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Electrodeposited nanoporous ruthenium oxide for simultaneous quantification of ascorbic acid and uric acid using chronoamperometry at two different potentials

Yejin Yang [1], Ara Jo [1], Youngmi Lee *, Chongmok Lee *

Department of Chemistry & Nano Science, Ewha Womans University, Seoul, 03760, South Korea

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ABSTRACT

Nanoporous ruthenium dioxide (RuO_2) was simply prepared by electrodeposition with potential cycling in $RuCl_3$ solution in the presence of reverse micelles of Triton X-100. The electrodeposited RuO_2 on Au substrate electrode showed high electroactivity for the oxidations of L-ascorbic acid (AA) and uric acid (UA), while AA oxidation started from a less positive potential compared to UA oxidation. Simultaneous quantitative analysis of AA and UA was successfully carried out via chronoamperometric measurements at two different applied potentials using RuO_2 deposited electrode. Due to the oxidation potential difference between AA and UA at RuO_2 electrode, only AA was oxidized at an applied potential of 0.20 V vs. SCE and both AA and UA were oxidized at 0.32 V vs. SCE. AA concentration was determined from the current measured at 0.20 V; and then UA concentration was estimated from the current measured at 0.32 V using the predetermined AA concentration. Electrodeposited nanoporous RuO_2 electrode exhibited current responses linearly proportional to AA and UA concentrations in a wide concentration range (0–1 mM) and fast response time ($\leq$1 s). The current sensitivities were $342.8 \pm 26.3\ \mu A\ mM^{-1}\ cm^{-2}$ for AA at 0.20 V; $377.8 \pm 18.4\ \mu A\ mM^{-1}\ cm^{-2}$ for AA at 0.32 V; and $344.2 \pm 11.6\ \mu A\ mM^{-1}\ cm^{-2}$ for UA at 0.32 V. In addition, RuO_2 electrode showed a high selectivity over interferents such as 4-acetamidophenol (AP), dopamine (DA), and glucose. Reasonable stability and repeatability of RuO_2 electrode were also confirmed. Selective quantification of AA and UA in an arbitrary mixture and a human urine sample demonstrated that RuO_2 electrode has practical utility in real sample analysis with satisfactory results.

1. Introduction

There is an increasing demand for biosensing platforms with low-costs and feasible application to human health. Several methods such as chemiluminescence [1,2], liquid chromatography [3], electrophoresis [4], fluorescence [5] and electrochemical technique [6–8] have been reported for biosensing. Among them, electrochemical technique is regarded as one of the most practical methods because the sample preparation is relatively simple and fast determination of analytes can be obtained with high sensitivity and low cost [9–11]. Especially, an amperometic measurement in which current is monitored at a constant applied potential would be a straightforward electrochemical method allowing fast analysis of analytes with a simple instrumentation. Recently, many nanomaterials have been synthesized in various methods. These nanomaterials having enlarged active surface areas have been used as good electrode materials for amperometric biosensors of which activity and sensitivity are highly enhanced by large surface area of the electrode materials [6,12].

Ascorbic acid (AA) is commonly known as vitamin C. The major role of AA is an anti-oxidant activity protecting cells from toxicity of reactive oxygen species. In medical aspect, AA is related to nausea, vomiting, diarrhea, and kidney stones [13] and widely used to treat infertility, mental illness, caner, and AIDS [14]. Uric acid (UA) is an end product of purine metabolism and the normal concentrations of UA for a healthy person are 240–520 μM in serum and 1.5–10 mM in urine [15,16]. The high level of UA in body fluids may cause diseases such as gout, cardiovascular disease, kidney stones, and some metabolic syndromes, and therefore determination of UA in human urine is important to notice the symptom of disease [17–20]. For these reasons, quantitative and selective analysis of AA and UA in biological samples is an important part of biological and clinical researches.

* Corresponding authors.
E-mail addresses: youngmilee@ewha.ac.kr (Y. Lee), cmlee@ewha.ac.kr (C. Lee).
[1] Authors equally contributed to this work.

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A few recent studies have dealt with voltammetric measurements for detection of AA and UA [21–23]. In fact, simultaneous quantification of AA and UA in their coexisting condition has been relied on voltammetry. Regardless of the advantages over voltammetry such as fast/straightforward analysis and simple instrumentation, amperometry in constant potential mode has not been reported for concurrent determination of AA and UA within the limit of our knowledge. In this study, we demonstrate amperometry with a constant applied potential to quantify both AA and UA concentrations using nanoporous ruthenium dioxide (RuO_2) film prepared with electrodeposition in a reverse micelle solution (Triton X-100/water). RuO_2 has been considered to be a good electrode material in various applications due to the high metallic conductivity and thermodynamic stability [24,25]. RuO_2 has been reported to be highly stable at physiological pH (~pH 7.4) even in anodic condition [26] and therefore RuO_2 is an attractive candidate for electrode materials in electrochemical sensing of biological species. Simple amperometric measurements at two different applied potentials give information about the concentrations of AA and UA. This report is the first study in which both AA and UA are amperometically detected using ruthenium-containing electrode materials. The contents of AA and UA were successfully analyzed in a real biological sample (human urine) without cross-interference between AA and UA which is a main drawback in the simultaneous determination.

