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Iron nanoparticles decorated multi-wall carbon nanotubes modified carbon paste electrode as an electrochemical sensor for the simultaneous determination of uric acid in the presence of ascorbic acid, dopamine and L-tyrosine

Arvind K. Bhakta [a], Ronald J. Mascarenhas [b,*], Ozma J. D'Souza [b], Ashis K. Satpati [c], Simon Detriche [d], Zineb Mekhalif [d], Joseph Dalhalle [d]

[a] Department of Postgraduate Studies and Research in Chemistry, St. Joseph's College (Autonomous), Lalbagh Road, Bangalore 560 027, Karnataka, India
[b] Electrochemistry Research Group, Department of Chemistry, St. Joseph's College, Lalbagh Road, Bangalore 560 027, Karnataka, India
[c] Department of Analytical Chemistry, Bhabha Atomic Research Centre, Anushakthi Nagar, Trombay, Mumbai 400 094, Maharashtra, India
[d] Laboratoire de Chimie et d'Electrochimie des Surface, University of Namur, 61 Rue de Bruxelles, B-5000 Namur, Belgium

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ABSTRACT

Iron nanoparticles decorated multi-wall carbon nanotubes modified carbon paste electrode (Fe-MWCNTs/MCPE) was prepared by bulk-modification method. The electrochemical impedance spectroscopy (EIS) suggests least charge transfer resistance at the modified electrode. The electrochemical behavior of UA was studied in 0.1 M phosphate buffer solution (PBS) of pH 3.0 using cyclic voltammetry (CV) while differential pulse voltammetry (DPV) was used for quantification. The spectroelectrochemial study of oxidation of UA at Fe-MWCNTs/MCPE showed a decrease in the absorbance of two peaks with time, which are ascribed to π to π^* and n to π^* transitions. Under optimum condition, the DPV response offered two linear dynamic ranges for UA in the concentration range 7.0×10^{-8} M–1.0×10^{-6} M and 2.0×10^{-6} M–1.0×10^{-5} M with detection limit $(4.80 \pm 0.35) \times 10^{-8}$ M (S/N = 3). The practical analytical application of this sensor was successfully evaluated by determination of spiked UA in clinical samples, such as human blood serum and urine with good percentage recovery. The proposed electrochemical sensor offers a simple, reliable, rapid, reproducible and cost effective analysis of a quaternary mixture of biomolecules containing AA, DA, UA and Tyr which was free from mutual interferences.

1. Introduction

Uric acid (UA) is the end product of the metabolism of purine, which is the nitrogen-containing component that occurs in nucleic acids. In the human body, UA is present in blood serum and in urine [1]. For a healthy human being, the normal concentration of UA in blood serum is in the range of 0.24–0.52 mM while that in urine is 1.49–4.46 mM [2]. Abnormalities in UA levels in the urine and in blood serum leads to various diseases such as gout, arthritis [3], cardiovascular diseases [4], neurological diseases [5], hypertension and renal insufficiency [6,7]. Moreover, studies have shown that a high level of uric acid has been found to directly inhibit insulin signaling and induce insulin resistance [8]. A recent study has revealed that excessive uric acid levels have a correlation to hyperthymic and irritable temperaments [9]. Determination of UA in body fluids, urine and blood may thus be used as powerful markers for early diagnosis of such diseases [10]. Therefore, there is a need for the development of a better sensor for the determination of UA in biological samples.

Though there are several diverse methods for the determination of UA such as chemiluminescence [11], ion exchange column chromatography [12], enzymatic [13], high performance liquid chromatography [14], spectrophotometry [15] and spectrofluorometry [16], these techniques have certain disadvantages such as their being often time consuming, expensive and complex. Electrochemical methods for UA determination have certain advantages such as simple, short detection time, reproducibility and ease of handling [17–21]. Moreover, when a reduction in cost is desired, especially for self monitoring, electrochemical techniques are useful and may be adopted in the construction of portable electrochemical devices.

Electrochemical methods constitute very useful techniques in the field of biological analysis, especially with regard to the determination of molecules such as norepinephrine, acetaminophen, n-acetylcysteine,

* Corresponding author.
E-mail address: ronaldmasc2311@yahoo.co.in (R.J. Mascarenhas).

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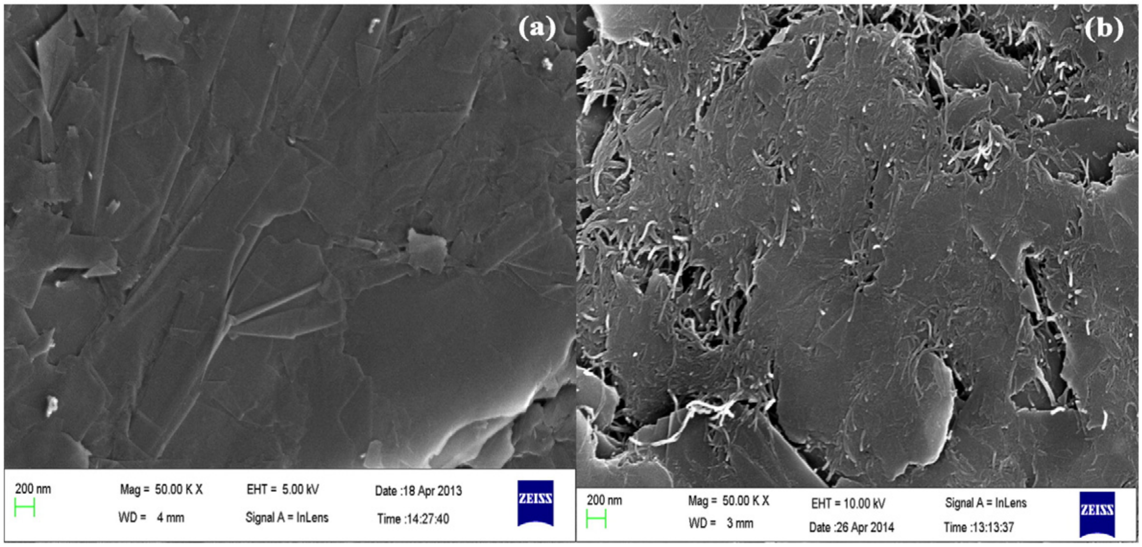

