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Electrochemical behavior of morphine at ZnO/CNT nanocomposite room temperature ionic liquid modified carbon paste electrode and its determination in real samples

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ABSTRACT

In this paper we report synthesis and application of ZnO/CNT nanocomposite and 1-methyl-3-butylimidazolium bromide as high sensitive sensors for voltammetric determination of morphine using carbon paste electrode. The ZnO/CNT nanocomposite was characterized with different methods such as TEM, SEM and XRD. The electrochemical oxidation of morphine on the new ZnO/CNTs ionic liquid carbon paste electrode (ZnO/CNTs/IL/CPE) was carefully studied. The oxidation peak potential of morphine on the ZnO/CNTs/IL/CPE appeared at 520 mV, which was about 75 mV decrease of the overpotential compared to that obtained on the traditional carbon paste electrode (CPE) and the oxidation peak current was increased for about 5.5 times. The electrochemical parameter of morphine on the ZnO/CNTs/IL/CPE was calculated with the charge transfer coefficient (α). Based on the relationship of the oxidation peak current and the concentration of morphine a sensitive analytical method was established with cyclic voltammetry. The linear range for morphine determination was in the range from 0.1 to 700 μmol L^{-1} and the detection limit was calculated as 0.06 μmol L^{-1} (3σ). Finally, the proposed method was also examined as a selective, simple and precise electrochemical sensor for the determination of morphine in real samples such as urine and ampoule.

1. Introduction

Carbon paste based electrode (CPE) is a special kind of heterogeneous carbon electrode consisting of a mixture prepared from carbon powder and a suitable water-immiscible or non-conducting binder [1–3]. CPEs are widely applicable in both electrochemical studies and electroanalysis thanks to their advantages such as very low background current, facility to prepare, large potential window, low cost, simple surface renewal processes and easiness of miniaturization [4,5].

As all we know, carbon nanotubes (CNTs) have received a tremendous amount of attention due to their unique and highly desirable electrical, thermal, and mechanical properties and have been widely used in analytical chemistry. This tendency is well manifested by several recently published excellent reviews [6–9]. The combination of CNTs with other nanomaterials is expected to be useful for catalysis, or making sensors. On the other hand, ZnO nanoparticles have advantages such as narrow size distribution, efficient surface modification, and desirable biocompatibility.

Recently room temperature ionic liquids (RTILs) are beginning to be used as a new kind of modifier to make an ionic liquid modified carbon paste electrode. RTILs are generally regarded as a compound entirely composed of organic cations and various inorganic anions that exist in the liquid state around room temperature. Because RTILs have many specific physical and chemical properties such as wide electrochemical window, high ionic conductivity and good solubility [10–12], they have been recognized as a useful non-aqueous media for various electrochemical processes [13–16].

Morphine is the most abundant alkaloid found in opium, the dried sap derived from shallowly slicing the unripe seedpods of the Papaver somniferum poppy [17]. Morphine is used to treat moderate to severe pain. Short-acting formulations are taken as needed for pain. To date, many analytical methods have been developed to determine of morphine concentrations, including high performance liquid chromatography [18–20], gas chromatography–mass spectroscopy [21,22], fluorimetry [23,24], chemiluminescence [25–27], surface plasma resonance (SPR) [28], and electrochemical methods [29–36].

We recently reported ionic liquid/carbon nanotube paste electrode as a novel electrochemical sensor for rapid and sensitive voltammetric determination of morphine [31,32]. In continuing efforts to improve this kind of sensors in morphine analysis, in this study we describe synthesis and application of novel ZnO/CNT nanocomposite as a novel nanosensor and 1-methyl-3-butylimidazolium bromide as suitable binder in carbon paste matrix for voltammetric determination of morphine. Compared with previous reports for determination of morphine using ionic liquid/carbon nanotube paste electrodes [31,32]; this modified electrode has the best dynamic range, limit of detection and

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sensitivity for morphine analysis. We also evaluate the analytical performance of the modified electrode for voltammetric determination of morphine in real samples such as patient urine and ampoule.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout.

A 1.0×10^{-2} mol L^{-1} morphine solution was prepared daily by dissolving 0.19 g morphine sulfate in water and the solution was diluted to 25 mL with water in a 25-mL volumetric flask. The solution was kept in a refrigerator at 4 °C in dark. More dilute solutions were prepared daily by serial dilution of the stock solution with water.

