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To cite this article: Saeid Ahmadzadeh, Fatemeh Karimi, Necip Atar, Elen Romao Sartori, Ehsan Faghieh-Mirzaei & Elahe Afsharmanesh (2017) Synthesis of CdO nanoparticles using direct chemical precipitation method: Fabrication of novel voltammetric sensor for square wave voltammetry determination of chlorpromazine in pharmaceutical samples, Inorganic and Nano-Metal Chemistry, 47:3, 347-353, DOI: [10.1080/15533174.2016.1186049](https://doi.org/10.1080/15533174.2016.1186049)

To link to this article: <https://doi.org/10.1080/15533174.2016.1186049>



Published online: 27 Jul 2016.



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Synthesis of CdO nanoparticles using direct chemical precipitation method: Fabrication of novel voltammetric sensor for square wave voltammetry determination of chlorpromazine in pharmaceutical samples

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ABSTRACT

A chemically modified electrode was constructed and applied to the electrooxidation of the chlorpromazine (CPZ). The oxidation peak potential of the CPZ at a surface of CdO/nanoparticles (NPs) ionic liquid carbon paste electrode (CdO/NPs/IL/CPE) appeared at 695 mV. The CdO/NPs were characterized with different methods such as transmission electron microscope and X-ray diffraction. Under optimized (pH 7.0), linear calibration curves were obtained in the range of 0.1–350 μM for CPZ, which shows adequate for the quantification in real samples. The proposed method was successfully applied to the determination of CPZ in both pharmaceutical and urine samples.

ARTICLE HISTORY

Received 27 March 2015
Accepted 1 May 2016

KEYWORDS

CdO nanoparticles; chemical precipitation method; chlorpromazine; ionic liquids; modified electrode

Introduction

Chlorpromazine (CPZ) is a phenothiazine drug with an aliphatic side chain, used in the management of psychotic conditions.^[1] It controls excitement, agitation, and other psychomotor disturbances in schizophrenic patients and reduces the manic phase of manic depressive conditions.^[1] CPZ works on a variety of receptors in the central nervous system, producing potent anticholinergic, antidopaminergic, antihistaminic, and antiadrenergic effects. Both the clinical indications and side effect profile of CPZ are determined by the broadness of its action: its anticholinergic properties cause constipation, sedation, and hypotension but also help relieve nausea.^[2] Several methods have been proposed for the determination of CPZ that include HPLC with UV detector,^[3] flow injection,^[4,5] potentiometry,^[6,7] spectrophotometric,^[8] gas chromatographic,^[9] spectrofluorimetric,^[10] capillary zone electrophoresis,^[11] electrochemical^[12,13] methods. Electrochemical based methods have more attention compare to other analytical methods for pharmaceutical, environmental and biological compounds analysis due to high sensitivity, low limit of detection, and simplicity.^[14–22]

Room temperature ionic liquids (RTILs) show many unique properties and great application potential in many fields, thus they have attracted many researchers' interest.^[23–28] Their application in electrochemical sensors is attracted mainly due to their promising properties such as tunable viscosity, high ionic conductivity, and wide electrochemical windows.^[29–35]

The application of nanotechnology in electrochemistry requires further studies for the development of new materials in the nanosize range.^[35–38] One of the better-known materials that has been widely used for modification of electrodes are metal-based nanoparticles and nanocomposite.^[39–42] The various applications of metal based nanoparticles are due to the specific chemical, surface, and microstructural properties of this material.^[43–45]

In this study, we describe the synthesis and application of CdO/NPs as a novel nanosensor and 1-butyl-3-methylimidazolium hexafluoro phosphate as a suitable binder in a carbon paste matrix for the voltammetric determination of CPZ. We also evaluate the analytical performance of the modified electrode for the voltammetric determination of CPZ in real samples such as drug, urine, and serum.

