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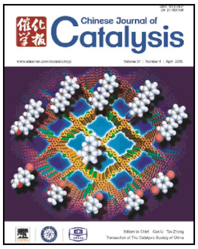

Article

Determination of isoproterenol in pharmaceutical and biological samples using a pyrogallol red multiwalled carbon nanotube paste electrode as a sensor

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ABSTRACT

Isoproterenol (ISPR) is an important catecholamine-based drug that is widely used in the treatment of heart disease. However, overdose of this drug is very dangerous to the human body. In this study, a new sensor based on a pyrogallol red modified-multiwalled carbon nanotube paste electrode (PGRMMWCNTPE) was prepared and used for high sensitivity determination of ISPR in aqueous solution. Electrocatalytic oxidation of ISPR at the PGRMMWCNTPE was investigated by chronoamperometry, cyclic voltammetry, and square-wave voltammetry. The values of the catalytic rate constant, electron transfer coefficient, and diffusion coefficient for ISPR oxidation were then calculated using voltammetric data. A linear calibration curve was constructed for ISPR concentration in the range 0.8–570 μmol/L with a detection limit of 0.47 μmol/L ISPR. The sensor was then applied to the determination of ISPR in urine and drug samples with satisfactory results.

1. Introduction

Isoproterenol (ISPR, isoprenaline) is a catecholamine-based drug that is widely used in asthmatic therapy, allergic emergencies, bronchial asthma, ventricular bradycardia, cardiac arrest, glaucoma, and as a styptic. ISPR under the brand name Isuprel in ampoule form is used to treat asthma, chronic bronchitis, and emphysema [1]. The cardiovascular effects of ISPR are similar to those of adrenaline and noradrenaline, which can relax almost any type of smooth muscle that contains adrenergic nerves. Adjusting the dose of medications by rapid determination of their concentration in biological fluids is very important. Hence, accurately determining their concentration is important. Analysis of catecholamine drugs in biological fluids, where they are found at relatively low concentrations, generally requires the use of selective and highly sensitive techniques with high detectability, such as high performance liquid chromatography with fluorometric [2] and/or with electrochemical [3,4] detection. Voltammetric systems for detecting drug and biological samples are cheap and sensitive techniques because they are widely used to analyze electroactive materials [5–10]. Electrochemical-based methods are fast, sensitive, selective, and simple methods for determining important electroactive materials in pharmaceutical and biological samples [11–20].

Modifying electrode substrates with nanomaterials such as graphene, metal oxide nanoparticles, metal-based nanoparticles, and carbon nanotubes (CNTs) for use in analytical sensing has been reported to result in low detection limits, a high linear dynamic range, high sensitivity, good selectivity, and the reduction of overpotentials [21–30]. CNTs are a class of nanomaterials that have a wide range of applications [31–35].

In this study, the suitability of a pyrogallol red modified-multiwalled carbon nanotube paste electrode (PGRMMWCNTPE) for the electrocatalytic determination of ISPR was investigated

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using cyclic voltammetry (CV) and square-wave voltammetry (SWV). The effect of different parameters, such as electrode composition, electrolyte, pH, potential scan rate, and interference on the potential was investigated by CV. The proposed sensor was then used to determine the concentration of ISPR in pharmaceutical and biological samples.

2. Experimental

For all of the electrochemical investigation, we used a potentiostat/galvanostat (Autolab PGSTAT 302N, the Netherlands) connected to a three-electrode cell (663 VA Stand, Metrohm, Herisau, Switzerland) linked to a computer (Pentium IV, 1200 MHz) with Autolab software. A platinum wire was used as the auxiliary electrode. The PGRMMWCNTPE and a Ag/AgCl/KCl$_{sat}$ electrode were used as the working and reference electrodes, respectively. The electrode prepared with CNTs was characterized by scanning electron microscopy (SEM, AIS 2100, Seron Technologies).

3. Results and discussion

3.1. SEM characterization

Figure 1 shows the typical morphologies of the carbon paste electrode (CPE) and the PGRMMWCNTPE characterized by SEM. As shown in Fig. 1(b), the mediator (pyrogallol red, PGR) is distributed on the surface of the modified electrode and the morphology of the modified electrode remains unchanged. This indicates that PGR and multiwall CNTs (MWCNTs) almost homogeneously distribute on the surface of the carbon paste matrix, which exhibits a unique three-dimensional structure.

3.2. Electrochemical investigation

The electrochemical behavior of the modified electrode was investigated by CV in phosphate buffer solution (PBS, pH 7.0). The experimental results show well-defined and reproducible anodic and cathodic peaks related to the PGR$_{(Red)}$/PGR$_{(Ox)}$ redox couple with quasi-reversible behavior and peak separation of $\Delta E_p = E_{pa} - E_{pc} = 180$ mV. These cyclic voltammograms were used to determine the relationship between the anodic peak current (I_{pa}) and the square root of the potential scan rate ($v^{1/2}$) (Fig. 2). From Fig. 2, I_{pa} is linearly dependent on $v^{1/2}$ with a correlation coefficient of $R^2 = 0.9996$. This indicates that the redox system shows Nernstian behavior.

