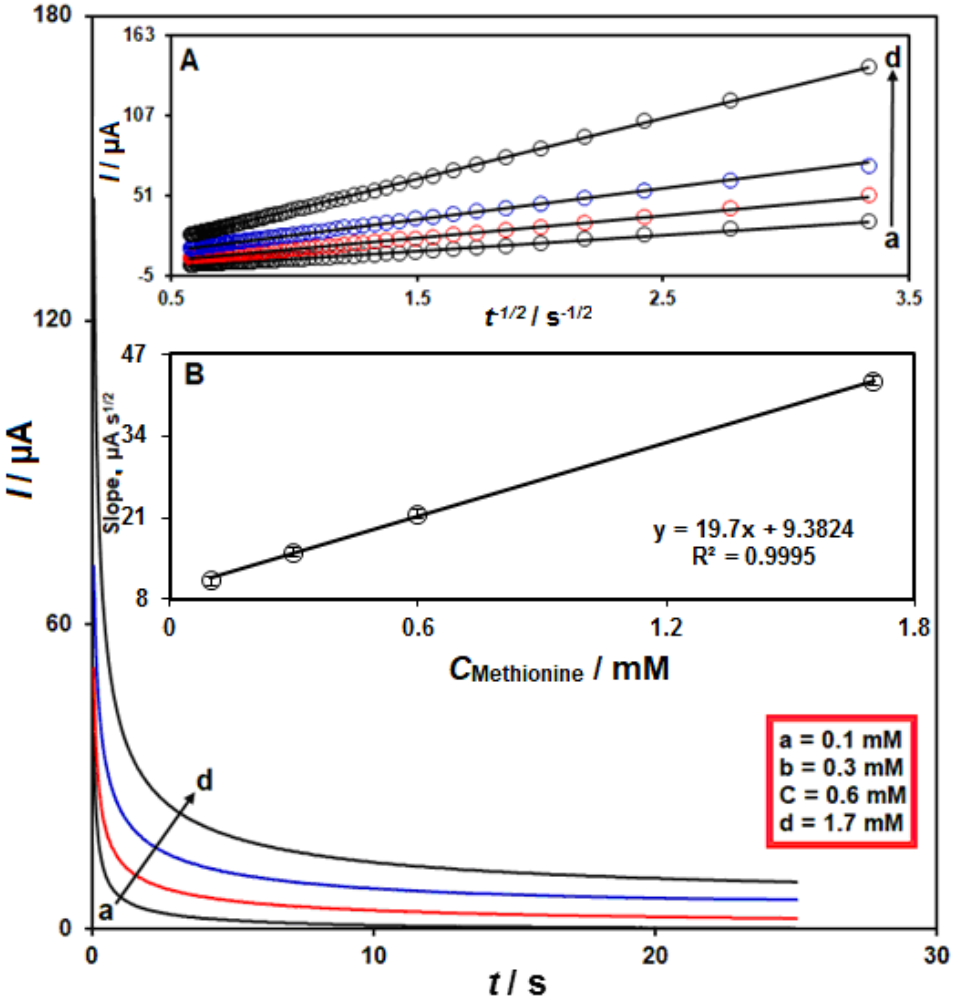

Figure 4. *Chronoamperometric responses of ZnO-BMIM.PF_6/CPE in 0.1 M PBS (pH 7.0) containing different concentrations of methionine from a: 0.1 to 1.7 mM. Inset A: the linear dependence between* I_{pa} */ µA* vs. $t^{-1/2}$ / $s^{-1/2}$*) and Inset B: linear dependence between slope values of I-*$t^{-1/2}$ *plots* vs. *methionine concentrations*

