RESEARCH PAPER

A New Sensor Based on Graphite Screen Printed Electrode Modified With Cu-Nanocomplex for Determination of Paracetamol

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ABSTRACT

Paracetamol is a non-steroidal anti-inflammatory drug used as an antipyretic agent for the alternative to aspirin. Conversely, the overdoses of paracetamol can cause hepatic toxicity and kidney damage. Hence, the determination of paracetamol receives much more attention in biological samples and also in pharmaceutical formulations. Here, we report a rapid and sensitive detection of the paracetamol based on screen-printed electrode (SPE) modified with Cu nanocomplex (Cu) in pH=7.0. The paracetamol is not stable in strong acidic and strong alkaline media, and is hydrolyzed and hydroxylated. However, it is stable in intermediate pHs due to the dimerization of paracetamol. The kinetics of the paracetamol oxidation was briefly studied and documented in the schemes. In addition, the characterization of Cu nanocomplex was probed by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). Moreover, the voltammetry determined the paracetamol with the linear concentration ranging from 10.0 to 1000.0 µM and the lower detection limit of 1.0 µM. This method was also successfully used to detect the concentration of paracetamol in pharmaceutical formulations and urine samples.

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INTRODUCTION

The liver plays a pivotal role in regulating various physiological processes and is the center of metabolism of nutrients such as carbohydrates, proteins and lipids. It is also involved in the metabolism and excretion of drugs and other xenobiotics and provides protection against foreign substances by detoxifying and eliminating them [1,2]. As a result, the liver is exposed to all types of toxic abuse from both endogenous and exogenous sources which may produce liver degeneration. Liver diseases have become one of the major causes of morbidity and mortality in man and hepatotoxicity due to drugs appears to be the most common contributing factor [3].

Paracetamol overdose can cause severe hepatotoxicity and nephrotoxicity. Paracetamol is activated and converted by cytochrome P450 enzymes to toxic metabolite NAPQI (N-acetyl-p-benzoquinoneimine) that causes oxidative stress and glutathione (GSH) depletion which is associated with its hepatotoxicity. In spite of the tremendous advances in modern medicine, there is no effective drug available that stimulates liver function, offers protection to the liver from damage or helps to regenerate hepatic cells [4-6].

Due to its importance, several analytical methods have been applied for the determination of paracetamol

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in pharmaceutical and clinical preparations. These methods include spectrophotometry, chemiluminescence, capillary electrophoresis, spectrofluorimetry, high performance liquid chromatography- electrospray ionization-tandem mass spectrometry, thin layer chromatography, micellar electrokinetic chromatography, micellar electrokinetic capillary chromatography, gas chromatography–mass spectrometry-based profiling [7-15] and electrochemical techniques [16-18].

Spectrophotometric and chemiluminescence methods involve an extraction process before detection, and liquid chromatography is time consuming, making these methods unsuitable for routine analysis. Because paracetamol is an electroactive compound that can be electrochemically oxidized, electrochemical sensors represent an interesting alternative for its rapid determination and quantification [19-20].

Screen-printed electrodes (SPE) have attracted much more interest and challenged the conventional three-electrode system due to its various advantages such as simple fabrication, small size, disposability, easy mass production at low cost, fast speed, high efficiency, portability, low cost and small sample size, these are promising sensors for chemical analytes [21-25]. Furthermore, chemical modification of the screen printed electrochemical sensors can be employed to produce specific and selective electrode for a definite target analytes.

In recent years, nanomaterials as chemical modifier have attracted a lot of attention. Among the various nanomaterials, inorganic nanoparticles are extremely important in the development of sensors. Not only can they be easily synthesized, but also cheaply mass produced. For this reason, they can also be more readily integrated into a variety of applications. Recently, inorganic nanoparticles of different kinds and dimensions have become widely exploited as versatile and sensitive sensors or probes [26-35]. The main objective of designing inorganic nanoparticles is enhancement the sensitivity in bio-sensing applications, and greatly benefits from their small size where their properties are strongly influenced by increasing their surface area. Thus, the combination of inorganic nanoparticles and sensors is one of the most exciting areas in modern analytical detection development because they offer excellent prospects for designing highly sensitive and selective sensors [36-41]. The copper (II) ions are redox active and play a crucial role in catalytic sites of oxidoreductases. The cyclic redox process enables these ions to act as pro or antioxidants [42].

