



# Development of an electrode modified on the basis of carbon nanoparticles and reduced graphene oxide for simultaneous determination of isoproterenol, uric acid and tryptophan in real samples



M. Mazloum-Ardakani\*, N. Rajabzadeh, A. Dehghani-Firouzabadi, A. Benvidi, B.B.F. Mirjalili, L. Zamani

Department of Chemistry, Faculty of Science, Yazd University, Yazd, I.R. Iran

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## ABSTRACT

In this research, the electrochemical properties of a carbon paste electrode modified by synthesized carbon nanoparticles (CNPs), reduced graphene oxide (RGO), and a novel derivative of hydroquinone, (Z)-4-(naphthalen-1-ylimino methyl) benzene-1, 2-diol, (NYB) were studied by cyclic voltammetry. The modified electrode was used as an electrochemical sensor for catalytic oxidation of isoproterenol (IP), and it exhibited an excellent electrocatalytic activity for IP with a good electrochemical performance, low overpotential and high conductivity. It was found that under optimum conditions (pH = 7.0) in cyclic voltammetry, the oxidation potential of IP would decrease to about 324 mV at the modified electrode as compared to an unmodified carbon paste electrode. Differential pulse voltammetry (DPV) exhibited two linear dynamic ranges of 0.5 to 80.0  $\mu\text{M}$  and 80.0 to 1000.0  $\mu\text{M}$  for IP. Also, the selectivity of the prepared electrochemical sensor was checked for determination of IP in the presence of uric acid (UA) and Tryptophan (Try). The detection limit for IP was found to be 0.065  $\mu\text{M}$ .

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## 1. Introduction

Chemically modified electrodes offer important advantages for electrochemical reactions such as minor overpotentials, higher reaction rates, extra sensitivity and improved selectivity [1–3]. Because of their unique physical and chemical properties such as small dimensional size, good stability, biocompatibility, good conductivity and excellent catalytic activity, nanomaterials have potential applications in the construction of electrochemical sensors and biosensors [4–7]. Nanomaterials prepared from metals, carbon or polymeric species, shaped into nanoparticles and nanotubes, can act as conduction centers and provide large catalytic surface areas for facilitating the transfer of electron [8–9]. Graphene is a one-atom-thick  $\text{sp}^2$  bonded carbon sheet. Because of its excellent mechanical, thermal and electronic properties, it has attracted much attention in fabrication of novel sensors [10]. Graphene oxide (GO) can be reverted back to conducting graphene by chemical reduction. Due to its high surface area, excellent conductivity and small band gap, reduced graphene oxide (RGO) is helpful in modification of electrodes [11]. Modification of electrodes with RGO and carbon nanoparticles (CNPs) can increase their surface area, and enhance their optical, electronic and catalytic properties. [2,12]. Also RGO and CNPs can lower the overpotential, increase the reaction rate and sensitivity and improve selectivity. Carbon paste electrodes (CPE) are

applicable in electrochemical and electroanalysis studies due to their advantages such as ease and speed of preparation and obtaining a new reproducible surface, very low background current, cheap, feasibility of incorporating different substances during the past modification. Catechol derivatives with redox behavior are electro active compounds that effectively shuttle electrons between the analyte and the electrode. These modifiers can reduce overpotential required for electrochemical reaction and can enhance the sensitivity and selectivity of the method.

Isoproterenol (IP) is a catecholamine drug widely used for hypertension and allergic emergencies, bronchitis, cardiac shock and heart attack. IP has positive inotropic and chronotropic effects on the heart and is used for bradycardia or heart block, but overdose of the drug may cause heart failure and arrhythmias [13]. IP is readily absorbed when given parenterally or as an aerosol. Absorption of sublingual or oral doses is unreliable. The drug is poorly absorbed from stomach, but well absorbed from small intestine, proximal colon, rectum and from the mucous membrane of the trachea. It is recognized that the dosage requirements for isoproterenol vary widely according to the route of administration; when the drug is given intravenously pharmacological effects are seen with only few micrograms (16–17), whereas using the oral route, tablets containing 180–360 mg are required daily to control chronic heart block [14].