2. Experimental methods

2.1. Reagents

Ruthenium chloride hydrate ($RuCl_3{\cdot}xH_2O$), Triton X-100, sodium chloride (NaCl), sodium dihydrogen phosphate (NaH_2PO_4), sodium hydrogen phosphate (Na_2HPO_4), L-ascorbic acid (AA), uric acid (UA), 4-acetamidophenol (AP), D-(+)-glucose and dopamine hydrochloride (DA) were supplied from Sigma-Aldrich (St. Louis, MO, USA, http://www.sigmaaldrich.com). Phosphate buffer solution (PBS, pH 7.4) was prepared by mixing 0.02 M NaH_2PO_4 and 0.08 M Na_2HPO_4. Using this PBS as a solvent, stock solutions of L-ascorbic acid (AA), uric acid (UA), 4-acetamidophenol (AP), D-(+)-glucose, and dopamine hydrochloride (DA) were prepared. All of the materials were of analytical grade and prepared without further purification.

2.2. Preparation of electroplated RuO_2 electrode

Before the electrodeposition of RuO_2, an Au disk electrode (Bioanalytical Systems, Inc. http://www.basinc.com) was wet-polished on a microcloth pad (Buehler) with 0.3 μm alumina slurries. To remove the alumina residue, the electrode was sonicated in ethanol and distilled water for 10 min. RuO_2 films were formed with a slightly modified method from previous reports where nanoporous Pt film was electrodeposited in reverse micelle phase solution [27,28]. A deposition solution for RuO_2 film formation was a mixture of $RuCl_3{\cdot}xH_2O$, Triton X-100 and 0.3 M NaCl aqueous solution (5:50:45 wt%) which forms reverse micelle phase. Au disk electrode (diameter, 1.6 mm) was used for cyclic voltammetry (CV) and amperometry, and Au rotating disk electrode (diameter, 3 mm) was used for linear sweep voltammetry (LSV). The electroplating of RuO_2 was performed in the prepared deposition solution at 50 °C by CV with scanning potential from 0.0 to −0.8 V (vs. SCE) at a scan rate of 0.05 V s^{-1} for 4 cycles. After the deposition, to remove any remaining Triton X-100, the electrode was immersed and rinsed in distilled water (50 °C) for 3 times and electrochemically cleaned in 0.1 M H_2SO_4 solution by scanning potential from 0.0 to 1.5 V (vs. SCE) for 2 cycles at a scan rate of 0.1 V s^{-1}.

2.3. Apparatus and measurements

The images of as deposited RuO_2 film surface were obtained by field emission scanning electron microscopy (FE-SEM, Jeol JSM-6700F, http://www.jeol.com) and high-resolution transmission electron microscopy (HR-TEM, Jeol JEM-2100F, 200 kV). The composition of RuO_2 was studied by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Theta Probe AR-XPS System, 1486.6 eV, http://www.thermofisher.com) with monochromated Al Kα photons.

Electrochemical measurements were carried out using RDE-1 (Bioanalytical Systems, Inc.) and CHI 705 workstation (CH Instruments, http://www.chinstruments.com) with a three-compartment cell system consisting of a Pt wire as the auxiliary electrode, the RuO_2-modified Au electrode as the working electrode, and a saturated calomel electrode (SCE) as the reference electrode. All electrochemical measurements were performed in a Faraday cage to increase the signal-to-noise ratio and all potential values in this paper were presented with respect to SCE.

LSV experiments were performed by scanning potential from −0.4 to 0.6 V with a scan rate of 10 mV s^{-1} and a rotating speed of 1600 rpm. Chronoamperometric measurements were carried out at 0.20 and 0.32 V (vs. SCE) with continuous stirring of the solutions. All electrochemical experiments were conducted in a 0.1 M PBS of pH 7.4.

3. Results and discussion

3.1. Electrodeposition and characterization of RuO_2

The electrochemical deposition solution for RuO_2 was composed of Ru precursor ($RuCl_3{\cdot}xH_2O$), Triton X-100 and NaCl aqueous solution. Triton X-100 is a nonionic surfactant and the binary mixture of Triton X-100 and water becomes an isotropic solution phase above 30 °C [29]. 50 wt% of Triton X-100 is a sufficient concentration to produce reverse micelle (L_2) phase at 40 °C [28]. This reverse micelle solution was reported as an effective medium for electroplating Pt films having a nanoporous structure [28]. In current study, RuO_2 was electrodeposited on a bare Au disk electrode in L_2 solution. The RuO_2 deposition was simply recognized with the observation of the electrode surface color change from gold to black. The surface morphology of electroplated RuO_2 films was characterized by FE-SEM. Fig. 1a shows an overall structure of RuO_2 film that was seen porous and quite uniformly deposited on the surface of the Au substrate electrode. In Fig. 1b, the SEM image with a higher magnification exhibits that the mean diameter of apparent particles was 150 ± 21.1 nm for 55 particles analyzed. Thickness of RuO_2 layer was 4.9 (± 0.64, n = 20) μm which was determined with SEM image (Fig. 1c). From the TEM image (Fig. 1d), it was observable that the apparent RuO_2 particle consisted of many smaller nanoparticles of which mean diameter was 1.7 ± 0.7 nm (n = 55). This result indicates that RuO_2 film has a highly porous morphology which is related to electrocatalytic activity of the electrode [30].

To estimate the electrode surface area we used Cu underpotential deposition (UPD) according to the literature [31] (Fig. S1). After measuring the area of the stripping peak we obtained the real surface area (RSA) of 1.07 cm^2 using conversion factor of 0.42 mC cm^{-2}. Geometric surface area (GSA) was obtained as our previous report [32]. Then the roughness factor, ratio of RSA to GSA, was calculated to be 37.8.

In addition, XPS analysis (Fig. 2) was performed to investigate the chemical state of Ru in the deposited film. The XPS spectrum for Ru (3p) range shows two peaks at 484.2 and 462.3 eV of binding energy, consistent with the ones of rutile RuO_2 fabricated with