Thus, in this paper, initially the preparation and suitability of a copper nanocomplex modified graphite screen printed electrode (Cu/SPE) as a new electrode in the electrocatalysis and determination of paracetamol in an aqueous buffer solution is described. Then, the analytical performance of the modified electrode in quantification of paracetamol is evaluated. Finally this new constructed electrochemical sensor is used for determination of paracetamol in real samples.

EXPERIMENTAL

Chemicals and Apparatus

Fourier transform infrared (FT-IR) spectra were recorded in transmission mode with a Perkin Elmer BX FT-IR infrared spectrometer. FT-IR spectra in the range of 4000–400 cm^{-1} were recorded in order to investigate the nature of the chemical bonds formed. SEM images of the samples were collected on JSM, 6380 LV equipped with an EDX microanalysis.

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with the General Purpose Electrochemical System (GPES) software. The screen-printed electrode (DropSens, DRP-110, Spain) consists of three main parts which are a graphite counter electrode, a silver pseudo-reference electrode and a graphite working electrode. A Metrohm 710 pH meter was used for pH measurements.

Paracetamol and all other reagents were analytical grade, and were obtained from Merck (Darmstadt, Germany), and the orthophosphoric acid and its salts were used to prepare buffers in the pH range of 2.0–9.0.

Synthesis of Cu(II) nanocomplex

Salophen ligand was synthesized similar to a previously described method [42]. Cu(II) nanocomplex is prepared by a facile low-temperature (<100 °C) synthesis route at atmospheric pressure via reaction of salophen ligand and copper chloride under reflux. Typically, $CuCl_2.6H_2O$ (1 mmol), salophen ligand (1 mmol) and methanol (20 ml) were mixed and sonicated (2 h, 60 °C). The obtained green solid was further purified by two-step processes using double solvent extraction with water and methanol. The solid was finally dried in a vacuum desiccator at 80 °C for 2 h prior to a further analysis or use.

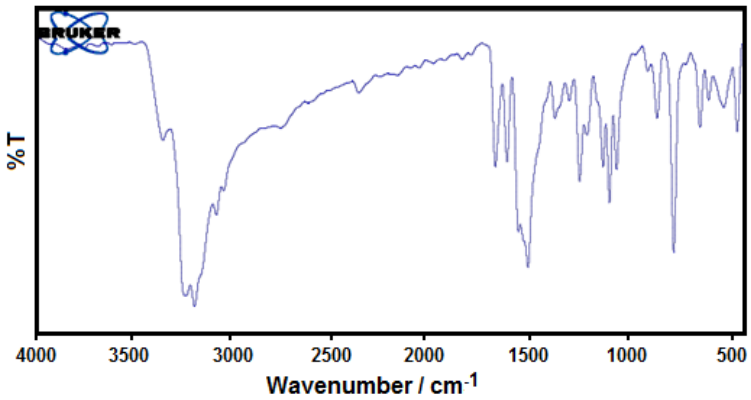

Fig. 1. FT-IR spectra of Cu nanocomplex

Preparation of modified electrode

The bare graphite screen printed electrode was coated with Cu(II) nanocomplex as follows. A stock solution of Cu(II) nanocomplex in 1 ml aqueous solution was prepared by dispersing 1 mg Cu(II) nanocomplex with ultrasonication for 1 h, and a 5 µl aliquot of the Cu(II) nanocomplex/ H_2O suspension solution was casted on the carbon working electrodes, and waiting until the solvent was evaporated in room temperature.

Preparation of real samples

Five paracetamol tablets (labeled 300 mg per tablet, Amin Pharmaceutical Company, Iran) were grinding. Then, the tablet solution was prepared by dissolving 300 mg of the powder in 25 mL water by ultrasonication. Then, different volumes of the diluted solution were transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The paracetamol content was analyzed by the proposed method using the standard addition method.