Quantitative analysis of methionine by DPV

To study the detection efficiency of ZnO-BMIM.PF_6/CPE, the DPV measurements were performed with the successive addition of methionine (0.04 to 330.0 µM) in 0.1 M PBS (pH 7.0) in the following conditions: step potential 0.01 V and pulse amplitude 0.025 V (Figure 5). From the recorded voltammograms, the increase of the I_{pa} is proportional to the increase of methionine concentration in a wide range from 0.04 to 330.0 µM. Furthermore, the linear dependence between the enhanced I_{pa} of methionine and its concentration is presented in the Inset of Figure 5. This dependence can be expressed by $I = 0.0812C_{Methionine} + 0.8557$ with a correlation coefficient of 0.999. The LOD was calculated according to the ensuing formula $3S_b/m$, where S_b denotes the standard deviation of the

blank (PBS) signal (obtained based on 12 measurements on the blank solution), and *m* denotes the slope of the corresponding calibration curve, and it was found to be 0.02 µM. The limit of quantification was found to be 0.04 µM. Table 1 lists the comparative characteristics of the as-prepared sensor with those of previously reported sensors for the determination of methionine.

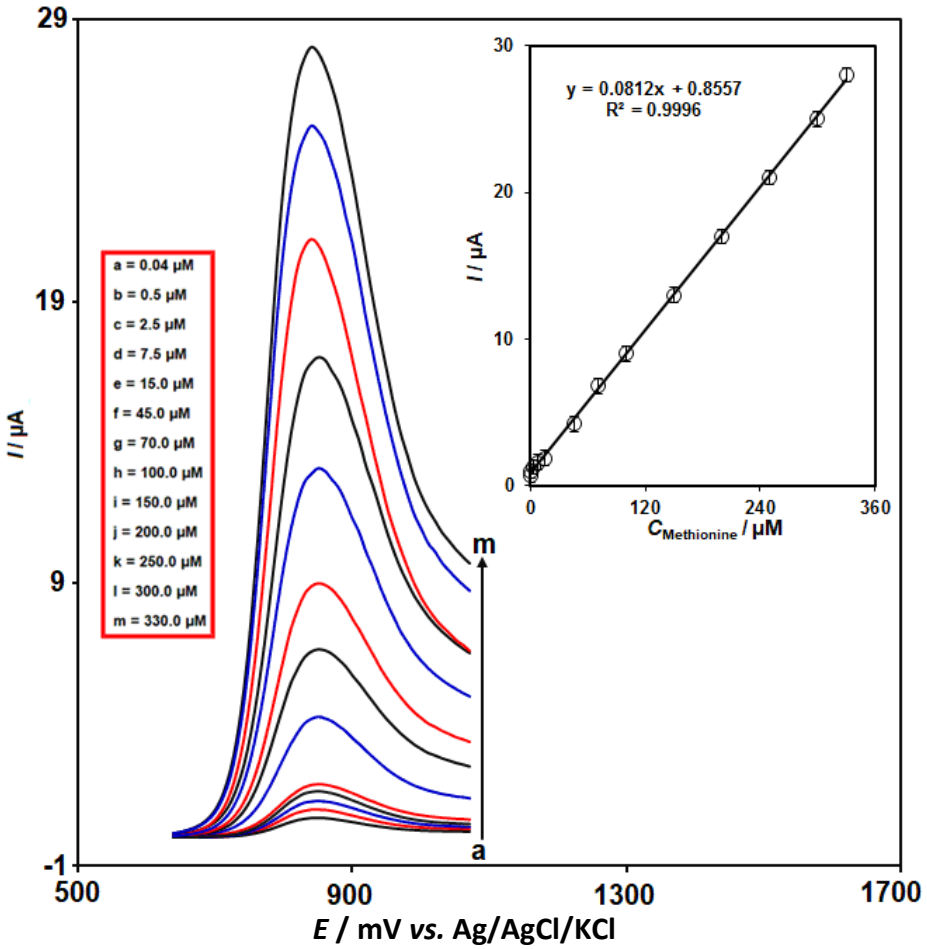

Figure 5. *DPVs of ZnO-BMIM.PF$_6$/CPE performed in 0.1 M PBS (pH 7.0) containing different concentrations of methionine (from a: 0.04 to m: 330.0 µM). Inset: the linear dependence between* I_{pa} *vs. methionine concentration*

Table 1. *Comparative results of ZnO-BMIM.PF$_6$/CPE based methionine sensor with previously reported sensors*