Experimental

Chemicals

All chemicals were of A.R. grade and were used as received without any further purification. Chlorpromazine was procured from Sigma. Mineral oil and Graphite powder (<50 μm) were obtained from Fluka. 1-Butyl-3-methylimidazolium hexafluorophosphate, NaH_2PO_4 , Na_2HPO_4 , and Na_3PO_4 were purchased from Sigma-Aldrich. All solutions were prepared using double distilled water having a specific conductivity of 0.4–0.9 μS .

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.

A 1.0 × 10⁻² mol L⁻¹ CPZ solution was prepared daily by dissolving 0.318 g CPZ in water in a 25 mL volumetric flask. The solution was kept in a refrigerator at 4°C in dark. More dilute solutions were prepared by serial dilution with water.

Apparatus

Cyclic voltammetry (CV), chronoamperometry, and square wave voltammetry (SWV) were performed using Autolab, potentiostat/galvanostat connected to a three-electrode cell, Metrohm Model 663 VA stand, linked with a computer (Pentium IV, 1200 MHz) and with Autolab software. The system was run on a PC using GPES and FRA 4.9 software. For impedance measurements, a frequency range of 100 kHz to 0.1 Hz was employed. 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.

X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu-Kα radiation (k = 1.54 Å). A pH-meter (Corning, Model 140) with a double junction glass electrode was used to check the pH of the solutions. Samples for transmission electron microscopy (TEM) analysis were prepared by evaporating a hexane solution of dispersed particles on amorphous carbon coated copper grids.

Preparation of the electrode

CdO/NPs/CPE was prepared by hand-mixing of 0.90 g of graphite powder and 0.10 g CdO/NPs plus paraffin and mixed well for 45 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. CdO/NPs/IL/CPE was prepared by mixing of 0.15 g of ionic liquids, 0.85 g of the liquid paraffin, 0.1 g of CdO/NPs, and 0.90 g of graphite powder. Then the mixture was mixed well for 70 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 CdO/NPs/IL/CPE.

Recommended procedure

CdO/NPs/IL/CPE was polished with a white and clean paper. To prepare a blank solution, 10.0 mL of the buffer solution (PBS, pH 7.0) was transferred into an electrochemical cell. The initial and final potentials were adjusted to 0.2 and 1.1 V versus Ag/AgCl, respectively. Then, different amounts of CPZ solution were added to the cell, using a micropipette, and the CV was recorded again to get the analytical signal (I_{ps}).

Preparation of real samples

For the tablets (labeled with amount of 25 mg), an accurately weighed portion of finely powdered sample obtained from five

tablets, The required amount of powder dissolved in 100 mL water with ultrasonication. Then, 1 mL of the solution plus 9 mL of the buffer (pH 7.0) was used for the analysis with standard addition method.

Urine samples were stored in the refrigerator immediately after collection. Ten milliliters of the sample was centrifuged for 40 min at 2000 rpm. The supernatant was filtered out using a 0.45 μm filter and then diluted four times with universal buffer solution (pH 7.0). 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 CPZ in real samples.

Injection (labeled with amount of 50 mg/2 mL), and pharmaceutical serum samples were used for determination of CPZ without any pretreatment procedure.

Pharmaceutical serum was used for real sample analysis without any pretreatment.

Results and discussion

Nanostructures characterization

CdO nanopowders were analyzed by XRD analyses. The XRD pattern of CdO/NPs nanopowders, in the 2θ range of 10–80°, is shown in Figure 1A. An average diameter of as-synthesized CdO nanoparticle was calculated from the broadness peak of (2θ~38) by using the Scherrer equation ($D = \frac{K\lambda}{\beta \cos\theta}$), and it is about 38.0 nm.

Also, Figure 1B shows EDAX analysis for CdO/NPs in the present work. As can be seen, presence of Cd and O elements confirm the synthesis of CdO/NPs carefully. The morphology of the as-grown nanostructures was characterized by TEM. Typical TEM micrograph of the CdO/NPs is shown in Figure 1C. Results confirm synthesis of CdO nanoparticles.