Phosphate buffer (sodium dihydrogen phosphate and disodium monohydrogen phosphate plus sodium hydroxide, 0.1 mol L^{-1}) solutions (PBS) with different pH values were used.

High viscosity paraffin ($d=0.88$ kg L^{-1}) from Merck was used as the pasting liquid for the preparation of the carbon paste electrodes.

2.2. Apparatus

Cyclic voltammetry, chronoamperometry, and square wave voltammetry were performed in an analytical system, μ-Autolab with (μ3AUT 71226) PGSTAT (Eco Chemie, the Netherlands). The system was run on a PC using NOVA 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 an unmodified carbon paste electrode (CPE), ZnO/CNTs/CPE, IL/CPE or a ZnO/CNTs/ILCPE. X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu-Ka radiation (k = 1.54 Å). Samples for transmission electron microscopy (TEM) analysis were prepared by evaporating a hexane solution of dispersed particles on amorphous carbon coated copper grids.

1-Methyl-3-butylimidazolium bromide (MBIDZBr) was synthesized according to the previous paper [16].

2.3. Synthesis of ZnO/CNTs

The commercial multi-walled carbon nanotubes with tube diameters of about 20–50 nm were used. The preparation of ZnO/CNT catalysts includes three steps. First, the chemical pretreatment of carbon nanotubes is required. A definite amount of carbon nanotubes was introduced into 40 cm^3 of nitric acid and sulfuric acid (3:1 in volume) solution, then 10 cm^3 of ethanol was dropped into the solution slowly, and the solution was agitated in a shaker at 70 °C and 150 rpm for 24 h. In the second step, certain amounts of purified CNTs (6 g) were dispersed into distilled water solution of NaOH (0.5 M; 100 ml) by ultrasonication for 15 min. The third step is the supporting of zinc oxide on carbon nanotubes by a direct deposition process. 7.4 g ZnO $(NO_3)_2\cdot2H_2O$ was dissolved in 100 cm^3 distilled water. In the constant magnetic stirring, the solution of ZnO $(NO_3)_2\cdot2H_2O$ was added drop wise to the solution of CNTs at 50 °C through a dropping funnel. The rate of addition of the salt solution was kept approximately at 20 ml/h. After completion of the precipitation procedure, the mixture was stirred at room temperature for 12 h, washed and filtered continually in distilled water (pH 7.5), and dried at 120 °C. The solid samples were then calcined at 200 °C for 1 h.

2.4. Preparation of the modified electrode

ZnO/CNTs/CPE was prepared by hand-mixing of 0.80 g of graphite powder and 0.20 g ZnO/CNTs plus paraffin at a ratio of 70/30 (*w*/*w*) and mixed well for 40 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. ZnO/CNTs/ILCPE was prepared by mixing of 0.3 g of 1-methyl-3-butylimidazolium bromide, 0.7 g of the liquid paraffin, 0.20 g of ZnO/CNTs, and 0.80 g of graphite powder. Then the mixture was mixed well for 40 min until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into one glass tube as described above to prepare ZnO/CNTs/ILCPE.

2.5. Preparation of real samples

Urine samples were stored in refrigerator immediately after collection (from the Sari Health Centre). Ten milliliters of the sample was centrifuged for 30 min at 2000 rpm. The supernatant was filtered out using a 0.45 μm filter and then diluted 5-times with the PBS (pH 8.0). The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment. The standard addition method was used for the determination of morphine in real samples.

0.10 mL of the solution injection solution (APP Pharmaceuticals, LLC Schaumburg 0.5 mg mL^{-1}) plus 10 mL of 0.1 mol L^{-1} buffer (pH 8.0) were used for the analysis.

3. Results and discussion

3.1. Nanostructures characterization

ZnO/CNT nanopowders were analyzed by XRD analyses. The XRD pattern of ZnO/CNT nanopowders, in the 2θ range of 10–80°, is shown in Fig. 1. It clearly proves the presence of ZnO nanoparticle, with a diffraction peak at about 26° from CNTs. An average diameter of as-synthesized ZnO nanoparticle was calculated from the broadness peak of (2θ = 36) by using Scherrer equation $\left(D=\frac{K\lambda}{\beta\cos\theta}\right)$, and it is about 22.0 nm.

