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Article

Electrocatalytic measurement of H_2O_2 concentration using bis(*N*-2-methylphenyl-salicyldenaminato)copper(II) spiked in a carbon paste electrode

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ABSTRACT

The electrochemical behavior of a bis(*N*-2-methylphenyl-salicyldenaminato)copper(II) complex spiked in a carbon paste electrode (BMPSCu-CPE) and its electrocatalytic reduction of H_2O_2 were examined using cyclic voltammetry, chronoamperometry, and differential pulse voltammetry. Cyclic voltammetry was used to study the redox properties of BMPSCu-CPE at various potential scan rates. The apparent charge transfer rate constant and the transfer coefficient for the electron transfer between BMPSCu and the carbon paste electrode (CPE) were 1.9 ± 0.1 s^{-1} and 0.43, respectively. BMPSCu-CPE had excellent electrocatalytic activity for H_2O_2 reduction in 0.1 mol/L phosphate buffer solution (pH 5.0), and it decreased the overpotential by 300 mV as compared to CPE alone. The diffusion coefficient and kinetic parameters such as the heterogeneous catalytic electron transfer rate constant and electron transfer coefficient for the reduction of H_2O_2 at the BMPSCu-CPE surface were also determined using electrochemical methods. Differential pulse voltammetry showed two linear dynamic ranges of 1.0–10.0 and 10.0–300.0 μmol/L and a detection limit of 0.63 μmol/L H_2O_2. The BMPSCu-CPE has excellent reproducibility and long term stability, and it was successfully applied for the determination of H_2O_2 in two pharmaceutical samples: an antiseptic solution and a hair dying cream.

1. Introduction

Much research has been conducted in recent years on how to measure H_2O_2 concentration present in samples in the areas of environmental control, clinical diagnosis, the food, chemical and pharmaceutical industries, and the biological and medical sciences [1–8]. H_2O_2 is also used as an oxidant in many liquid-based fuel cells [2–8], and it is present in a variety of commercial products such as cosmetics and pharmaceutical products [9,10]. Furthermore, H_2O_2 has emerged as an important byproduct of enzymatic reactions in the field of biosensing [11–17]. The accurate and reliable determination of H_2O_2 concentration has been widely investigated using techniques such as titrimetry [18], spectrometry [19], chemiluminescence [20,21], chromatography [22–24], and electrochemical methods [10,25,26]. The electrochemical methods have been found appropriate for H_2O_2 determination because of their simplicity, efficiency, high sensitivity, relatively low cost, and ease of operation [27–29]. However, the direct electrochemical detection of H_2O_2 at many bare electrodes is not good enough for analytical applications. This is due to slow electrode kinetics and high overpotential required for its redox reactions. So, redox mediators have been used to decrease the overpotential and increase the electron transfer kinetics. Different electron transfer

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mediators such as methylene green [30], platinum and iridium [31–33], vanadium doped zirconia [34], iodine [35], and Prussian blue [36] cadmium sulfide nanoparticles [37] have been used to improve the determination of H_2O_2.

Electrochemical reactions catalyzed by transition metal complexes have received considerable attention in the past several decades, and metal complexes are well recognized for their excellent electrocatalytic properties [38,39]. The electrochemical characteristics and electrocatalytic activity of Cu complexes have been studied by several groups [40–42]. Wang et al. [43] investigated the electrocatalytic activity of a new Cu complex for the reduction of bromate, nitrite, and H_2O_2. Marques et al. [44] studied the electrochemical reduction of O_2 and H_2O_2 catalyzed by a Cu(II)-2,4,6-tris(2-piridil)-1,3,5-triazine complex adsorbed on a graphite electrode. The overpotential decrease of the H_2O_2 reduction at the carbon paste electrode (CPE) spiked with a bis(*N*-2-methylphenyl-salicyldenaminato)copper(II) complex (BMPSCu-CPE) surface is comparable to or more than those reported in the literature [43,44]. A CPE spiked with different mediators has been widely used for the electrocatalytic reaction of different analytes [45,46]. In this study, we employed a BMPSCu-CPE for the electrocatalytic reduction of H_2O_2. Our findings indicated that this modified electrode offered many advantages including good stability, good repeatability, excellent reproducibility, high surface charge transfer rate constant, low detection limit, and technical simplicity in the electrocatalytic detection of H_2O_2. To evaluate the utility of the modified electrode for analytical applications, it was used for the voltammetric determination of H_2O_2 in two pharmaceutical formulations.

2. Experimental

2.1. Apparatus and chemicals

All the electrochemical experiments were carried out with an EG&G PARSTAT 2273 equipped with a Power Suite software. A three-electrode assembly in an electrochemical cell containing a BMPSCu-CPE as the working electrode, a Pt wire as the counter electrode, and a Ag/AgCl/KCl (sat'd) as the reference electrode was used for the experiments. All of the potentials were measured versus the Ag/AgCl/KCl (sat'd) electrode. The pH values were measured with a Metrohm model 691 pH/mV meter.

H_2O_2 (30%), graphite fine powder, and viscous paraffin were obtained from Merck Company and used as received. All the other chemicals, also purchased from Merck Company, were of analytical reagent grades and were used without any further purification. Doubly distilled water was used in the experiments. The solutions were prepared just prior to use, and all the experiments were carried out at the ambient temperature of the laboratory (about 25 °C). All the test solutions were deaerated by passing high purity N_2 (99.999%) through them for 30 min before the electrochemical experiments. A continuous flow of N_2 was maintained in the sample solutions during the experiments. The buffer solutions (0.1 mol/L) were made up from H_3PO_4, and the pH was adjusted with 2.0 mol/L NaOH. The pharmaceutical samples of an antiseptic solution and a hair dye cream were purchased from Fuadara Company (Iran).