Voltammetric investigation

The microscopic areas were calculated from the slope of the I_p-ν^{1/2} relation (taking concentration of K₄Fe(CN)₆ as 1.0 mmol L⁻¹, concentration of KCl electrolyte as 0.10 mol L⁻¹, n = 1, D_R = 7.6 × 10⁻⁶ cm s⁻¹). The peak currents (i_p) change linearly with the square root of scan rate (ν^{1/2}) for above solution at a surface of different electrode, meaning that the electrochemical process is controlled by diffusion. The active areas of the modified and bare electrodes are estimated according to the Randles-Sevcik equation:

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} \nu^{1/2} C \quad (1)$$

It is 0.21 cm² (average of four measurements) for the (CdO/NPs/IL/CPE), 0.18 cm² for ILs/CPE, 0.16 cm² for CdO/NPs/CPE and 0.09 cm² for the CPE.

Scheme 1 shows propose mechanism for electrooxidation of CPZ at a surface of modified electrode.^[46] According to the scheme 1 mechanism, first oxidation signal is independent of pH value and second oxidation peak in dependent of pH. So, we selected first oxidation peak potential with relative potential windows for more investigation.

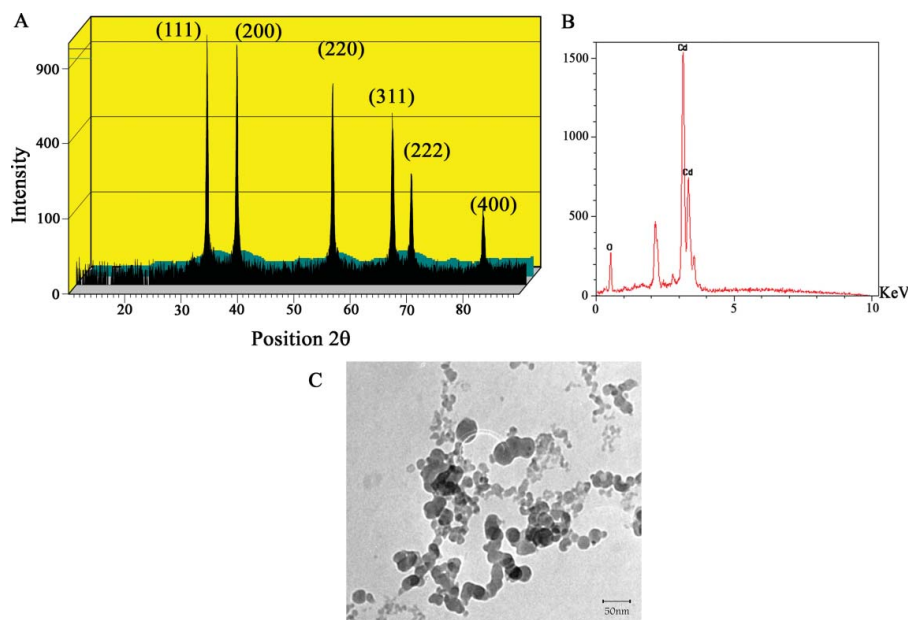
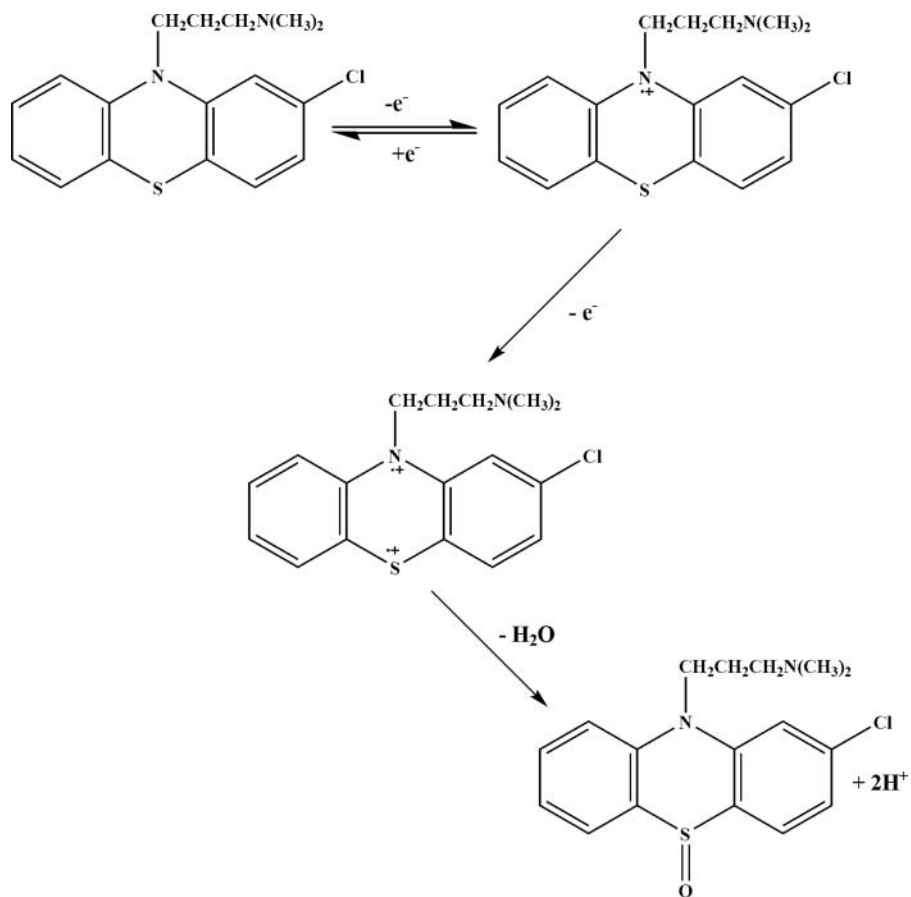