The morphology of the as-grown nanostructures was characterized by SEM and TEM techniques. Typical SEM micrograph of the ZnO/CNTs is shown in Fig. 2a. Results show the presence of ZnO nanostructure grown on carbon nanotubes. The elemental composition of ZnO/CNT nanocomposites was confirmed by the EDX measurement as shown in Fig. 2b. The EDX measurement shows that the composition of ZnO/CNTs alloy was 23 at.% of Zn, 62% C and 15.0 at.% O, indicating a ratio of 1:2.7 to ZnO/CNTs. Fig. 3 presents a typical TEM image of ZnO/CNT nanocomposite. Results show the core of particles supported on carbon nanotubes. Since the corresponding XRD pattern presented in Fig. 1 detected only CNTs and ZnO, it was believed that the core and nanotubes of particles should be ZnO and carbon nanotubes, respectively.

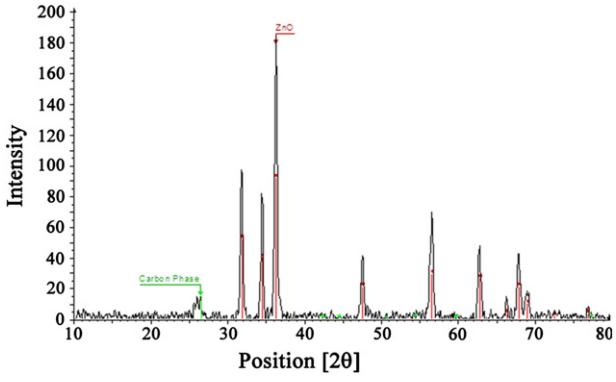


Fig. 1. XRD patterns of as-synthesized ZnO/CNT nanocomposite.

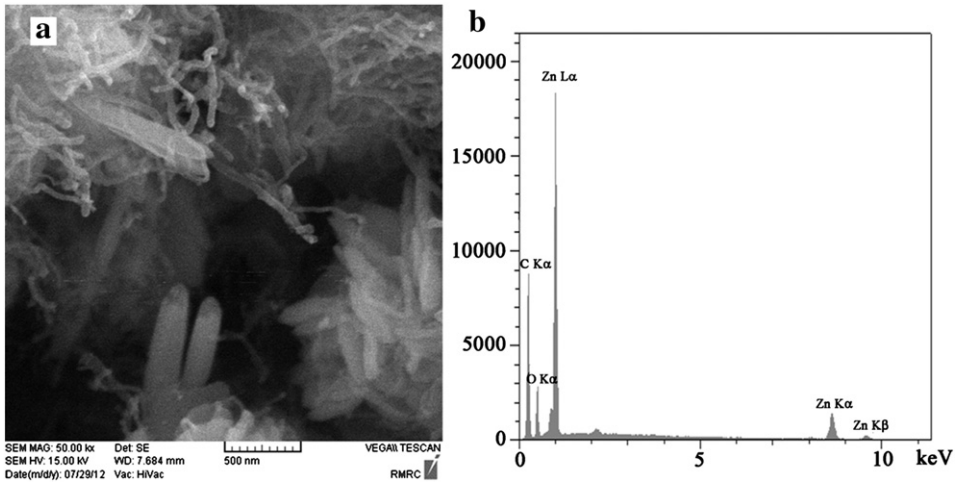


Fig. 2. (a) SEM image of ZnO/CNTs. (b) EDX pattern of as-synthesized ZnO/CNT composites.

3.2. Electrochemical investigation

Morphine can be oxidized at positive potential depending on the electrode type and solution pH [37]. Scheme 1 shows the electrooxidation reaction of morphine. According to Scheme 1, we anticipated that the oxidation of morphine would be pH dependent. In order to ascertain this, the voltammetric response of morphine at a surface of ZnO/CNTs/ILCPE was obtained in solutions with varying pH. Result shows that the peak potential of the redox couple was pH dependent with a slope of −69.0 mV/pH unit at 25 °C which was equal to the anticipated Nernstian value for a one-electron, one-proton electrochemical reaction. It can be seen that the maximum value of the peak current appeared at pH 8.0 (Fig. 4), so this value was selected throughout the experiments.

Fig. 5 (inset) shows the current density derived from the cyclic voltammogram responses of 500 μmol L^{-1} morphine (pH 8.0) at the surface of different electrodes with a scan rate of 50 mV s^{-1}. The results show that the presence of ZnO/CNT nanocomposite and IL together causes the increase in the active surface of the electrode.