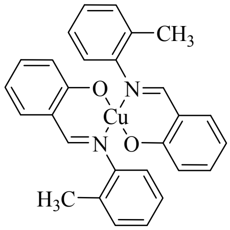
The BMPSCu (see Scheme 1) was synthesized in the laboratory as reported in our previous work [47]. Briefly, the Schiff base ligand was synthesized by the condensation reaction of salicylaldehyde (10 mmol) and 2-methylaniline (10 mmol). Then it was treated in methanol (20 mL) at room temperature for 30 min, and an orange powder was obtained with a yield of 72%. The powder was filtered off and recrystallized in diethyl ether solution at room temperature [47]. To make BMPSCu, 2.5 mmol (0.499 g) of $Cu(NO_3)_2\cdot H_2O$ was slowly added to 40.0 mL of methanol solution containing 5.0 mmol of the Schiff base, and the resulting solution was stirred for 1.0 h at room temperature. The brown precipitate obtained was collected by filtering and washed with 10.0 mL of methanol. The Cu complex was recrystallized from dichloromethane/acetone (1:1, v/v), and brown plate-like crystals were obtained with a yield of 40%. Anal. Calc. for $C_{28}H_{24}CuN_2O_2$: C 69.48, H 5.00, N 5.79; Found: C 69.57, H 4.80, N 5.85%. IR (KBr, cm^{-1}): υ(C=N) = 1607, υ(C–O) = 1326. Electronic spectra in $CHCl_3$: *d*–*d*, λ_{max} (ε) 635 nm (148 mol^{-1} L cm^{-1}).

2.2. Preparation of BMPSCu-CPE

The carbon paste containing the modifier was prepared by thoroughly hand-mixing graphite powder (100.0 mg) and BMPSCu (10.0 mg) in a mortar with a pestle. Paraffin oil was added to the mixture, and they were mixed well to obtain a uniform wetted carbon paste of the modifier, BMPSCu-CP. To fabricate a BMPSCu-CP electrode (BMPSCu-CPE), the paste was inserted into the bottom of a glass tube (2 mm in diameter and 10 cm long). A copper wire was introduced into the opposite side to establish electrical contact. The electrode surface was smoothed using white paper. The modified electrode surface can be easily and reproductively renewed by slightly polishing it on a smooth paper. An unmodified CPE was prepared by mixing graphite powder and paraffin to obtain a wetted paste. Then it was fabricated as described above.

2.3. Pharmaceutical sample preparation

An antiseptic solution (0.5 mL, 0.882 mol/L) and a hair dye cream (1.764 mol/L) were separately transferred to a flask and diluted to volume of 100.0 mL with twice distilled water. 0.3 mL portion of each solution was diluted in a voltammetric cell to 10.0 mL of a 0.1 mol/L phosphate buffer (pH 5.0), and the differential pulse voltammograms were recorded.



Scheme 1. Structure of bis(*N*-2-methylphenyl-salicyldenaminato) copper(II) complex, BMPSCu.

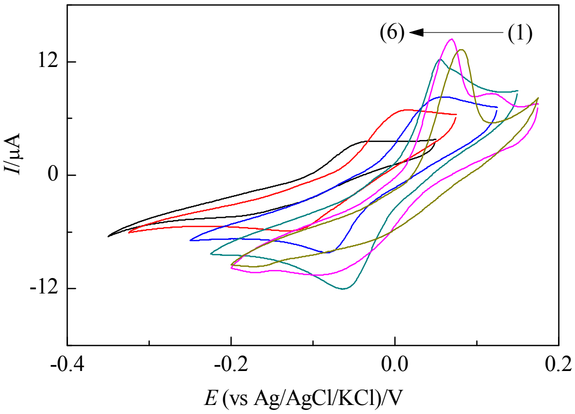


Fig. 1. Cyclic voltammograms of Cu-CPE at various buffered pH at a potential scan rate of 25 mV/s. Curves (1)–(6) correspond to pH of 2, 3, 4, 5, 6, and 7.

3. Results and discussion

3.1. *Electrochemical behavior of BMPSCu-CPE*

The electrochemical behavior of BMPSCu-CPE was studied using a cyclic voltammetry method in a phosphate buffer solution (0.1 mol/L, pH = 2.0–7.0) at the potential scan rate of 25 mV/s (Fig. 1). The results indicated that the stability of the modified electrode was pH dependent, and there was higher stability at pH 5.0 as compared to other pH values. Therefore, the electrochemical behavior and electrocatalytic activity of the modified electrode were studied in a phosphate buffer solution (0.1 mol/L, pH 5.0).

Figure 2 shows the cyclic voltammograms of BMPSCu-CPE in the potential range of 0.15 to –0.25 V at different potential scan rates. The redox couple which appeared in this figure was attributed to the redox reaction of Cu(II)/Cu(I) of the BMPSCu complex. The formal potential of this redox couple, obtained from the equation $E^{0'} = E_{pa} - \alpha(E_{pa} - E_{pc})$ [48] and using $\alpha = 0.43$ (see below), was –10 mV and it was almost independent of the potential scan rate in the range of 5–75 mV/s. The peak-to-peak potential separation ($\Delta E_p = E_{pa} - E_{pa}$) at the potential scan rate of 10 mV/s was 125 mV. However, at higher potential scan rates, the separation between the peak potentials increased with an increase in the scan rates. This result indicated that the electrochemical process of the BMPSCu was quasi-reversible, and the rate of the redox process was controlled by charge transfer kinetics. The plots of peak current versus potential scan rates are shown in inset (a) of Fig. 2. The anodic and cathodic peak currents (I_p) were proportional to the potential scan rate, suggesting that the redox process for BMPSCu-CPE was a surface-confined process. The surface coverage of the modified electrode was estimated by [49]:

$$I_p = n^2F^2A\Gamma v/4RT \quad (1)$$

where n represents the number of electrons involved in the electrochemical reaction, A is the surface area (0.0962 cm^2) of BMPSCu-CPE, Γ is the surface coverage (mol/cm^2), and the other symbols have their usual meanings. From the slope of the anodic and cathodic peak currents versus potential scan rate (Fig. 2, inset (a)), the surface coverage of the BMPSCu complex on the CPE surface was 2.5×10^{-9} mol/cm^2 for $n = 1$. Insets (b) and (c) of Fig. 2 show the variations in the anodic and cathodic peak potentials (E_{pa} and E_{pc}) as a function of the potential sweep rate. When the potential scan rate was increased, the anodic peak potential shifted to the positive direction, but the cathodic peak potential shifted to the negative direction. Figure 2 inset (c) shows that the peak potential separation ($n\Delta E_p$)

