



Enhanced electrocatalytic oxidation of isoniazid at electrochemically modified rhodium electrode for biological and pharmaceutical analysis



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ABSTRACT

A simple and sensitive electrochemical method has been proposed for the determination of isoniazid (INZ). For the first time, rhodium (Rh) modified glassy carbon electrode (GCE) has been employed for the determination of INZ by linear sweep voltammetry technique (LSV). Compared with the unmodified electrode, the proposed Rh modified electrode provides strong electrocatalytic activity toward INZ with significant enhancement in the anodic peak current. Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM) results reveal the morphology of Rh particles. With the advantages of wide linearity (70–1300 μM), good sensitivity (0.139 $\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$) and low detection limit (13 μM), this proposed sensor holds great potential for the determination of INZ in real samples. The practicality of the proposed electrode for the detection of INZ in human urine and blood plasma samples has been successfully demonstrated using LSV technique. Through the determination of INZ in commercially available pharmaceutical tablets, the practical applicability of the proposed method has been validated. The recovery results are found to be in good agreement with the labeled amounts of INZ in tablets, thus showing its great potential for use in clinical and pharmaceutical analysis.

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1. Introduction

Isoniazid (INZ) is an antibiotic and pulmonary tuberculosis agent that has been widely used for suppressing the activity of *Mycobacterium tuberculosis* [1,2]. In order to prevent tuberculosis, INZ has been prescribed in single or with drugs such as pyrazinamide, rifampicin and ethambutol HCl at fixed dosages [3,4]. However, regular uptake of INZ tablets may cause hepatic problems. Thus, monitoring the dosage levels of INZ at regular intervals during the treatment is mandatory. Hydrazine formed through the metabolism of INZ induced hepatotoxicity, causing fatal conditions [5]. Therefore, it is highly essential to monitor the changes in the INZ level in human body fluids for providing effective therapeutic treatments [6]. Owing to the increased use of this drug in clinical analysis, it is important to develop a sensitive method for the determination of INZ in pharmaceutical samples [7].

In the recent years, numerous methods including titrimetry, spectrophotometry, chemiluminescence, high performance liquid

chromatography, fluorimetry, capillary electrophoresis and electrochemical methods have been used for the determination and quantification of INZ [8–15]. Among these techniques, electrochemical methods are very simple, cheaper, sensitive and selective. Nevertheless, determination of INZ at bare GCE leads to slow electrode kinetics [16], large over potential and low sensitivity. To overcome these limitations, several efforts have been made to develop different modified electrodes for the determination of INZ. However, most of these electrodes suffer from severe fouling effects. In order to overcome the fouling effect, electrode material and electrolyte should be selected carefully. For instance, Quintino et al. used the alkaline medium to minimize the fouling effect produced by INZ on GCE [17]. Yan et al. used nafion modified ordered mesoporous carbon/GC electrode to overcome the fouling effect produced by INZ [18]. In recent years, nanomaterials modified electrodes have been used as sensing platforms for the selective determination of INZ [19–24]. The modification of electrode surface with nanomaterials facilitated the electron-transfer due to their high conductivity, large surface area, good catalytic activity and biocompatibility.

In recent years, metal particle modified electrodes have received considerable attention in the electrochemical field. Among various

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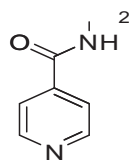


Fig. 1. Chemical structure of the INZ.

metal particles, Rh particles have been widely used in the electrochemical and biosensor fields for sensing biological molecules [25,26] due to its excellent electrocatalytic activity and interesting optical properties [27–29]. Rh particles have been prepared with the use of N,N-bis-succinamide-based dendrimer as a stabilizer [30]. Rh hydrosols have been prepared by dispersing bulk Rh in NaOH solutions [31]. Rh and its compounds have also been prepared through laser deposition on smooth graphite disk [32,33]. However, these approaches are expensive and time consuming. Among these methods, electrochemical deposition method is comparatively simple and less time consuming. Owing to its advantages, we have used electrochemical technique to deposit Rh particles on GCE.

Herein, the electrochemical determination of INZ at Rh particles modified GCE in pH 7 phosphate buffer solution was demonstrated. High conductivity and sensitivity of Rh particles was more helpful for the determination of INZ with good sensitivity. The practical applicability of this sensor was successfully demonstrated in the real and pharmaceutical samples. As shown in Table 1, the performance of our sensor is comparable with other modified electrodes reported in the literature. The chemical structure of the INZ is shown in Fig. 1.

