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Highly sensitive determination of promazine in pharmaceutical and biological samples using a ZnO nanoparticle-modified ionic liquid carbon paste electrode

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ABSTRACT

In this work we describe the first report for the determination of promazine using a nanostructure-modified ionic liquid carbon paste electrode in aqueous solutions. To achieve this goal, a novel modified carbon paste electrode using ZnO nanoparticles and 1-methyl-3-butylimidazolium bromide as a binder (ZnO/NPs/ILs/CPE) was fabricated. The oxidation peak potential of promazine at the surface of the ZnO/NPs/ILs/CPE appeared at 685 mV, which was about 65 mV lower than the oxidation potential at the surface of CPE under similar conditions. Also, the peak current was increased to about 4.0 times higher at the surface of ZnO/NPs/ILs/CPE compared to that of CPE. The linear response range and detection limit were found to be 0.08–450 and 0.04 μmol/L, respectively. The modified electrode was successfully used for the determination of promazine in real samples with satisfactory results.

1. Introduction

Electrochemical sensors satisfy many of the requirements in analysis, such as high selectivity, easy preparation, good selectivity and sensitivity, and fast response [1–6]. Furthermore, the limited amount of electrode materials makes only a restricted number of electroactive materials suitable for electrochemical detection with high sensitivity and selectivity [7–10]. So, efforts have been made to modify the electrode surfaces for the purpose of lowering the overpotential, improving the sensitivity with high current density for effective enrichment of the desired substance and/or restraining the effect of interferences [11–14].

Promazine is a medicine that belongs to the phenothiazine class of antipsychotics. An old drug used to treat schizophrenia, promazine is still being prescribed alongside newer agents such as olanzapine and quetiapine. It has predominantly anticholinergic side effects, though extra pyramidal side effects are not uncommon either [15]. The monitoring of promazine is significant for quality assurance in the pharmaceutical industry and for obtaining optimum therapeutic concentrations in body fluids to minimize toxicity [16]. Therefore, the detection of this drug is important in biological samples such as urine and drug tablets. In comparison to other methods for determination of promazine, the proposed electrochemical sensor has attracted more interest due to its sensitivity, low cost, accuracy, high dynamic range and simplicity.

To the best of our knowledge, there are no reports for the application of ZnO/NPs-modified carbon ionic liquid paste electrode for the determination of promazine. The electrochemical behaviors of promazine at ZnO/NPs/ILs/CPE, carbon paste electrode modified with ionic liquid (IL/CPE), ZnO/NPs carbon paste electrode (ZnO/NPs/CPE), and carbon paste electrode (CPE) were investigated. The results showed the superiority of ZnO/NPs/ILs/CPE to the other electrodes in terms of both reversibility and sensitivity. We also evaluate the analytical performance of ZnO/NPs/ILs/CPE for the voltammetric determination of promazine in real samples such as drug tablets, urine and serum.

2. Experimental

2.1. Chemicals and apparatus

In this study we used a Potentiostat/Galvanostat (μ-Autolab with PGSTAT 302 N (Eco Chemie, the Netherlands) coupled with a Pentium IV personal computer connected to an HP laser jet 6L printer, and experiments were performed in a three-compartment

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cell. 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 a ZnO/NPs/ILs/CPE. All chemicals were of A.R. grade and were used as received without any further purification. Promazine was purchased from Sigma. Mineral oil was obtained from Fluka. Graphite powder (<50 μm) was purchased from Fluka. All solutions were prepared using double distilled water having a specific conductivity of 0.4–0.9 μS. ZnO nanoparticles were synthesized according to our previous report [17].

2.2. Preparation of the electrode

ZnO/NPs/ILs/CPE was prepared by mixing 0.2 g of ionic liquids, 0.8 g of the liquid paraffin, 0.1 g of ZnO/NPs, and 0.90 g of graphite powder. Then the mixture was well mixed for 60 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/NPs/ILs/CPE. ZnO/NPs/CPE was prepared by hand–mixing of 0.90 g of graphite powder and 0.10 g ZnO/NPs plus paraffin and mixed well for 60 min until a uniformly wetted paste was obtained.

3. Results and discussion

ZnO/NPs were analyzed by XRD analyses. The XRD pattern of ZnO/NPs, in the 2θ range of 10–90°, is shown in Fig. 1A. The average grain size of the samples was estimated with the help of the Scherrer equation using the diffraction intensity of (1 0 1; $2\theta = 42.327^{o}$) peak. The mean grain size (D = 38 nm) of the particles was determined from the XRD line broadening measurement using the Scherrer equation. The morphology of the as-grown nanostructures was characterized by SEM. Typical SEM micrograph of the ZnO/NPs is shown in Fig. 1B. The presence of dark points in this figure in nanoscale size confirms that this nanoparticle was synthesized.

