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A novel electrochemical sensor based on Cu-phthalocyanine and Au nanoparticles for the efficient sensing of L-phenylalanine in biological samples

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Abstract
Monitoring the blood levels of phenylalanine, an essential amino acid, plays a vital role in the treatment of phenylketonuria. Cu-phthalocyanine (CuPC) and Au nanoparticles (AuNPs)-mediated non-enzymatic carbon paste electrode (CPE) has been developed for the electrochemical monitoring of L-phenylalanine (L-phe). The oxidation signal of L-phe was not observed on bare CPE or AuNPs/CPE. Although AuNPs was not involved in the apparition of L-phe oxidation peak, it enhanced the oxidation current. Using AuNPs-CuPC/CPE, we have successfully determined the different concentrations of L-phe with no need to any enzyme on the electrode surface. The performance characteristics of this sensor were accomplished with differential pulse anodic stripping voltammetry (DPASV) and cyclic voltammetry (CV). After optimizing the experimental parameters, L-phe gave a linear response over the concentration range of 1.0-130.0 µM with the detection limit of 0.41 µM. The practical applications of the modified electrode were demonstrated by measuring the concentration of L-phe in blood serum and urine samples.

Keywords
L-phenylalanine sensing; Biological samples; Electrochemical sensor; Gold nanoparticles

1. INTRODUCTION

Untreated phenylketonuria (PKU) is a hereditary metabolic disorder that caused by a genetic mutation in phenylalanine hydroxylase (PAH) and is characterized by elevated blood phenylalanine (Phe) [1]. The mainstay of the treatments is to maintain blood phenylalanine levels within the limits considered safe for the patient's age [2]. L-phenylalanine is an essential amino acid which is a constituent of many central nervous system neuropeptides [3]. It is the only form of phenylalanine found in proteins. The body uses phenylalanine to make chemical messengers [4]. Phe is a precursor for Tyr, the monoamine signaling molecules dopamine, norepinephrine and epinephrine, and the skin pigment melanin [5]. Nowadays, multiple analytical methods have been developed to monitor Phe. The Guthrie method, the bacterial inhibition assay, is generally used for screening neonatal PKU [6]. However, the method is a semi-quantitative test and has disadvantages of low sensitivity and poor precision [7]. Other methods used are as follows: enzymatic sensors [8], molecularly imprinted polymer sensors [9, 10], chemiluminescence based sensors [3], spectrofluorimetric [7, 11-13] and flow-injection techniques [9, 14]. These methods are time-consuming, expensive and often need the pretreatment step. Also, some of them suffer from low sensitivity and selectivity in the corresponding determinations. To overcome these defects, electrochemical methods are used for the elegant and sensitive properties such as selectivity, reproducibility, low cost and simplicity of this approach. The enzymatic electrochemical biosensors are suffering from very low stability. Because of that, we considered fabricating a non-enzymatic, sensitive, simple, rapid and also low-cost sensor for the determination of low concentrations of L-Phe [15, 16]. Carbon-based electrodes are the mostly used electrodes for the electrochemical determination of Phe [16, 17]. However, a few studies have been reported on the use of carbon paste electrode for this purpose [18]. AuNps is one of the available and useful materials for modifying carbon paste electrodes [19]. In recent years, AuNPs has received epidemic attention because of their widespread application in the fields of catalysis, electronics, and biosensors. AuNPs, due to their large aspect ratio, biocompatibility and high electrical conductivity have also been widely employed as a modifier in

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voltammetry for analysis of various species [20, 21]. Copper phthalocyanine, often referred to as CuPc, is also a leading material used in electrochemical sensors [22]. It is extremely valued for its superior properties such as light fastness, tinting strength, covering power and resistance to the alkalies and acids effects. CuPc is also insoluble in water and most other solvents and it can be easily processed into a thin film for use in device fabrication [23, 24]. The most important advantages of CuPc are its high chemical stability, semiconduction, and uniform growth [25, 26].
The aim of this work is develpoping a new sensor for determination of L-phe in biological samples. For this purpose, a carbon paste electrode modified with AuNPs and CuPC (AuNPs-CuPC/CPE) was constructed, then the voltammetric behavior of L-phe at the surface of AuNPs-CuPC/CPE was investigated using differential pulse anodic stripping voltammetry (DPASV) for the determination of L-phe in blood plasma and urine samples.