The urine specimens were kept in a refrigerator after sampling. To prepare the test samples, 10 millilitres of these were taken or centrifuged at 2000 rpm for 15 min. After filtering the supernatant with a 0.45 µm filter, different volumes of it were diluted in 25 mL volumetric flasks using PBS (pH=7.0). The diluted urine sample was spiked with different amounts of paracetamol.

RESULTS AND DISCUSSION

Morphology and structure of Cu nanocomplex

FT-IR spectra provide valuable information about the coordination behavior of the ligands with the copper ion. The FT-IR spectrum of Cu nanocomplex exhibits the characteristic bands of (O-H), (C=N), (C=C), (C-O) and (C-H) appearing at 3358-3086, 1668-1609, 1503, 1293-1053 and 846, 762, 629 cm^{-1}, respectively (Fig. 1). Also, the spectra of Cu nanocomplex show new absorptions in the region of 495 and 440 cm^{-1} attributable to the Cu-N and Cu-Cl stretching mode [42].

The morphology of the product was examined by SEM. Fig. 2 depicts the SEM pictures of Cu nanocomplex. From the graph, it was observed that the Cu nanocomplex, which are plate, are not agglomerated and they are seen as less than 45 nm.

The EDX analysis was performed to further confirm the composition of the obtained products. Fig. 3 shows that the products are composed of Cu and Cl.

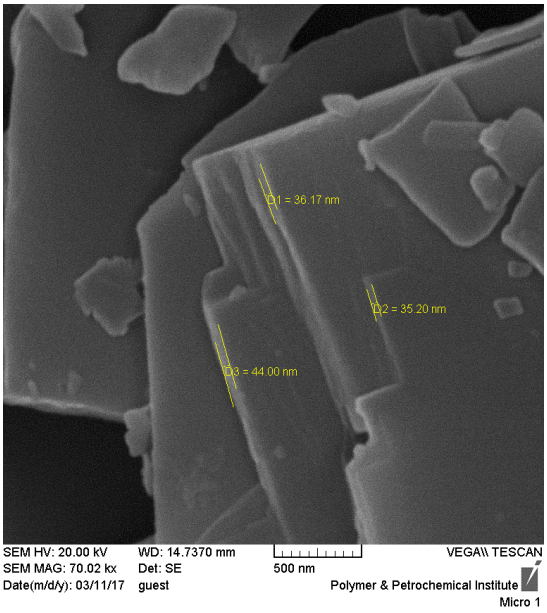

Fig. 2. SEM micrographs of the Cu nanocomplex

Electrochemical profile of the analyte on the Cu/SPE

Due to the fact that the electrochemical behaviour of paracetamol is pH-dependent, optimizing the pH of the solution is necessary for obtaining the best results. Furthermore, the results showed that the best results during the electro-oxidation of paracetamol at the surface of the modified electrodes could be obtained at pH=7. Fig. 4 illustrates the cyclic voltammograms of a 1000.0 µM paracetamol obtained using Cu/SPE (Curve a) and an unmodified SPE (Curve b). As it can be easily noticed, the maximum oxidation of paracetamol occurs at 300 mV in the case of Cu/SPE that is around 200 mV more negative than that observed in the case of the unmodified SPE.

Effect of scan rate on the results

Fig. 5 illustrates the effects of potential scan rates on the oxidation currents of paracetamol, indicating that increasing the scan rate has increased the peak