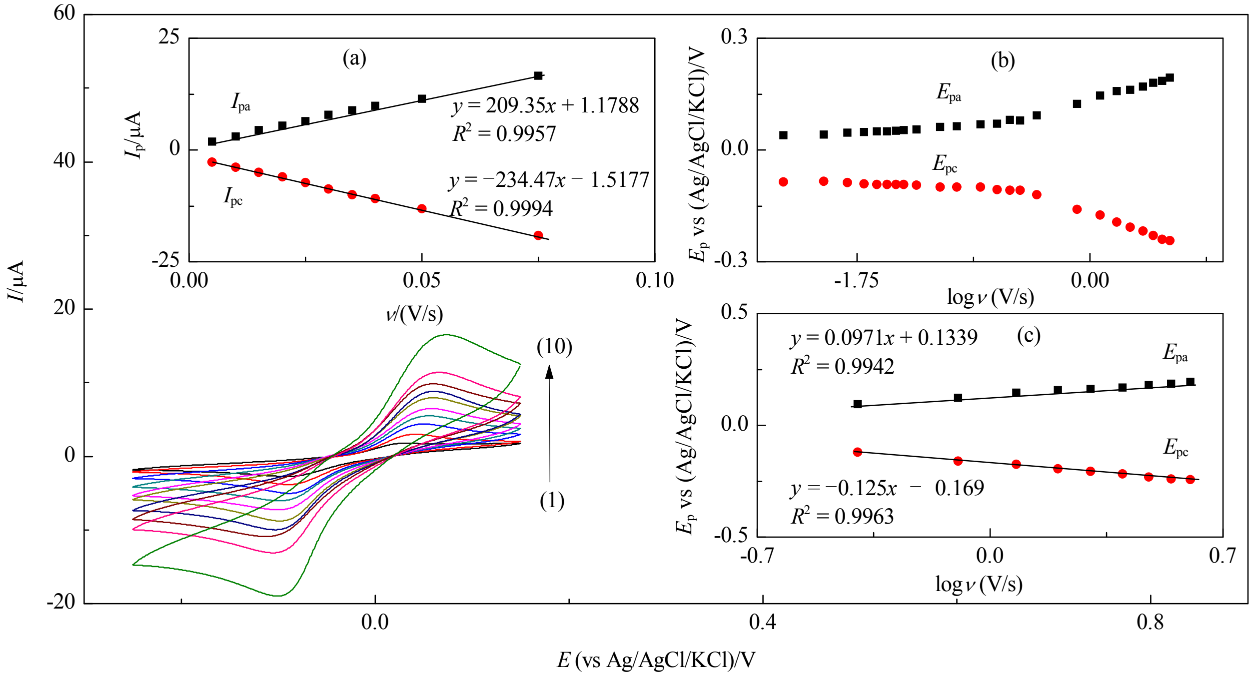


Fig. 2. Cyclic voltammograms of BMPSCu-CPE in phosphate buffer solution (0.1 mol/L, pH 5.0) at various potential scan rates. (1)–(10) correspond to 5, 10, 15, 20, 25, 30, 35, 40, 50, and 75 mV/s potential scan rates. Insets: (a) Variation of peak current (I_p) vs potential scan rates (v); (b) Variation of peak potential (E_p) vs log$v$; (c) Magnification of the plots of (b) for fast potential scan rates.

value was larger than 200 mV, and that the anodic and cathodic peak potentials were proportional to the logarithm of the potential scan rates higher than 400 mV/s. Under these conditions, the electron transfer coefficient (α) and the surface electron transfer rate constant (k_s) corresponding to electron transfer between BMPSCu and the CPE can be determined from the slopes of the plots in Fig. 2, inset (c), according to the Laviron theory [50]. Based on the Laviron procedure, in the case of $n\Delta E_p > 200$ mV, it is possible to determine α from the slope of $E_p = f(\log v)$. The graph $E_p = f(\log v)$ yielded two straight lines with the slope $2.3RT/\alpha_a nF$ for the anodic peak and $-2.3RT/\alpha_c nF$ for the cathodic peak. Figure 2 inset (c) shows that the slopes of E_{pa} and E_{pc} versus $\log v$ were 0.097 and –0.125, respectively. So, the estimated values for the kinetic parameters of α_a ($\alpha_a = 1-\alpha_c$) and α_c (anodic and cathodic transfer coefficient) were 0.61 and 0.47. We accordingly used the value of 0.43 for α_c (α) in subsequent studies. Also, the following equation can be used to estimate the electron transfer rate constant (k_s) between CPE and BMPSCu:

$$\log k_s = \alpha\log(1-\alpha) + (1-\alpha)\log\alpha - \log(RT/nFv) - \alpha(1-\alpha)nF\Delta E_p/2.3RT \qquad (2)$$

In Eq. (2), v is the potential scan rate, and all the other symbols have their usual meanings. Based on ΔE_p corresponding to the different potential scan rates of 400–4000 mV/s, k_s was found to be 1.9 ± 0.1 s^{-1} for pH 5.0, which is in good agreement with the value reported by Yu et al. [51], and is higher than those reported by others [1,52].

3.2. Electrocatalytic reduction of H_2O_2 at BMPSCu-CPE

The potentials of the different electrodes for the electrocatalytic reduction of H_2O_2 were obtained by the cyclic voltammetric responses of an unmodified CPE and BMPSCu-CPE in the absence and presence of 1.0 mmol/L H_2O_2 solution. Figure 3 shows the cyclic voltammograms of the unmodified CPE and BMPSCu-CPE in 0.1 mol/L phosphate buffer (pH 5.0) solution at the scan rate of 25 mV/s.

