

FULL PAPER

CuO nanoflowers modified glassy carbon electrode for the electrochemical determination of methionine

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This study reported the electrochemical sensor for sensitive determination of methionine based on CuO nanoflowers (CuO NFs) supported on glassy carbon electrode (GCE). Therefore, we utilized cyclic voltammetry (CV), chronoamperometry (CHA) as well as differential pulse voltammetry (DPV) for characterizing the sensor performance. This CuO NFs/GCE has been found to have very good electrochemical catalytic activity toward methionine oxidation. The oxidation overpotential of methionine decreased significantly and its oxidation peak current increased dramatically at CuO NFs/GCE. Moreover, the sensor showed a linear response for detecting methionine in the broad ranges from 1.0-300.0 μM with a low limit of detection (LOD) equal to 0.3 μM . Finally, we employed CuO NFs/GCE as a highly sensitive tool to analyze methionine in real sample (urine).

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Introduction

It is widely accepted that methionine (α -amino- γ -methyl mercaptobutyric acid) is one of the sulfur-bearing mono-carboxylic amino acids as one of the supplies of sulfur in body, which is essentially responsible for biological methylation reaction as well as prevention of disorders in the skin, hair and nail [1]. Although methionine has been considered as one of the essential amino acids, it is not synthesized in body and thus may be readily provided from the food supplies so pharmaceuticals can be commercially provided in the market. In addition, it is crucial for forming the blood protein, globulin as well as albumin, contributes to the reduction of the level of cholesterol via elevating the lecithin generation in livers, and keeps the cells' normal growth [2]. This drug

has been proposed to be helpful for curing acquired immune deficiency syndrome (AIDS)-related myelopathy [3] as well as different kinds of cancers [4]. Furthermore, it is found in the humans' fluids such as in the blood plasma [5,6], urine and serum [7]. However, abnormal concentrations of methionine largely cause the coronary artery disease in humans [8] as well as hypermethioninemia and hyperhomocysteinemia in the infants [9]. Consequently, variations in the concentrations of methionine in human fluids have correlation with numerous acute illnesses. Due to its clinical and physiological significance, the determination of methionine in human fluids is very important. Over the past years, many analytical methods have been developed to detect methionine like

high-performance liquid chromatography (HPLC)[10], colorimetric [11,12], enzymatic [13], capillary electrophoresis–UV [6], photoelectrochemical [14], gas chromatography–mass spectrometry [15], spectrophotometric [16] and electrochemical techniques [17-19].

On the other hand, electrochemical sensors fulfil several needs specifically because of simplified preparation, higher sensitivity and selectivity and faster responses [20-31]. In case of the use of the unmodified electrodes for detecting this analyte, many challenges like decreased sensitivity, slower electron transfer kinetics, duplicability, decreased stability on a wide range of solution compounds, as well as greater overpotential would occur, in which the electron transfer processes will be seen [32]. Nonetheless, chemical modification of the electrodes surfaces has been considered as one of the current approaches for designing the electrochemical sensors that is a developed strategy of the electro-chemical analyses [33-43].

Since nano-materials enjoy very acceptable features, researchers have largely considered them. Moreover, nano-particles (NPs) may function as the conduction centers simplifying the electron transfer and providing larger catalytic surface area. Researchers have also presented diverse nanomaterials to modify the surface of electrodes and ameliorate their electrochemical features [44-51].

In addition, experts in the field have been considerably attracted by the transition metal oxides because of their manifold features like thermal durability, different optical and electrical features as well as mechanical strength that led to their extensive utilization in particular in sensing interfaces [52,53]. Amongst diverse metal oxides, researchers have commonly applied copper oxide (CuO) for sensors because of their innate catalytic and electronic characteristics. Furthermore, CuO nano-structure shows numerous

morphologies using the controlled synthetic processes that may exhibit effective electron transfer in the small sizes [54,55].