Various methods have been developed to detect IP, including chemiluminescence [15], chromatography [16] and spectrophotometry [17]. These methods are often time-consuming and expensive. As IP is structurally electroactive, it is suitable for electrochemical detection by

\* Corresponding author.

E-mail address: [mazloum@yazd.ac.ir](mailto:mazloum@yazd.ac.ir) (M. Mazloum-Ardakani).

electrochemical methods such as amperometric and voltammetric techniques, which are inexpensive and sensitive methods of determining IP [18].

Uric acid (UA) is a product of the metabolic breakdown of purine nucleotides. Monitoring of UA is essential because a high concentration of uric acid in blood can lead to several diseases such as gout and hyperuricemia [19]. Some methods, like chemiluminescence [20], enzymatic-spectrophotometric [21] and electrochemical methods [22–25], have been employed for the detection of UA.

Tryptophan (Try) is a routine constituent of most protein-based foods and a precursor of neurotransmitter serotonin [26]. It is indispensable to human nutrition for establishing and maintaining a positive nitrogen balance. Some electrochemical techniques have been already developed to determine Try [27–30].

In this paper, for the first time, the electrochemical behavior of a novel synthesized derivative of hydroquinone, (Z)-4-(naphthalen-1-ylimino methyl) benzene-1, 2-diol, (NYB) was studied at CNPs and RGO modified CPE. Initially, the preparation of a CPE modified with NYB, RGO and CNP (NYB/CNP/RGO/CPE) was reported as a new electrode in the electrocatalysis and determination of IP. Then, the analytical performance of the modified electrode was evaluated for simultaneous determination of IP, UA and Try. The NYB/CNP/RGO/CPE could resolve the overlapping anodic peaks of IP, UA and Try into three well-defined voltammetric peaks by differential pulse voltammetry (DPV). This modified electrode was effective in detecting IP, UA and Try in a mixture with good results.

In our previous works [2,29], we used CNPs in electrode modification. In the present study, we used a combination of RGO, CNPs and NYB for detection of IP. Due to the unique properties of RGO and CNPs, a lower detection limit, a wider linear range, and a lower overpotential were obtained. This is what makes the present study distinct from our previous ones [29]. The experimental results indicate that NYB/CNP/RGO/CPE offers several advantages such as high repeatability, high sensitivity and good stability. Also, the detected potential difference between the three compounds is large enough to allow simultaneous determination of IP, UA and Try in mixtures without any significant interference. These properties along with very low detection limit (65 nM) and ease of preparation and surface regeneration make the proposed modified electrode very suitable for detection of the three compounds. The detection limit and the linear range for IP in this study are comparable to those in other works [29,31–38].

## 2. Experimental

### 2.1. Apparatus and reagents

All the electrochemical measurements were performed using a potentiostat/galvanostat  $\mu$ Autolab Type III (Eco Chemie B. V.) with GPES 4.9 software. A three-electrode cell was used at  $25 \pm 1$  °C. An Ag/AgCl (KCl, Sat.) electrode, a platinum wire and a carbon paste electrode modified by NYB, RGO and CNP (NYB/CNP/RGO/CPE) were used as reference, auxiliary and working electrodes respectively. A Metrohm 691 pH/ion meter was used for pH measurements. All the solutions were freshly prepared with double distilled water. IP, UA, Try and the other reagents were of analytical grades (Merck). Phosphate buffers (0.1 M) were prepared from orthophosphoric acid and its salts in the pH range of 2.0–12.0. Graphite powder (Merck) and paraffin oil (Merck) were used to prepare carbon pastes.

