



Original scientific paper

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

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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.PF₆). The results by cyclic voltammetry showed that the prepared electrode (ZnO-BMIM.PF₆/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.PF₆/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.PF₆/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 toxemia, 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 Qs-BMIM.PF₆ for detection of methionine. The ZnO-BMIM.PF₆ 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 Qs were reported in our previous work [58]. Figure 1 shows the FE-SEM image of ZnO hollow Qs.

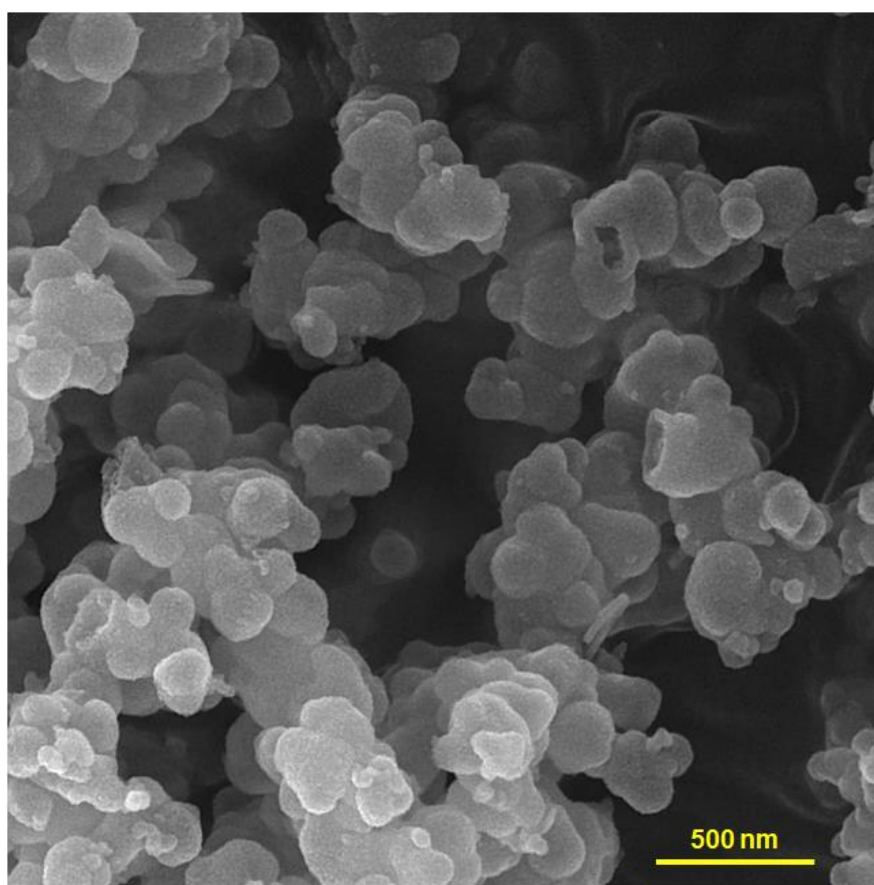


Figure 1. FE-SEM image of ZnO hollow Qs

Preparation of ZnO-BMIM.PF₆/CPE

The ZnO-BMIM.PF₆ 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 Qs for 5 min until a homogeneous blend was formed. Then, paraffin oil and BMIM.PF₆ in the ratio 3:1 was added to the blend of graphite and ZnO hollow Qs, which was mixed again for at least 30 min to obtain the ZnO-BMIM.PF₆ 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.PF₆/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.PF₆/CPE, the CVs were recorded at different scan rates in 0.1 M KCl solution containing 1.0 mM K₃[Fe(CN)₆] as a redox probe. Using the Randles–Ševčík equation, the value of the ESCA for ZnO-BMIM.PF₆/CPE (0.297 cm²) was found 3.3 times greater than unmodified CPE.