Electrochemical sensor	Linear range, µM	LOD, µM	Sensitivity	Ref.
Pt-doped TiO_2 nanoparticles (NPs) carbon nanotubes (CNTs)/glassy carbon electrode (GCE)	0.5 - 100	0.1	29.085 µA μM^{-1} cm^{-2}	[1]
Colloidal gold-cysteamine/CPE	1.0 - 100	0.59	-	[12]
Fullerene-C_{60}/Au electrode	-	8.2	50 mA M^{-1}	[59]
Ni-doped carbon ceramic electrode	2 - 90	2	5.6 nA μM^{-1}	[60]
Graphitic carbon nitride nanosheets/GCE	0.1 - 200	0.32×10^{-3}	1.16 µA μM^{-1} cm^{-2}	[61]
ZnO-BMIM.PF_6/CPE	0.04 - 330.0	0.02	0.0812 µA μM^{-1}	This work

Stability and reproducibility studies of ZnO-BMIM.PF$_6$/CPE sensor towards the determination of methionine

Studies related to the stability of ZnO-BMIM.PF_6/CPE sensors were performed by recording the current response of the designed sensor towards 75.0 µM methionine over 20 days. The results

showed that the electrode response retained 95.9 % of its initial value after 20 days. These results indicated that the designed sensor has good stability.

Also, the reproducibility of the prepared sensor (ZnO-BMIM.PF_6/CPE) was evaluated by recording the current response of five electrodes prepared independently under the same conditions. All five prepared electrodes showed almost the same responses and the relative standard deviation (RSD) was 2.7 % in the determination of 75.0 µM methionine.

Interferences studies

The effect of the possible interferences from some species such as Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, Al^{3+}, Cl^-, SO_4^{2-}, S^{2-}, glucose, acetaminophen, epinephrine, norepinephrine, uric acid, tryptophan, glycine, phenylalanine, and L-serine on the electrochemical response of methionine was evaluated at the surface of ZnO-BMIM.PF_6/CPE sensor. It was observed that these species did not show significant interference for the determination of methionine (no signal change more than ± 5 %). These results confirmed that the developed sensor has good selectivity for the determination of methionine.

Methionine analysis in real samples

To evaluate the practical performance of the developed sensor (ZnO-BMIM.PF_6/CPE), the determination of methionine in the urine sample was conducted. The standard addition method was employed for the analysis of methionine by the DPV technique. By adding the known concentrations of methionine to the urine sample, measurements were performed. The recovery and RSD values are summarized in Table 2. The summarized results in Table 1 show acceptable recovery values (between 98.0 and 102.7 %) and RSD values (n = 5) of ≤3.3 %, which confirm that the developed sensor could be used for real-time analysis.

Table 2. *Real sample analysis for the determination of methionine spiked into the urine samples*

Sample	Amount, µM		Recovery, %	RSD, %
	Spiked	Found		
Urine	0	-	-	-
	5.0	4.9±0.05	98.0	3.3
	7.5	7.7±0.04	102.7	2.9
	10.0	10.1±0.06	101.0	1.7
	12.5	12.4±0.05	99.2	2.4

Conclusions

In this study, the efficient and accurate detection of methionine was reported based on ZnO hollow QSs-BMIM.PF_6 modified CPE. The obtained results demonstrated that the ZnO-BMIM.PF_6/CPE sensor was well developed and showed an enhanced electrochemical response towards methionine oxidation. The ZnO-BMIM.PF_6/CPE can be used to determine methionine in the concentration from 0.04 to 330.0 µM with an LOD of 0.02 µM. Finally, excellent precision (RSD ≤3.3 %) and accuracy (recovery for spiked samples ranging from 98.0 to 102.7 %) were obtained.