2. EXPERIMENTAL

2.1. Chemicals

A 6.0×10^{-4} M L-phe solution in 0.10 M phosphate buffer was prepared daily and was kept in a refrigerator in dark. More dilute solutions were prepared by serial dilution with phosphate buffer. Cu-phthalocyanine with analytical reagent grade and Au nanoparticles with the average size of 10.0 nm were purchased from Merck (Germany) and Nano Zino company (Iran), respectively. All other chemicals used in this work were of analytical grade purchased from Merck (Germany) unless otherwise stated. Double distilled water was used to prepare the solutions used in this investigation.

2.2. Apparatus

All voltammetric experiments were performed with an Autolab PGSTAT 302N electrochemical system from Metrohm (Switzerland) interfaced with a personal computer for data acquisition and potential control. The system was run on a PC using Nova 1.8 software. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl/KCl (sat) electrode as a reference electrode was used. The working electrode was either a bare carbon paste electrode (CPE) or a modified one.

2.3. Fabrication of the modified electrode

15.0 mg of CuPc was hand mixed with 485 mg of graphite powder and 3.0 mL of AuNPs (100.0 µM) using a syringe in a mortar and pestle. 0.23 g of paraffin was added to the mixture and mixed well for 50 min until a uniformly wetted paste was obtained. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper. The unmodified carbon paste electrode was prepared in the same way without adding AuNPs and CuPC to the mixture. The electrodes were stored at room temperature.

2.4. Experimental procedure

Differential pulse anodic stripping voltammetry (DPASV) was used to record the voltammograms of L-phe. For this purpose, AuNPs-CuPC/CPE was immersed into the electrochemical cell containing L-phe in 0.10 M phosphate buffer (pH 7.0). Accumulation of L-phe was carried out for 250 s while the solution was stirring at 200 rpm. Then, the corresponding voltammogram was recorded by scanning the electrical potential from 0.95 V to 1.10 V using differential pulse voltammetry employing a step potential of 5.0 mV and modulation amplitude of 50.0 mV. Cyclic voltammetric experiments were carried out by sweeping the potential between 0.30 V and 1.30 V.

2.5. Preparation of real samples

Blood plasma samples utilised without any pre-treatment, except for dilution.The blood plasma sample was diluted with 0.10 M phosphate buffer (1:2, v/v) and stored in the refrigerator. For preparing the urine sample, 10.0 mL of the sample was centrifuged for 25 min at 3000 rpm and then the obtained supernatant was filtered through a 0.45-µm filter. For the voltammetric determination, the sample was diluted (1:2, v/v) with 0.10 M phosphate buffer. Standard addition method was used for the determination of L-phe in both real samples.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behaviors of different electrodes

In order to compare the electrochemical behaviors of the electrodes, AuNPs/CPE, CuPc/CPE, and AuNPs-CuPC/CPE were separately used to record the cyclic voltammogram of L-phe. The obtained results are illustrated in Fig. 1. As can be seen, at the surface of CuPc/CPE the cyclic voltammogram exhibits an anodic peak related to the oxidation of the L-phe with the current of 2.83 µA in the forward scan of the potential (Fig. 1C.) while no peak is observed using AuNPs/CPE. As shown in Fig. 1D, the potential of the peak recorded at the surface of AuNPs-CuPC/CPE shows about 50 mV negative shift compared with CuPC/CPE. Also, a significant increase of about 3.5 µA in the oxidation peak current (Fig. 1D) is seen. So, AuNPs-CuPC/CPE can be used to record the oxidation signal of L-phe as a well-defined peak

with an improved sensitivity in comparison with CuPC/CPE and AuNPs/CPE. Figure 1A reveals that AuNPs-CuPC/CPE in a blank sample shows no peak indicating no interference from the modifiers.