2. Experimental

2.1. Chemicals

Isoniazid (4-pyridinecarboxylic acid hydrazide) was purchased from Sigma–Aldrich. Rh(III) chloride hydrate was purchased from Strem chemicals (USA). The supporting electrolyte used for all the experiments was pH 7 phosphate buffer solution (PBS), which was prepared by using 0.05 M of Na₂HPO₄ and NaH₂PO₄ solutions. All other chemicals were of analytical grade and used without further purification.

Table 1

Comparison of analytical parameters of isoniazid at Rh/GCE with other modified electrodes.

Method	Electrode	pH	Detection limit (μM)	Linear range (μM)	References
Amperometry	Nf/OMC ⁱ modified GC	7.0, PBS	0.084	0.1–370	[18]
LSV ^a	Poly-L-histidine/SPCE ^b	PBS ^c	0.5	1.5–210	[38]
LSV	ARS ^d -modified GC ^e	6.0, PBS	3.94	10–800	[39]
CV	OPPy ^f -modified GC	9.0, NH ₃	3.15	3.99–126	[40]
CV	PASA ^g -modified GC	PBS	0.01	0.05–10	[41]
SWV ^h	Poly-L-histidine/SPCE	7.0, PBS	0.25	0.15–11	[38]
DPV	DME ^j electrode	PBS	–	0.06–100	[14]
LSV	Rh-modified GC	7.0, PBS	13	70–1300	This work

^a LSV – linear sweep voltammetry.

^b SPCE – screen printed carbon paste electrode.

^c PBS – phosphate buffer solution.

^d ARS – Alizarin Red S.

^e GC – glassy carbon electrode.

^f OPpy – overoxidized polypyrrole.

^g PASA – poly(amidosulfonic acid).

^h SWV – square wave voltammetry.

ⁱ OMC – ordered mesoporous carbon.

^j DME – dropping mercury electrode.

2.2. Apparatus

CHI 1205 electrochemical workstation (CH Instruments) was employed for cyclic voltammetry (CV) and linear sweep voltammetry (LSV) studies. Hitachi S-3000 H, scanning electron microscope (SEM) and Hitachi S-4700 field emission scanning electron microscope (FESEM) were used for the surface morphological investigations of the composite. A conventional three-electrode system consisting of a Rh modified glassy carbon electrode (GCE) as a working electrode (active surface area = 0.079 cm²), a Ag/AgCl electrode (Sat. KCl) as a reference electrode and a platinum wire with 0.5 mm diameter as a counter electrode were employed for electrochemical experiments. All the electrochemical measurements were carried out under nitrogen saturated conditions.

2.3. Electrochemical deposition of Rh particles

Prior to modification, the GCE surface was first polished with alumina slurry on BAS polishing pad, followed by successive sonication in ethanol and double distilled water. After bath sonication, the electrode was rinsed with double distilled water and allowed to dry at room temperature for few minutes and further employed for the electrochemical deposition process. For the electrode fabrication, we employed CV technique. GCE was immersed in 1 mM Rh(III) chloride hydrate/0.2 M H₂SO₄ solution and 30 consecutive cycles were recorded in the potential range 1 to –0.3 V at the scan rate of 100 mV s^{–1} [34]. The as-modified Rh/GCE was subsequently rinsed twice with doubly distilled water, dried at ambient conditions and employed for the detailed electrochemical studies.

2.4. Preparation of samples

2.4.1. Lab sample

0.05 M of INZ sample was prepared in pH 7.0 PBS in a 25 mL volumetric flask through ultra-sonication in a cold-water bath. The as-prepared sample solution was stored in the refrigerator at 4 °C when not in use. The samples were prepared 30 min before each analysis.

2.4.2. Real samples (human urine and blood plasma)

Human urine samples were obtained from two healthy persons aged around 25 years and the samples were stored in a refrigerator at 4 °C. About 25 mL of urine samples were centrifuged at 3000 rpm for 15 min. Then, 1 mL of the supernatant was collected and further diluted 10 fold with pH 7.0 PBS to avoid the complex interferences.

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