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Original scientific paper

ZnO/1-hexyl-3-methylimidazolium chloride paste electrode, highly sensitive lorazepam sensor

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Abstract

The measurement of pharmaceutical compounds in biological fluids is considered an effective way to evaluate their effectiveness. On the other hand, lorazepam is a drug with good efficiency in treatment and some side effects, which measurement is very important. In this study, the ZnO nanoparticle was synthesized as an electrocatalyst by chemical precipitation method. Then, a simple modification on paste electrode (PE) by ZnO nanoparticle (ZnO-NPs) and 1-hexyl-3-methylimidazolium chloride (HMImCl) was made and a new sensor was used for sensing of lorazepam. The HMImCl/ZnO-NPs/PE showed catalytic behavior on oxidation signal of lorazepam and improved its signal about 2.17 times compared to unmodified PE. On the other hand, oxidation potential of lorazepam was reduced about 110 mV at surface of HMImCl/ZnO-NPs/PE compared to unmodified PE that confirm accelerating the electron exchange process after modification of sensor by HMImCl and ZnO-NPs as powerful catalysts. The HMImCl/ZnO-NPs/PE was used for monitoring of lorazepam in water and injection samples and results showed recovery data 98.5 to 103.5 % that are acceptable for a new sensor.

Keywords

Pharmaceutical sensor; modified sensor; nano-catalyst; ionic liquid

Introduction

Medicines, as one of the most important substances used in human life, have many positive and negative effects, which have attracted the attention of many researchers [1,2]. Although drugs play an important role in the treatment of diseases, the harmful effects of some of them on the body as well as the harmful effects on the environment have caused many studies to be done on this group of compounds [3]. Measuring medicinal compounds is one of the most important studies in this field and can provide a lot of information during patient treatment or its role in environmental pollution [4,5]. In between of analytical methods in sensing of pharmaceutical compounds [6-10], electrochemical methods showed more attentions due to many advantages such as easy modification for sensitive sensing, low cost and wide range applications [11].

The lorazepam is one of famous medicines used to treat anxiety [12]. There are several reports of adverse effects of lorazepam use such as dizziness, tiredness and weakness [13]. Therefore, monitoring of this medicine is very important during treatment [14]. Due to high over-voltage and low redox signal of lorazepam, the sensing of it is so hard with usual electrochemical sensors [11]. To overcome to this problem, modification and amplification of electrochemical sensors is necessary [15]. Modification of electrodes is one of the proven solutions to increase the sensitivity and selectivity of electrochemical sensors [16-21]. Different types of mediators such as polymers, nanomaterials, ionic liquids, MOF *etc.* were suggested for modification and amplification of electrochemical sensors in recent years [22-30].

Nanotechnologies opened a new approach in science and improve many of chemical and physical properties of materials [31-36]. With this way, nanomaterials were selected as first choice in different branches of science [37-42]. Due to high electrical conductivity of some nanomaterials such as metal nanoparticles and carbon-based nanomaterials, they were used for modification of electrochemical sensors [43-45]. On the other hand, ionic liquids showed good advantage as binder for fabrication of paste electrode and improved electrical conductivity of modified paste electrodes [46-51].

In this research work, the HMImCl/ZnO-NPs/PE was fabricated and used as new approach for monitoring of lorazepam with good limit of detection compared to previous suggested electrochemical sensors. The HMImCl/ZnO-NPs/PE showed acceptable analytical data in sensing of lorazepam in real samples with recovery data 98.5 - 103.5%. Modification of electrode improved oxidation current of lorazepam about 2.17 times and reduced its oxidation potential for about 110 mV compared to unmodified electrode.

Experimental

Materials and instruments

Zinc nitrate hexahydrate and sodium hydroxide were purchased from Merck Company and used for synthesis of ZnO nanoparticles. 1-Hexyl-3-methylimidazolium chloride, graphite powder, paraffin oil and diethyl ether were purchased from Sigma-Aldrich Company and used for fabrication of paste electrode. Phosphoric acid purchased from Merck was used for preparation phosphate buffer solution. The I - V signals were recorded by Vertex – Ivium (potentiostat/galvanostat) connected with HMImCl/ /ZnO-NPs/PE as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode.