In the present work, a simplified, sensitive as well as precise electroanalytical procedure to determine methionine has been shown to be possible by utilizing synthesized CuO NFs modified GCE. The CuO NFs/GCE exhibit greater electrocatalytic activity, wide linear range and high sensitivity for determination of methionine over unmodified GCE. The CuO NFs/GCE was successfully employed for sensitive detection of methionine in urine sample.

Experimental phase

Instruments and chemicals

An Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was utilized to measure electrochemicals. A platinum wire as the auxiliary electrode, CuO NFs/GCE as the working electrode and an Ag/AgCl/KCl (3.0 M) as reference electrode were used for electrochemical measurements. The ortho-phosphoric acid as well as the respective salts (KH_2PO_4 , K_2HPO_4 , K_3PO_4) with a pH ranging between 2.0 and 9.0 were utilized to procure buffer solution. The pH values were measured using a pH-meter (Metrohm 692 model, Herisau, Switzerland). Methionine and all other reagents were of the analytical grade, and they were obtained from Merck (Darmstadt, Germany). The phosphate buffer solution (PBS) was produced from concentrate phosphoric acid and its salts.

Preparation of electrode

The GCE was modified with CuO NF using a simple drop-casting method. To prepare the CuO NF stock solution in 1 mL of aqueous solution, the CuO NF (1 mg) was distributed by 30-minute ultrasonication. After that, a 5 μL CuO NF suspension was dropped on the screen-printed working electrode surface.

Then, the solvent was evaporated at an ambient temperature.

Results and discussion

Electrochemical behaviours of methionine on the various surface of electrodes

For studying electrochemical behaviours of *methionine* based on pH, providing an optimized pH-value could be of high significance to obtain acceptable outputs. Hence, the modified electrode was used for running experimentations under different pH amount ranging from 2.0 to 9.0. In the last step, the most promising outputs were seen

in the case of electrooxidation of methionine at the pH equal to 7.0.

Figure 1 depicts CVs for methionine oxidation, at bare GCE (a), and CuO NFs/GCE (b) in 0.1 M PBS (pH of 7.0) solution containing 100.0 μM methionine at scan rate of 50 mV s^{-1} . The anodic peak potential for methionine oxidation on the bare GCE was about 1280 mV, while on the CuO NFs/GCE, the peak potential was around 1000 mV. This reduction of around 280 mV proposes that the CuO NFs possesses highly efficient electrocatalytic activity considering the oxidation of methionine.

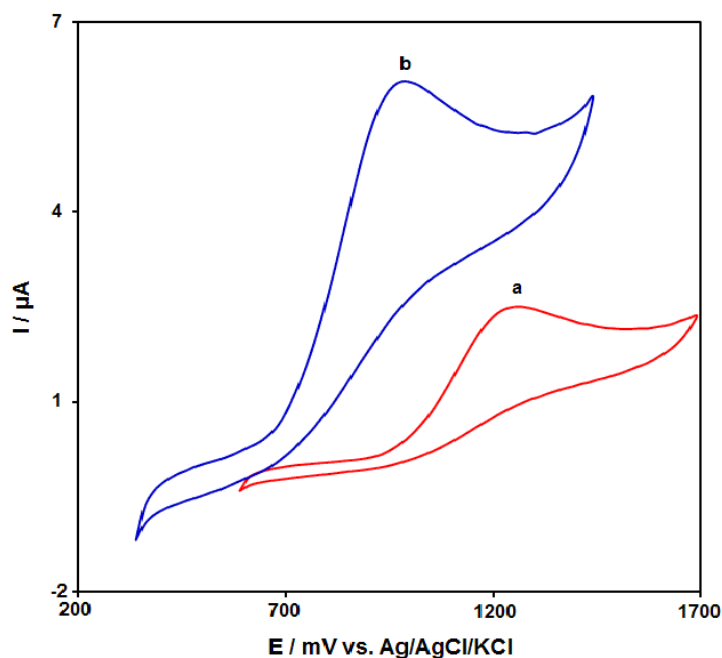


FIGURE 1 CVs of (a) bare GCE and (b) CuO NFs/GCE in the presence of 100.0 μM methionine. Scan rate was 50 mVs^{-1}

Effect of scan rate on the results

The relationship among scan rate and peak current presented promising data with respect to electrochemical mechanisms. Hence, the influence of scan rate onto the peak current of methionine was studied by

LSV in the range of 10 to 400 mVs^{-1} in PBS (0.1 M, pH equal to 7.0) (Figure 2). The electrode response of methionine was a diffusion-controlled process since the peak current of oxidation was proportional to the square root of the scan rate (Figure 2, inset).