As can be seen, there was a quasi-reversible redox couple for BMPSCu-CPE, while no redox response was observed at the unmodified CPE. The cyclic voltammetric response of the electrocatalytic reduction of 1.0 mmol/L of H_2O_2 at BMPSCu-CPE appeared at a potential of –100 mV (Fig. 3(4)) while at the unmodified CPE, a peak potential with a weak current was observed at 400 mV (Fig. 3(2)). Therefore, a significant decrease of 300 mV was achieved in the reduction of the overvoltage of H_2O_2. Also, the comparison of the voltammograms of (3) and (4) in Fig. 3 showed that upon the addition of H_2O_2, the cathodic current increased markedly while the corresponding anodic current disappeared. This result showed that BMPSCu-CPE had good electrocatalytic activity for the reduction of H_2O_2. The possible electrocatalytic reduction process of H_2O_2 at the modified electrode surface can be described by the $E_qC'_i$ mechanism [43,53].

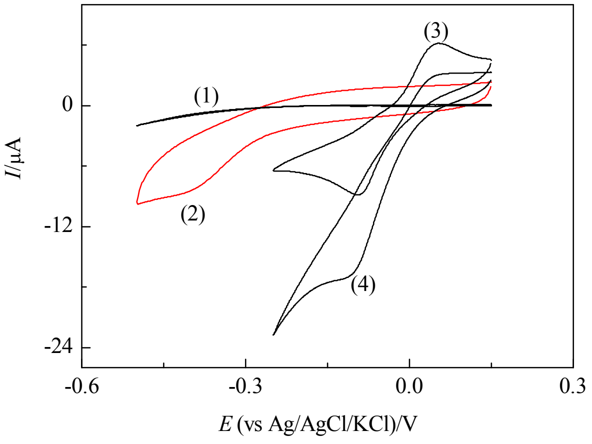
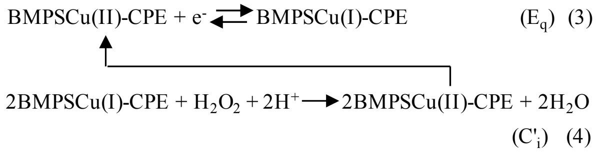


Fig. 3. Cyclic voltammograms of an unmodified CPE in 0.1 mol/L phosphate buffer solution (pH 5.0) at the potential scan rate of 25 mV/s in absence (1) and presence (2) of 1.0 mmol/L H_2O_2. (3) same as (1) and (4) same as (2) for BMPSCu-CPE.



$$\text{BMPSCu(II)-CPE} + e^- \rightleftharpoons \text{BMPSCu(I)-CPE} \qquad (E_q) \quad (3)$$

$$2\text{BMPSCu(I)-CPE} + H_2O_2 + 2H^+ \longrightarrow 2\text{BMPSCu(II)-CPE} + 2H_2O \qquad (C'_i) \quad (4)$$

Figure 4 shows the cyclic voltammograms of BMPSCu-CPE

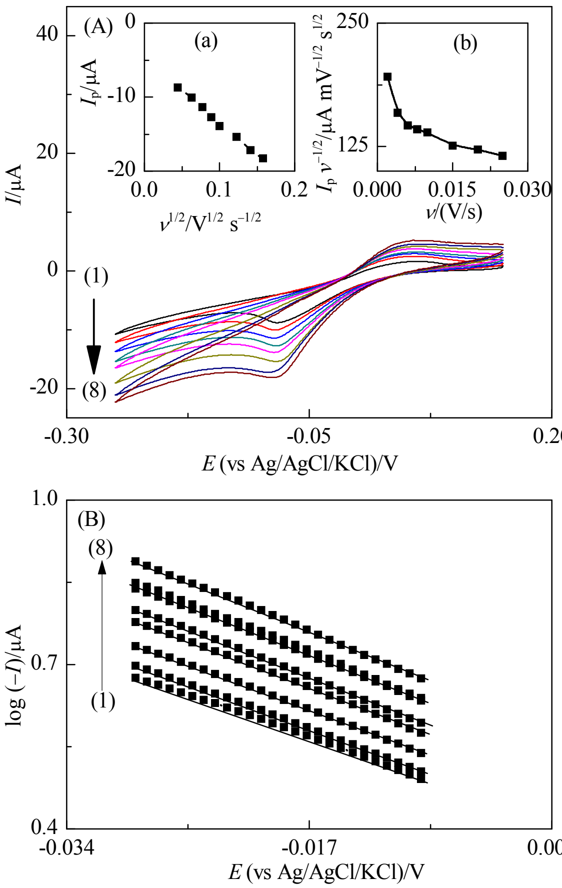


Fig. 4. (A) Cyclic voltammograms of BMPSCu-CPE in 0.1 mol/L phosphate buffer solution (pH 5.0) containing 1.0 mmol/L H_2O_2 at different potential scan rates. (1)–(8) correspond to 2, 4, 6, 8, 10, 15, 20, and 25 mV/s. Insets: (a) variation of the electrocatalytic peak current (I_p) vs square root of potential scan rate ($v^{1/2}$) and (b) variation of the potential scan rate normalized current ($I_p v^{-1/2}$) vs potential scan rate ($v^{1/2}$). (B) Tafel plots derived from the cyclic voltammograms recorded at (A).

in 0.1 mol/L phosphate buffer solution (pH 5.0) containing 1.0 mmol/L of H_2O_2 at different potential scan rates. It can be noted from Fig. 4 that with an increasing potential scan rate, the peak potential for the electroreduction of H_2O_2 shifted to more negative potentials, suggesting kinetic limitation in the reaction between the redox active sites of the modified electrode and H_2O_2. However, the catalytic peak current increased linearly with the square root of the potential scan rate (Fig. 4, inset (a)), suggesting that the reaction was diffusion limited at a sufficient overpotential. Also, the plot of the scan rate normalized current ($Iv^{-1/2}$) versus the potential scan rate (Fig. 4, inset (b)) exhibited a shape typical of a E_qC_i catalytic process. The number of electrons participating in the reduction process of H_2O_2 at the modified electrode surface (n) was found to be 1.8 (~ 2). This calculation was done by using the slope of the straight line of I_p versus $v^{1/2}$ (Fig. 4, inset (a)). The following equation describes the slope of the plot for a totally irreversible diffusion controlled process [54].

