Journal of Electroanalytical Chemistry 783 (2016) 167–175

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Simultaneous determination of ascorbic acid, dopamine, uric acid, tryptophan, and nitrite on a novel carbon electrode

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ARTICLE INFO

Article history:
Received 22 September 2016
Received in revised form 10 November 2016
Accepted 12 November 2016
Available online 15 November 2016

Keywords:
Carbon electrode
Graphene nanosheet
Electrocatalytic response
Simultaneous determination
Biomolecules

ABSTRACT

A novel carbon electrode for simultaneous determination of ascorbic acid (AA), dopamine (DA), uric acid (UA), tryptophan (Trp), and nitrite (NO_2^-) was fabricated by chemical vapor deposition of carbon layers on a Ta wire. The carbon electrodes were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), cyclic voltammetry (CV), and differential pulse voltammetry (DPV). The carbon electrodes are composed of stacked graphene nanosheets. The carbon electrode exhibited excellent electro-catalytic activities, high selectivity and sensitivity toward the oxidation of AA, DA, UA, Trp, and NO_2^- in pH 7.0 phosphate buffer solution. For AA, DA, UA, Trp, and NO_2^-, the corresponding DPV current signals have appeared as five well resolved oxidation peaks with peak potential differences of 204 mV (AA-DA), 152 mV (DA-UA), 312 mV (UA-Trp), and 128 mV (Trp-NO_2^-). For simultaneous determination, the linear responses for AA, DA, UA, Trp, and NO_2^- were obtained in concentration ranges of 6 to 1500, 0.4 to 100, 1 to 250, 0.4 to 100, and 6 to 1500 μM with detection limits of 5 μM, 0.2 μM, 0.8 μM, 0.4 μM, and 3 μM, respectively. The carbon electrode was proved to be applicable for the determination of the above analytes in serum samples.

1. Introduction

The ascorbic acid (AA), dopamine (DA), uric acid (UA), tryptophan (Trp), and nitrite (NO_2^-) usually coexist in biological matrixes, and they are crucial molecules for physiological processes in human metabolism [1–3]. AA is known for its antioxidant properties and is a critical human vitamin. It has been used to prevent and treat scurvy, the common cold, mental illness, cancer, and AIDS [4,5]. DA is an important neurotransmitter in the mammalian central nervous system. Abnormal levels of DA will lead to neurological disorders such as Parkinsonism and schizophrenia [6–8]. UA is the primary end product of purine metabolism. The extreme abnormalities of UA levels will lead to some diseases such as gout and hyperuricemia [9]. Nitrite (NO_2^-) is used for the curing of meat because it prevents bacterial growth, and it is a color and flavor enhancer [10]. After ingestion, NO_2^- is a potential hazard to human health. When NO_2^- is present at abnormal concentration in blood, it is will lead to methemoglobinemia [11]. Many papers have reported that NO is a neurotransmitter or a neuromodulator. The NO can be oxidized to NO_2^- in the central nervous system. Some groups also have reported that NO can affect the release of DA [12,13]. Trp is an essential amino acid required for the biosynthesis of proteins. It is important in nitrogen balance and maintenance of muscle mass and body weight in humans [14–16]. Therefore, the simultaneous determination of AA, DA, UA, Trp, and NO_2^- is important for studies of physiological function and disease diagnosis.