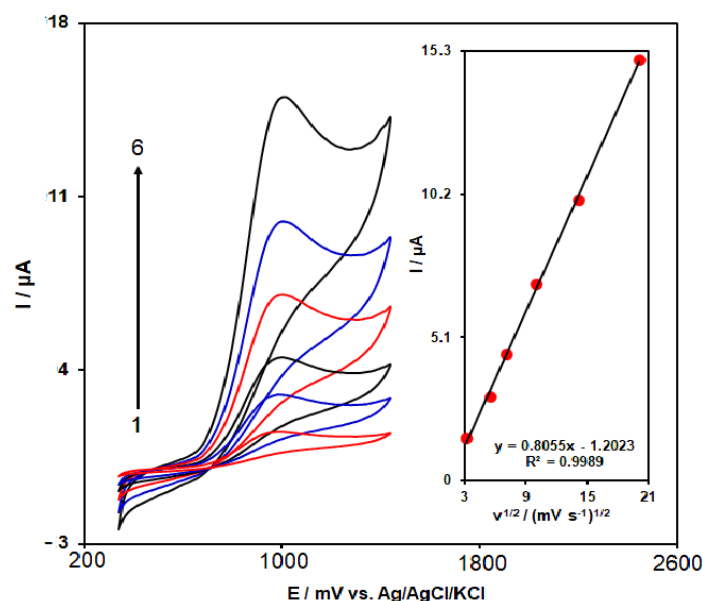


FIGURE 2 CVs of CuO NFs/GCE in 50.0 μM of methionine at different scan rates; (10, 30, 50, 100, 200 and 400 mV s^{-1}). Inset: Variation in the peak current vs. $v^{1/2}$

Chronoamperometric analyse

Chronoamperometric study was used for calculating the diffusion coefficient (D) of methionine on the surface CuO NFs/GCE at an optimum condition. Figure 3 displays chronoamperometric results of diverse

concentrations of the methionine sample in PBS considering pH of 7.0. In addition, Cottrell equation is proposed in the case of the chronoamperometric analyses of electroactive moiety on the basis of the mass transfer restricted states [56]: Hence, D mean value equaled to $2.0 \times 10^{-5} \text{ cm}^2/\text{s}$.

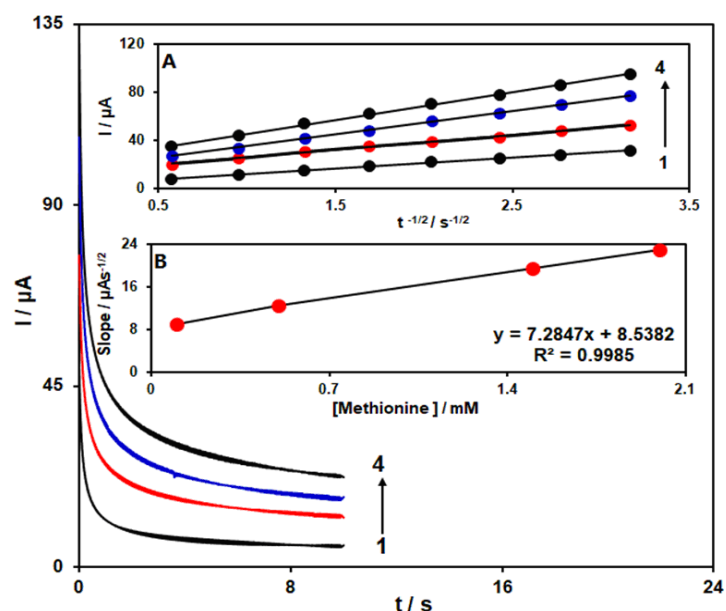


FIGURE 3 Chronoamperograms of CuO NFs/GCE in different concentration of methionine. (0.1, 0.5, 1.5 and 2.0 mM) Insets: (A) Plots of I vs. $t^{-1/2}$. (B) Plot of the slope against methionine concentration