Fig. 1. FE-SEM images of (a) CPE and (b) Fe-MWCNTs/MCPE.

folic acid, epinephrine, uric acid, levodopa, carbidopa and isoproterenol while also being useful in environmental analysis — for example with regard to the determination of hydroxylamine in water samples [22–30].

L-Tyrosine (Tyr) is an important amino acid which is considered nonessential because the human body can make it from another amino acid called phenylalanine. In the human body, Tyr is used to make catecholamines. Tyr plays a crucial role in biological systems as it is a predecessor of hormones as well as of neurotransmitters such as thyroxin and DA respectively, in addition to other physiologically essential biomolecules [31]. Tyr is often added to food products and to pharmaceutical formulations [32]. Tyr is critical to mental and physical health as it is needed to produce catecholamines through an iron-containing enzyme called tyrosine hydroxylase.

DA is a vital neurotransmitter which belongs to a group of catecholamines and abnormalities in the metabolism of DA may cause brain diseases such as schizophrenia and Parkinsonism [33]. AA is an essential vitamin which has been used for the treatment of common cold, mental illness, cancer and AIDS [34]. AA is present in the mammalian brain along with DA. It also participates in several biological reactions [35]. Therefore, the simultaneous determination of these molecules is definitely desirable since they play an important role in fields such as analytical chemistry, neuro-chemistry, biomedicine, and diagnostic research.

The major difficulty in the electrochemical detection of UA at an unmodified electrode is the presence of interferences from co-existing molecules such as AA and DA which have oxidation potentials similar to that of UA [36]. This problem is overcome by the modification of the electrode using materials such as polymers [37–39], carbon based materials [40–42] and noble metal nanoparticle [43,44].

Carbon nanotubes are nanomaterials with properties such as extraordinary tensile strength, excellent electrical conductivity and high chemical stability [45]. These properties help carbon nanotubes find potential applications in the field of chemical and biological sensors [46–49]. Carbon nanotubes are basically categorized into two types: multi-wall carbon nanotubes (MWCNTs) [50] and single wall carbon nanotubes (SWCNTs) [51]. The unique electronic properties of carbon nanotubes show better electron transfer rates when used as electrode material and offer excellent prospects for development of miniaturized electronic devices. Metal nanoparticles possessing broad range of dimensions are expected to be endowed with size-dependent optical, magnetic, electronic and chemical properties appropriate for catalysts, optoelectronic devices, as well as for chemical and biosensor applications [52–54]. Iron nanoparticle/clusters have important properties — primarily, mechanical and magnetic properties — which have several applications such as in the domains of data storage, catalysis, magnetic fluids, biomedical applications, magnetic recording and media. They are also endowed with a high ratio of surface-atoms, which results in high catalytic activity [55–58].

CPE has been used as a working electrode for many biosensor applications because of its simple method of preparation, easy renewability of the surface, compatibility with various types of modifiers, cost effectiveness and, more importantly biocompatibility [59–61]. In our earlier studies, we have demonstrated how different electrode materials influence the electrochemical reaction rate, as well as the selectivity of electroactive species, by developing sensors using different modifiers in CPE matrix [62–69]. To the best of our knowledge, iron nanoparticles decorated MWCNTs have so far not been exploited for their potential applications as sensors. Therefore, in this paper, our focus was directed towards the preparation of iron nanoparticles decorated MWCNTs modified CPE so as to utilize the beneficial characteristics of the modifier for the sensitive, simultaneous determination of UA in the presence of interfering molecules such as AA, DA and coexisting biologically important molecule Tyr which is the precursor of DA. The spectroelectrochemical study of UA using MCPE is not reported in the extant literature. Hence Fe-MWCNTs/MCPE is employed to study the electrochemical reaction mechanism of UA at the solution electrode interface. Ultimately, driven by the need to make it relevant as well as reliable for practical applications, the sensor was applied in the sensitive determination of UA in real samples such as blood serum and urine without subjecting it to any preliminary treatment.

2. Experimental

2.1. Reagents

UA, Tyr (SRL), DA (Sigma), AA, $HClO_4$, H_3PO_4, KH_2PO_4 and NaOH pellets (all of analytical grade) were purchased from Merck and were used as such. All chemicals were purchased from Labsupplies (India) Pvt. Ltd., Bangalore. All aqueous solutions were prepared using ultra pure water (>18.2 MΩ cm) from Milli-Q Plus system (Millipore India Pvt. Ltd., Bangalore). Stock solutions of UA, AA, DA and Tyr (25 mM) were prepared using 0.1 M NaOH, ultra pure water, 0.1 M perchloric acid and 0.1 M NaOH respectively. 0.1 M Phosphate buffer solution of