Synthesis of ZnO nanoparticles

The 100 mL zinc nitrate hexahydrate (0.5 M) were stirred in Erlenmeyer flask for 15 min and then 100 mL sodium hydroxide (0.5 M) were added dropwise and stirred form 30 min. White precipitate of zinc hydroxide was washed for 10 times by distilled water and then dried ate 100 °C for 16 h. The white powder was calcinated at 250 °C for 4 h and ZnO nano-powder was obtained.

Fabrication of HMImCl/ZnO-NPs/PE

For fabrication of HMImCl/ZnO-NPs/PE; 90 mg ZnO-NPs + 910 mg graphite powder were mixed in mortar and pestle and 15 mL diethyl ether was superimposed. After evaporation of diethyl ether, the paraffin oil + HMImCl with ratio of (7:3 vol.%) were used as binders and sample hand mixed for 1 h. The HMImCl/ZnO-NPs paste was inserted into the end of a glass tube for fabrication of HMImCl/ZnO-NPs/PE in the presence of copper wire.

Results and discussion

Electrochemical investigations

The electrochemical behavior of lorazepam was investigated in the pH range 5.0 to 7.0 and results are shown in Figure 1.

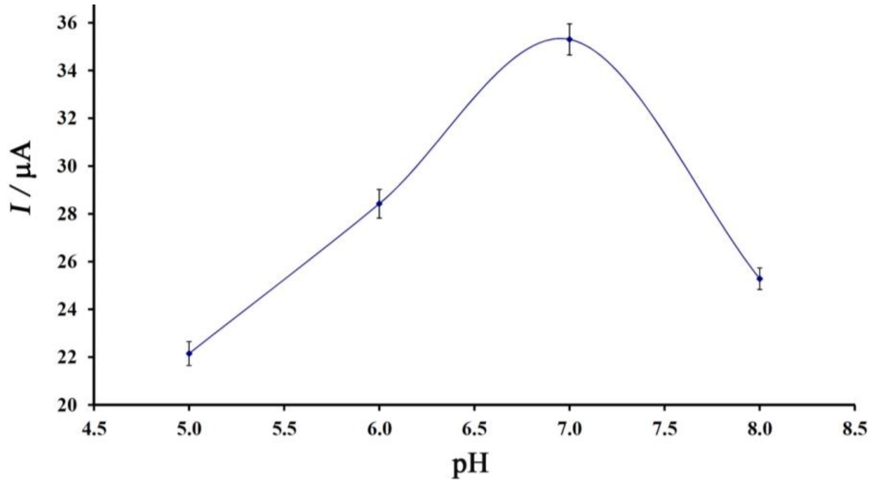

Figure 1. *Oxidation peak current-pH diagram for sensing of 300 μM lorazepam using HMImCl/ZnO-NPs/PE as electroanalytical sensor (n=4)*

As can be seen, with increasing pH from 5.0 to 7.0, the oxidation signal of 300 μM lorazepam increased and then decreased. Therefore, pH 7.0 was selected as optimum condition for monitoring of lorazepam using HMImCl/ZnO-NPs/PE as electroanalytical sensor.

The oxidation signal of 200 μM lorazepam was recorded at surface of PE (Figure 2a), ZnO-NPs/PE (Figure 2b), HMImCl/PE (Figure 2c) and HMImCl/ZnO-NPs/PE (Figure 2d), respectively.