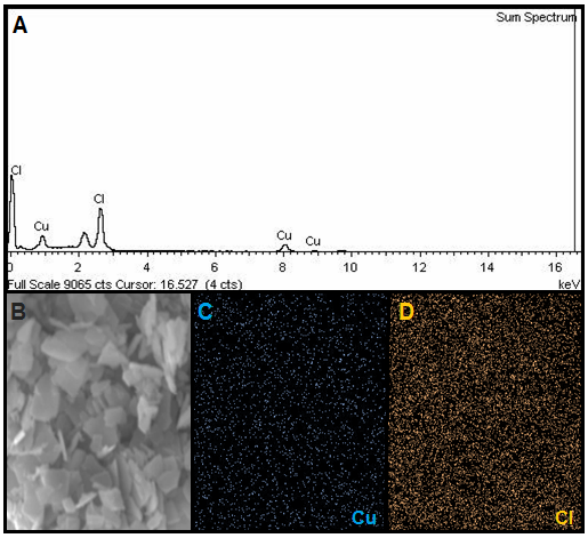

Fig. 3. EDX spectra of Cu nanocomplex

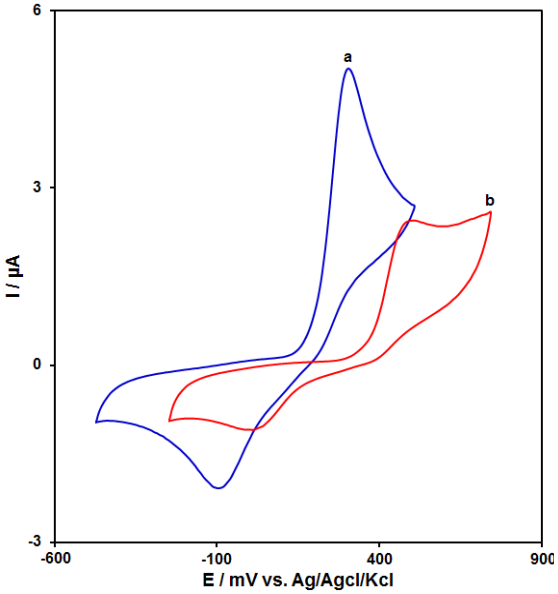

Fig. 4. Cyclic voltammograms of (a) Cu/SPE and (b) bare SPE in 0.1 M PBS (pH 7.0) in the presence of 1000.0 µM aracetamol at the scan rate 50 mVs^{-1}

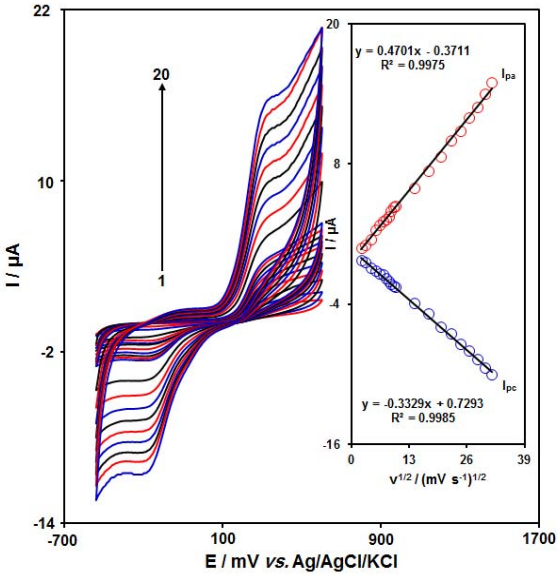

Fig. 5. Cyclic voltammograms of Cu/SPE in 0.1 M PBS (pH 7.0) containing 100.0 µM paracetamol at various scan rates; numbers 1-20 correspond to 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mV s^{-1}, respectively. Inset: variation of anodic and cathodic peak current vs. $v^{1/2}$

currents. Also, based on the fact that the plot of I_p against the square root of the potential scan rate ($\nu^{1/2}$) for paracetamol was linear, it was concluded that the oxidation process is diffusion controlled.

Further Tafel curve of paracetamol was plotted using the data from the rising sections (i.e. the Tafel regions) of the current–voltage curves obtained at 10 mVs^{-1} (Fig. 6). The Tafel regions of the current potential curve is influenced by the electron transfer kinetics of the electrode reactions. The results showed Tafel slope of 0.1716 V, which indicates one electron (Fig. 6) rate determining step (RDS) for the electrode process [43] for charge transfer coefficient (α) of 0.65.