Results and discussion

Electrocatalytic response of ZnO-BMIM.PF₆/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.PF₆ 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.PF₆) 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.PF₆/CPE (voltammogram b) towards the 150.0 μM methionine in 0.1 M PBS (pH 7.0).

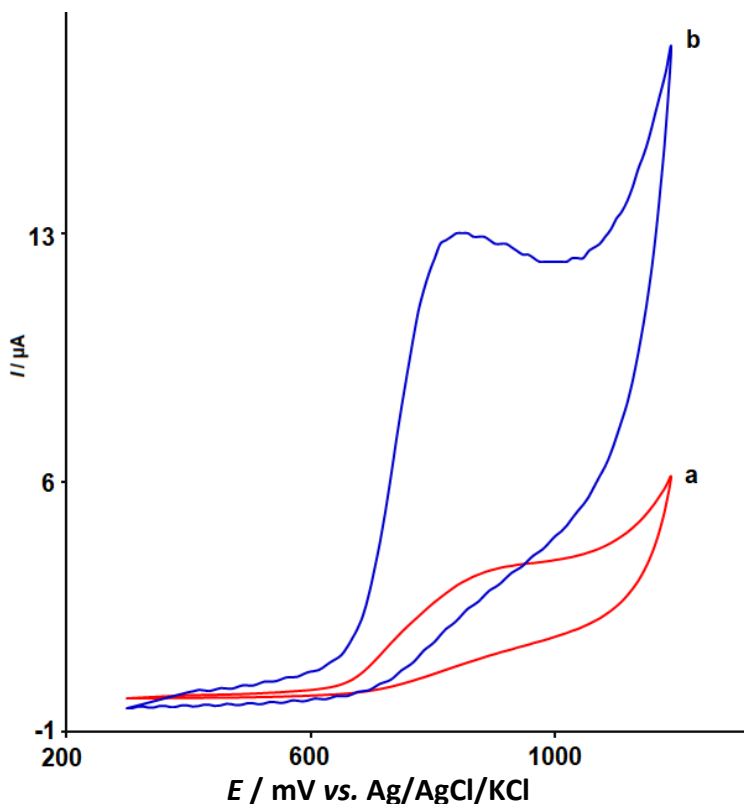


Figure 2. CVs of unmodified CPE (a) and ZnO-BMIM.PF₆/CPE (b) in 0.1 M PBS (pH 7.0) containing 150.0 μM methionine at a scan rate of 50 mV s⁻¹

As can be seen, a broad oxidation peak with a low anodic peak current (I_{pa}) was shown for unmodified CPE. The ZnO-BMIM.PF₆/CPE clearly improves the oxidation of methionine, as evident from the increase of the I_{pa} (from 3.5 to 13.0 μ A) 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.PF₆/CPE were recorded at different scan rates (10 to 250 mV/s) in 0.1 M PBS containing 100.0 μ M 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 ($v^{1/2}$) ($I_{pa} = 1.8901 v^{1/2} - 2.9739$) (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.PF₆/CPE.

