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ORIGINAL ARTICLE

Fabrication of poly (Solid Red A) modified carbon nano tube paste electrode and its application for simultaneous determination of epinephrine, uric acid and ascorbic acid

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Abstract In this study, a stable electroactive thin film of poly(Solid Red A) has been deposited on the surface of a carbon nano tube paste electrode by cyclic voltammetric technique in an pH 7 phosphate buffer solution (PBS) containing Solid Red A. A higher catalytic activity was obtained for electrocatalytic oxidation of ascorbic acid (AA), epinephrine (EP), and uric acid (UA) in pH 7 PBS at over oxidized poly (Solid Red A) film modified carbon nano tube paste electrode (PSRA/MCNTPE) due to an enhanced peak current and well-defined peak separations compared with both bare carbon nano tube paste electrode (BCNTPE) and PSRA/MCNTPE. The electrode surfaces were characterized by field emission scanning electron microscopy (FESEM). Individual and simultaneous determination of AA, EP, and UA were carried out by cyclic voltammetry and differential pulse voltammetry. The reduction peak current was proportional to the EP and UA concentrations in the range of 2.0×10^{-6}–9.0×10^{-6} M and 7.0×10^{-6}–2×10^{-5} M, respectively. The modified electrode showed good sensitivity, selectivity, stability, and was employed for the determination of EP and UA in real samples.

1. Introduction

The development of voltammetric sensors for the determination of EP, UA and AA has received significant attention throughout the previous couple of years. The importance of EP within the body is well known and documented (Banks, 2001; Chen and Peng, 2003). It belongs to the cluster of substances known as catecholamine neurotransmitters which include norepinephrine and dopamine (Chen and Peng,

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2003). They are mainly necessary for message transfer in the mammalian central nervous system. Changes in the concentration of EP in the body can result in several diseases, therefore its detection and quantification in physiological pH conditions is of great interest. The determination of EP has been reported using chromatographic ways (Shelkovnikov and Gonick, 2004), spectroscopic methods (Efremov et al., 2008), chemiluminescence (Su et al., 2005), capillary electrophoresis (Wei et al., 2005), flow injection analysis (Du et al., 2003), and various electrochemical methods (Ozoemena et al., 2008; Li et al., 2009; Yogeswaran et al., 2007; Beitollahi et al., 2008; Mazloum-Ardakani et al., 2010; Wang et al., 2004). Electrochemical methods offer a simple, cost effective and fast method of analyzing biologically and environmentally vital molecules. The EP electrooxidation at bare electrodes is joined with problems of slow electron transfer rate and adsorptions of EP on the electrode surfaces leading to passivation (Beitollahi et al., 2008; Wang et al., 2002).

AA is known for its reductive properties and for its use on a broad scale as an antioxidant agent in foods and drinks, it is also important for therapeutic purposes and biological metabolism. Thus, recent advances in the food and pharmaceutical industries and a need for nutritional assessment have necessitated the development of a selective, simple and accurate method to determine AA, and it is present in the mammalian brain in the presence of many neurochemical amines together with EP and UA. AA has been used for the prevention and treatment of diseases (Arrigoni and Tullio, 2002) up to now, to detect EP with high selectivity and sensitivity is still a most useful target of electroanalytical research (Wang et al., 2002, 2004; Beitollahi et al., 2011; Salimi et al., 2004).

UA (2,6,8-trihydroxypurine,) is the primary product of purine metabolism (Kaur and Halliwell, 1990). Physiological UA serum levels range from 41 to 88 mg mL^{-1} and urinary excretion is typically 250–750 mg per day (Zheng et al., 2001). Its abnormal concentration level in a human body may be the symptoms of several diseases, such as gout, hyperuricemia, and Lesch-Nyhan syndrome. Leukemia, pneumonia, and so on are also associated with enhanced urate levels (Kang and Shiu, 2001; Miland et al., 1995). So it is desirable to have a simple and direct method for monitoring the concentration of UA in biological fluids. UA and EP are coexistent in biological fluids of human, so the simultaneous detection of UA and EP in a mixture is quite attractive to biological and chemical researches. Individual determination of UA or EP has been reported by many researches however, simultaneous determination of them is rarely presented.