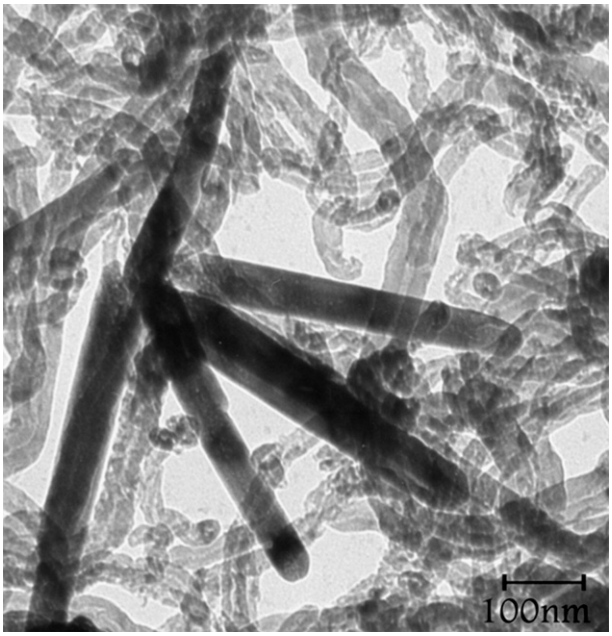
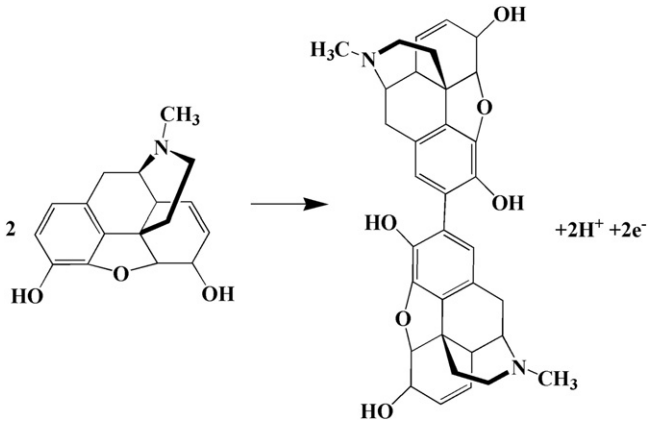


Fig. 3. TEM image of ZnO nanoparticles deposited on sidewalls of MWCNTs.

The direct electrochemistry of morphine on the modified electrode was investigated by linear sweep voltammetry. Fig. 5 showed the typical linear voltammogram responses of 500 μmol L^{-1} morphine at pH 8.0 at the surface of different electrodes with a scan rate of 50 mV s^{-1}. ZnO/CNTs/ILCPE exhibited significant oxidation peak current around 520 mV with the peak current of 62.3 μA (Fig. 5, curve a). In contrast, low redox activity peak was observed at ZnO/CNTs/CPE (Fig. 5, curve c) and at unmodified CPE (Fig. 5 curve d) over the same potential range. The morphine oxidation peaks potential at ZnO/CNTs/CPE and at CPE were observed around 580 and 595 mV vs. the Ag/AgCl/KCl_{sat} reference electrode with the oxidation peak currents of 21.0 and 11.5 μA, respectively. In addition, at the surface of bare IL/CPE, the oxidation peak appeared at 540 mV with a peak current of 35.0 μA (Fig. 5, curve b), which indicated that the presence of ILs in CPE could enhance the peak currents and decrease the oxidation potential (decreasing the overpotential). A substantial negative shift of the currents starting from oxidation potential for morphine and dramatic increase of current of morphine indicated the catalytic ability of ZnO/CNTs/ILCPE to morphine oxidation. The results indicated that the presence of ZnO/CNTs on ZnO/CNTs/ILCPE surface had great improvement with the electrochemical response, which was partly due to excellent characteristics of ZnO/CNT nanocomposite such as good electrical conductivity, high chemical stability, and high surface area. The suitable electronic properties of ZnO/CNTs together with the ionic liquid gave the ability to promote charge transfer reactions, good anti-fouling properties, especially when mixed with a higher conductive compound such as ILs when used as an electrode.



Scheme 1. The mechanism for electrooxidation of morphine at a surface of electrode.