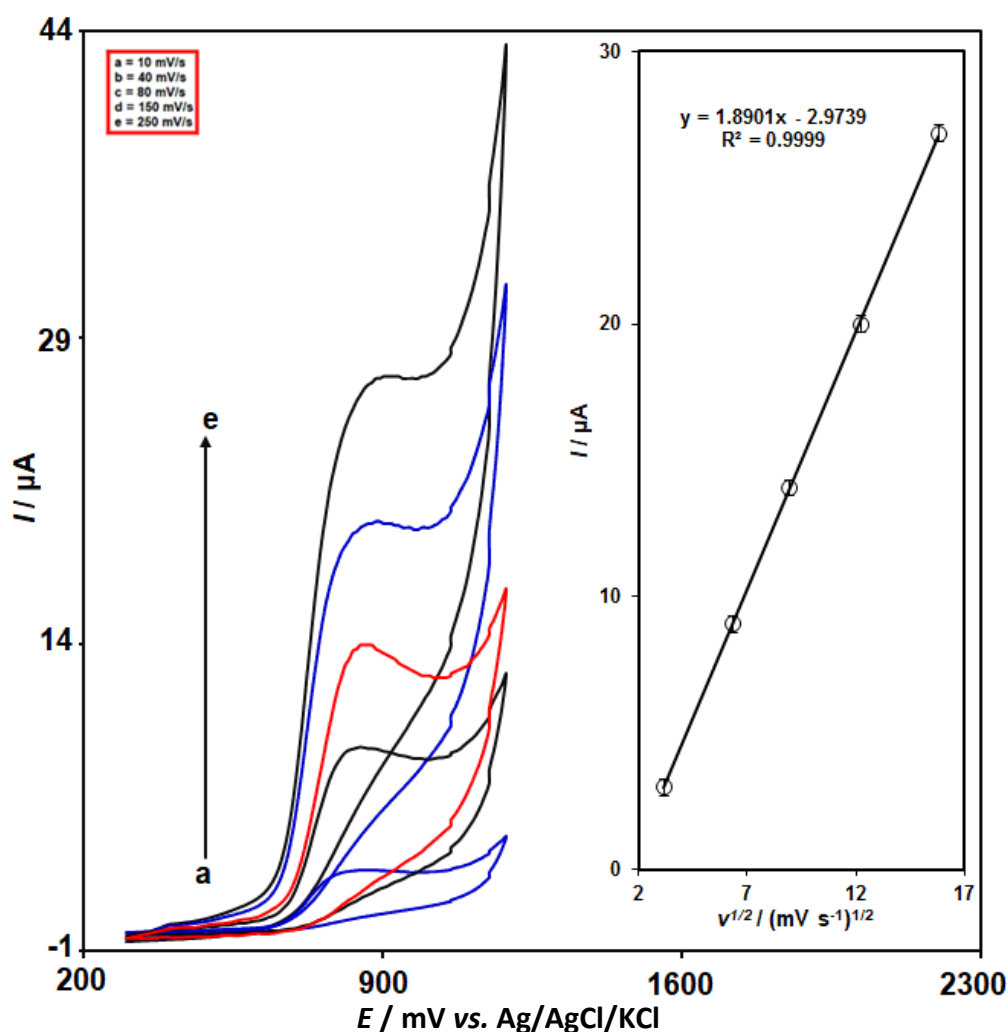


Figure 3. CVs of ZnO-BMIM.PF₆/CPE performed at different scan rates (from a: 10 to e: 250 mV s^{-1}) in 0.1 M PBS (pH 7.0) containing 100.0 μM methionine. Inset: the linear dependence between I_{pa} vs. $v^{1/2}$

Chronoamperometric measurements of methionine at ZnO-BMIM.PF₆/CPE

To measure the diffusion coefficient (D) of methionine, the chronoamperometric responses of ZnO-BMIM.PF₆/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 $19.7 \mu\text{A s}^{1/2} \text{mM}^{-1}$ was obtained. From the slope of the resulting plot and using Cottrell's equation, the D of methionine on the surface of ZnO-BMIM.PF₆/CPE was found to be $1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