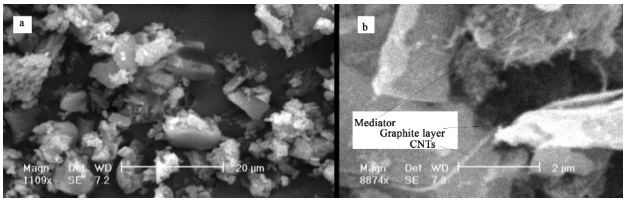

Fig. 1. SEM images of (a) the CPE and (b) the PGRMMWCNTPE.

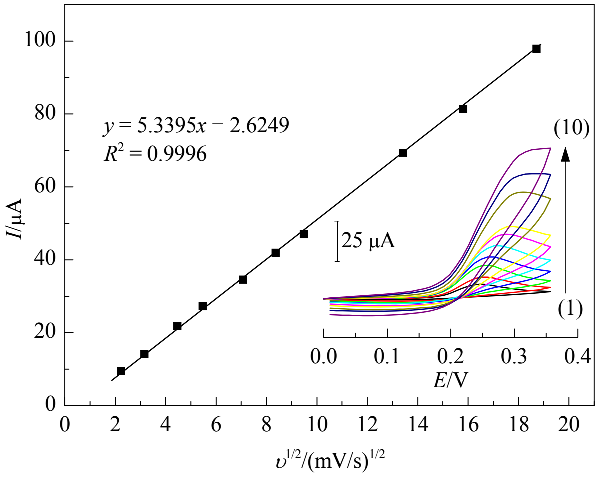

Fig. 2. Plot of I_{pa} versus $v^{1/2}$ for the oxidation of ISPR by the PGRMMWCNTPE. The inset shows cyclic voltammograms for various scan rates of 5 (1), 10 (2), 20 (3), 30 (4), 50 (5), 70 (6), 90 (7), 180 (8), 250 (9), and 350 mV/s (10) in 0.1 mol/L PBS (pH 7.0).

One important objective of the present study was to develop a modified sensor capable of electrocatalytic oxidation of ISPR. We obtained the cyclic voltammetric responses for the electrochemical oxidation of 500 μmol/L ISPR at the PGRMMWCNTPE (Fig. 3) and at the PRG-modified CPE (PGRCPE). In Fig. 3, curves (4) and (5) are the same as curves (3) and (2) but without the mediator.

These results show that the sensor produces a large anodic peak current in the presence of ISPR without a cathodic counterpart (Fig. 3, curves (3) and (2)). Curve (1) shows the cyclic voltammogram of the PGRMMWCNTPE in PBS (pH 7.0). The current observed is associated with ISPR oxidation and not oxidation of the modifier, which was determined by comparing the current in the presence and absence of ISPR. At the surface of the MWCNT paste electrode (MWCNTPE) and the CPE without mediator, ISPR was oxidized at around 357 mV. The electroactivity of ISPR on the PGRMMWCNTPE and the PGRCPE was significant (Fig. 3) with a strongly defined peak potential at around 277 mV (vs. Ag/AgCl/KCl$_{sat}$). Thus, a decrease in the overpotential and enhancement of the peak current for ISPR oxidation were achieved with the PGRMMWCNTPE and the

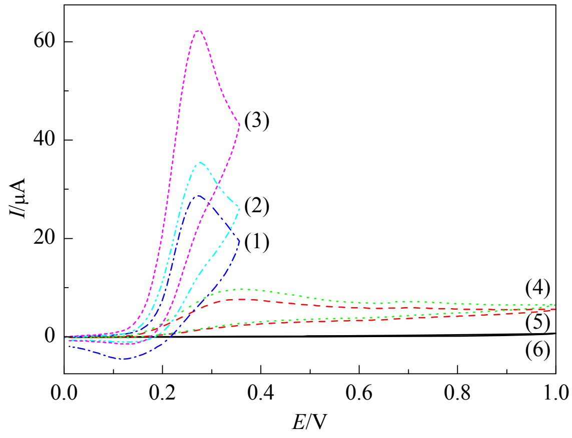

Fig. 3. Cyclic voltammograms of PBS at the PGRMMWCNTPE (1), 500 μmol/L ISPR at the PGRCPE (2), PGRMMWCNTPE (3), CNPE (4), and CPE (5), and PBS at the CNPE (6). Conditions: 0.1 mol/L PBS (pH 7.0) and scan rate 20 mV/s.