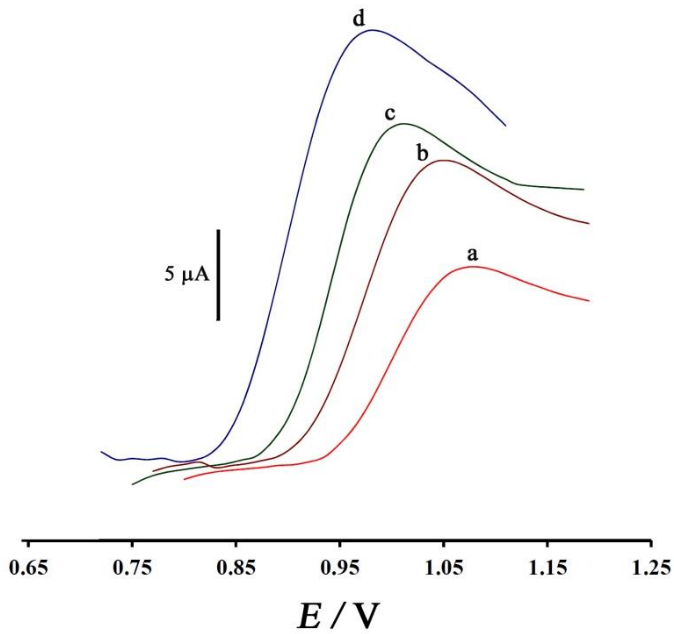

Figure 2. *Linear sweep voltammograms of 200 μM lorazepam at surface of PE (a), ZnO-NPs/PE (b), HMImCl/PE (c) and HMImCl/ZnO-NPs/PE (d); pH 7.0*

The oxidation peak currents of 10.85 μA, 16.53 μA, 18.55 μA and 23.6 μA were detected for monitoring of 200 μM lorazepam at surface of PE, ZnO-NPs/PE, HMImCl/PE and HMImCl/ZnO-NPs/PE, respecttively. As can be seen, with moving PE to HMImCl/ZnO-NPs/PE, the oxidation current of lorazepam increased due to high electrical conductivity and synergic effect of two conductive mediators. This result confirms synergic effect of two mediators after modification of PE and fabrication of a highly sensitive voltammetric sensor to monitoring of lorazepam.

The linear sweep voltammogarms of 300 μM lorazepam at surface of HMImCl/ZnO-NPs/PE and in the scan rate range 10 to 100 mV/s were recorded and signals are presented in the inset of Figure 3.

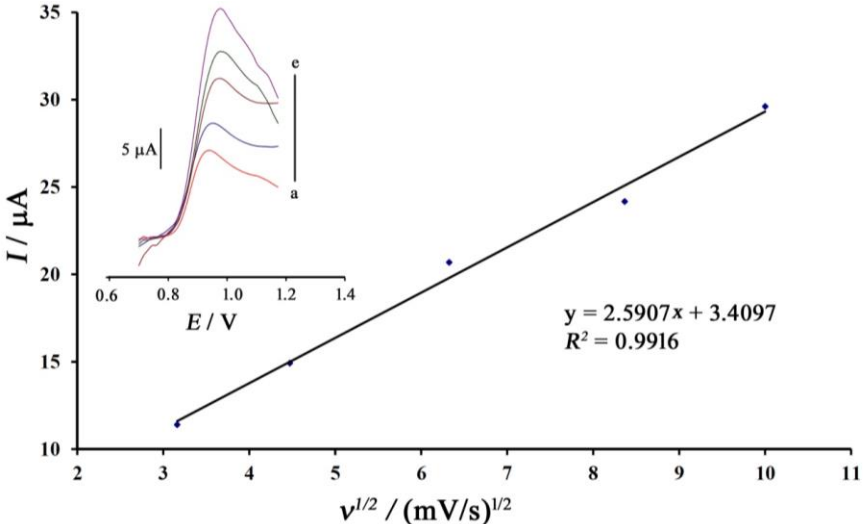

Figure 3. *Peak current vs. $v^{1/2}$ plot for oxidation of 300 μM lorazepam at surface of HMImCl/ZnO-NPs/PE. Linear sweep voltammogarms of 300 μM lorazepam at scan rates; a) 10; b) 20; c) 40; c) 70 and e) 100 mV / s (n=4)*

As can be seen, a linear relation between oxidation signals of 300 μM lorazepam and $v^{1/2}$ with equation $I = 2.5907 v^{1/2} + 3.4097$ ($R^2 = 0.9916$) that confirms diffusion process [52-55] to lorazepam oxidation at surface of HMImCl/ZnO-NPs/PE. On the other hand, positive shift in oxidation potential of lorazepam with increase in scan rate confirms kinetic limitation in redox reaction of this drug.

The Tafel plot relative to oxidation of 300 μM lorazepam at scan rate 10 mV/s are shown in Figure 4. Using Tafel equation and Tafel slope, the value of α was calculated 0.33, that confirms irreversible behavior to redox reaction of lorazepam.