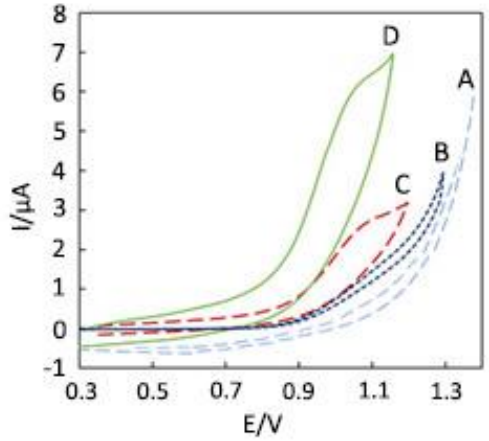

Fig. 1. Cyclic voltammograms in 0.10 M phosphate buffer pH=7.0 at the surface of (A) AuNPs-CuPC/CPE without L-phe and with 50.0 µM L-phe at the surface of (B) AuNPs/CPE (C) CuPC/CPE and (D) AuNPs-CuPC/CPE. Scan rate: 100 $mV.s^{-1}$

3.2. Effect of the percentage of the modifiers on the electrode response

As mentioned in the previous section, the modifiers play a crucial role in the detection of the oxidation peak current of L-phe. So, the effect of the amount of AuNPs and CuPc as modifiers was studied by varying their percentages in AuNPs-CPc/CPE in the range of 1–10% with respect to the graphite powder. It was found that the peak current increased with increasing the percentages of the modifiers until 5% AuNPs and 3% CuPc and then remained unchanged. It was clear that increasing the percentage of modifier has some dire consiquences, increasing the background noise and appearing the AuNPs peak, for instance. Therefore, 5% AuNPs and 3% CuPc were used for the preparation of the modified AuNPs-CPc/CPE in the next experiments.

3.3. Effect of pH on the electrode response

Since protons contribute in the electrode reaction of L-phe [15], the influence of pH on the anodic current of target-phe was investigated. Figure 2A indicates the response of AuNPs-CuPC/CPE to L-phe at different pHs (5.0-9.0). As can be seen, the maximum oxidation current is observed at pH 7.0. Thus, pH 7.0 is the optimal point chosen for subsequent experiments. In addition, the peak potential of L-phe shifts toward more negative values with increasing pH (Fig. 2B). Also, the plot of peak potential vs. pH is linear over the pH range of 5.0 to 9.0 with the regression equation of Epa (V) = 1.465−0.065 pH (R2 = 0.9918). The value of the slope (0.065) is close to the Nernst slope 0.059 V pH-1, suggesting that an equal number of protons and electrons are involved in the electrode process of L-phe.

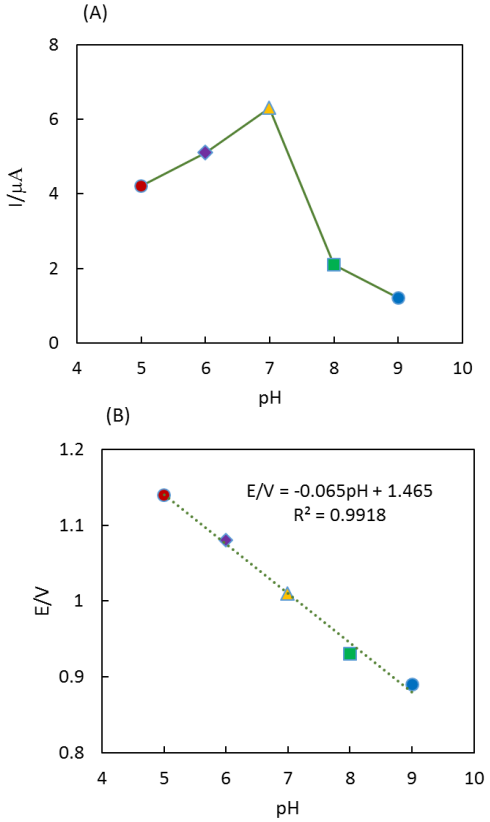

Fig. 2. (A) Effect of pH on the current response of 50.0 µM L-phe potential in 0.10 M phosphate buffer at the surface of AuNPs-CuPc/CPE (B) plot of pH vs. the oxidation peak potential