Figure 1. (A) XRD patterns of as-synthesized CdO nanoparticles. (B) EDAX analysis for CdO nanoparticle. (C) TEM image of CdO nanoparticles.

Figure 2 inset shows the current density derived from the cyclic voltammograms of 500 μM CPZ (pH 7.0) at the surface of different electrodes with a scan rate of 50 mV s^{-1} . The results show that the presence of CdO/NPs and ILs together causes the increase of the electrode. The direct electrochemistry of CPZ on the modified electrode was

investigated by cyclic voltammetry. Figure 2 shows cyclic voltammograms of 500 μM CPZ at pH 7.0 at the surface of different electrodes with a scan rate of 50 mV s^{-1} . CdO/NPs/IL/CPE exhibited significant oxidation peak current around 695 mV with the peak current of 33.2 μA (Figure 2, curve a). In contrast, low redox activity peak was observed



Scheme 1. Electro-oxidation reaction of chlorpromazine.

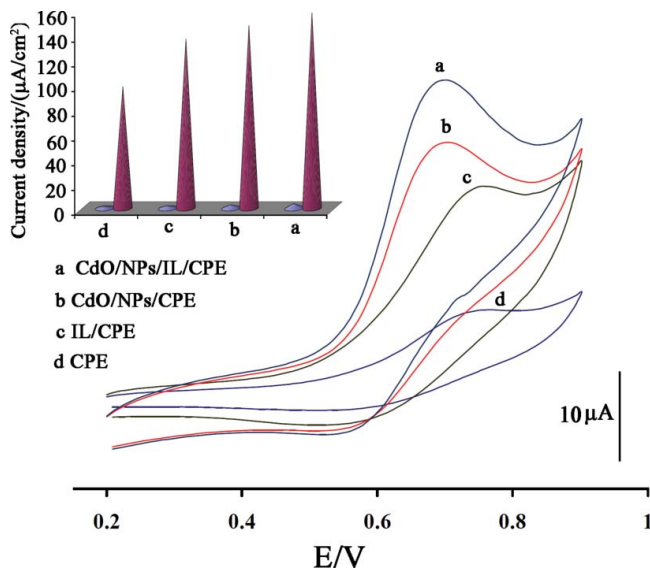


Figure 2. Cyclic voltammograms of (a) CdO/NPs/IL/CPE, (b) IL/CPE, (c) CdO/NPs/CPE, and (d) CPE in the presence of 500 μM CPZ at pH 7.0, respectively. Inset: the current density derived from cyclic voltammogram responses of 500 μM CPZ at pH 7.0 at the surface of different electrodes.

at CdO/NPs/CPE (Figure 2, curve c) and at unmodified CPE (Figure 2, curve d) over the same condition. The CPZ oxidation peak potential at CdO/NPs/CPE and at CPE observed around 740 and 765 mV versus the reference electrode with the oxidation peak current of 21.9 and 8.85 μA , respectively. In addition, at the surface of bare ILs/CPE, the oxidation peak appeared at 700 mV with the peak current was 26.6 μA (Figure 2, curve b), which indicated 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 CPZ and dramatic increase of current of CPZ indicated the catalytic ability of CdO/NPs/IL/CPE to CPZ oxidation. The results indicated that the presence of CdO/NPs on CdO/NPs/IL/CPE surface had great improvement with the electrochemical response, which was partly due to excellent characteristics of CdO/NPs such as good electrical conductivity, high chemical stability, and high surface area. The suitable electronic properties of CdO/NPs 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.

The effect of scan rate (ν) on the oxidation current of CPZ was also examined (Figure 3 inset). The results showed that the peaks current increased linearly with increasing the square root of scan rate that ranged from 10 to 250 mV s^{-1} according to the following regression equation (Figure 3):

$$I_p = 8.7974 \nu^{1/2} - 9.6389 \quad (2)$$

$\times (r^2 = 0.9975, I \text{ in } \mu\text{A}, \nu \text{ in } \text{mV s}^{-1})$

The result shows that the electrode process is controlled under the diffusion step. On the other hand, the peak potential

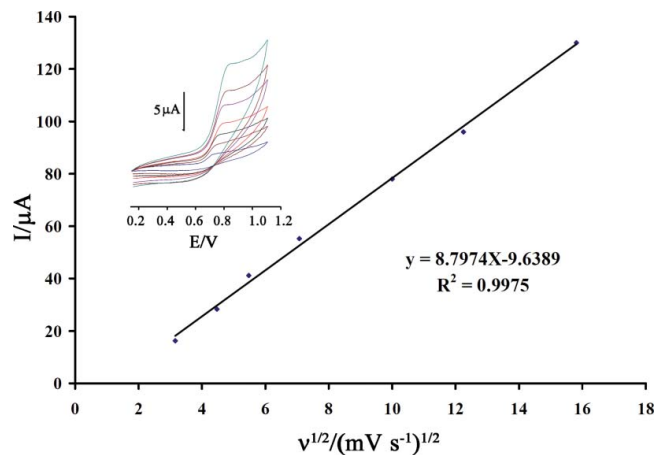


Figure 3. Plot of I_{pa} versus $\nu^{1/2}$ for the oxidation of CPZ at CdO/NPs/IL/CPE. Inset shows cyclic voltammograms of CPZ at CdO/NPs/IL/CPE at different scan rates (from inner to outer) of 10, 20, 30, 50, 100, 150.0, and 250 mV s^{-1} in 0.1 M phosphate buffer, pH 7.0.

shifts in negative direction when the scan rate increases, meaning that the electrochemical reaction is irreversible.