References

[1] F. Chekin, S. Bagheri, S. B. Abd Hamid, Synthesis of Pt doped TiO_2 nanoparticles: characterization and application for electrocatalytic oxidation of l-methionine, *Sensors and Actuators B: Chemical* **177** (2013) 898-903. https://doi.org/10.1016/j.snb.2012.12.002

[2] J. D. Finkelstein, Methionine metabolism in mammals, *The Journal of Nutritional Biochemistry* **1** (1990) 228-237. https://doi.org/10.1016/0955-2863(90)90070-2

[3] Y. Yang, S. Han, Synergistic enhanced of carbon dots and eosin Y on fenton chemiluminescence for the determination of methionine, *Microchemical Journal* **163** (2021) 105902. https://doi.org/10.1016/j.microc.2020.105902
[4] Y. Li, S. Mei, S. Liu, X. Hun, A photoelectrochemical sensing strategy based on single-layer MoS_2 modified electrode for methionine detection, *Journal of Pharmaceutical and Biomedical Analysis* **165** (2019) 94-100. https://doi.org/10.1016/j.jpba.2018.11.059
[5] T. Hoshi, S. H. Heinemann, Regulation of cell function by methionine oxidation and reduction, *The Journal of Physiology* **531** (2001) 1-11. https://doi.org/10.1111/j.1469-7793.2001.0001j.x
[6] L. Vitali, F. Della Betta, A. C. O. Costa, F. A. S. Vaz, M. A. L. Oliveira, J. P. Vistuba, G. A. Micke, New multilayer coating using quaternary ammonium chitosan and κ-carrageenan in capillary electrophoresis: Application in fast analysis of betaine and methionine, *Talanta* **123** (2014) 45-53. https://doi.org/10.1016/j.talanta.2014.01.047
[7] K. Borowczyk, G. Chwatko, P. Kubalczyk, H. Jakubowski, J. Kubalska, R. Głowacki, Simultaneous determination of methionine and homocysteine by on-column derivatization with o-phtaldialdehyde, *Talanta* **161** (2016) 917-924. https://doi.org/10.1016/j.talanta.2016.09.039
[8] P. C. Huang, N. Gao, J. F. Li, F. Y. Wu, Colorimetric detection of methionine based on anti-aggregation of gold nanoparticles in the presence of melamine, *Sensors and Actuators B: Chemical* **255** (2018) 2779-2784. https://doi.org/10.1016/j.snb.2017.09.092
[9] Y. Wang, S. Liu, Z. Liu, J. Yang, X. Hu, A l-tryptophan-Cu (II) based fluorescence turn-on probe for detection of methionine, *Journal of Luminescence* **147** (2014) 107-110. https://doi.org/10.1016/j.jlumin.2013.11.006
[10] M. Zhou, A. Wang, C. Li, X. Luo, Y. Ma, Flow-based determination of methionine in pharmaceutical formulations exploiting TGA-capped CdTe quantum dots for enhancing the luminol-KIO_4 chemiluminescence, *Journal of Luminescence* **183** (2017) 206-211. https://doi.org/10.1016/j.jlumin.2016.11.007
[11] V. R. R. Bernardo-Boongaling, N. Serrano, J. J. García-Guzmán, J. M. Palacios-Santander, J. M. Díaz-Cruz, Screen-printed electrodes modified with green-synthesized gold nanoparticles for the electrochemical determination of aminothiols, *Journal of Electroanalytical Chemistry* **847** (2019) 113184. https://doi.org/10.1016/j.jelechem.2019.05.066
[12] L. Agüý, J. Manso, P. Yáñez-Sedeño, J. M. Pingarrón, Colloidal-gold cysteamine-modified carbon paste electrodes as suitable electrode materials for the electrochemical determination of sulphur-containing compounds: application to the determination of methionine, *Talanta* **64** (2004) 1041-1047. https://doi.org/10.1016/j.talanta.2004.05.002
[13] Y. Tangal, D. Coban, S. Cogal, A WSe_2@poly (3,4-ethylenedioxythiophene) nanocomposite-based electrochemical sensor for simultaneous detection of dopamine and uric acid, *Journal of Electrochemical Science and Engineering* **12** (2022) 1251-1259. https://doi.org/10.5599/jese.1375
[14] H. Karimi-Maleh, R. Darabi, F. Karimi, C. Karaman, S. A. Shahidi, N. Zare, M. Baghayeri, L. Fu, S. Rostamnia, J. Rouhi, State-of-art advances on removal, degradation and electrochemical monitoring of 4-aminophenol pollutants in real samples, *Environmental Research* **222** (2023) 115338. https://doi.org/10.1016/j.envres.2023.115338
[15] M. Vardini, N. Abbasi, A. Kaviani, M. Ahmadi, E. Karimi, Graphite electrode potentiometric sensor modified by surface imprinted silica gel to measure valproic acid, *Chemical Methodologies* **6** (2022) 398-408. https://doi.org/10.22034/chemm.2022.328620.1437
[16] S. Tajik, H. Beitollahi, H. W. Jang, M. Shokouhimehr, A screen printed electrode modified with Fe_3O_4@polypyrrole-Pt core-shell nanoparticles for electrochemical detection of 6-