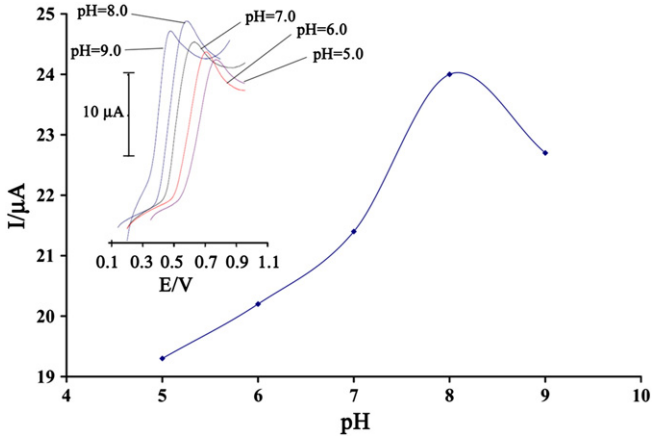


Fig. 4. Current-pH curve for electrooxidation of 150.0 μmol L^{-1} morphine at ZnO/CNTs/ILCPE with a scan rate of 50 mV s^{-1}. Inset: influence of pH on linear sweep voltammograms of morphine at a surface of the modified electrode, (pH 5, 6, 7, 8, and 9, respectively).

The effect of scan rate (υ) on the oxidation current of morphine was also examined (Fig. 6 inst). The results showed that the peak current increased linearly with increasing the square root of scan rate that ranged from 6 to 50 mV s^{-1} according to regression equation of:

$$I_p = 5.8124\nu^{1/2} - 9.5450\left(r^2 = 0.9926, I \text{ in } \mu A, \nu \text{ in } mV\,s^{-1}\right). \quad (1)$$

The result shows that the electrode process is controlled under the diffusion step. On the other hand, the peak potential shifts in negative direction when the scan rate increases, meaning that the electrochemical reaction is quasi-reversible. At higher scan rate, the dependence of the peak potential (E_{pa}) and ln(ν) showed a linear relationship with a regression equation of:

$$E_p = 0.0493\ln(\nu) + 0.3661\left(r^2 = 0.9919, E_p \text{ in } V, \nu \text{ in } V\,s^{-1}\right). \quad (2)$$

According to the following equation [38]:

$$E_{pa} = E^{0/} + m\left[0.78 + \ln\left(D^{1/2}k_s^{-1}\right) - 0.5\ln m\right] + (m/2)\ln(\nu) \quad (3)$$

with

$$m = RT/[(1-\alpha)n_\alpha F. \quad (4)$$

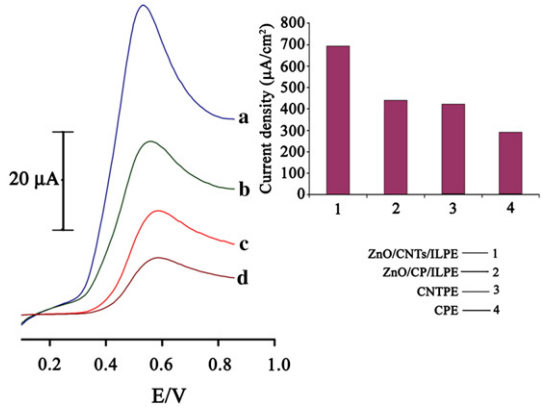


Fig. 5. Linear sweep voltammograms of a) ZnO/CNTs/ILCPE, b) IL/CPE, c) ZnO/CNTs/CPE and d) CPE in the presence of 500 μmol L^{-1} morphine at a pH 8.0, respectively. Inset: the current density derived from linear sweep voltammogram responses of 500 μmol L^{-1} morphine at pH 8.0 at the surface of different electrodes with a scan rate of 50 mV s^{-1}.

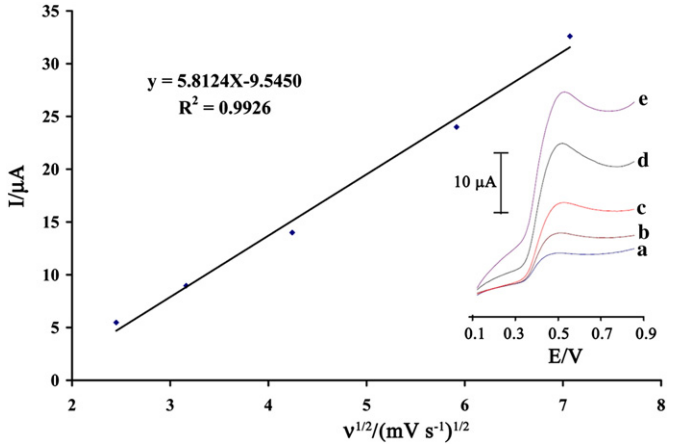


Fig. 6. Plot of I_{pa} versus $\nu^{1/2}$ for the oxidation of morphine at ZnO/CNTs/ILCPE. Inset shows linear sweep voltammograms of morphine at ZnO/CNTs/ILCPE at different scan rates of a) 6, b) 10, c) 18, d) 35, and d) 50 mV s^{-1} in 0.1 M phosphate buffer, pH 8.0.