To obtain further information on the rate determining step, a Tafel plot was developed for the CPZ at a surface of CdO/NPs/IL/CPE using the data derived from the raising part of the current–voltage curve (Figure 4). The slope of the Tafel plot is equal to $n(1-\alpha)F/2.3RT$, which comes up to 0.1916 V decade $^{-1}$. We obtained α as 0.69.

Chronoamperometric measurements of CPZ at CdO/NPs/IL/CPE were carried out by setting the working electrode potential at 800 mV vs. Ag/AgCl/KCl $_{sat}$ for the various concentration of CPZ in buffered aqueous solutions (pH 7.0; Figure 5A). For an electroactive material (CPZ in this case) with a diffusion coefficient of D , the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation. Experimental plots of I versus $t^{-1/2}$ were employed, with the best fits for different concentrations of CPZ (Figure 5B). The slopes of the resulting straight lines were then plotted vs. CPZ concentration. From the resulting slope and Cottrell equation the mean value of the D was found to be $1.3 \times 10^{-5} \text{ cm}^2/\text{s}$.

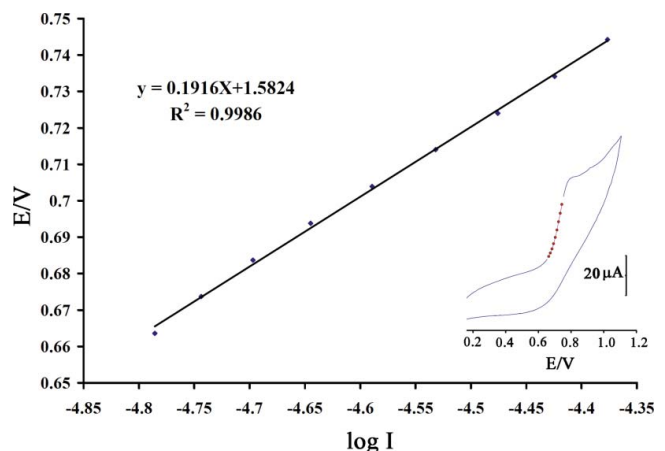


Figure 4. Tafel plot for CdO/NPs/IL/CPE in 0.1 M PBS (pH 7.0) with a scan rate of 50 mV s^{-1} in the presence of 600 μM CPZ.

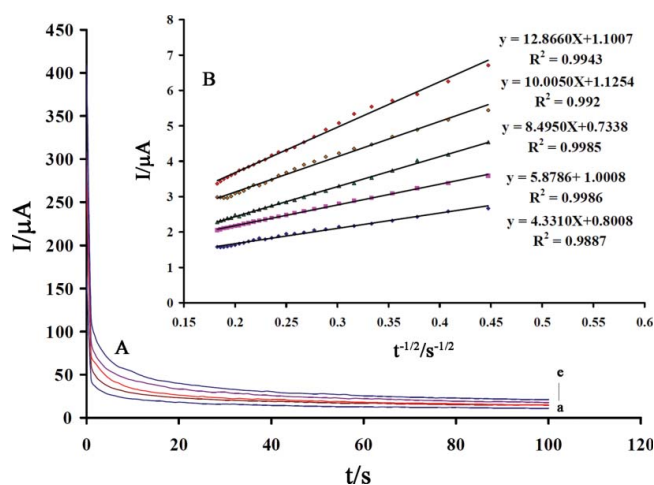


Figure 5. (A) Chronoamperograms obtained at CdO/NPs/IL/CPE in the presence of (a) 100, (b) 150, (c) 200, (d) 250, and (e) 300 μM CPZ in the buffer solution (pH 7.0). (B) Cottrell's plot for the data from the chronoamperograms.