mercaptopurine and 6-thioguanine, *Talanta* **232** (2021) 122379. https://doi.org/10.1016/j.talanta.2021.122379

[17] R. S. Kumar, G. K. Jayaprakash, S. Manjappa, M. Kumar, A. P. Kumar, Theoretical and electrochemical analysis of L-serine modified graphite paste electrode for dopamine sensing applications in real samples, *Journal of Electrochemical Science and Engineering* **12** (2022) 1243-1250. https://doi.org/10.5599/jese.1390

[18] H. Pyman, Design and fabrication of modified DNA-Gp nano-biocomposite electrode for industrial dye measurement and optical confirmation, *Progress in Chemical and Biochemical Research* **5** (2022) 391-405. https://doi.org/10.22034/pcbr.2022.367576.1236

[19] S. Tajik, H. Beitollahi, F. Garkani Nejad, M. Safaei, P. Mohammadzadeh Jahani, (2022). Electrochemical sensing of Sudan I using the modified graphite screen-printed electrode, *International Journal of Environmental Analytical Chemistry* **102** (2022) 1477-1490. https://doi.org/10.1080/03067319.2020.1738418

[20] S. Cheraghi, M. A. Taher, H. Karimi-Maleh, F. Karimi, M. Shabani-Nooshabadi, M. Alizadeh, A. Al-Othman, N. Erk, P. K. Y. Raman, C. Karaman, Novel enzymatic graphene oxide based biosensor for the detection of glutathione in biological body fluids, *Chemosphere* **287** (2022) 132187. https://doi.org/10.1016/j.chemosphere.2021.132187

[21] R. Zaeimbashi, A. Mostafavi, T. Shamspur, Synthesis of vanadium oxide nanoplates for electrochemical detection of amaranth in food samples, *Journal of Electrochemical Science and Engineering* **12** (2022) 1153-1163. https://doi.org/10.5599/jese.1394

[22] H. Roshanfekr, A simple specific dopamine aptasensor based on partially reduced graphene oxide–AuNPs composite, *Progress in Chemical and Biochemical Research* **6** (2023) 61-70. https://doi.org/10.22034/pcbr.2023.381280.1245

[23] S. Z. Mohammadi, H. Beitollahi, E. Bani Asadi, Electrochemical determination of hydrazine using a ZrO_2 nanoparticles-modified carbon paste electrode, *Environmental Monitoring and Assessment* **187** (2015) 122. https://doi.org/10.1007/s10661-015-4309-9

[24] S. B. Arpitha, B. K. Swamy, J. K. Shashikumara, An efficient electrochemical sensor based on ZnO/Co_3O_4 nanocomposite modified carbon paste electrode for the sensitive detection of hydroquinone and resorcinol, *Inorganic Chemistry Communications* **152** (2023) 110656. https://doi.org/10.1016/j.inoche.2023.110656

[25] S. N. Zakiyyah, D. R. Eddy, Firdaus, M. L. Eddy, T. Subroto, Y. W. Hartati, Screen-printed carbon electrode/natural silica-ceria nanocomposite for electrochemical aptasensor application, *Journal of Electrochemical Science and Engineering* **12** (2022) 1225-1242. https://doi.org/10.5599/jese.1455

[26] H. Karimi-Maleh, Y. Liu, Z. Li, R. Darabi, Y. Orooji, C. Karaman, F. Karimi, M. Baghayeri, J. Rouhi, L. Fu, Calf thymus ds-DNA intercalation with pendimethalin herbicide at the surface of ZIF-8/Co/rGO/C_3N_4/ds-DNA/SPCE; A bio-sensing approach for pendimethalin quantification confirmed by molecular docking study, *Chemosphere* **332** (2023) 138815. https://doi.org/10.1016/j.chemosphere.2023.138815

