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Simultaneous determination of adrenaline, uric acid, and cysteine using bifunctional electrocatalyst of ruthenium oxide nanoparticles

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ABSTRACT

In this study, ruthenium oxide nanoparticles were electrochemically deposited on the surface of a glassy carbon electrode (RuON-GCE). Electrochemical studies indicate that a modified electrode (RuON-GCE) plays the role of an excellent bifunctional electrocatalyst for the oxidation of adrenaline (AD) and uric acid (UA) in two different potentials. The charge transfer coefficient (α) and the heterogeneous charge transfer rate constant (k') between the analytes and the electrodeposited nanoparticles were determined using cyclic voltammetry experiments. Through a different pulse voltammetric (DPV) method, the plot of the electrocatalytic current versus AD and UA concentrations emerged to be constituted of two linear segments with different sensitivities. Furthermore, the detection limits of AD and UA were estimated. In DPV, RuON-GCE could separate the oxidation peak potentials of AD, UA, and cysteine (Cys) present in the same solution though, at the bare GCE, the peak potentials were indistinguishable. Finally, the modified electrode activity was studied for the electrocatalytic determination of AD in an injection solution and UA in a human urine sample. The results were found satisfactory.

1. Introduction

Metal nanoparticles are of great fundamental and practical interest due to their unique physical properties, chemical reactivity, and potential applications in electronics, catalysis, and biochemistry [1]. Nanoparticles of many metals such as gold [2,3], platinum [4], palladium [5], ruthenium [6], and silver [7] have been studied with a wide variety of experimental techniques. The importance of ruthenium lies in its unique activity as a catalyst for different synthesis and redox processes [8]. Also, due to the different oxidation states of ruthenium derivatives and their electrochemical reversibility, these compounds have been used as excellent electron transfer mediators for the modification of different electrode surfaces [9].

Catecholamines, such as adrenaline (AD), are an important kind of compounds for the message transfer in the mammalian central nervous system. They exist as an organic cation in the nervous tissue and the biological body fluid [10,11]. AD in the body affects the regulation of blood pressure and the heart rate, lipolysis, immune system, and glycogen metabolism [12]. Many life phenomena are related to the concentration of AD in blood [13]. Low levels of AD have been found in patients with Parkinson's disease [14,15]. Thus, it is significant to develop a method for the quantitative determination of AD in order to study its physiological function and to diagnose some diseases in clinical medicine [16]. Different methods have been reported for the quantitative determination of AD [17–25]. Among them, electrochemical methods are of particular importance [22–25]. Ease of operation, low cost, small value of required analyte, and high sensitivity are the advantages of electrochemical methods over all other methods.

Uric acid (UA) is a chief nitrogenous component of biological fluids such as urine and blood serum [26]. This

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compound is a relatively water-insoluble end product of purine metabolism in humans and is excreted via urine [27]. Abnormal levels of UA are liable to result in several diseases such as gout, hyperuricemia, and pneumonia [28]. An elevated UA concentration in serum causes kidney damages and cardiovascular diseases [29]. In a healthy human being, the typical concentration of UA in urine is within a mili-molar range (~2 mM), whereas in blood it is in a micro-molar range (120–450 μM) [30]. Thus, the detection of UA level dissolved in human physiological fluids is indispensable for the diagnosis of patients suffering from these disorders associated with altered purine biosynthesis and catabolism. Various techniques have been developed to determine UA concentration [31–36]. Among the various methods used to detect uric acid, electrochemical methods are known to be the most popular because a low detection limit, high selectivity, and sensitivity can be easily acquired where matrix plays an important role [26–30,37–39].

Amino acids are known to be precursors for various significant biological substances. Cysteine (2-amino-3-mercaptopropanoic acid, Cys) is one of the 20 amino acids commonly found in natural proteins [40]. It is widely used in the food industry as an antioxidant and in the pharmaceutical industry for drug formulation [41]. Cysteine also has several pharmaceutical applications; it is used in some antibiotics and for the treatment of skin damages and as a radioprotective agent [42]. Cysteine is critical for the proper metabolism of a number of essential biochemicals such as heparin, biotin, lipoid acid, coenzyme A, and glutathione. It has been used as a prospective radiation protector and cancer indicator in a number of pathological conditions including Parkinson's and Alzheimer's diseases as well as autoimmune deficiency syndrome (AIDS) [43]. Therefore, it is important to determine Cys in many biological, medical, and clinical studies. Due to its crucial role in biological functions and its clinical significance, many attempts have been made to determine Cys [44–49]. Compared with other methods, electrochemical detection offers inherent advantages of simplicity, ease of miniaturization, high sensitivity, and relatively low cost [50–52].

