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ORIGINAL ARTICLE

Novel functionalized multiwalled carbon nanotube-glassy carbon electrode for simultaneous determination of ascorbic acid and uric acid

Tahereh Rohani [a,b,*], **Mohammad Ali Taher** [c]

[a] *Payame Noor University, P.O. Box 19395-4697, Tehran, Iran*
[b] *Department of Chemistry, Payame Noor University, Kerman, Iran*
[c] *Department of Chemistry, Shahid Bahonar University of Kerman, P.O. Box 76175-133, Kerman, Iran*

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Abstract In this study the electrochemical behavior of ascorbic acid (AA) and uric acid (UA) at the surface of glassy carbon electrodes (GCEs) modified by multi-walled carbon nanotubes (MWCNTs) functionalized with Fe^{3+} complex was investigated. The voltammetric studies using the modified electrode showed two well-resolved anodic peaks for AA and UA with a potential difference of ~0.4 V, revealing the possibility of the simultaneous electrochemical detection of these compounds. First, the electrochemical behavior of ferric/ferrous at Fe^{3+} complex/MWNTs/nafion (FeCMN) modified electrode was studied. The results showed an adsorption-controlled reaction at the modified electrode. Then, the behavior of ascorbic acid and uric acid at the modified electrode was investigated. The optimum analytical conditions were sought. Linear calibration plots were obtained over the range of 4.0 to 600 μmol l^{-1} and 0.3 to 490 μmol l^{-1} with detection limits (3σ) of 2.57 μmol l^{-1} and 0.137 μmol l^{-1} for AA and UA, respectively.

The electrode with the best conditions was applied for selective determination of AA and UA in biological matrices.

1. Introduction

Ascorbic acid (AA) is a soluble vitamin widely present in many biological systems and in multivitamin preparations; it is commonly used to supplement inadequate dietary intake and as an anti-oxidant (Yu and Chen, 1997). AA has been used for prevention and treatment of common cold, mental illness, infertility, cancer, and in some clinical manifestations of HIV infections (Arrigoni and Tullio, 2002). Uric acid (UA) is the primary product of purine metabolism in the human body

* Corresponding author at: Department of Chemistry, Payame Noor University, Kerman, Iran. Tel.: +98 341 3643853; fax: +98 341 3643852.
E-mail address: th_rohani@yahoo.com (T. Rohani).
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(Kaur and Halliwell, 1990). It has been proved that abnormalities of UA levels are symptoms of gout, hyperuricemia (Harper, 1977), Lesch–Nyhan syndrome (Nyhan, 2005), multiple sclerosis (Toncev et al., 2002) and oxidative stress (Becker, 1993). Other diseases such as leukemia and pneumonia are also associated with enhanced urate levels (Miland et al., 1996). As UA and AA are usually coexistent in biological fluids of blood and urine, it is important to develop a technique to selectively detect UA and AA conveniently in routine assay (Kalimuthu et al., 2006). Among several methods of determination, electrochemical methods have received much interest because they are more selective, less expensive, less time consuming and can potentially be applied to a real-time determination *in vivo* (Matos et al., 2000). Because of irreversible oxidation of UA and AA in aqueous solution, electrochemical procedures have been greatly developed to determine UA and AA based on their electrochemical activities. However, direct electro-oxidation of UA and AA requires high overpotentials at bare electrodes (Gao et al., 1997; Kachoosangi et al., 2006), in addition, UA and AA are oxidized at a very close potential valve, which results in poor selectivity for simultaneous determination of UA and AA. To solve this problem, most of the attention has been focused on electrochemical procedures using modification of electrode surfaces for selective electrocatalytic determination of AA and UA (Shahrokhian and Gholkhani, 2006; Yao et al., 2007; Zen and Hsu, 1998; Gilmartin et al., 1992).