Calibration plot and detection limit

In this step, DPV was applied for determining methionine content with different concentration gradients at a pH of 7.0 (Figure 4). It was found that the peak currents of methionine oxidation at CuO NFs/GCE surface linearly depended on methionine concentrations above the range of 1.0–300.0 μM . The linear equation was as follows: $y=0.0588x+0.2534$, and the correlation coefficient was 0.9995. Also, the detection limit, C_m , of methionine was obtained using the following equation:

$$C_m=3S_b/m$$

The detection limit was 0.3 μM .

Analysis of real samples

Finally, the performance of CuO NFs/GCE as a new electrochemical sensor for analyzing of methionine in different samples of urine was evaluated. Table 1 shows obtained data as well as the recovery data proved the ability CuO NFs/GCE as a sensitive sensor in the case of the analysis of methionine in real samples.

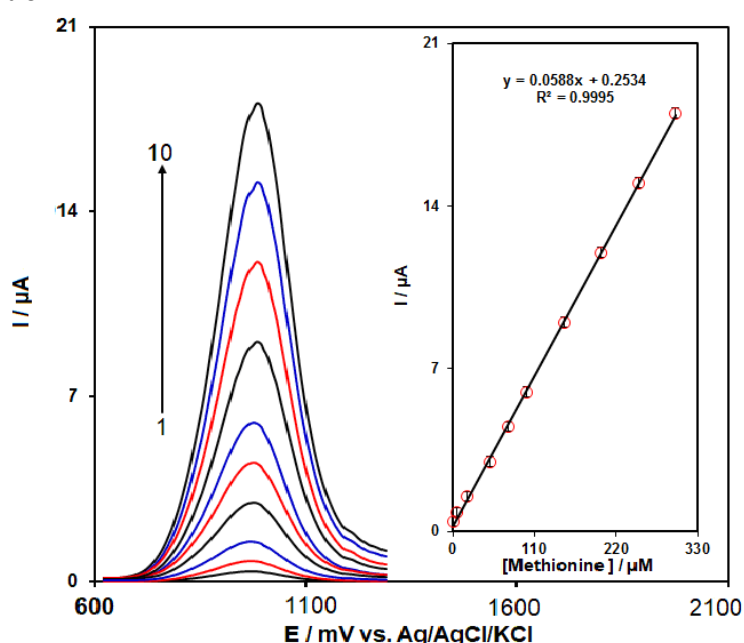


FIGURE 4 DPVs of CuO NFs/GCE in different concentrations of methionine (1.0, 5.0, 20.0, 50.0, 75.0, 100.0, 150.0, 200.0, 250.0 and 300.0 μM). Inset: plot of the peak current vs. methionine concentration

Table 1. The application of CuO NFs/GCE for the determination of methionine in urine ($n=5$)

Spiked (μM)	Found (μM)	Recovery (%)	R.S.D. (%)
0	-	-	-
7.0	6.9	98.6	3.2
12.0	12.2	101.7	1.8
17.0	16.9	99.4	2.9
22.0	22.5	102.3	2.4

Conclusion

This research provided one of the effective affordable analytical procedure for sensing methionine in PBS with the use of a CuO NFs modified GCE. The results indicated the

greater surface area of electrode by the presence of CuO NFs that led to the effective interface for electrochemical reaction of methionine. By DPV, the proposed modified electrode linearly responded in the broad

ranges from 1.0-300.0 μM with the LOD equal to 0.3 μM . Also, the results showed CuO NFs/GCE sensitivity to determine methionine in urine samples with reasonable accuracy, which reflected the possible utilization of this technique to detecting methionine in real samples.

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