A major problem to detect AD is the interference from UA, which largely coexists with neurotransmitters in body fluids and has a nearly identical oxidation potential range on unmodified electrodes [53,54]. Also, the response of highly concentrated UA interferes with and/or blocks the detection signals of Cys [55]. So, the simultaneous detection of AD, UA, and Cys in a mixture is quite attractive to biological and chemical research.

A bifunctional electrocatalyst is able to catalyze the redox reaction of two species simultaneously. Developing such an electrocatalyst has been a challenge in recent years [9,56–58]. In our previous studies, we introduced new bifunctional sensors for the simultaneous electrocatalytic oxidation of hydrazine-hydroxylamine [9] and ascorbic acid-glutathione [58] in mixtures. The aim of the present work is to utilize a ruthenium oxide nanoparticles modified glassy carbon electrode (RuON-GCE) as a bifunctional electrocatalyst for the electrocatalytic oxidation of AD and UA. In addition, the modified electrode has been used successfully for the simultaneous determination of AD, UA, and Cys in a mixture.

2. Experimental

Adrenaline (AD), uric acid (UA), cysteine (Cys), $RuCl_3{\cdot}xH_2O$, hydrochloric acid, phosphoric acid, and 0.05 μm analytical reagent grade alumina were purchased from Merck and used as received. An injection solution of AD (from Darou Pakhsh, Iran) was purchased in a local drugstore. The required phosphate buffer solutions (0.1 M) were prepared with H_3PO_4, and the pH was adjusted with 2.0 M NaOH. All the aqueous solutions were prepared with doubly distilled water. UA, AD, and Cys solutions were prepared just prior to use and all the experiments were carried out at room temperature.

To prepare the modified electrode at first, a glassy carbon electrode (GCE) was carefully polished mechanically with a 0.05 μm Al_2O_3 slurry on a polishing cloth to a mirror finish and then rinsed with doubly distilled water. Then the cleaned bare GCE (BGCE) was modified as described in the literature [9]. In brief, BGCE was immersed in a 0.1 M HCl solution containing about 1.0 mM of ruthenium (III) chloride, and the ruthenium oxide nanoparticles were electrodeposited on the electrode surface by 20 cycles of a potential scan between −500 and 1700 mV at 50 mV/s. The ruthenium oxide nanoparticle modified glassy carbon electrode (RuON−GCE) was rinsed thoroughly with water and placed in a 0.1 M phosphate buffer solution (pH 2.0). Subsequently, the potential was scanned for 10 cycles at 100 mV/s over the −300 to 600 mV range so as to obtain a stable redox response for the surface immobilized film. The results show that the current response of the redox couples first decreases and then remains almost constant. The initial decay of the current response may be due to the removal of RuON that is weakly adsorbed to the electrode surface.

An Autolab potentiostat-golvanostat PGSTAT 30 (Eco Chemie, Ultrecht, the Netherlands) equipped with a GPES 4.9 software, in conjunction with a three-electrode system and a personal computer, was used for electrochemical measurements. A saturated calomel reference electrode (SCE), a platinum wire counter electrode, and ruthenium oxide nanoparticles electrodeposited on a GCE (RuON-GCE) intended as a working electrode were employed for the electrochemical studies. The pH was measured with a Metrohm model 691 pH/mV-meter. The morphology of the BGCE and RuO-GCE surfaces was characterized by scanning electron microscopy (LEO 4401, UK) at an acceleration voltage of 20 kV. As previously described [9], the surface morphologies of BGCE and RuON-GCE are indicated when RuON are electrodeposited on the BGCE surface. The scanning electron microscopy, SEM, of bare GCE and RuON−GCE are given on Scheme S1. A comparison of Scheme S1A and S1B indicates that the nanoparticles of the ruthenium oxide with a size of approximately 50 to 100 nm are distributed on the BGCE surface. As demonstrated in the literature [59–62], the distributed nanoparticles are ruthenium oxide nanoparticles.