[27] O. Daliri Shamsabadi, Investigation of antimicrobial effect and mechanical properties of modified starch films, cellulose nanofibers, and citrus essential oils by disk diffusion method, *Asian Journal of Green Chemistry* **8** (2024) 1-14. https://doi.org/10.48309/ajgc.2024.398370.1394

[28] H. Alinezhad, P. Hajiabbas Tabar Amiri, S. Mohseni Tavakkoli, R. Muslim Muhiebes, Y. Fakri Mustafa, Progressive types of Fe_3O_4 nanoparticles and their hybrids as catalysts, *Journal of Chemical Reviews* **4** (2022) 288-312. https://doi.org/10.22034/jcr.2022.325255.1137

[29] O. K. Akeremale, Metal-organic frameworks (MOFs) as adsorbents for purification of dye-contaminated wastewater: a review, *Journal of Chemical Reviews* **4** (2022) 1-14. https://doi.org/10.22034/jcr.2022.314728.1130

[30] S. Li, Y. Zhang, Y. Yuan, F. Chang, K. Zhu, G. Li, L. Yang, Design and synthesis of dispersed Ni_2P/Co nano heterojunction as bifunctional electrocatalysis for boosting overall water splitting, *International Journal of Hydrogen Energy* **48** (2023) 3355-3363. https://doi.org/10.1016/j.ijhydene.2022.10.129
[31] B. Baghernejad, M. Alikhani, Nano-cerium oxide/aluminum oxide as an efficient catalyst for the synthesis of xanthene derivatives as potential antiviral and anti-inflammatory agents, *Journal of Applied Organometallic Chemistry* **2** (2022) 140-147. https://doi.org/10.22034/jaoc.2022.154819
[32] I. Alao, I. Oyekunle, K. Iwuozor, E. Emenike, Green synthesis of copper nanoparticles and investigation of its antimicrobial properties, *Advanced Journal of Chemistry, Section B* **4** (2022) 39-52. https://doi.org/10.22034/ajcb.2022.323779.1106
[33] M. S. Jabar, S. A. W. Al-Shammaree, Cytotoxicity and anticancer effect of chitosan-Ag NPs-doxorubicin-folic acid conjugate on lungs cell line, *Chemical Methodologies* 7 (2023) 1-14. https://doi.org/10.22034/chemm.2023.359769.1604
[34] D. Palke, Synthesis, physicochemical and biological studies of transition metal complexes of DHA schiff bases of aromatic amine, *Journal of Applied Organometallic Chemistry* **2** (2022) 81-88. https://doi.org/10.22034/jaoc.2022.349187.1055
[35] M. Ozdal, S. Gurkok, Recent advances in nanoparticles as antibacterial agent, *ADMET and DMPK* **10** (2022) 115-129. https://doi.org/10.5599/admet.1172
[36] B. Bonhoeffer, A. Kordikowski, E. John, M. Juhnke, Numerical modeling of the dissolution of drug nanocrystals and its application to industrial product development, *ADMET and DMPK* **10** (2022) 253-287. https://doi.org/10.5599/admet.1437
[37] F. Garkani Nejad, S. Tajik, H. Beitollahi, I. Sheikhshoaie, Magnetic nanomaterials based electrochemical (bio) sensors for food analysis, *Talanta* **228** (2021) 122075. https://doi.org/10.1016/j.talanta.2020.122075
[38] S. Z. Mohammadi, F. Mousazadeh, M. Mohammadhasani-Pour, Electrochemical detection of folic acid using a modified screen printed electrode, *Journal of Electrochemical Science and Engineering* **12** (2022) 1111-1120. https://doi.org/10.5599/jese.1360
[39] J. A. Buledi, N. Mahar, A. Mallah, A. R. Solangi, I. M. Palabiyik, N. Qambrani, F. Karimi, Y. Vasseghian, H. Karimi-Maleh, Electrochemical quantification of mancozeb through tungsten oxide/reduced graphene oxide nanocomposite: A potential method for environmental remediation, *Food and Chemical Toxicology* **161** (2022) 112843. https://doi.org/10.1016/j.fct.2022.112843
[40] A. Hajializadeh, An electrochemical sensor for detection of vanillin in food samples using $CuFe_2O_4$ nanoparticles/ionic liquids modified carbon paste electrode, *Journal of Electrochemical Science and Engineering* **12** (2022) 1193-1203. https://doi.org/10.5599/jese.1395
[41] Z. Zhang, H. Karimi-Maleh, In situ synthesis of label-free electrochemical aptasensor-based sandwich-like AuNPs/PPy/$Ti_3C_2T_x$ for ultrasensitive detection of lead ions as hazardous pollutants in environmental fluids, *Chemosphere* **324** (2023) 138302. https://doi.org/10.1016/j.chemosphere.2023.138302
[42] S. Tajik, H. Beitollahi, F. Garkani Nejad, M. Safaei, K. Zhang, Q. Van Le, M. Shokouhimehr, Developments and applications of nanomaterial-based carbon paste electrodes, *RSC Advances* **10** (2020) 21561-21581. https://doi.org/10.1039/D0RA03672B
[43] H. Karimi-Maleh, C. T. Fakude, N. Mabuba, G. M. Peleyeju, O. A. Arotiba, The determination of 2-phenylphenol in the presence of 4-chlorophenol using nano-Fe_3O_4/ionic liquid paste electrode as an electrochemical sensor, *Journal of Colloid and Interface Science* **554** (2019) 603-610. https://doi.org/10.1016/j.jcis.2019.07.047