The value of m = 0.098 is calculated from Eq. (4). Therefore, the electron transfer coefficient (α) is approximately 0.73 for the irreversible electrode process. In addition, the value of α was calculated for the oxidation of morphine at pH 8.0 for both the ZnO/CNTs/ILCPE and unmodified CPE using the following equation [39]:

$$\alpha n_\alpha = 0.048/\left(E_P - E_{P/2}\right) \quad (5)$$

where $E_{P/2}$ is the potential corresponding to $i_{P/2}$. The values for αn_α were found to be 0.73 and 0.59 at the surface of both ZnO/CNTs/ILCPE and unmodified CPE, respectively. Those values show that the overpotential of morphine oxidation is reduced at the surface of ZnO/CNTs/ILCPE, and also that the rate of electron transfer process is greatly enhanced. This phenomenon is, thus, confirmed by the larger I_{pa} values recorded during linear sweep voltammetry at ZnO/CNTs/ILCPE.

The chronoamperometry as well as the other electrochemical methods was employed for the investigation of electro-oxidation of morphine at ZnO/CNTs/ILCPE. Chronoamperometric measurements of morphine at ZnO/CNTs/ILCPE were done (not shown) for various concentrations of morphine. For an electroactive material (morphine in this case) with a diffusion coefficient of D, the current for the

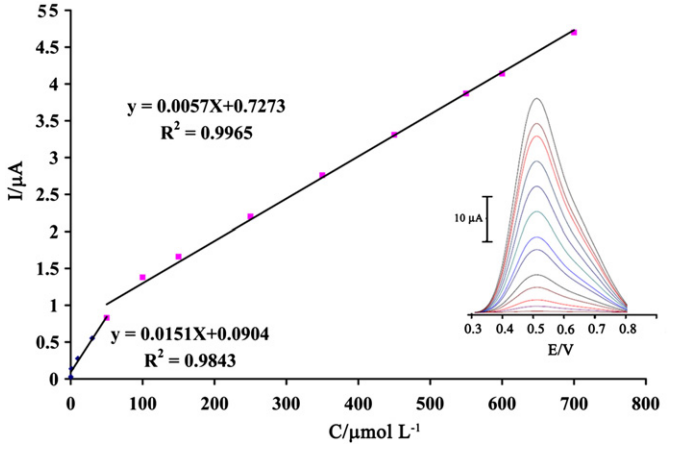


Fig. 7. The plots of the electrocatalytic peak current as a function of morphine concentration. Inset shows the SWVs of ZnO/CNTs/ILCPE in 0.1 mol L^{-1} phosphate buffer solution (pH 8.0) containing different concentrations of morphine. From inner to outer correspond to 0.1, 1.0, 10.0, 30.0, 50.0, 100.0, 150.0, 250.0, 350.0, 450.0, 550.0, 600.0 and 700.0 μmol L^{-1} of morphine.

Table 1
Determination of morphine in drug and urine samples.

Sample	Added (μmol L^{-1})	Expected (μmol L^{-1})	Founded (μmol L^{-1})	Published method (μmol L^{-1}) [37]	F_{ex}	F_{tab}	t_{ex}	$t_{tab(95\%)}$
Injection solution	–	10.0	10.3 ± 0.5	10.5 ± 0.7	4.5	19	2.2	3.8
	20.0	30.0	29.6 ± 0.7	30.5 ± 0.6	–	–	–	–
	20.0	50.0	50.8 ± 0.9	51.0 ± 1.1	–	–	–	–
Urine	–	–	<Limit of detection	–	–	–	–	–
	5.0	5.0	5.5 ± 0.6	5.6 ± 0.8	8.5	19	2.8	3.8
	10.0	15.0	15.5 ± 0.5	15.7 ± 0.8	–	–	–	–
Urine*	–	–	4.7 ± 0.3	5.1 ± 0.6	7.5	19	2.3	3.8
	5.3	10.0	10.5 ± 0.6	10.6 ± 0.8	–	–	–	–