In the past few decades, electrochemical techniques have received considerable interest for the detection of biomolecules and environmental pollutants because of their high sensitivity, rapid response, simple operation, and low costs [17–22]. In recent years, many researchers have detected AA, DA, UA, Trp, and NO_2^- as well as other electrically active materials [23–25]. AA, DA and UA were simultaneously determined with a hemin-functionalized graphene oxide/glassy carbon electrode (GCE) [26], MgO nanobelts/GCE [27], Au@Pd-reduced graphene oxide/GCE [28], nitrogen doped porous carbon nanopolyhedra/GCE [29], and amino-group functionalized mesoporous Fe_3O_4-graphene sheets/GCE [30]. The DA, UA, and Trp were also simultaneously determined with ruthenium red-MWCNT/F-doped SnO_2 thin films [31]. The AA, DA, UA and NO_2^- were simultaneously determined with CTAB-functionalized graphene oxide/multi-walled carbon nanotube (MWCNT)/GCE [32], lanthanum-MWCNT/GCE [33], gold nanoclusters/poly(3-amino-5-mercapto-1,2,4-triazole)/GCE [34], and chloro[3,7,12,17-tetramethyl-8,13–divinylporphyrin-2,18-dipropanoato(2-)]iron(III)/MWCNTs/GCE [1]. The AA, DA, UA, and Trp were simultaneously determined with silver nanoparticles/reduced graphene oxide (RGO)/GCE [35], Fe-mesoporous polyaniline-Nafion/GCE [36], gold nanoparticles/overoxidized-polyimidazole/GCE [37], and graphene sheets with 3,4,9,10-

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http://dx.doi.org/10.1016/j.jelechem.2016.11.026
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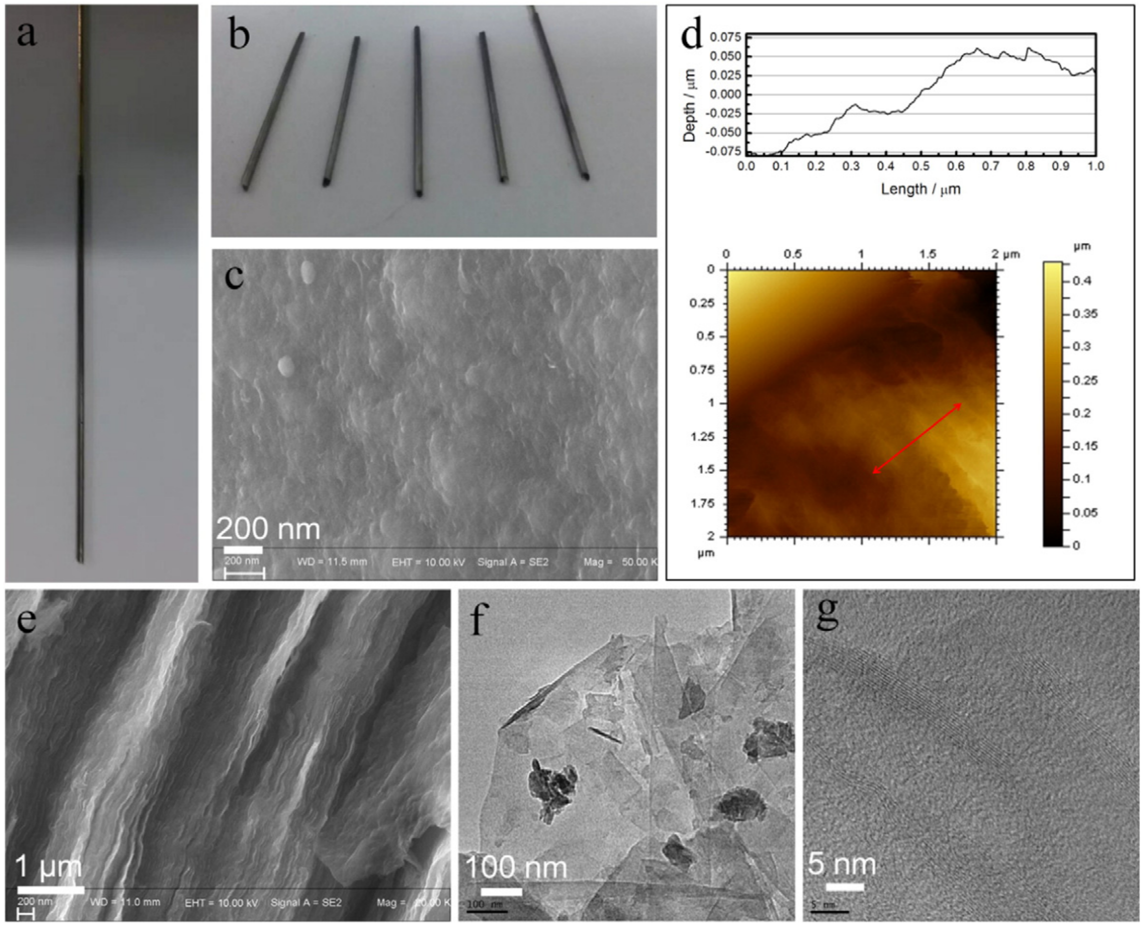