[44] Z. Mehdizadeh, S. Shahidi, A. Ghorbani-HasanSaraei, M. Limooei, M. Bijad, Monitoring of amaranth in drinking samples using voltammetric amplified electroanalytical sensor, *Chemical Methodologies* **6** (2022) 246-252. https://doi.org/10.22034/chemm.2022.324073.1423

[45] O. V. Larina, P. I. Kyriienko, D. Y. Balakin, M. Vorokhta, I. Khalakhan, Y. M. Nychiporuk, V. Matolín, S. O. Soloviev, S. M. Orlyk, Effect of ZnO on acid-base properties and catalytic performances of ZnO/ZrO_2-SiO_2 catalysts in 1,3-Butadiene production from ethanol-water mixture, *Catalysis Science & Technology* **9** (2019) 3964–3978. https://doi.org/10.1039/C9CY00991D

[46] Z. Li, L. Guo, Z. Feng, S. Gao, H. Zhang, X. Yang, G. Pan, Metal-organic framework-derived ZnO decorated with CuO for ultra-high response and selectivity H_2S gas sensor. *Sensors and Actuators B: Chemical* **366** (2022) 131995. https://doi.org/10.1016/j.snb.2022.131995

[47] K. Zhu, J. Chen, C. Guo, H. Wang, H. Li, P. Xue, J. M. Lee, Hierarchically constructed ZnO/Co_3O_4 nanoheterostructures synergizing dendrite inhibition and polysulfide conversion in lithium–sulfur battery, *ACS Materials Letters* **4** (2022) 1358-1367. https://doi.org/10.1021/acsmaterialslett.2c00266

[48] K. Saxena, A. Kumar, N. Chauhan, M. Khanuja, B. D. Malhotra, U. Jain, Electrochemical immunosensor for detection of h. Pylori secretory protein vaca on g-C_3N_4/ZnO nanocomposite-modified au electrode, *ACS Omega* **7** (2022) 32292-32301. https://doi.org/10.1021/acsomega.2c03627

[49] V. B. Raghavendra, S. Shankar, M. Govindappa, A. Pugazhendhi, M. Sharma, S. C. Nayaka, Green synthesis of zinc oxide nanoparticles (ZnO NPs) for effective degradation of dye, polyethylene and antibacterial performance in waste water treatment, *Journal of Inorganic and Organometallic Polymers and Materials* **32** (2022) 614–630. https://doi.org/10.1007/s10904-021-02142-7