$$\text{Slope} = 3.01 \times 10^5 n\,[(1-\alpha)n_\alpha]^{1/2} ACD^{1/2} \quad (5)$$

where $(1-\alpha)n_\alpha = 0.40$ (as obtained below from the Tafel plot), A, D, and C are the electrode area (cm²), diffusion coefficient (cm²/s), and substrate concentration (mol/cm³), respectively. For the case of low potential scan rates (v) and a large catalytic rate constant (k'), Andrieux and Saveant [55] showed that I_p is proportional to $v^{1/2}$for a heterogeneous reaction, in accordance with Eq. (6):

$$I_p = 0.496n\text{F}ADC_bv^{1/2}(nF/RT)^{1/2} \quad (6)$$

where D and C_b are the diffusion coefficient (cm²/s) and the bulk concentration (mol/cm³) of H_2O_2, respectively, and the other symbols have their own usual meanings. Low values of k' resulted in coefficient values lower than 0.496. For low potential scan rates (6–25 mV/s), this constant was found to be 0.23 for BMPSCu-CPE with a net surface area (A) of 0.0962 cm², and $D = 7.01 \times 10^{-6}$ cm²/s (obtained by chronoamperometry as below) in the presence 1.0 mmol/L of H_2O_2. Using the approach of Andrieux and Saveant [55] and using the data of Fig. 2 in their paper [52], a value of $k' = (7.4 \pm 2.9) \times 10^{-4}$ cm/s was calculated.

In order to obtain information on the rate determining step, the Tafel plots were drawn using the data from the rising part of the cyclic voltammograms (known as the Tafel region) recorded at different potential scan rates (Fig. 4(B)). This part of the voltammogram was affected by the electron transfer kinetics between H_2O_2 and BMPSCu-CPE. These data can be used to evaluate the kinetic parameters of H_2O_2 electrocatalytic reduction at the modified electrode surface. Referring to Eq. (7) [56], the charge transfer coefficient (α) of the electrode process can be evaluated from the slope of the cathodic Tafel plot if the rate determining step of the electrode process includes a one-electron transfer, $n_\alpha = 1$.

$$\text{Cathodic Tafel slope} = -\alpha n_\alpha F/2.3RT \quad (7)$$

Based on the above results and from the slopes of the Tafel plots in Fig. 4(B), the cathodic charge transfer coefficient, α_{ave}, was evaluated as 0.60±0.03. The exchange current density, j_0, is accessible from the intercept of the Tafel plots [56]. The j_0 of H_2O_2 at the BMPSCu-CPE surface was found to be 33.1±4.1 μA/cm².

3.3. *Chronoamperometric studies*

The diffusion coefficient of H_2O_2 in solution can be estimated by a chronoamperometric experiment. For an electroactive material with a diffusion coefficient D, the current response under diffusion control is described by Cottrell's equation [56]:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \quad (8)$$

In this equation, I is the current controlled by the diffusion of H_2O_2 from the bulk solution to the electrode/solution interface. Figure 5(a) shows the experimental plots of I versus $t^{-1/2}$ with the best fits for the different concentrations of H_2O_2. The plots were derived from the chronoamperogram data at BMPSCu-CPE and different H_2O_2 concentrations at a potential step of –220 mV. As can be seen in Fig. 5(a), the plots of I versus $t^{-1/2}$ were straight lines. The slopes of the resulting straight lines were then plotted versus the H_2O_2 concentration (Fig. 5(b)).

The slope in Fig. 5(b) of 7.01×10^{-6} cm²/s was calculated for the diffusion coefficient, D, of H_2O_2 under the working conditions. Although this value is in good agreement with the values reported by others [57], it is higher than that reported by Yu et al. [48] and Kumar et al. [58].

3.4. *Differential pulse voltammetric (DVP) determination of H_2O_2 at BMPSCu-CPE*

Figure 6(a) shows the DPV data obtained for the reduction of different concentrations of H_2O_2 at the BMPSCu-CPE surface. The dependence of the electrocatalytic peak current, corrected for any residual current of the modified electrode in the sup-

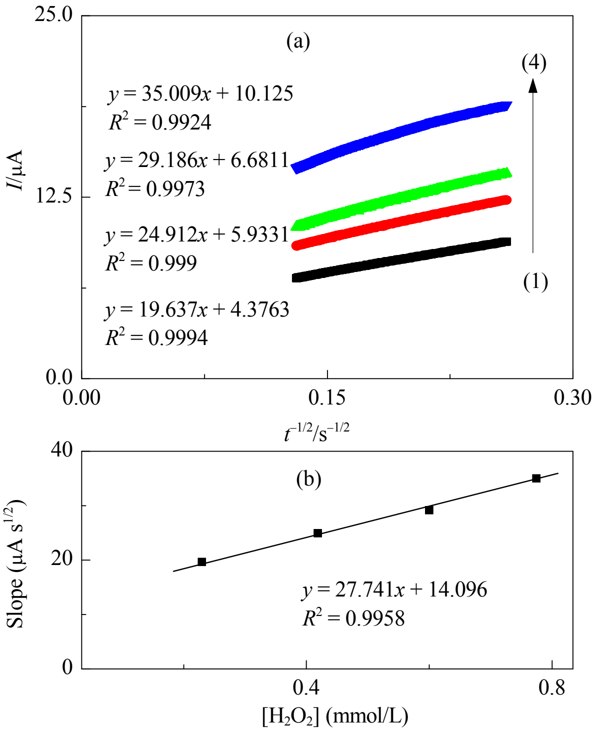


Fig. 5. (a) Plot of I vs $t^{1/2}$ from chronoamperogram data recorded at the BMPSCu-CPE surface in 0.1 mol/L phosphate buffer solution (pH 5.0) at a potential step of −220 mV for different concentrations of H_2O_2. Numbers of (1)–(4) correspond to 0.2, 0.4, 0.6, and 0.8 mmol/L. (b) Plot of the slopes of the straight lines *vs* H_2O_2 concentration.