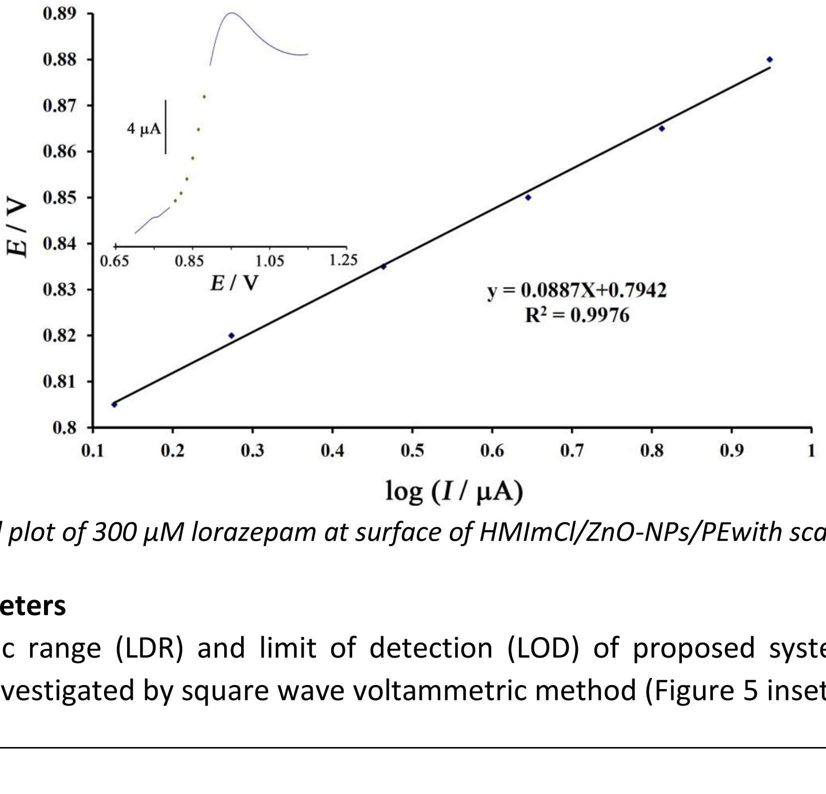

Figure 4. *Tafel plot of 300 μM lorazepam at surface of HMImCl/ZnO-NPs/PEwith scan rate 10 mV/s*

Analytical parameters

Linear dynamic range (LDR) and limit of detection (LOD) of proposed system for sensing of lorazepam was investigated by square wave voltammetric method (Figure 5 inset).

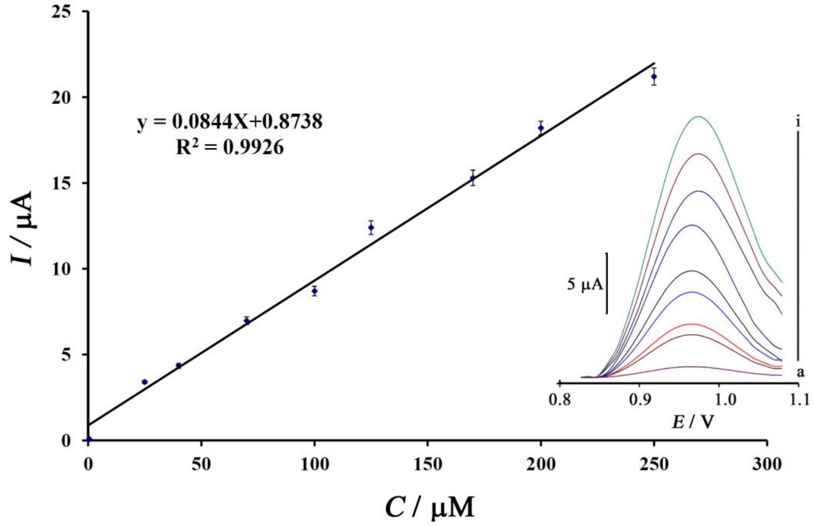

Figure 5. *Current – concentration curve for monitoring of lorazepam using HMImCl/ZnO-NPs/PE. Inset) square wave voltammograms of lorazepam at surface of HMImCl/ZnO-NPs/PE at concentrations of 1) 0.5; 2) 25; 3) 40; 4) 70; 5) 100; 6) 125; 7) 170; 8) 200 and 9) 250 µM (n=4)*

A linear relation in the concentration range 0.5 to 250 µM with equation $I = 0.0844C + 0.8738$ ($R^2 = 0.9926$) was detected for sensing of lorazepam using HMImCl/ZnO-NPs/PE as electro-analytical sensor. The detection limit 0.1 µM was reported for sensing of lorazepam using HMImCl/ZnO-NPs/PE in this study.

