Electrochimica Acta 177 (2015) 118–127

Contents lists available at ScienceDirect

Electrochimica Acta

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

Electrodeposition of platinum nanosheets on C_{60} decorated glassy carbon electrode as a stable electrochemical biosensor for simultaneous detection of ascorbic acid, dopamine and uric acid

Xuan Zhang *, Li-Xia Ma, Yi-Chi Zhang

College of Chemistry, Chemical Engineering & Biotechnology, Donghua University, Shanghai 201620, China

ARTICLE INFO

Article history:
Received 12 January 2015
Accepted 31 January 2015
Available online 2 February 2015

Keywords:
Platinum nanosheets electrocatalyst
Fullerene
Ascorbic acid
Dopamine
Uric acid

ABSTRACT

Platinum nanosheets (Pt NSs) were fabricated on fullerene (C_{60}) decorated glassy carbon electrode (GCE) (denoted as Pt NSs/C_{60}/GCE) through a simple potentiostatic deposition method. In the coexistence of ascorbic acid (AA), dopamine (DA) and uric acid (UA), the as-prepared Pt NSs/C_{60}/GCE electrode exhibited three well-resolved voltammetric peaks ($\Delta E_{AA-DA} = 176$ mV, $\Delta E_{DA-UA} = 132$ mV, $\Delta E_{AA-UA} = 308$ mV) in the differential pulse voltammetry (DPV) measurements, allowing a simultaneous detection of these biomolecules. There are linear relationships between current intensities and concentrations in the region of 10–1800 μM (AA), 0.5–211.5 μM (DA), and 9.5–1187 μM (UA), and the limits of detection (LOD) (S/N = 3) are down to 0.43 μM, 0.07 μM and 0.63 μM for AA, DA and UA, respectively. The as-prepared Pt NSs/C_{60}/GCE electrode displayed a good reproducibility and storage stability and was successfully used for detection of AA, DA and UA in real plasma and urine samples.

1. Introduction

Dopamine (DA), ascorbic acid (AA) and uric acid (UA) are very important biomolecules involved in many physiological processes. For example, DA, a crucial neurotransmitter, can adjust the function of central nervous and cardiovascular systems, and its abnormal level will lead to various neurological diseases such as schizophrenia, Alzheimer's, and Parkinson's disease [1,2]. AA, one of the essential vitamins known as vitamin C, is extensively used in food processing and pharmaceuticals due to its antioxidant peculiarity, and its deficiency may result in cataract, scurvy, atherosclerosis and other diseases [3,4]. UA, a primary end product of purine metabolism, has been known to associated to several diseases such as gout and hyperuricemia [5,6]. Usually these functional biomolecules are coexisted in physiological fluids at different concentration levels, where the normal concentrations of DA, AA and UA are reported to be 0.01–1 μM [7], ~100 μM [7], and 200–430 μM [6], respectively. Therefore, it is highly desired to develop sensitive, selective and simultaneous detection methods for these important biomolecules in a variety of fields including healthcare, biological analysis, clinical diagnostics and pathological researches.

Due to DA, UA and AA are electroactive, electrochemical technique gained particular attention because of its advantages of rapid response, high sensitivity and selectivity, easy operation in vivo [8,9]. Nevertheless, it is difficult to voltammetrically resolve DA, AA and UA at conventional bare electrodes due to their very close oxidation potential [7]. To fulfill the demand of simultaneous determination, the electrode materials must be capable of well separating oxidation peaks of analytes. As a consequence, various modified electrodes have recently been employed to design and fabricate electrochemical biosensors, particularly based on nanometerials such as metal nanoparticles (NP) and carbon nanomaterials [10]. Special attention has been paid on noble metal nanoparticles (Pt, Au, etc.) due to their morphology-dependent electrocatalytic activities and mediated fast electron transfer in the surfaces of electrodes [10]. Regarding to the carbon nanomaterials, carbon nanotubes (CNTs) and graphene are mostly used in electrocatalysis due to their stable physical and chemical properties, large specific surface area, good conductivity, biocompatibility and synergistic effect on catalytic activity [10–29]. In contrast, fullerene (C_{60}), another allotropic nanocarbon, received less attention in electrocatalysis [30–32], even its potential application in novel electrode materials has been noted near two decades ago [33]. Recently, C_{60}-based electrode materials have been used for electrochemical detection of several small organic molecules with good performance [34–36]. For example, C_{60} hollow microspheres have showed high sensitivity for DA and UA with the detection

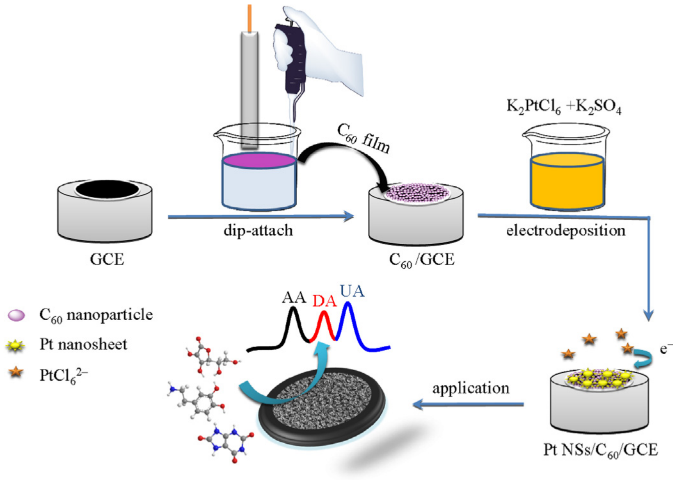
---

* Corresponding author. Tel.: +86 21 67792619.
E-mail address: xzhang@dhu.edu.cn (X. Zhang).

http://dx.doi.org/10.1016/j.electacta.2015.01.202
0013-4686/© 2015 Elsevier Ltd. All rights reserved.

limit of 0.1 nM and 1 μM respectively, revealing that nanostructured fullerene materials are more preferred for an electrode materials [34]. In addition, recent large advancement on self-assembly of fullerene will provide new opportunities for C_{60}-modified electrodes [37–39].