3.4. Effect of accumulation time on the electrode response

The amount of non-oxidized L-phe accumulated on the surface of AuNPs-CuPC/CPE plays an important role in the electrochemical response of L-phe. Therefore, suitable accumulation time results in the greater presence of L-phe on the electrode surface and subsequent increase of the oxidation current. So, we studied the peak current obtained after different accumulation times in the range of 100 to 350 s. According to the obtained results (Fig. 3), the electrochemical signal of L-phe increased with increasing the accumulation time from 100 s to 250 s and then remained constant with further increasing the time. Finally, 250 s was suitable for the preconcentration of L-phe.

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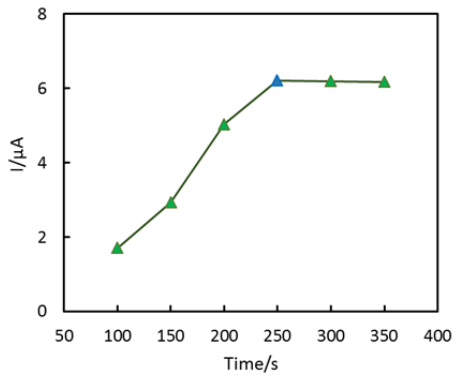


Fig. 3. Influence of accumulation time on the oxidation peak current of 50.0μM L-Phe in 0.10 M phosphate buffer (pH=7.0) at the surface of AuNPs-CuPc/CPE

3.5. Effect of scan rate on the electrode response

The effect of scan rate on the anodic peak current of L-phe at the surface of AuNPs-CuPC/CPE was investigated in 0.10 M phosphate buffer containing 50.0 μM L-phe. Fig, 4 illustrates the corresponding cyclic voltammograms recorded at different scan rates of 10-100 mV s-1. As it can be seen, an increase of the scan rate increases the peak current of L-phe while the peak potentials do not shift considerably. Since the oxidation current is linearly proportional to the scan rate (inset of Fig. 4), the electrode process is controlled by adsorption rather than diffusion.

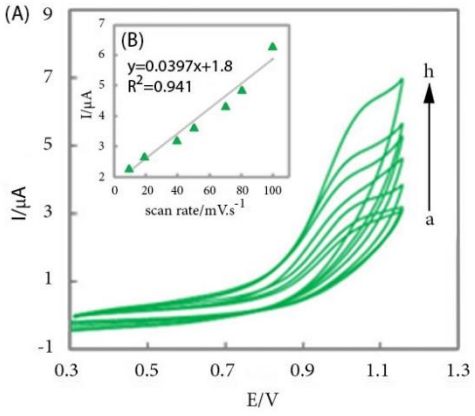


Fig. 4. (A) CVs of 50.0 μM L-Phe in 0.10 M phosphate buffer (pH 7.0) recorded at different scan rates (a to h: 10, 20, 40, 50, 70, 80 and 100 mV s^(-1)) at the surface of AuNPs-CuPC/CPE. (B) the plot of the peak current vs. scan rate

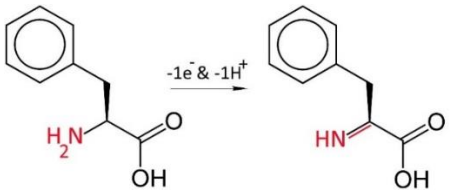
The following regression equation correlates the oxidation peak current of L-phe to scan rate:

Ipa (μA) = 0.0397 ν +1.8 (R2=0.941)

Number of the electrons involved in the electrochemical process is then calculated using the equation,

Ep−Ep/2=47.7/αnαmV at 25ºC

From the obtained CV, Ep−Ep/2 is found to be 100 mV. If there is no information available about charge transfer coefficient (α), it can be taken as 0.5 for completely irreversible reaction [27]. Hence, by substituting the values of α and Ep−Ep/2 in the equation, the number of the electrons involved in the oxidation of L-phe is calculated to be 1. The probable mechanism of the oxidation of L-phe is shown in Scheme 1 which is a one-electron- and one-proton-transfer process and loss of one electron and one proton results in the formation of 2-imino-3-phenylpropanoic acid [15].