The electrochemical oxidation of the promazine occurs at the nitrogen atom in a potential range of (0.0–0.8 V). This signal is independent of pH value [18]. So, we select pH 7.0 to mimic biological conditions for the analysis. The microscopic areas were calculated from the slope of the $I_p - \nu^{1/2}$ relation (taking concentration of $K_4Fe(CN)_6$ as 1.0 mmol/L, concentration of KCl electrolyte as 0.10 mol/L, n = 1, $D_R = 7.6 \times 10^{-6}$ cm/s) for all of the electrodes. It is 0.25 cm^2 (average of five measurements) for the (ZnO/NPs/ILs/CPE), 0.19 cm^2 for ILs/CPE, 0.14 cm^2 for ZnO/NPs/CPE and 0.09 cm^2 for the CPE. Fig. 2A (inset) shows the current density derived from the cyclic voltammograms of 400 μmol/L promazine (pH 7.0) at the surface of different electrodes with a scan rate of 50 mV/s. The results show that the presence of both ZnO/NPs and ILs causes the good conductivity of the electrode. Fig. 2A shows cyclic voltammograms of 400 μmol/L promazine at pH 7.0 at the surface of different electrodes with a scan rate of 50 mV/s. ZnO/NPs/ILs/CPE exhibited a significant oxidation peak current around 685 mV with the peak current of 41.6 μA (Fig. 2A, curve d). In contrast, low redox activity peak was observed at ZnO/NPs/CPE (Fig. 2A, curve b) and at unmodified CPE (Fig. 2 curve a) under the same conditions. The promazine oxidation peak potential at ZnO/NPs/CPE and at CPE observed around 740 and 750 mV *vs.* the reference electrode with the oxidation peak current of 19.2 and 10.1 μA, respectively. In addition, at the surface of bare ILs/CPE, the

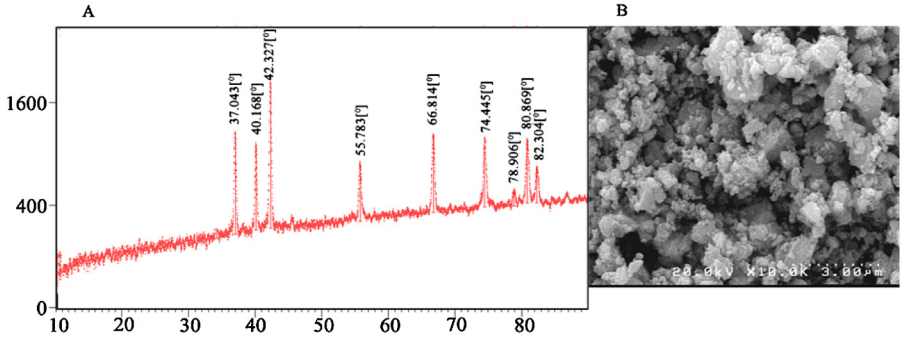

Fig. 1. (A) XRD patterns of as-synthesized ZnO/NPs. (B) SEM images of ZnO/NPs.

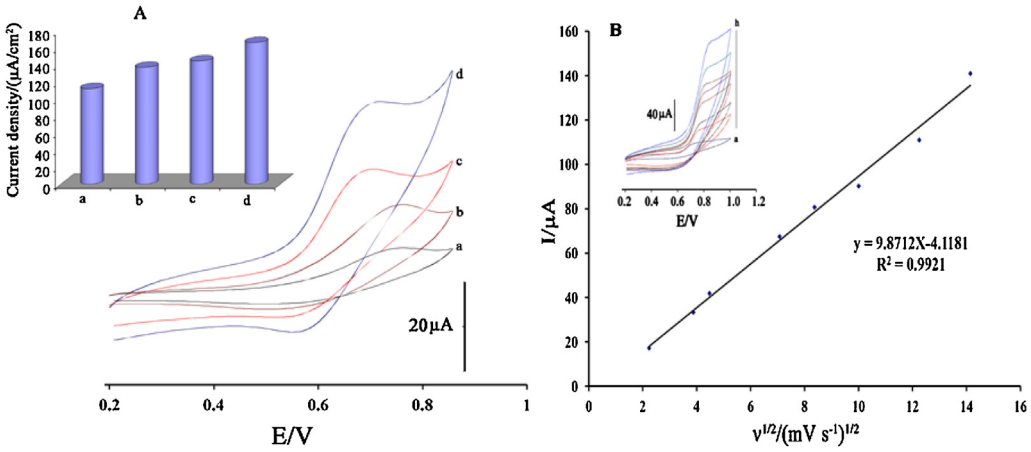

Fig. 2. (A) Cyclic voltammograms of (a) CPE, (b) ZnO/NPs/CPE, (c) ILs/CPE and (d) ZnO/NPs/ILs/CPE in the presence of 400 μmol/L promazine at pH 7.0, respectively. Inset: the current density derived from cyclic voltammogram responses of 400 μmol/L promazine at pH 7.0 at the surface of different electrodes. (B) Plot of Ipa versus $\nu^{1/2}$ for the oxidation of promazine at ZnO/NPs/ILs/CPE. Inset shows cyclic voltammograms of promazine at ZnO/NPs/ILs/CPE at different scan rates (a–h) of 5, 15, 20, 50, 70, 100.0, 150.0 and 200 mV/s in 0.1 mol/L phosphate buffer, pH 7.0.