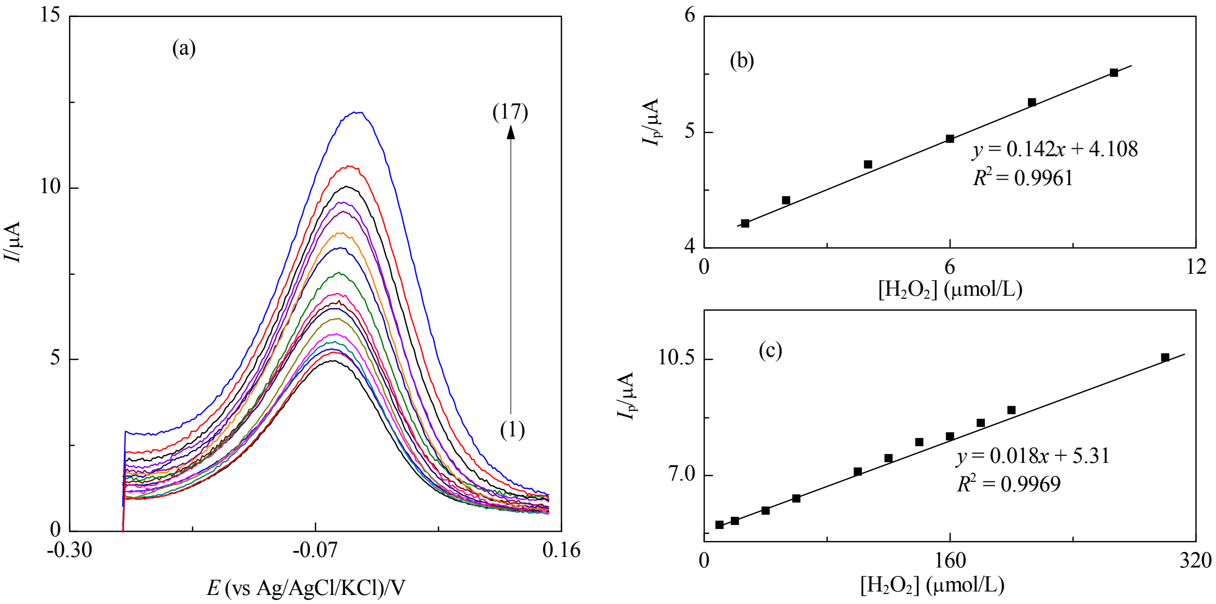


Fig. 6. (a) Differential pulse voltammograms of BMPSCu-CPE in 0.1 mol/L phosphate buffer solution (pH 5.0) containing different concentrations of H_2O_2. (1)–(17) correspond to 1.0–300.0 μmol/L H_2O_2. (b) and (c) show the plots of the electrocatalytic peak current as a function of H_2O_2 concentration for two concentration ranges of 1.0–10.0 and 10.0–300.0 μmol/L H_2O_2, respectively.

porting electrolyte, on the H_2O_2 concentration is shown in Fig. 6(b) and (c). They show clearly that the plot of the peak current versus H_2O_2 concentration is made up of two linear segments with different slopes of 0.142 and 0.018 μA μmol^{-1} L, corresponding to two different ranges of 1.0–10.0 and 10.0–300.0 μmol/L. A comparison of the sensitivities of the two linear segments indicated a decrease of sensitivity in the second linear range of the calibration plot.

It is well known that when an analyte concentration increases in a solution, the thickness of the diffusion layer and mass transfer limitation are reduced [56]. Therefore, it is logical to conclude that under these conditions, the electron transfer kinetics between the analyte and the electrodeposited modifier at the electrode surface is mainly responsible for the current limitation. In other words, the decrease of the sensitivity of the calibration plot in the higher concentration range of H_2O_2 (Fig. 6(c)) was likely due to the electron transfer kinetic limitation between H_2O_2 and BMPSCu(I)-CPE already shown in Eq. (4). In Table 1, some of the analytical parameters obtained for H_2O_2 determination at the modified electrode surface are compared with those previously reported by others [43,44,51, 58–60]. As can be seen, the linear range and the detection limit has been improved in comparison with those previously reported for other modified electrodes.

3.5. Interference study

The selectivity and applicability of BMPSCu-CPE for the determination of H_2O_2 in the presence of the usual interfering species was evaluated by the investigation of the effect of some common species that accompany H_2O_2 in real samples. This study was done for a phosphate buffer solution (0.1 mol/L, pH 5.0) containing 100.0 μmol/L of H_2O_2. The tolerance limit was defined as the molar ratio of the interference species to H_2O_2 that caused a relative error of 5% for H_2O_2 determination. The results presented in Table 2 indicated that the nitrite ion and L-cysteine have serious interfering effects on H_2O_2 determination.

3.6. Determination of H_2O_2 in real samples

To confirm the usefulness of BMPSCu-CPE, the applicability and reliability of this modified electrode were tested for the determination of H_2O_2 in two pharmaceutical samples of an antiseptic solution and a hair dye cream. The pharmaceutical samples were prepared as described in Section 2.3. The measurements were performed using the calibration curve shown in Fig. 6(b). Table 3 presents the nominal values on the label for these products, and the values obtained using the differential

Table 1
Comparison of some parameters of the electrocatalytic detection of H_2O_2 at different modified electrode surfaces.

Modifier	Method	pH	Linear range (μmol/L)	Detection limit (μmol/L)	Ref.
$[Cu_2(Dpq)_2(Ac)_2(H_2O)_2]\ (ClO_4)_2\cdot H_2O$	CV	2.0	2000–20000	—	[43]
$[Cu(II)(TPT)]^{2+}$	CV	5.3	—	—	[44]
Gallium hexacyanoferrate	Amperometry	6.8	4.9–400.0	1.0	[51]
poly(*p*-aminobenzene sulfonic acid)	Amperometry	7.0	50–550	10	[58]
MnO_2	Amperometry	7.4	100–690	2.0	[59]
PNMA (SDS)/Co	DPV	13.0	5–48	3.0	[60]
Bis(*N*-2-methylphenyl-salicyldenaminato)copper(II)	DPV	5.0	1.0–10.0, 10.0–300.0	0.63	this work

Table 2

Interference studies of some species on the determination of 100.0 μmol/L of H_2O_2 (in 0.1 mol/L phosphate buffer solution, pH 5.0) at the BMPSCu-CPE surface using differential pulse voltammetry.