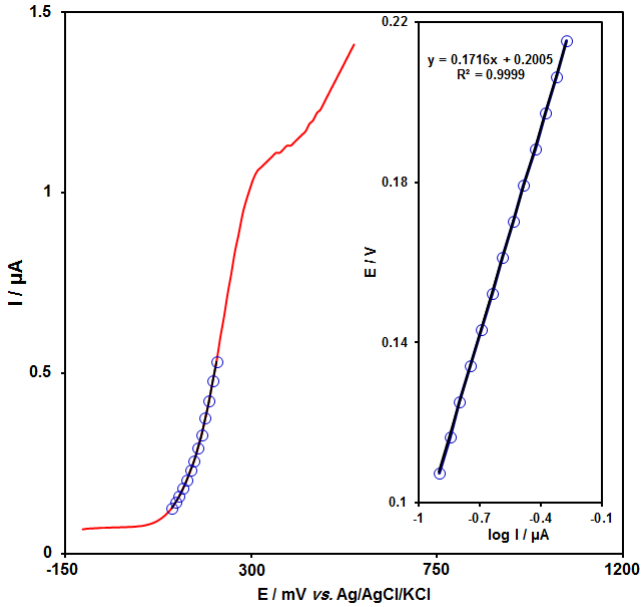

Fig. 6. LSV (at 10 mV s^{-1}) of electrode in 0.1 M PBS (pH 7.0) containing 100.0 µM paracetamol. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV

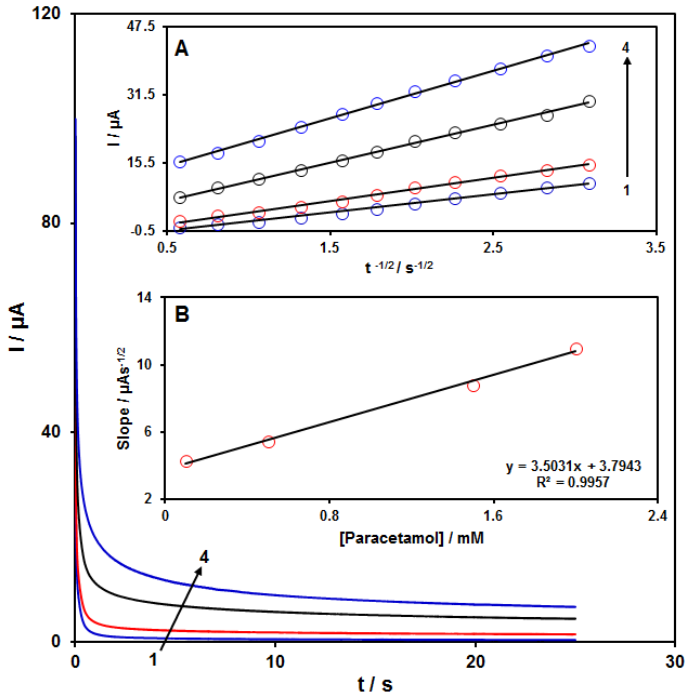

Fig. 7. Chronoamperograms obtained at Cu/SPE in 0.1 M PBS (pH 7.0) for different concentrations of paracetamol. The numbers 1–4 correspond to 0.1, 0.5, 1.5, and 2.0 µM of paracetamol. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 1–4. (B) Plot of the slope of the straight lines against paracetamol concentration

Chronoamperometric analyses

The chronoamperometric analyses of the paracetamol samples using the Cu/SPE and the results obtained for the different paracetamol samples in PBS (pH 7.0) are illustrated in Fig. 7. For chronoamperometric analysis of electroactive materials under mass transfer limited conditions, the Cottrell equation is [43]:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

where D and C_b are the diffusion coefficient ($cm^2\ s^{-1}$) and the bulk concentration (mol cm^{-3}), respectively. Experimental plots of I vs. $t^{-1/2}$ were employed with the best fits for different concentrations of paracetamol (Fig. 7A). The slopes of the resulting straight lines were then plotted vs. paracetamol concentration (Fig. 7B). From the resulting slope and Cottrell equation the mean value of the D was found to be 1.05×10^{-6} cm^2/s.