Nanomaterials have received nice attention in recent years in numerous fields because of their huge potential. Among them, carbon nanotubes (CNTs) have become the topic of intense investigation since their discovery in 1991 by Iijima (1991). Such considerable interest reflects the unique behavior of CNTs, together with their outstanding electrical, chemical, mechanical and structural properties that make them a very attractive material for a large range of applications (Cravotto et al., 2011; Farma et al., 2013; Ajayan, 1999). The benefits of both single-wall (SW) and multi-wall (MW) CNTs, such as high surface area, smart conductance, favorable electronic properties and electrocatalytic effect make them adequate for the construction of electrochemical sensors and biosensors (Beitollahi et al., 2008; Salinas-Torres et al., 2011; Manjunatha et al., 2014).

Polymer modified electrodes have obtained important attention among the researchers for biosensor applications. Electropolymerization is a good method to prepare Polymer modified electrodes as adjusting electrochemical parameters can control film thickness, permeation and charge transport characteristics (Pariente et al., 1994; Sun et al., 1998; Ni et al., 1999; Chen and Peng, 2003).

Electrochemical techniques give an easy, cost less and fast way of analyzing biologically and environmentally molecules (Beitollahi et al., 2014, 2011a; Raoof et al., 2006; Taleat et al., 2008). However, the main drawback for the voltammetric detection of EP in real samples is the interference of the concomitant compounds, such as ascorbic acid (AA) and uric acids (UA), which usually lead in overlapped voltammetric response due to their very similar oxidation peak potentials (Mohammadi et al., 2013; Mokhtari et al., 2012). Recently, chemically modified electrode surface has been proved to be a successful method to solve this problem, and various materials and techniques have been used (Tajik et al., 2013; Raoof et al., 2007) the modified electrodes have many advantages like good biocompatibility, stability and easiness of the preparation (Raoof et al., 2005; Beitollahi et al., 2011b; Mazloum-Ardakani et al., 2010).

In continuation of our studies concerning the preparation of modified electrodes (Manjunatha et al., 2009a,b,c,d, 2010a, 2011a; Manjunatha et al., 2010b, 2011b; Manjunatha et al., 2012a,b, 2013), in this work, the PSRA/MCNTPE was used for the determination of EP, AA and UA individually and also simultaneously. A carbon nano tube paste electrode (CNTPE) consists of a mixture of multiwall carbon nanotube powder and silicone oil as a binder, which is immiscible with water. The well fabricated PSRA/MCNTPE showed an exceptionally low background current, a wide operating potential window, convenient modification, renewability, miniaturization, and low cost. The electrochemical properties of these modified electrodes and their responses toward the simultaneous determination of EP, AA and UA have been investigated by cyclic voltammetric and differential pulse voltammetric techniques. To our knowledge, there is no report about the voltammetric behaviors and determination of EP at PSRA/MCNTPE.

2. Experimental

2.1. Reagents

Solid Red A, EP, AA, UA, Silicone oil were obtained from Sigma Aldrich Malaysia. Solid Red A was prepared from 25×10^{-4} M stock solution by dissolving in 0.1 M sodium hydroxide solution. EP, AA and UA and other chemicals were of analytical grade and used without further purification. EP was prepared 25×10^{-3} M stock solution by dissolving in 0.1 M perchloric acid solution, AA was prepared 25×10^{-3} M stock solution by dissolving double distilled water and 25×10^{-3} M stock solution of UA by dissolving in 0.1 M sodium hydroxide solution. In all the measurements, the supporting electrolyte used was 7 pH 0.2 M PBS. Spectroscopically