



Carbon nanoparticles with tosyl functional group for distinguishing voltammetric peaks of ascorbic acid and uric acid



Mandana Amiri ^{a,*}, Hamideh Imanzadeh ^b, Alireza Banaei ^b

^a Department of Chemistry, University of Mohaghegh Ardabili, Ardabil, Iran

^b Department of Chemistry, Payame Noor University, Ardabil, Iran

ARTICLE INFO

Article history:

Received 20 April 2014

Received in revised form 20 October 2014

Accepted 7 November 2014

Available online 12 November 2014

Keywords:

Ascorbic acid

Uric acid

Voltammetric sensor

Tosyl functionalized carbon nanoparticles

ABSTRACT

In this approach, electro-oxidation of a mixture of uric acid and ascorbic acid at the surface of tosyl surface carbon nanoparticles/glassy carbon electrode has been performed. The electro-oxidation of these compounds at bare electrode is sluggish and there is no suitable peak separation between them. However, using functionalized carbon nanoparticles, two well-defined anodic peaks with a considerable enhancement in the peak current and a remarkable peak potential separation near 452 mV is obtained. The porous interfacial layer of the carbon nanoparticles modified electrode with a high specific surface area increases the conductive area; molecules can penetrate through the conductive porous channels onto the electrode more easily so leading to higher sensitivity and selectivity. The dynamic linear ranges of 1.0×10^{-5} to 3.0×10^{-3} M and 1.0×10^{-7} to 1.0×10^{-4} M with detection limits 1.0×10^{-5} M and 2.0×10^{-8} M (for S/N = 3) were obtained for ascorbic acid and uric acid, respectively. Analytical utility of the modified electrode has been examined successfully using human urine samples and vitamin C commercial tablets.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Carbon based materials are widely used as electrode materials for many applications. New types of nanostructured carbons are now widely investigated and employed as a substrate for surface modification and optimization [1–6]. Carbon nanoparticles with sulfonic acid functionalization are in large scale industrial use (e.g. as colorants; Emperor 2000, Cabot Corp.) and these particles have recently been exploited to electrode surface modification [7–9]. Nanoparticulate carbon film has electrochemical properties different from bulk carbon materials. These materials are attractive for sensing and biosensing applications [9–11]. CNPs generally exhibit extremely high surface areas, high conductivity, and a multitude of reactive surface and adsorption sites [12]. CNPs may be considered more economical than other nano-carbons, as they are produced commercially in bulk quantities and also often formed as waste by-products during the formation of other nano-materials such as CNTs.

Ascorbic acid (AA), Vitamin C, is an essential nutrient found mainly in fruits and vegetables and one of the most important cellular antioxidants. Ascorbic acid helps to produce collagen, a protein needed to develop and maintain healthy teeth, bones, gums, cartilage, vertebrae discs, joint linings, skin and blood vessels [13]. There is evidence that large doses of ascorbic acid contribute to the development of kidney

stones [14]. In addition the concentration of AA in foodstuffs, beverages and pharmaceuticals can be an index of quality since it varies during production and storage stages [15].

Uric acid (UA), is the principal final product of purine metabolism in the human body [16]. The increasing of UA concentration in serum causes kidney damage and cardiovascular disease [17]. It can be concluded the determination of the concentration of UA in human blood or urine is a powerful indicator in diagnosing diseases.

UA and AA commonly coexist in biological fluids of humans, mainly in serum, blood and urine. The major problem with simultaneous determination of UA and AA by electrochemical methods is the closeness of the oxidation potentials of these two compounds which results in an overlapped voltammetric response which makes their signal discrimination very difficult [18].

There are a lot of attempts to obtain a suitable method for the determination of AA and UA in the presence of each other recently [19–29]. The electrochemical determination of uric acid and ascorbic acid have been reported using various modified electrodes such as amorphous silica gel modified carbon paste electrode [19], poly (Evans Blue) modified-GCE [20], gold nanoparticles modified glassy carbon electrode (GCE) [21] palladium nanoparticle loaded carbon nanofibers modified carbon paste electrode [22], ordered mesoporous carbon/Nafion composite film modified-GCE [23], polyacrylic acid-coated multi-wall carbon nanotubes modified screen printed carbon electrode [24], LaFeO₃ nanoparticles modified-GCE [25], a hematopylin multi-wall carbon nanotube modified glassy carbon electrode [26], a multi-walled carbon nanotubes modified glassy carbon electrode [27], carbon paste/cobalt

* Corresponding author.

E-mail address: mandanaamiri@uma.ac.ir (M. Amiri).

Schiff base composite electrode [28] and lanthanum-multiwalled carbon nanotube nanocomposites (a-MWCNTs) modified GCE [29].

In this approach, we have employed a thin film of tosyl carbon nanoparticles to modify glassy carbon electrode for simultaneous determination of AA and UA at submicromolar concentration level in biological samples. Table 1 compares some of the recent applied methods for determination of AA and UA with the present research. The aim of this work is to determine those compounds in the presence of each other with good analytical results. The easy renewability, and simplicity of presented electrode could be very interesting for analytical means.

2. Experimental

2.1. Materials

Carbon nanoparticles with surface tosyl groups (tosyl-CNP) were obtained from Cabot (ca. 9 to 18 nm diameters, Emperor 2000™, Cabot Corporation). Uric acid was purchased from Alfa Aesar. All other chemicals such as ascorbic acid, KH_2PO_4 , H_3PO_4 , KOH, $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, acetic acid and potassium acetate were analytical reagent grade from Merck. All aqueous solutions were prepared with deionized water. The buffer solutions were prepared using $\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ for pH 2.0 and 3.0, $\text{KH}_2\text{PO}_4/\text{KOH}$ for pH 6.0 and 7.0 and potassium acetate/acetic acid for buffered solution pH 4.0 and 5.0. Measurement of the pH was carried out on each freshly made solution prior to experiments. Voltammetric experiments were carried out in the buffered solutions, deoxygenated by purging the pure nitrogen. Deionized water was taken from a Millipore water purification system.