Calibration curves

The peak currents obtained for paracetamol using the Cu/SPE were used for the quantitative analysis of the paracetamol in water solutions. Given the advantage of differential pulse voltammetry (DPV) in terms of improved sensitivity and better characteristics for analytical applications, the modified electrode was used as the working electrode in DPV analyses in a range of paracetamol solutions in 0.1 M PBS, and the results (Fig. 8) show that there is a linear relation

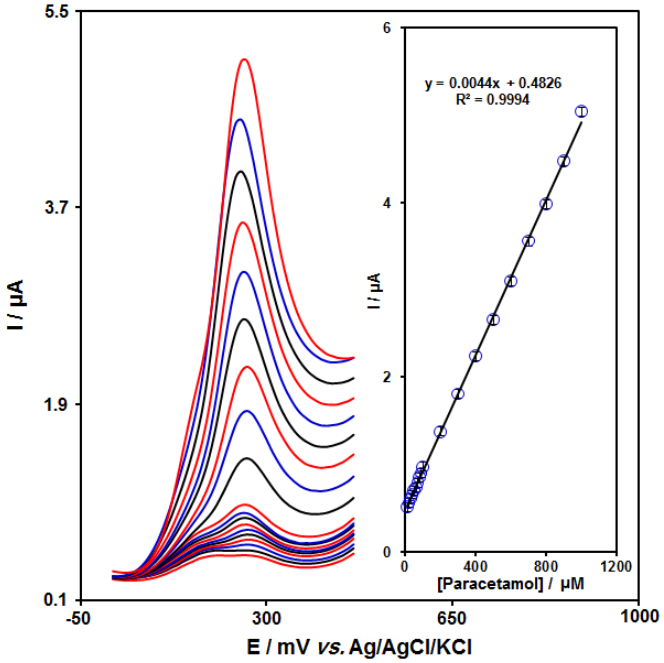

Fig. 8. DPVs of Cu/SPE in 0.1 M (pH 7.0) containing different concentrations of paracetamol. From inner to outer correspond to 10.0. 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0, 200.0, 300.0, 400.0, 500.0, 600.0, 700.0, 800.0, 900.0 and 1000.0 µM of paracetamol. Inset: plot of the electrocatalytic peak current as a function of paracetamol concentration in the range of 10.0-1000.0 µM

Table 1. The application of Cu/SPE for determination of paracetamol in paracetamol tablet and urine samples (n=5). All concentrations are in µM.

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Paracetamol tablet	0	10.0	-	3.3
	2.5	12.3	98.4	2.7
	5.0	15.2	101.3	2.3
	7.5	17.9	102.3	1.9
	10.0	19.8	99.0	2.8
Urine	0	-	-	-
	7.5	7.6	101.3	2.8
	12.5	12.2	97.6	1.8
	17.5	18.1	103.4	3.1
	22.5	22.3	99.1	2.5

between the peak currents and concentrations of paracetamol over the concentration range of 10.0-1000.0 μM (with a correlation coefficient of 0.9994), and a detection limit (3σ) of 1.0 μM was obtained.

Analysis of real samples

To assess the applicability of the modified electrode for the determination of paracetamol in real samples, the described method was applied to the determination of paracetamol in paracetamol tablets and urine samples. For the purpose of this analysis, the standard addition method was used and the results are given in Table 1. The observed recovery of paracetamol was satisfactory and the reproducibility of the results was demonstrated based on the mean relative standard deviation (R.S.D.).

CONCLUSION

A Cu nanocomplex modified SPE was successfully fabricated. Compared with bare SPE, the responses of Cu/SPE were significantly enhanced. The reason is the increase of the electrochemical active surface area and the conductivity of the electrode by introducing Cu nanocomplex. Additionally, the Cu/SPE exhibited an excellent electrocatalytic activity for paracetamol oxidation in neutral aqueous media. The excellent catalytic ability of the modified electrode was attributed to the effect of Cu nanocomplex, which would accelerate electron transfer. The Cu/SPE was applied to the determination of paracetamol in real samples with satisfactory results.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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