± Shows the standard deviation.
* Sampling was made after 2.5 h from a man who is sick and used morphine.

electrochemical reaction (at a mass transport limited rate) is described by the Cottrell equation [40]:

$$I = nFAD^{1/2} C_b \pi^{-1/2} t^{-1/2}. \quad (6)$$

Under diffusion control, a plot of I versus $t^{-1/2}$ will be linear, and from the slope the value of D can be obtained. The mean value of the D was found to be 5.55×10^{-6} cm^2/s.

3.3. Stability and reproducibility

The repeatability and stability of ZnO/CNTs/ILCPE were investigated by linear sweep voltammetric measurements of 50.0 μmol L^{-1} morphine. The relative standard deviation (RSD%) for seven successive assays was 0.92%. When using five different electrodes, the RSD% for five measurements was 1.5%. When the electrode is stored in the laboratory, the modified electrode retains 97% of its initial response after a week and 94% after 40 days. These results indicate that ZnO/CNTs/ILCPE has a good stability and reproducibility, and could be used for morphine analysis.

3.4. Interference studies

The influence of various substances as potentially interfering compounds for the determination of morphine was studied under the optimum conditions with 5.0 μmol L^{-1} morphine at pH 8.0. The potential interfering substances were chosen from the group of substances commonly found with morphine in pharmaceuticals and/or in biological fluids. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error of less than ± 5% for the determination of morphine. After the experiments, we found that neither 1000-fold of glucose, sucrose, lactose and fructose, nor 800-fold of K^+, Li^+, Ca^{2+}, Mg^{2+}, Al^{3+}, NH_4^+, SO_4^{2-}, Cl^- and ClO_4^-, nor 500-fold methionine, alanine, phenylalanine, valine, tryptophan, histidine and glycine affected the selectivity. Nor did saturation solution of starch; neither 200-fold of urea and thiourea were interfered with the determination of morphine.

3.5. Calibration plot and limit of detection

Since square wave voltammetry has a much higher current sensitivity than linear sweep voltammetry, it was used for the determination of morphine (Fig. 7 inset). The plot of peak current vs. morphine concentration consisted of two linear segments with slopes of 0.0151 and 0.0057 μA μmol^{-1} L in the concentration ranges of 0.1 to 50.0 μmol L^{-1} and 50.0 to 700.0 μmol L^{-1}, respectively (Fig. 7). The decrease in sensitivity (slope) of the second linear segment is likely due to kinetic limitation. According to the method mentioned in Refs. [41–60], the lower detection limit, C_m, was obtained by using the equation $C_m = 3s_b/m$, where s_b is the standard deviation of the blank response (μA) and m is the slope of the calibration plot. The data analysis presents the value of lower limit detection of morphine to be 0.06 μmol L^{-1}.

3.6. Determinations of morphine in real samples

In order to demonstrate the ability of the modified electrode to the determination of morphine in real samples, determinations of morphine in pharmaceutical and in urine samples were examined. The results are given in Table 1. These results demonstrated the ability of ZnO/CNTs/ILCPE for voltammetric determination of morphine with high selectivity and good reproducibility. Also, the results from the statistical calculation indicate good agreement between the mean values (t-test) and the precisions (F-test) of the data obtained by the proposed and the published method [37].

4. Conclusion

In this paper we report synthesis of ZnO/CNT nanocomposite as a high sensitive sensor for voltammetric determination of morphine using carbon paste electrode. The synthesized nanocomposite was characterized with different methods such as SEM, TEM, XRD, and EDX. ZnO/CNTs/ILCPE combines the features of ZnO/CNT nanocomposite and room temperature ionic liquid to play a good voltammetric sensor. Hence it shows high sensitivity and reproducibility in sensing of morphine. Compared with traditional CPE, a decrease of overpotential of oxidation of morphine was about 75 mV with 5.5-fold increment in the oxidation peak current when using ZnO/CNTs/ILCPE. Under the optimum conditions, the oxidation peak current was proportional to the morphine concentration in the range of 0.1 to 700 μmol L^{-1} with the detection limit of 0.06 μmol L^{-1}. The proposed method was successfully applied to the morphine detection in real samples such as drug and urine.

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