Interference species	Molar ratio (Interference/H_2O_2)
Ascorbic acid	10:1
Uric acid	20:1
Dopamine	20:1
Glucose	20:1
L-Cysteine	1:2
NaCl	100:1
Na_2SO_4	100:1
Na_2NO_2	5:1

Table 3

Determination of hydrogen peroxide in two pharmaceutical samples of antiseptic solution and a hair dye cream using BMPSCu-CPE (DPV method) and the titration method.

Sample	Labeled value (mol/L)	Our method (mol/L)	Titration method (mol/L)
Antiseptic solution	0.882	0.864 ± 0.022 (*n* = 3)	0.860 ± 0.04 (*n* = 3)
Hair coloring cream	1.764	1.717 ± 0.085 (*n* = 3)	1.730 ± 0.07 (*n* = 3)

pulse voltammetry method, and those obtained by a classical potassium permanganate titration method [61].

The good agreement among these results showed the successful application of our proposed method to determine H_2O_2 in pharmaceutical samples. Also, statistical tests such as the t test and F test did not show any significant difference between the values and precision of the results obtained experimentally and those registered on the label of the pharmaceutical inhalation product at the 95% confidence level.

3.7. Stability and reproducibility of BMPSCu-CPE

The stability of BMPSCu-CPE was evaluated by cycling it 100 times in the potential range between –0.25 and 0.15 V at the potential scan rate of 25 mV/s in 0.1 mol/L phosphate buffer solution (pH 5.0). The redox peak current of BMPSCu-CPE remained almost unchanged in these continuous cycles. The storage stability of the modified electrode was also very good as the current response decreased by only 3% after it was kept for more than two months under ambient conditions. Using the modified electrode, the relative standard deviation (RSD) corresponding to 20 replicate measurements of 100.0 μmol/L H_2O_2 was 1.7%. The detection limit of H_2O_2 (C_m) was 0.63 μmol/L using the equation $C_m = 3s_{bl.}/m$ [62], where $s_{bl.}$ is the standard deviation of the blank solution response at the BMPSCu-CPE surface (0.03 μA for $n = 10$) and m is the slope of the calibration plot (0.142 μA μmol^{-1} L) in the first linear range (1.0–10.0 μmol/L).

4. Conclusions

A bis(*N*-2methylphenyl-salicyldenaminato)copper(II) (BMPSCu) modified carbon paste electrode (BMPSCu-CPE) was prepared and tested for its electrocatalytic reduction of H_2O_2. The kinetic parameters of the electron transfer rate constant, k_s, and the transfer coefficient, α, corresponding to the redox reaction of BMPSCu were obtained. The electrocatalytic reduction of H_2O_2 was significantly improved at the BMPSCu-CPE surface in comparison to a bare CPE. The heterogeneous catalytic electron transfer rate constant, k', and α were also determined for the reduction of H_2O_2 at the modified electrode surface using cyclic voltammetry. Differential pulse voltammetric measurements exhibited two linear ranges of 1.0–10.0 and 10.0–300.0 μmol/L and a detection limit of 0.63 μmol/L for H_2O_2. The modified electrode was successfully applied to determine H_2O_2 in two pharmaceutical samples. A low detection limit, excellent catalytic activity, good repeatability for H_2O_2 determination, simplicity of preparation, good reproducibility, and low cost of the modified electrode are the important advantages of BMPSCu-CPE.

References

[1] Salimi A, Hallaj R, Soltanian S, Mamkhezri H. *Anal Chim Acta*, 2007, 594: 24

[2] Choudhury N A, Raman R K, Sampath S, Shukla A K. *J Power Sources*, 2005, 143: 1

[3] Hasegawa S, Shimotani K, Kishi K, Watanabe H. *Electrochem Solid-State Lett*, 2005, 8: A119

[4] Kim T, Hwang J S, Kwon S. *Lab Chip*, 2007, 7: 835

[5] Kjeang E, Brolo A G, Harrington D A, Djilali N, Sinton D. *J Electrochem Soc*, 2007, 154: B1220

[6] Miley G H, Luo N, Mather J, Burton R, Hawkins G, Gu L F, Byrd E, Gimlin R, Shrestha P J, Benavides G, Laystrom J, Carroll D. *J Power Sources*, 2007, 165: 509

[7] Raman R K, Shukla A K. *Fuel Cells*, 2007, 7: 225

[8] Ramanavicius A, Kausaite A, Ramanaviciene A. *Biosens Bioelectron*, 2005, 20: 1962

[9] Campanella L, Roversi R, Sammartino M P, Tomassetti M. *J Pharm Biomed Anal*, 1998, 18: 105

[10] Quintino M S M, Winnischofer H, Araki K, Toma H E, Angnes L. *Analyst*, 2005, 130: 221

[11] Cosnier S, Szunerits S, Marks R S, Novoa A, Puech L, Perez E, Rico-Lattes I. *Electrochem Commun*, 2000, 2: 851

[12] Gouda M D, Kumar M A, Thakur M S, Karanth N G. *Biosens Bioelectron*, 2002, 17: 503

[13] Shan D, Zhu M J, Xue H G, Cosnier S. *Biosens Bioelectron*, 2007, 22: 1612

[14] Shin M C, Kim H S. *Biosens Bioelectron*, 1996, 11: 161

[15] Wei A, Sun X W, Wang J X, Lei Y, Cai X P, Li C M, Dong Z L, Huang W. *Appl Phys Lett*, 2006, 89: 123902/1

[16] Willner I, Riklin A, Shoham B, Rivenzon D, Katz E. *Adv Mater*, 1993, 5: 912

[17] Zou Y J, Xiang C L, Sun L X, Xu F. *Biosens Bioelectron*, 2008, 23: 1010

[18] Hurdis E C, Romeyn H Jr. *Anal Chem*, 1954, 26: 320

[19] Clapp P A, Evans D F, Sheriff T S S. *Anal Chim Acta*, 1989, 218: 331

[20] Kok G L, Holler T P, Lopez M B, Nachtrieb H A, Yuan M. *Environ Sci Technol*, 1978, 12: 1072