Scheme 1. Probable oxidation mechanism of L-phe [18]

3.6. Analytical performance for the detection of L-phe

Using the optimized operational parameters, DPASV responses of AuNPs-CuPC/CPE for different concentrations of L-phe were recorded. Figure 5A shows the obtained voltammograms. It is clear that the peak currents are linearly correlated with L-phe concentrations in the range of 1.0-130.0 μM range (Fig. 5B). The linear regression equation is I (μA) = 0.1013 C (μM) + 1.0209 (R2=0.9917) where I is the anodic peak current and C is the concentration of L-phe. The theoretical limit of detection (LOD) calculated as 3 Sb/m, where Sb is the standard deviation for the intercept of the regression line and m is the slope of the linear calibration plot, is found to be 0.41 μM.

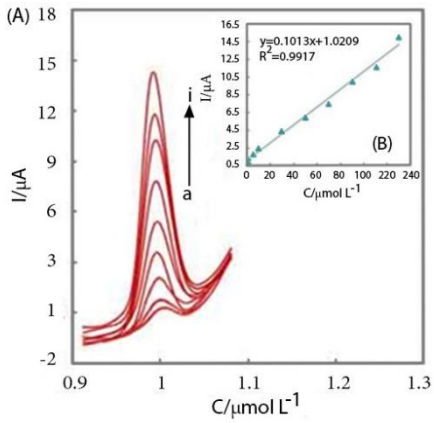


Fig. 5. The DPASVs of the anodic peak current at the surface of AuNPs-CuPc/CPE in 0.10 M phosphate buffer pH=7.0 containing different concentrations of L-Phe (a to i: 1.0, 5.0, 10.0, 30.0, 50.0, 70.0, 90.0, 110.0, 130.0 μM). Inset: calibration curve extracted from the voltammogram plots

3.7. Repeatability, reproducibility, and stability of AuNPs-CuPC/CPE

Repeatability of the DPASV behaviors of AuNPs/-CuPC/CPE was checked separately at 1.0 µM and 30.0 µM L-phe for 6 repetitive measurements under the optimized conditions. The relative standard deviations (RSD) of the obtained peak currents were calculated to be ±2.32% and 1.92%, respectively for 1.0 µM and 30.0 µM. Such reasonable errors demonstrated that the AuNPs/CuPC/CPE could be repeatedly used for the detection of L-phe. Reproducibility was also checked with 8 AuNPs-CuPC/CPE applied for the determination of 50.0 µM L-phe under the optimized conditions. The obtained results confirmed a good reproducibility with the RSD% of 1.62% for the electrochemical signal of L-phe.

3.8. Analysis of real samples

In order to evaluate the practical application of AuNPs-CuPC/CPE in real samples, it was employed for the determination of L-phe concentration in blood serum and urine samples. The prepared samples were analyzed three times using the proposed electrode under the optimized conditions.

The results obtained are reported in Table 1. Satisfactory spiked recoveries indicate that AuNPs-CuPC/CPE is capable of voltammetric determination of L-phe in biological samples.

Table 1. Determination of L-phe in real samples

Sample	Added (µM)	Found[a] (µM)	Recovery (%)
Blood plasma	0.0	78.4±4.1	-
	20.0	97.2±5.8	94.0
	40.0	136.9±8.1	99.2
Urine	0.0	2.5±0.1	-
	10.0	11.6±2.1	91.0
	20.0	30.7±3.6	94.0

[a] Mean±standard deviation (n=3)

3.9. Comparison of the proposed method with some of the previously reported ones

A comparison of the analytical performance of the proposed method with some previously reported voltammetric methods for the determination of L-phe [15, 28--33] is shown in Table 2. The data reveals that the AuNPs-CuPC/CPE shows a superior analytical performance in terms of the detection limit and linear dynamic range over the others. In addition, the present method is simple and does not involve any pretreatment step.