In continuous of electrochemical investigation we selected electrochemical impedance spectroscopy as powerful electrochemical techniques frequently in surface modification studies.^[47–50] Impedance measurements were performed in the frequency range from 0.1 to 100,000 Hz. Figure 6 shows Nyquist diagrams of the imaginary impedance (Z_{im}) versus the real impedance (Z_{re}) of the EIS obtained at CPE (curve a), CdO/NPs/CPE (curve b), IL/CPE (curve c), and CdO/NPs/IL/CPE (curve d) in the presence of 500 $\mu\text{mol L}^{-1}$ CPZ at pH 7.0, respectively. It can be seen that the all of the electrodes exhibits an almost straight line that is characteristic of a diffusion-limiting step of the electrochemical process. Nyquist diagrams follow the theoretical shapes and include a squeezed semicircle portion, observed at higher frequencies, which corresponds to the electron transfer limited process. The respective semicircle diameters at the high frequency, corresponding to the electron transfer resistance at the electrode surface. The curve corresponding to CPE is a big semicircle plus a straight line (Figure 6a). For CdO/NPs/CPE, IL/CPE, and CdO/NPs/IL/CPE, R_{ct} decreases dramatically (Figures 6b–d), indicating that CdO/NPs and IL can act as an effective electron conduction pathway between the electrode and electrolyte.

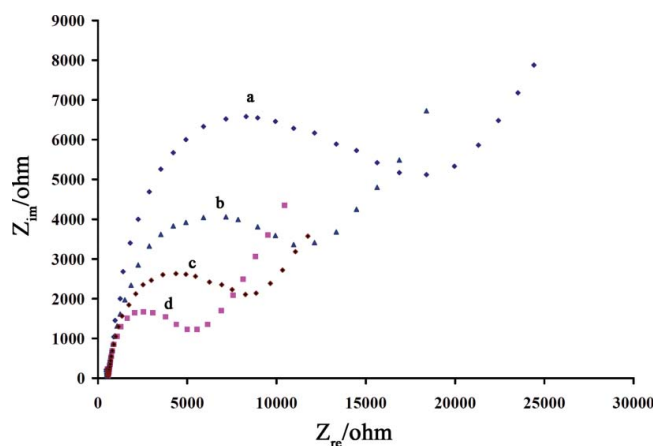


Figure 6. Nyquist plots of CPE (a), CdO/NPs/CPE (b), IL/CPE (c), and CdO/NPs/IL/CPE (d) in the presence of 500 μM CPZ. Conditions: pH, 7.0; E_{dc} , +0.6 V versus Ag/AgCl; E_{ac} , 5 mV; frequency range, 0.1–100,000 Hz.

Table 1. Comparison of the efficiency of some electrochemical methods in the determination of CPZ.

Electrode	pH	LOD (μM)	LDR (μM)	Ref.
Graphene paste electrode	4.0	0.006	0.01–9.0	[12]
Modified Gold electrode	9.0	0.1	0.6–10.0	[13]
Glass carbon electrode	9.0	0.13	0.14–3.36	[51]
Carbon paste electrode	7.0	0.07	0.1–350	This work

Therefore, CdO/NPs/IL/CPE composite electrode has good electronic conductivity for electro-oxidation of CPZ.

Figures of merit

Square wave voltammetry (SWV) was used to determine CPZ concentrations. The SW voltammograms clearly show that the plot of peak current versus CPZ concentration is linear for 0.1–350 μM of CPZ, the regression equation being $I_p(\mu\text{A}) = (0.0885 \pm 0.0032)C_{\text{CPZ}} + (2.0897 \pm 0.1431)$ ($r^2 = 0.9955$, $n = 10$), where C is μM concentration of CPZ and I_p is the peak current. The detection limit was 0.07 μM CPZ according to the definition of $Y_{\text{LOD}} = Y_B + 3\sigma$. The detection limit, linear dynamic range, and sensitivity to CPZ with the proposed sensor are comparable to, and even better than, those recently developed using voltammetric methods. Table 1 presents comparisons of the results obtained from the proposed method and those from electrochemical methods recently reported.