2.2. Instruments

Voltammetric experiments were performed using a Metrohm Computrace Voltammetric Analyzer model 797 VA. A conventional three-electrode system was used with a glassy carbon electrode (GCE), a saturated Ag/AgCl reference electrode and a Pt wire as the counter electrode. A digital pH/mV/Ion meter (Metrohm) was applied for the preparing of the buffer solutions, which were used as the supporting electrolyte in voltammetric experiments. The scanning electron microscope (SEM) images were obtained using LEO 1430VP.

2.3. Preparation and characterization of the modified electrode

Pretreatment of GCE was done using 2500 emery (Germany) rinsed thoroughly with water. A stable suspension of CNP containing 1 mg/ml in doubly distilled deionized water using 30 min ultrasonic agitation was prepared. 2 μL of this suspension was cast on the pretreated GCE surface and dried in the air to remove solvent for 20 min in 25 °C. The obtained modified GCE (MGCE) was characterized by cyclic voltammetry (CV) and scanning electron microscopy (SEM).

Table 1
The characteristics of some sensors for simultaneous determination of UA–AA are summarized.

LOD (UA) (μM)	LOD (AA) (μM)	ΔE (V)	Electrode	Reference
0.2	3	0.306	Gold nanoparticles-GCE	[21]
0.008	0.008	0.315	CPE-Me-Cosal	[28]
–	–	0.400	Polyelectrolyte-GCE	[30]
6.4	44	0.400	Organoclay film-GCE	[31]
0.2	10	0.452	GCE-CNP	This work

3. Results and discussion

3.1. Characterization of the GCE/tosyl-CNP modified electrode

3.1.1. Scanning electron microscopy

To study of the surface morphology of the tosyl-CNP thin film, scanning electron microscopy (SEM) has been utilized. Scanning electron micrographs of the surface of bare and tosyl-CNP modified glassy carbon electrode have been shown in Fig. 1a and b, respectively. The deposition of tosyl-CNP suspension on the surface of GCE resulted in a completely rough surface which increases the area of the modified surface and finally, response sensitivities in voltammetric determinations. Fig. 1b of the carbon nanoparticle material confirms a particle size in the order of 40–100 nm radiuses. It seems the tosyl-CNPs aggregate during the preparation of suspension and deposition. Due to the porous nature of this film water and electrolyte can readily access the film whereas electrical contact and conductivity via carbon nanoparticles is maintained.

3.1.2. Electrochemical characterization: capacitive currents

The surface characteristics and microscopic area of the modified and the bare GCE were obtained by comparison of the CV responses in 0.1 M phosphate buffer pH 2.0 (not shown). Capacitance values of ca. 52 μF and 200 μF for a bare glassy carbon electrode and for a modified glassy carbon electrode (ca. 2 μg carbon) were estimated. A one order of magnitude increase in capacitive current suggests a significantly increased active electrode surface area (with ca. 2 μL tosyl-CNPs). This increase in area can be further controlled by changing the amount of film deposited at the electrode surface.

3.1.3. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was employed to investigate the impedance changes of the electrode surface due to the modification procedure. Fig. 1c shows the Nyquist plots of $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ at the GCE and GCE/tosyl-CNP. In these studies, high frequency zone, which appears as a nearly semicircle plot, can be ascribed to the kinetic limitations (R_{ct}) of the electrochemical reaction. On the other hand, the linear behavior of Z_{lm} versus Z_{Re} in a low frequency region is characteristic of a diffusion-controlled electrode process in GCE/tosyl-CNP. As can be seen in Fig. 1c, a semicircle with a very large diameter is observed at GCE. However, the diameter of the semicircle is significantly reduced with GCE/tosyl-CNP which suggests that the surface of the modified electrode exhibits lower electron transfer resistance and greatly increases the electron transfer rate.

3.2. Voltammetric behavior of AA and UA at the surface of bare GCE and GCE/tosyl-CNP

Cyclic voltammograms have been recorded at the surface of bare GCE (dashed line) and GCE/tosyl-CNP (solid line) in the presence of 0.1 mM AA (Fig. 2a) and UA (Fig. 2b) in 0.1 M phosphate buffer of pH 2.0.

The electro-oxidation of AA occurs at approximately 0.315 V and the voltammetric peak is rather broad, suggesting slow electron transfer kinetics. However, as can be seen in Fig. 2a, a sharp anodic peak at a less positive potential at 0.202 V is obtained for AA at the surface of modified electrode. The same behavior can be seen for UA. The increasing peak current for oxidation of UA is more than ten times at the surface of GCE/tosyl-CNP (Fig. 2b). A significant increase of the anodic peak currents in conjunction with the sharpness of the peak, which is related to a reduction of the overpotential of the process at the surface of the modified electrode, revealed that the modified electrode could act as a very effective promoter to enhance the kinetics of the electrochemical process.

It can be resulted that the increase in the capacitive current is observed, but also the faradaic current responses are substantially

Download English Version:

<https://daneshyari.com/en/article/1428392>

Download Persian Version:

<https://daneshyari.com/article/1428392>

[Daneshyari.com](https://daneshyari.com)