Table 2. Comparison of our method with some other methods for the determination of L-Phe

Method	Modifier	Linear range	LOD	Reference
Linear sweep voltammetry	Fe_2O_3/GO[a]	0.10–1.0 µM	0.01 µM	[15]
Amperometry	PAH[b]/NADPH[c]/GO	50.0 µM–9.10 mM	25.0 µM	[28]
CV	PAH/Chitosan/AuNPs	up to 3.0 mM	15.0 µM	[29]
CV	PADH[d]/ Aminated cellulose membrane/ Gutaraldehyde	0.50-6.0 mM	0.5 mM	[30]
Amperometry	AuNPs/ERGO[e]	0.0-20.0 mg/dl	3.17 µM	[31]
Amperometry	Carbon/ZIF[f]-67 encapsulated PtPd	20 nM–200 µM	0.02 µM	[32]
DPA[g]	PADH/Carbon/PAD[h]/ ERGO	1–600 µM	0.2 µM	[33]
SDPV	AuNPs/CuPC	1.0-130.0 µM	0.42 µM	This work

4. CONCLUSION

In the present study, a carbon-paste electrode modified with AuNPs and CuPC was used for the determination of trace amounts of L-phe using DPASV. At the surface of AuNPs-CuPC/CPE, oxidation of L-phe was catalyzed and the peak potential of L-phe was shifted by 50 mV to a less positive potential. It was found that the operational parameters such as the percentage of the mediators, accumulation time and pH affected the stripping voltammetric behavior of L-phe. AuNPs-CuPC/CPE showed satisfactory reproducibility and repeatability with RSDs less than 3%. In addition, the present method is simple, accurate, and does not require any pretreatment step such as extraction of the analyte from the real samples.

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ساخت حسگر الکتروشیمیایی جدید با نانوذرات مس فتالوسیانین و طلا برای سنجش L- فنیل آلانین در نمونه‌های بیولوژیکی

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چکیده

پایش میزان فنیل آلانین که یک اسید آمینه ضروری است در خون، نقش حیاتی در درمان فنیل کتونوری ایفا می کند. در این کار الکترود خمیر کربن غیر آنزیمی اصلاح شده با واسطه نانوذرات مس فتالوسیانین و طلا برای اندازه گیری الکتروشیمیایی L- فنیل آلانین توسعه داده شده است. سیگنال اکسیداسیون L- فنیل آلانین در الکترود خمیر کربن خالی و الکترود اصلاح شده فقط با نانو ذرات طلا مشاهده نشد. اگرچه نانو ذرات طلا در ظهور پیک اکسیداسیون L- فنیل آلانین نقشی نداشت اما جریان اکسیداسیون را افزایش داد. با استفاده از الکترود خمیر کربن اصلاح شده با نانو ذرات طلا و مس فتالوسیانین، می توان غلظت های مختلف L- فنیل آلانین را بدون نیاز به هیچ آنزیمی روی سطح الکترود تعیین کرد. ویژگی های عملکرد این حسگر با ولتامتری عریان سازی آندی پالس تفاضلی و ولتامتری چرخه ای انجام شد. پس از بهینه سازی پارامترهای تجربی، L- فنیل آلانین پاسخ خطی در محدوده غلظت ۱/۰ تا ۱۳۰/۰ میکرومولار پاسخ خطی داشت و حد تشخیص ۰/۴۱ میکرومولار محاسبه شد. از الکترود اصلاح شده برای اندازه گیری غلظت L- فنیل آلانین در نمونه های سرم خون و ادرار نشان استفاده شد.

کلید واژه ها

حسگر L - فنیل آلانین، حسگر الکتروشیمیایی، سنجش نمونه های زیستی، نانو ذرات طلا.