[50] N. Salahuddin, S. Awad, M. Elfiky, Vanillin-crosslinked chitosan/ZnO nanocomposites as a drug delivery system for 5-fluorouracil: study on the release behavior via mesoporous ZrO_2–Co_3O_4 nanoparticles modified sensor and antitumor activity, *RSC Advances* **12** (2022) 21422-21439. https://doi.org/10.1039/d2ra02717h

[51] S. Ameen, M. S. Akhtar, H. K. Seo, H. S. Shin, An electrochemical sensing platform based on hollow mesoporous ZnO nanoglobules modified glassy carbon electrode: Selective detection of piperidine chemical, *Chemical Engineering Journal* **270** (2015) 564–571. https://doi.org/10.1016/j.cej.2015.02.052

[52] J. Zhang, H. Lu, L. Zhang, D. Leng, Y. Zhang, W. Wang, C. Wang, Metal–organic framework-derived ZnO hollow nanocages functionalized with nanoscale Ag catalysts for enhanced ethanol sensing properties, *Sensors and Actuators B* **291** (2019) 458-469. https://doi.org/10.1016/j.snb.2019.04.058

[53] S. Wang, X. Wang, G. Qiao, X. Chen, X. Wang, H. Cui, Core-double shell ZnO@ In_2O_3@ZnO hollow microspheres for superior ethanol gas sensing, *Sensors and Actuators B* **341** (2021) 130002. https://doi.org/10.1016/j.snb.2021.130002

[54] R. Chokkareddy, S. Kanchi, G. G. Redhi, A novel IL-f-ZnONPs@MWCNTs nanocomposite fabricated glassy carbon electrode for the determination of sulfamethoxazole, *Journal of Molecular Liquids* **359** (2022) 119232. https://doi.org/10.1016/j.molliq.2022.119232

[55] P. Ranjan, M. Abubakar Sadique, S. Yadav, R. Khan, An electrochemical immunosensor based on gold-graphene oxide nanocomposites with ionic liquid for detecting the breast cancer CD44 biomarker, *ACS Applied Materials & Interfaces* **14** (2022) 20802-20812. https://doi.org/10.1021/acsami.2c03905

[56] M. A. Mohamed, N. N. Salama, M. A. Sultan, H. F. Manie, M. M. A. El-Alamin, Sensitive and effective electrochemical determination of butenafine in the presence of itraconazole using

titanium nanoparticles-ionic liquid based nanocomposite sensor, *Chemical Papers* **77** (2023) 1929-1939. https://doi.org/10.1007/s11696-022-02593-3

[57] K. Kunpatee, S. Traipop, O. Chailapakul, S. Chuanuwatanakul, Simultaneous determination of ascorbic acid, dopamine, and uric acid using graphene quantum dots/ionic liquid modified screen-printed carbon electrode, *Sensors and Actuators B* **314** (2020) 128059. https://doi.org/10.1016/j.snb.2020.128059

[58] S. Z. Mohammadi, S. Tajik, F. Mousazadeh, E. Baghadam-Narouei, F. Garkani Nejad, ZnO hollow quasi-spheres modified screen-printed graphite electrode for determination of carmoisine, *Micromachines* **14** (2023) 1433. https://doi.org/10.3390/mi14071433

[59] W. E. Tan, J. E. Goh, Electrochemical oxidation of methionine mediated by a fullerene-C60 modified gold electrode, *Electroanalysis* **20** (2008) 2447-2453. https://doi.org/10.1002/elan.200704335

[60] A. Salimi, M. Roushani, Electrocatalytic oxidation of sulfur containing amino acids at renewable Ni-powder doped carbon ceramic electrode: application to amperometric detection L-cystine, L-cysteine and L-methionine, *Electroanalysis* **18** (2006) 2129-2136. https://doi.org/10.1002/elan.200603639

[61] A. Ajith, S. A. John, Cost Effective Electrochemical sensor for L-Methionine based on graphitic carbon nitride sheets modified electrode, *Electroanalysis* **35** (2023) e202200063. https://doi.org/10.1002/elan.202200063