Stability and reproducibility

The repeatability and stability of CdO/NPs/IL/CPE was investigated by cyclic voltammetric measurements of 30.0 μM CPZ. The relative standard deviation (RSD%) for nine successive assays was 1.4%. When using five different electrodes, the RSD% for seven measurements was 2.4%. When the electrode stored in the laboratory, the modified electrode retains 96% of its initial response after a week and 92% after 45 days. These results indicate that CdO/NPs/IL/CPE has good stability and reproducibility, and could be used for CPZ.

Interference study

The influence of various substances as potentially interfering compounds with the determination of CPZ was studied under the optimum conditions 10.0 μM CPZ at pH 7.0. The potentially interfering substances were chosen from the group of

Table 2. Interference study for the determination of 10.0 μM CPZ under the optimized conditions.

Species	Tolerance limits (W/W)
Glucose, Fructose, Lactose, Sucrose,	950
Hystidine, Alanine, Phenyl alanine, Glycine, L-Theronine,	800
L-isoleucin, Na^+ , Al^{3+} , F^- , SO_4^{2-} , K^+ , Cl^- , SCN^- , Br^- , Mg^{2+} , Ca^{2+} , CO_3^{2-} and Li^+	
Methionine, Tryptophan, Ascorbic acid*	400
Starch	Saturation
Urea, Thiourea	300

*After addition of 1 mmol L^{-1} ascorbate oxidase.

Table 3. Determination of CPZ in real samples.

Sample	Added (μM)	Expected (μM)	Founded (μM)	HPLC method (μM)	F_{ex}	F_{tab}	t_{ex}	$t_{\text{tab}(95\%)}$
Urine	—	—	<Limit of detection	<Limit of detection	—	—	—	—
	10.0	10.0	10.25 ± 0.36	10.31 ± 0.41	9.5	19	2.4	3.8
Tablet	—	15.0	14.85 ± 0.45	15.08 ± 0.52	8.5	19	2.1	3.8
Injection	5.0	5.0	5.22 ± 0.28	4.85 ± 0.36	10.1	19	2.8	3.8
Pharmaceutical	—	—	<Limit of detection	<Limit of detection	—	—	—	—
Serum	20.0	20.0	20.44 ± 0.55	20.68 ± 0.4	11.5	19	3.2	3.8

F_{ex} is calculated F-value; F_{tab} is the F value obtained from one-tailed table of F-test; t_{ex} is calculated value of t-student test; t_{tab} is the t-value obtained from the table of student t-test.

substances commonly found with CPZ in pharmaceutical and biological samples. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than $\pm 5\%$ for the determination of CPZ. The results are shown in Table 2. Those results confirm the suitable selectivity of the proposed method for determination of these compounds.

Analytical applications in pharmaceutical and clinical preparations

To evaluate the applicability of the proposed sensor for the pharmaceutical and biological applications, the modified electrode was employed for the analysis of CPZ injections as well as tablet and urine. Standard addition method was used for measuring CPZ concentration in the real samples. The proposed method was compared with a HPLC method too. The results are given in Table 3, confirm that the modified electrode retained its efficiency for the determination of CPZ in real samples.

Conclusion

The CdO/NPs/IL/CPE was developed as a high-sensitive sensor for the quick determination of CPZ in pharmaceutical samples. The CdO/NPs/IL/CPE showed good improvement to the electrode process of CPZ compare to the unmodified CPE. Compared to unmodified CPE, a decrease of overpotential of oxidation of CPZ with 3.75-fold increment in the oxidation peak current observed when using CdO/NPs/IL/CPE as a high sensitive and novel sensor. Under the optimum conditions in voltammetric determination, the oxidation peak current was proportional to the CPZ concentration in the range of 0.1–350 μM with the detection limit of 0.07 μM . Finally, the propose sensor was successfully used for the determination of CPZ in real samples.

Acknowledgments

The authors would like to thank Kerman University of Medical Sciences, Kerman, Iran, for support.

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