Fig. 1. (a) Carbon electrode. (b) Carbon electrodes after extracting the Ta wire. (c) Surface SEM image of a carbon electrode. (d) AFM image and line profile of the carbon layer. (e) Cross-section SEM image of carbon electrode. (f) TEM image and (g) HRTEM image of the graphene nanosheets.

perylentetracarboxylic acid (PTCA)/GCE [38]. However, the oxidation potentials of these electro-active species are too close and more difficult to separate on common electrodes such as bare GCE. This results in poor sensitivity and selectivity. Although various materials have been used to modify electrodes to solve this problem, developing a facile method to simultaneously measure AA, DA, UA, Trp, and nitrite remains a challenge. To the best of our knowledge, no report has yet described the simultaneous determination of AA, DA, UA, Trp, and NO_2^-.

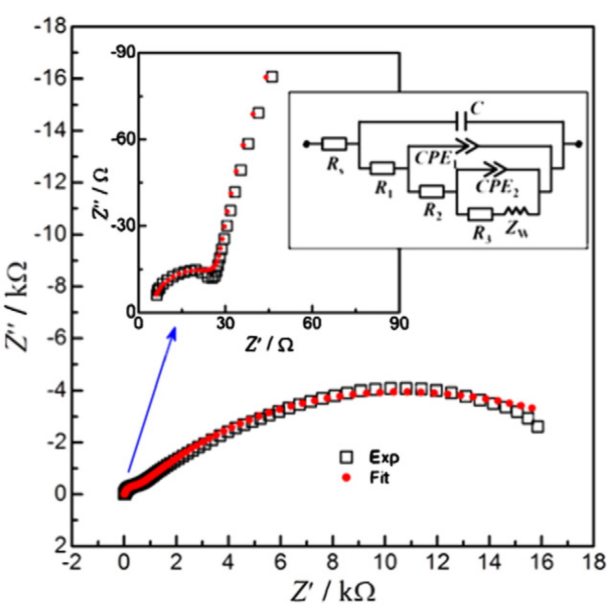

Fig. 2. Nyquist diagram of the carbon electrode in 0.1 M KCl containing 5.0 mM $K_3Fe(CN_6)$ and 5.0 mM $K_4Fe(CN)_6$. Insets: enlarged high-frequency region and equivalent circuit.

Recently, graphene has attracted much attention in fabricating electrochemical biosensors because of its unique properties such as exceptional thermal and mechanical properties, large surface-to-volume ratio and high electrical conductivity [39–45]. Graphene-modified electrodes offer high sensitivity and selectivity but are easily removed from the base electrode to markedly reduce the effective lifetime. When developing a carbon electrode which is composed of stacked graphene nanosheets, the performance and life expectancy of the electrodes is improved. Chemical vapor deposition (CVD) growth can produce large-area single- and few-layer graphene sheets [46]. Graphene grown by the CVD method exhibits high carrier mobility, very low sheet resistance, high optical transparency, and outstanding mechanical properties suggesting that it has high quality and great potential for applications of electrochemical devices.

In the present paper, graphene nanosheets were facilely deposited on Ta wire surface by CVD method. The carbon electrode was successfully employed in the simultaneous determination of AA, DA, UA, Trp, and NO_2^-. The attractive response performance of the carbon electrode served as a sensing electrode, and its potential merits are detailed.

2. Experimental

2.1. Reagents and materials

The AA, DA, UA, L-Trp, and nitrite were purchased from Sigma Aldrich (USA). Hexacyanoferrate (II) trihydrate ($K_4[Fe(CN)_6]\cdot 3H_2O$), disodium hydrogen phosphate (Na_2HPO_4), and sodium dihydrogen