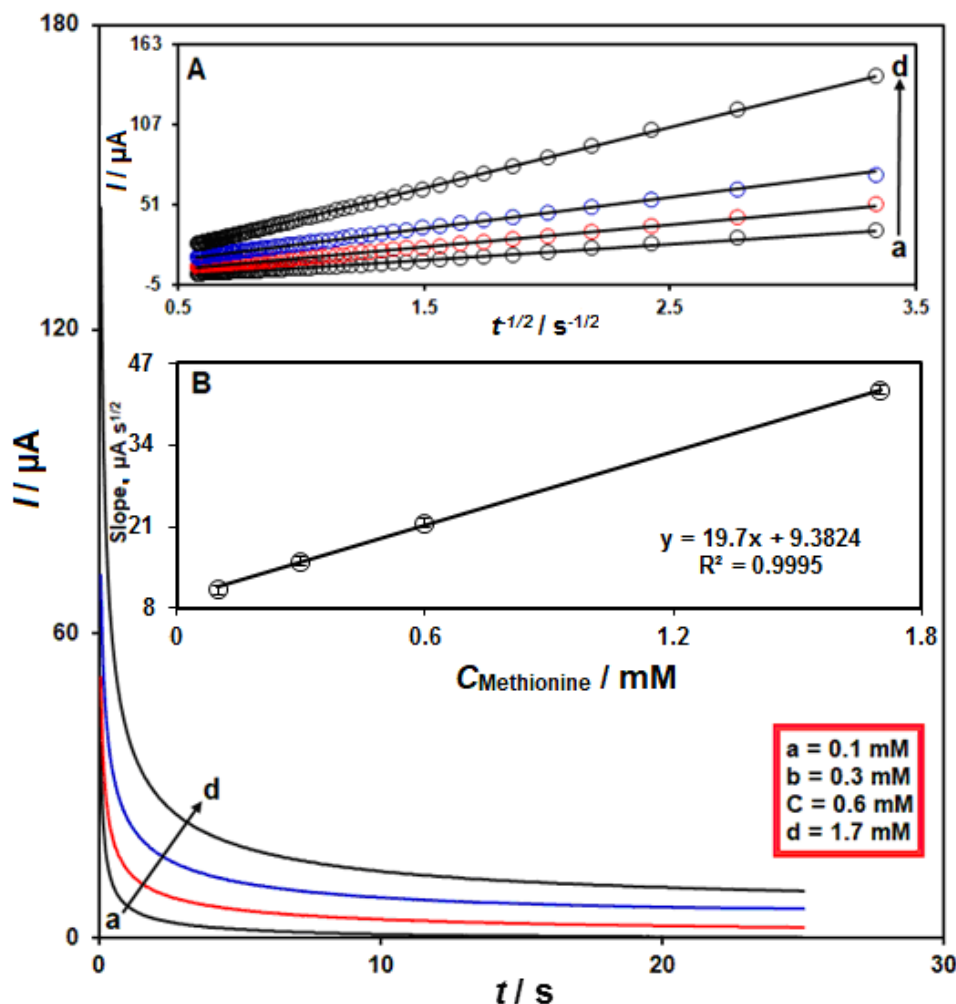


Figure 4. Chronoamperometric responses of ZnO-BMIM.PF₆/CPE in 0.1 M PBS (pH 7.0) containing different concentrations of methionine from a: 0.1 to 1.7 mM. Inset A: the linear dependence between $I_{pa} / \mu\text{A}$ vs. $t^{-1/2} / \text{s}^{-1/2}$) and Inset B: linear dependence between slope values of $I-t^{-1/2}$ plots vs. methionine concentrations

Quantitative analysis of methionine by DPV

To study the detection efficiency of ZnO-BMIM.PF₆/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 $I = 0.0812C_{\text{Methionine}} + 0.8557$ 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 $0.02 \mu\text{M}$. The limit of quantification was found to be $0.04 \mu\text{M}$. Table 1 lists the comparative characteristics of the as-prepared sensor with those of previously reported sensors for the determination of methionine.

