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Comparison of electrochemical property between multiwalled carbon nanotubes and porous graphitized carbon monolith modified glassy carbon electrode for the simultaneous determination of ascorbic acid and uric acid

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ABSTRACT

In this work, glassy carbon electrode (GCE) was modified with porous graphitized carbon monolith (CM) as a new nanomaterials and multi-walled carbon nanotubes (MWCNTs) for simultaneous determination of ascorbic acid (AA) and uric acid (UA). Scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were employed for the surface analysis of the modified electrodes. In this simultaneous detection, the electrochemical response of AA and UA on MWCNTs/GCE exhibited broad anodic peaks and were resolved into separated CV peaks at +45 mV and +254 mV, respectively. In comparison, two well resolved peaks of CM/GCE were obtained at -39 mV and +233 mV with flat base-lines for oxidation of AA and UA, respectively. Under the optimum conditions, the performance of porous graphitized carbon monolith were superior to MWCNTs modified glassy carbon electrode. For CM/GCE, the oxidation peak current was linearly dependent on AA and UA concentration in the range 0.195–4.04 mM and 0.094–1.90 mM, with the correlation coefficients (R^2) greater than 0.997. Detection limits ($S/N = 3$) were found 0.39 μM and 0.15 μM for AA and UA, respectively. The recoveries of the AA and UA from spiked human serum were 76.0–94.2%. In addition, the CM/GCE showed high sensitivity, good reproducibility and long-time stability at least 1 month without significant loss of electrochemical signal.

1. Introduction

Ascorbic acid [1] is well known for its antioxidant properties. It plays an important role in several enzymatic reactions and as the defense against oxidative stress [2], acting as a radical scavenger in different metabolic processes that involve redox mechanisms [3]. In addition, it is also used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS [4,5].

Uric acid (2,6,8-trihydroxypurine, UA), is the primary end product of purine metabolism. Abnormal levels of UA in human plasma are symptoms of several diseases, such as gout, hyperuricemia and Lesch-Nyan disease [6,7].

AA and UA usually coexist in biological samples. Electrochemical determination shows overlapping oxidation peaks at solid electrodes. Therefore, simultaneous determination of these compounds is a special interest in sensor system. A major problem of these determinations is a surface fouling thus results in poor reproducibility.

A number of techniques are available for the determination of AA and UA including spectrophotometry [8,9] and chromatography [10,11]. These techniques are time consuming requiring the use of organic solvents and are relatively expensive. Electroanalytical techniques overcome many of these disadvantages with additional benefits of low detection sensitivity, reproducibility and ease of miniaturization. Various modified glassy carbon electrodes (GCE)

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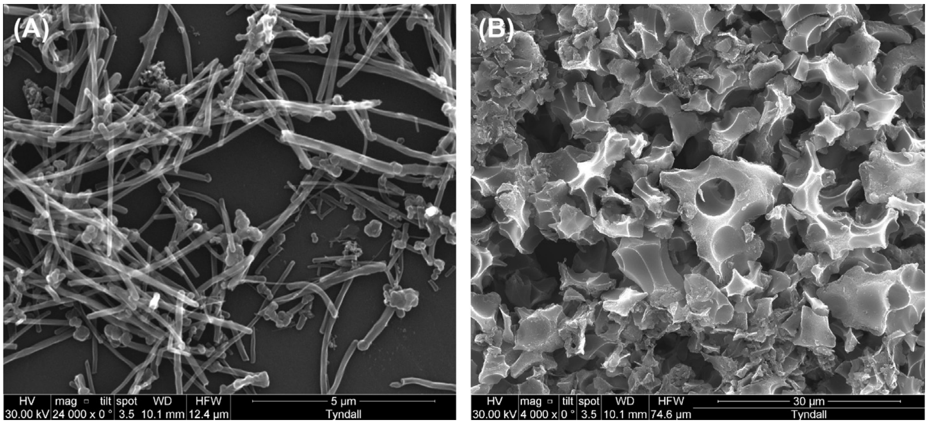

Fig. 1. The SEM images (A) of MWCNTs and (B) of CM.

have been designed for simultaneous determination by voltammetric techniques for example, modified GCE with carbon nanotubes [12–14], palladium nanoparticle–load carbon nanofibers modified electrode [15], single-walled carbon nanotube modified electrode [16], and multiwalled carbon nanotube modified ormosil composite [17]. It can be seen that, nanomaterials have been used as a modifier in chemically modified electrode for analysis of drug molecules [18–20], metal ions [21,22] and biomolecular compound such as guanine, adenine and thymine [23–25].