[21] Li B X, Zhang Z J, Jin Y. *Anal Chem*, 2001, 73: 1203

[22] Effkemann S, Pinkernell U, Karst U. *Anal Chim Acta*, 1998, 363: 97

[23] Pinkernell U, Effkemann S, Karst U. *Anal Chem*, 1997, 69: 3623

Graphical Abstract

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Electrocatalytic measurement of H_2O_2 concentration using bis(*N*-2-methylphenyl-salicyldenaminato)copper(II) spiked in a carbon paste electrode

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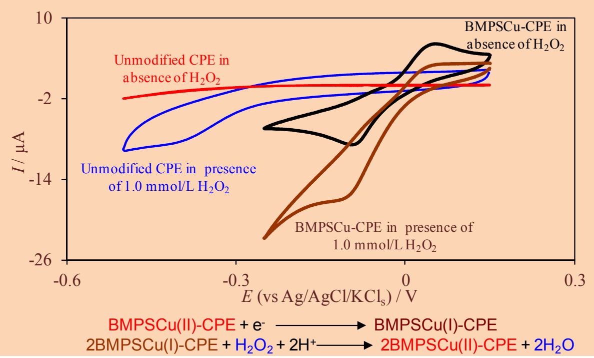

A Cu(II) complex (BMPSCu) used for the electrocatalytic reduction of H_2O_2 gave excellent activity. It successfully detected H_2O_2 in two pharmaceutical samples.

[24] Hong J G, Maguhn J, Freitag D, Kettrup A. *Fresenius J Anal Chem*, 1998, 361: 124
[25] Gorton L, Johansson G. *J Mol Catal*, 1986, 38: 157
[26] Ivama V M, Serrano S H P. *J Braz Chem Soc*, 2003, 14: 551
[27] Ivandini T A, Sato R, Makide Y, Fujishima A, Einaga Y. *Diamond Relat Mater*, 2005, 14: 2133
[28] Santhosh P, Manesh K M, Gopalan A, Lee K P. *Anal Chim Acta*, 2006, 575: 32
[29] Shen Y, Träuble M, Wittstock G. *Anal Chem*, 2008, 80: 750
[30] Wang B, Dong S. *Talanta*, 2000, 51: 565
[31] Cox J A, Jaworski R K. *Anal Chem*, 1989, 61: 2176
[32] Li X Y, Liu Y X, Zheng L C, Dong M J, Xue Z H, Lu X Q, Liu X H. *Electrochim Acta*, 2013, 113: 170
[33] Li B L, Chen J R, Luo H Q, Li N B. *J. Electroanal Chem*, 2013, 706: 64
[34] Doménech A, Alarcón J. *Anal Chim Acta*, 2002, 452: 11
[35] Miah M R, Ohsaka T. *Anal Chem*, 2006, 78: 1200
[36] Fiorito P A, Córdoba de Torresi S I. *Talanta*, 2004, 62: 649
[37] Salimi A, Rahmatpanah R, Hallaj R, Roushani M. *Electrochim Acta*, 2013, 95: 60
[38] Gao G G, Xu L, Wang W J, An W J, Qiu Y F, Wang Z Q, Wang E B. *J Phys Chem B*, 2005, 109: 8948
[39] Salimi A, Alizadeh V, Hadadzadeh H. *Electroanalysis*, 2004, 16: 1984
[40] Kulesza P J, Faulkner L R. *J Electroanal Chem Interf Electrochem*, 1989, 259: 81
[41] Kulesza P J, Roslonek G, Faulkner L R. *J Electroanal Chem Interf Electrochem*, 1990, 280: 233
[42] Chen S M. *J Electroanal Chem*, 1998, 457: 23
[43] Wang X L, Zhao H Y, Lin H Y, Liu G C, Fang J N, Chen B K. *Electroanalysis*, 2008, 20: 1055
[44] Dias V L N, Fernandes E N, da Silva L M S, Marques E P, Zhang J J, Brandes Marques A L. *J Power Sources*, 2005, 142: 10
[45] Kalcher K, Kauffmann J M, Wang J, Švancara I, Vytras K , Neuhold C, Yang Z. *Electroanalysis*, 1995, 7: 5
[46] Gorton L. *Electroanalysis*, 1995, 7: 23
[47] Vafazadeh R, Hayeri V, Willis A C. *Polyhedron*, 2010, 29: 1810
[48] Ju H X, Shen C Z. *Electroanalysis*, 2001, 13: 789
[49] Sharp M, Petersson M, Edstrom K. *J Electroanal Chem Interf Electrochem*, 1979, 95: 123
[50] Laviron E. *J Electroanal Chem Interf Electrochem*, 1979, 101: 19
[51] Yu H, Sheng Q L, Zheng J B. *Electrochim Acta*, 2007, 52: 4403
[52] Ju H X, Liu S Q, Ge B X, Lisdat F, Scheller F W. *Electroanalysis*, 2002, 14: 141
[53] Lin H Y, Wang X L, Hu H L, Chen B K, Liu G C. *Solid State Sci*, 2009, 11: 643
[54] Antoniadou S, Jannakoudakis A D, Theodoridou E. *Synth Met*, 1989, 30: 295
[55] Andriex C P, Saveant J M. *J Electroanal Chem Interf Electrochem*, 1978, 93: 163
[56] Bard A J, Faulkner L R. Electrochemical Methods: Fundamentals and Applications. New York: Wiley, 2001
[57] Miomandre F, Audebert P, Maumy M, Uhl L. *J Electroanal Chem*, 2001, 516: 66
[58] Kumar S A, Chen S M. *J Mol Catal A*, 2007, 278: 244
[59] Lin Y H, Cui X L, Li L Y. *Electrochem Commun*, 2005, 7: 166
[60] Ojani R, Raoof J-B, Norouzi B. *J Solid State Electrochem*, 2010, 14: 621
[61] Jeffery G H, Bassett J, Mendham J, Denney R C. Vogel's Textbook of Quantitative Chemical Analysis. 5th Ed. Essex: Longman Scientific and Technical, 1989
[62] Skoog D A, Holler F J, Nieman T A. Principles of Instrumental Analysis. 5th Ed. Philadelphia: Harcourt Brace & Company, 1998