Stability, selectivity and real sample analysis

The stability of HMImCl/ZnO-NPs/PE for monitoring of 200 µM lorazepam was investigated in period time 70 days. Results shown in Figure 6 confirm that HMImCl/ZnO-NPs/PE has good stability for sensing of lorazepam in 2 months.

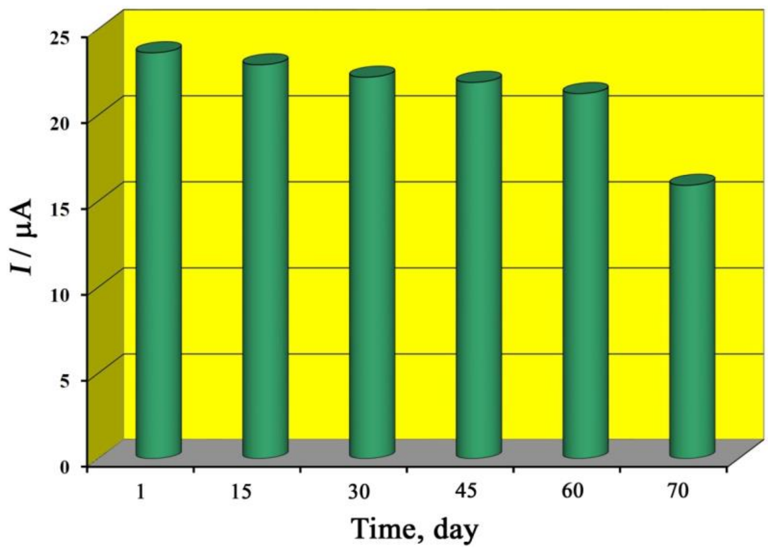

Figure 6. *Current – days diagram for oxidation of 200 µM lorazepam at surface of HMImCl/ZnO-NPs/PE*

On the other hand, selectivity of HMImCl/ZnO-NPs/PE in sensing of 15 µM lorazepam was investigated and results with acceptable error 5 % are reported in Table 1. As can be seen in Table 1, there is not any important interference observed for monitoring of 15 µM lorazepam using HMImCl/ZnO-NPs/PE and this sensor showed good selectivity in monitoring of lorazepam.

In the final step, ability of HMImCl/ZnO-NPs/PE in monitoring of lorazepam in water, dextrose saline and injection samples was checked, and results are reported in Table 2. As can be seen, the

HMImCl/ZnO-NPs/PE detected lorazepam with recovery range 98.5 to 103.5 % that are acceptable values for a new sensor.

Table 1. *Interference study results for monitoring 15 µM lorazepam using HMImCl/ZnO-NPs/PE as sensor*

Species	Tolerant limits ($W_{substance}$/$W_{lorazepam}$)
Cl^-, Br^-, Ca^{2+}, K+, Na^+	1000
Glucose	700
Starch	Saturation

Table 2. *Application of HMImCl/ZnO-NPs/PE for sensing of lorazepam in real samples*

Sample	*C* / µM			Recovery, %
	Added	Expected	Founded	
Water	---	---	<LOD	---
	10.00	10.00	10.35±0.54	103.5
Injection	---	2.00	2.03±0.05	---
	10.00	12.00	11.82±0.45	98.5
Dextrose saline	---	---	<LOD	---
	10.00	10.00	10.31±0.51	103.1

Conclusions

In this study, a new and simple analytical plan was described for monitoring of lorazepam in aqueous solution. The suggested sensor (HMImCl/ZnO-NPs/PE in this case) showed good selectivity for monitoring of lorazepam. The pH 7.0 was selected as optimum condition in voltammetric analysis. In addition, HMImCl/ZnO-NPs/PE was successfully used to monitor of lorazepam in the concentration range 0.5 to 250 µM with detection limit 0.1 µM. The modification of PE by HMImCl and ZnO-NPs improved oxidation signal of lorazepam about 2.17 times compared to unmodified PE. On the other hand, no specific interference for monitoring of lorazepam has been reported at surface of HMImCl/ZnO-NPs/PE. The HMImCl/ZnO-NPs/PE showed two-month stability for monitoring of lorazepam in aqueous solution.

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