Carbon nanotubes have emerged as one kind of porous nanostructured material receiving considerable interest [26–28]. There are two classes of nanotubes: single-walled carbon nanotubes (SWCMTs) and multi-walled carbon nanotubes (MWCNTs). The latter multi-walled carbon nanotubes (MWCNTs) are especially important nanomaterials and modifiers due to their ability to promote electron transfer in electrochemical reactions, improve sensitivity and chemical inertness when used as electrode materials in electrochemical devices [29].

Furthermore, porous graphitized carbon monolith (CM) is a new class of carbon materials with interesting physicochemical properties [30] and its high surface area makes it a potential material for biomolecules immobilization and biosensing applications. To our knowledge, the CM modified electrodes have not yet been reported or compared with MWCNTs for the determination of ascorbic acid (AA) and uric acid (UA) concentration.

The novelty of this paper lies in the use and comparison of new nanomaterial modified surfaces on glassy carbon electrodes using porous graphitized carbon monolith and MWCNTs for simultaneous determination of AA and UA in a mixed solution. Scanning electron microscopy (SEM) was used to study the modified surfaces. The electrochemical properties of the modified electrodes were investigated by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and amperometry. It was found that the porous graphitized carbon monolith modified glassy carbon electrode has potential to be used for sensitive and simultaneous voltammetric determination of AA and UA in a mixed solution. In addition, the electroanalytical performance of the porous graphitized carbon monolith were found to be superior to the MWCNTs modified glassy carbon electrode.

2. Experimental

2.1. Reagents

All the reagents used were of analytical grades and aqueous solutions were prepared with deionized water (Millipore, Ireland). Ascorbic acid (AA), uric acid (UA), NaOH, KH_2PO_4, K_2HPO_4, H_3PO_4, $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$ and KCl were all obtained from Sigma–Aldrich (Dublin, Ireland).

Stock solution of AA (0.2453 M) was prepared daily by dissolving a suitable amount of the reagent in water. UA solution (0.0235 M) was prepared by dissolution in a small volume of 0.1 M NaOH solution and subsequent dilution with water.

Phosphate-buffered solutions of different pH were prepared by mixing solutions of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4 at different ratios. The solution pH was adjusted by adding 1.0 M H_3PO_4 solution where necessary.

Multi-walled carbon nanotubes (MWCNTs) with a diameter of 110–170 nm were purchased from Sigma–Aldrich (Dublin, Ireland). The detailed synthesis and characterization of the CM can be found in Ref. [30].

2.2. Apparatus

The electrochemical measurements were performed using a CHI 1040A electrochemical workstation (CH Instruments, Austin, TX) at room temperature. A three-electrode system consisted of a glassy carbon working electrode (GCE, 3 mm diameter) modified with MWCNTs and CM dispersed in DMF were used as working electrodes, a Ag/AgCl (3 M NaCl) reference electrode (BAS, West Layette, IN), and a platinum wire counter electrode (Sigma–Aldrich, Dublin, Ireland). The convection transport during the amperometric determination was performed with magnetic stirring.

The surface morphology of the modified electrodes was examined by a JEOL 2100 High Resolution Scanning Electron Microscope (SEM, UK). A Hitachi scanning electron microscope (SEM, S-2600N, Tokyo, Japan) equipped with an Energy Dispersive X-ray (EDX) spectrometer, LN2-free analytical silicon drift detector (INCA x-act, Oxford Instruments, UK) was used for topographical analysis of the electrodes.

2.3. Preparation of GCE modified with MWCNTs and CM dispersion

GCEs were polished with 0.3 and 0.05 µm alumina slurry and then sonicated in water first for 5 min and then in ethanol for another 5 min.

For MWCNTs and CM, a mass of 1 mg MWCNTs and 5 mg CM were dispersed in 1 mL N,N-dimethylformamide (DMF), then ultrasonicated for 30 min and for 16 h respectively, until a homogenous suspension of MWCNTs and CM was obtained.

Then, 4 µL of MWCNTs and CM dispersions were carefully dropped on the top of polished GCE, allowing the solvent to evaporate at room temperature. The electrodes so obtained constitute the MWCNTs/GCE and CM/GCE, respectively. Finally, modified