### 2.2. General procedure for the synthesis of (4-naphthalen-1-ylimino) methyl benzene-1, 2-diol

A mixture of 3, 4-dihydroxy benzaldehyde (1 mmol),  $\alpha$ -naphthylamine (1 mmol), ethanol (5 mL) and 50% nano-TiCl<sub>4</sub>.SiO<sub>2</sub> (0.1 g) was refluxed for an appropriate time. The progress of the reaction was monitored by thin-layer chromatography. After completion

of the reaction, the mixture was cooled to room temperature and filtered to isolate the product from the catalyst. The catalyst was separated from the product by boiling ethanol. The crude solid product was purified by recrystallization procedure in ethanol:water, 80:20. Spectroscopic data: FT-IR:  $\nu$  (KBr) = 2500–3300 (OH), 1615 (C=N), 1509, 1460, 1335, 1263, 1201, 827, 701 cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>): 7–8 (m, 9H, Ar–C–H), 8.4 (s, 1H, N=C–H), 6.8 (s, 1H, Ar–C–H), 3–4 (brs, 2H, OH) ppm.

### 2.3. Preparation of nanomaterials (RGO and CNPs)

Graphene nanosheets were prepared and characterized (SEM, XPS, UV and IR) according to our previous work [39]. For the reduction of GO, this suspension in purified water (150 mg/50 mL) was added to 50  $\mu$ L of a hydrazine solution (98%) with 200  $\mu$ L of an ammonia solution (30%). After being refluxed at 90 °C for 12 h, the solution was cooled down. Subsequently, it was centrifuged, and the precipitates were washed with deionized water and then dried at 60 °C in vacuum for 24 h. Also, CNPs with a diameter of 11.3 nm were synthesized and characterized (SEM) in our laboratory [2].

### 2.4. Preparation of the electrode

To obtain the best conditions in the preparation of NYB/CNP/RGO/CPE, we optimized the ratio of NYB, RGO and CNP. The maximum peak current intensity of IP could be obtained in the optimum condition. The NYB/CNP/RGO/CPE was prepared by mixing 0.465 g of graphite powder, 0.005 g of NYB, 0.015 g of CNP, 0.015 g of RGO and ~0.7 mL of paraffin oil using a mortar and pestle until a uniform paste was prepared. This paste was then packed into the end of a glass tube (ca. 10 cm long and 3.5 mm i.d.). A copper wire inserted into the carbon paste provided an electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it with a weighing paper.

### 2.5. Preparation of real samples

An ampoule (0.2 mg mL<sup>-1</sup>, Galena Siena Srl, Italy) was prepared, and 1.0 mL of the solution was diluted to 10.0 mL by a phosphate buffer solution (pH 7.0). Then, 0.7 mL of this solution was diluted to a 10.0 mL volume by a phosphate buffer solution (pH = 7.0) and transferred to the electrochemical cell for the analysis. Also, different amounts of IP, UA and Try were added to the same solution diluted from the IP ampoule for simultaneous determination. The serum sample was centrifuged, filtered, and diluted with PBS (pH 7.0) without any further treatment. The diluted serum sample was spiked with different amounts of IP, UA and Try. Urine samples were stored in a refrigerator after collection. 10.0 mL of the sample was centrifuged for 10 min and diluted to 50.0 mL with PBS. Ten mL of the solution was transferred into a voltammetric cell to be analyzed without any further pretreatment.

## 3. Results and discussion

### 3.1. Electrochemical properties of NYB

It should be noted that one of the advantages of NYB as an electrode modifier is its insolubility in aqueous media. Therefore, we prepared NYB/CNP/RGO/CPE and investigated its electrochemical properties in an aqueous solution (pH = 7.0) using cyclic voltammetry (CV). We expect the peak potential to be pH dependent, because NYB has a hydroquinone structure. The effect of pH on the electrochemical behavior of a modified electrode in 0.1 M phosphate buffer at different pH values was studied by CVs. It was observed that the anodic and cathodic peak potentials of NYB/CNP/RGO/CPE shift to negative values with increasing pH (Fig. 1). A potential-pH diagram was constructed by plotting the

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