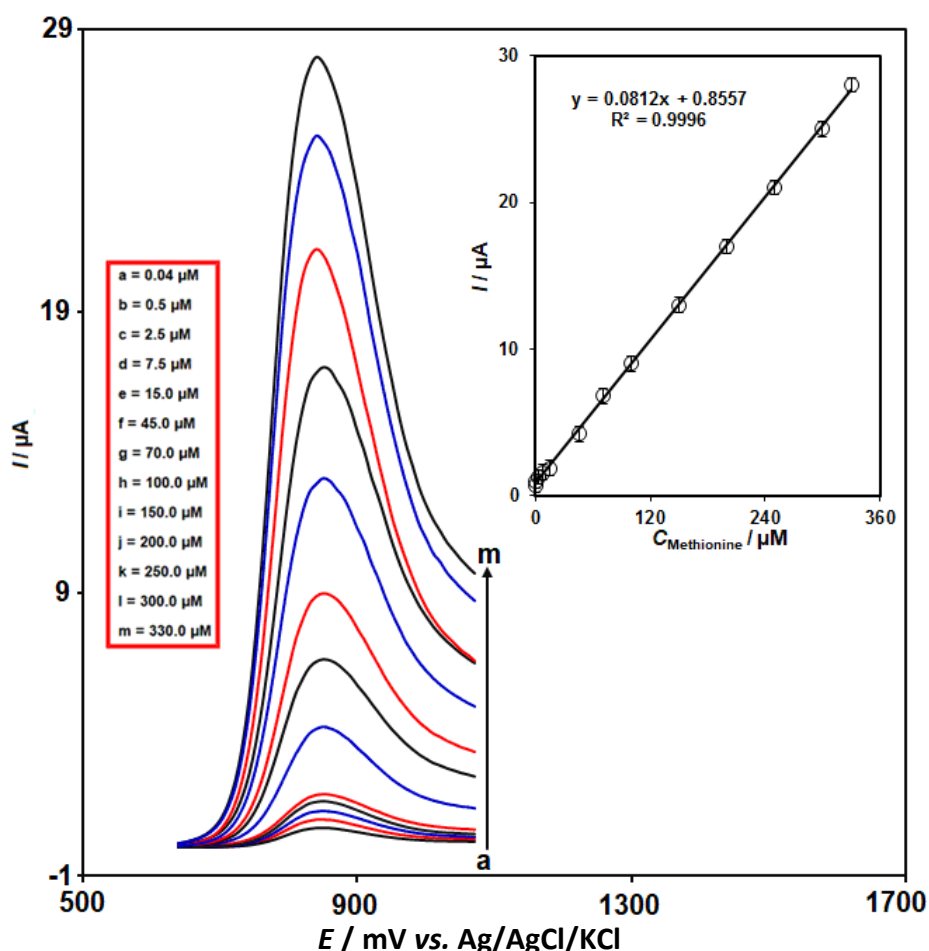


Figure 5. DPVs of ZnO-BMIM.PF₆/CPE performed in 0.1 M PBS (pH 7.0) containing different concentrations of methionine (from a: 0.04 to m: 330.0 μM). Inset: the linear dependence between I_{pa} vs. methionine concentration

Table 1. Comparative results of ZnO-BMIM.PF₆/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	$29.085 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$	[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	$5.6 \text{ nA} \mu\text{M}^{-1}$	[60]
Graphitic carbon nitride nanosheets/GCE	0.1 - 200	0.32×10^{-3}	$1.16 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$	[61]
ZnO-BMIM.PF ₆ /CPE	0.04 - 330.0	0.02	$0.0812 \mu\text{A} \mu\text{M}^{-1}$	This work

Stability and reproducibility studies of ZnO-BMIM.PF₆/CPE sensor towards the determination of methionine

Studies related to the stability of ZnO-BMIM.PF₆/CPE sensors were performed by recording the current response of the designed sensor towards $75.0 \mu\text{M}$ 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.PF₆/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⁺, Ca²⁺, Mg²⁺, NH₄⁺, Al³⁺, Cl⁻, SO₄²⁻, S²⁻, 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.PF₆/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.PF₆/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.PF₆ modified CPE. The obtained results demonstrated that the ZnO-BMIM.PF₆/CPE sensor was well developed and showed an enhanced electrochemical response towards methionine oxidation. The ZnO-BMIM.PF₆/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.

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