Nowadays, carbon nanotubes (CNTs) have attracted much interest directed toward exploiting unique thermal, mechanical, electronic, and chemical properties (Popov, 2004) since they were first discovered. Due to these unique properties, CNTs have received great attention for the preparation of electrochemical sensors (Gooding, 2005; Wang, 2005). CNTs can be functionalized with organic compounds without any damage to their electrical and chemical properties (Wang, 2005; Sun et al., 2006). Functionalization of carbon nanotubes is an effective way to enhance their physical properties and improve their solubility. However, the aromatic character of nanotubes is a restriction to any possible additional reactions. Some of the functionalization approaches were through the formation of covalent bonds (Bahr et al., 2001; Pompeo and Reasaco, 2002; Dyke and Tour, 2003), while others had utilized noncovalent interactions (O'Connell et al., 2001; D. Chattopadhyay et al., 2003). Both noncovalent and covalent modifications of the surface were developed to improve solubility.

In the present study, glassy carbon electrodes (GCEs) were modified by multi-walled carbon nanotubes (MWCNTs) functionalized with Fe^{3+}–2-(5-bromo-2-pyridylazo)-5-diethyl amino phenol (5-Br-PADAP) complex.

Our results showed that Fe^{3+}complex/MWCNTs/nafion modified GCE (FeCMN/GCE) could be used for the determination of AA in the presence of UA. The peak separation between AA and UA was wide enough to provide an attractive ability for the simultaneous determination of AA and UA, with lower detection limit and excellent selectivity. The proposed modified electrode could be applied to the simultaneous determination of AA and UA concentrations in real samples with satisfactory results.

2. Experimental

2.1. Reagents

MWCNTs (95% purity) with an average outer diameter of 3–20 nm, length of 1–10 μm, number of walls 3–15 and surface area of 350 $m^2\ g^{-1}$ were obtained from Plasma Chem. GmbH (Berlin, Germany). UA and AA were purchased from Merck and used as received. Nafion perfluorinated ion exchange resin (5.0 wt% solution in lower aliphatic alcohols/H_2O mixture) and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) (Fig. 1) were purchased from Sigma. 2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol solution (1.0 mmol l^{-1}) was prepared in ethanol. Other reagents used in this study were of analytical grade and were used as received. Doubly distilled, deionized water was used for all experiments. Phosphate buffer solutions (PBS) were prepared from H_3PO_4 and NaH_2PO_4 (0.1 mol l^{-1}); we adjusted the pH range with 0.1 M H_3PO_4 and NaOH solutions and used the solutions as supporting electrolytes. All solutions were prepared with doubly distilled water. The electrolyte solutions were deoxygenated with nitrogen bubbling before each voltammetric experiment. All experiments were performed under nitrogen atmosphere at room temperature.

2.2. Apparatus

Voltammetric experiments were performed using a Computrace Voltammetric Analyzer (Model 757 Metrohm). All voltammograms were recorded with a three-electrode system consisting of an Ag/AgCl electrode as the reference electrode, a platinum wire as the auxiliary electrode, and the modified GC electrode as the working electrode. A Metrohm 710 pH meter was used for pH adjustments. All the electrochemical experiments were carried out under pure nitrogen atmosphere at room temperature (23 ± 1 °C).

2.3. Preparation of functionalized MWCNTs with Fe^{3+}–5-Br-PADAP complex

Raw MWCNTs were heated at 350 °C for 30 min to remove amorphous carbon. Prior to use, MWCNTs were oxidized with concentrated HNO_3 according to the literature, in order to create binding sites onto the surface of MWCNTs (Tan et al., 2005) The treatment was carried out by the dispersion of 50 ml of concentrated HNO_3 to 5.0 g of MWCNTs, and then refluxing for 5 h at 80 °C. Afterward, the oxidized

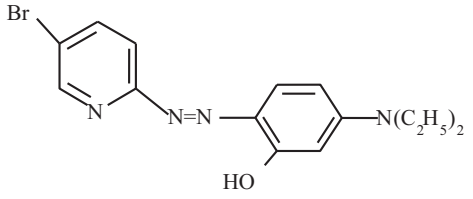

Figure 1 Chemical structure of 5-Br-PADAP.