In this work, with taking advantage of our earlier work on self-assembly of fullerenes [40–42], we will present a study on electrochemically fabrication of Pt nanosheets (Pt NSs) on pristine C_{60} nanoparticles decorated glassy carbon electrode (GCE) (denoted as Pt NSs/C_{60}/GCE) and its biosensing performance. The as-prepared Pt NSs/C_{60}/GCE were successfully applied to simultaneous determination of AA, DA and UA with the well-resolved peak potentials, enhanced activity and stability compared to that on the bare GCE at physiological pH 7.0. The developed method was successfully used to detect AA, DA and UA in real plasma and urine samples, demonstrating that the Pt NSs/C_{60}/GCEs could serve as potential C_{60}-based electrode materials for a practical application in simultaneous determination of AA, DA and UA.



Scheme 1. Illustration of fabrication process of the Pt NSs/C_{60}/GCE electrode.

2. Experimental

2.1. Materials

C_{60} (Bucky USA, purity 99.5%), potassium chloroplatinate (Institute of Shanghai Fine Chemical Material, AR), ascorbic acid, dopamine and uric acid were all purchased from Acros (Beijing, China). Other chemicals were analytical grade and used as received. Phosphate buffer solutions (0.1 M PBS) were prepared by mixing 0.1 M K_2HPO_4 and 0.1 M KH_2PO_4 and the desired pH value was obtained by adjusting with 0.1 M HCl and 0.1 M NaOH. The stock solution of AA (0.3 M), DA (0.1 M) and UA (0.05 M) were prepared freshly in PBS buffer. Milli-Q water (18.2 MΩ cm) was used throughout the experiments.

2.2. Apparatus

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were finished on Hitachi S-4800 and JEOL JEM-2100F, respectively. Electrochemical measurements were carried out on CHI-660D electrochemical workstation (Chenhua, Shanghai) by using a conventional three-electrode system, including glassy carbon electrode (GCE) as working electrode, Pt wire as counter electrode, saturated calomel electrode (SCE) or Ag/AgCl electrode as reference electrode, respectively.

2.3. Preparation of the Pt NSs/C_{60}/GCE

Before fabricating the working electrode, C_{60} NPs were similarly prepared by a rapid reprecipitation method as described [43]. In brief, 3 mL C_{60} toluene solution (1.3 mg mL^{-1}) was slowly injected into 16 mL acetonitrile in a round-bottom flask under ultrasonication. After further 10 min ultrasonication, C_{60} nanoparticles were obtained by centrifuging, washing with ethanol and drying under vacuum at 40 °C.

The fabrication procedures for Pt NSs/C_{60}/GCE electrochemical biosensor were depicted in Scheme 1. Firstly, the glassy carbon electrode (GCE, 3.0 mm diameter) was sequentially polished with 0.3 and 0.05 μm alumina oxide powder, and ultrasonically rinsed with nitric acid (v: v, 1: 1), ethanol, and water, respectively. Then C_{60} decorated GCE (C_{60}/GCE) was fabricated by spreading C_{60} NPs dispersion in ethanol (1 mg mL^{-1}) onto the water surface to form a homogeneous C_{60} film (30 μg cm^{-2}), and transferring the formed compact C_{60} film onto GCE by a previously reported dip-attach method [34]. Finally, the Pt nanosheets were fabricated on C_{60}/GCE by a potentiostatic deposition method. Briefly, C_{60}/GCE was immersed into the solution of K_2PtCl_6 (5 mM) + K_2SO_4 (5 mM), and an electrodeposition was carried out at a constant potential of −0.35 V (vs. Ag/AgCl) [44]. The amount of Pt loading (34.7 μg cm^{-2} for a typical experiment) was determined from coulometry by assuming a 100% current utilization. Cyclic voltammetry (CV) scanning from −0.2 to 1.0 V (vs. SCE) was carried out in 0.5 M H_2SO_4 for 20 cycles with the scan rate of 50 mV s^{-1}, to get stable Pt NSs/C_{60}/GCE electrode materials for further biosensor application. For comparison, C_{60}/GCE and Pt NSs/GCE electrodes were also fabricated by following a similar procedure.

2.4. Electrochemical measurements

The CV and linear sweep voltammetry (LSV) were performed from −0.1 to 0.5 V, −0.3 to 0.6 V and −0.3 to 0.5 V (vs. SCE) with the scan rate of 50 mV s^{-1}, respectively. The differential pulse voltammetry (DPV) was carried out in 0.1 M PBS + 0.1 M KCl at pH 7.0 from −0.3 to 0.5 V (vs. SCE), with step potential of 4 mV, amplitude of 50 mV, pulse width of 0.2 s and pulse period of 0.5 s, respectively. The current-time curves were recorded in 0.1 M PBS + 0.1 M KCl at pH 7.0 under stirring at a constant potential of 0.3 V (for AA) and 0.4 V (for DA and UA). All electrochemical measurements were carried out under nitrogen atmosphere at room temperature.

3. Results and discussion

3.1. Characterization of electrodes

Fig. 1 showed the SEM and TEM images of C_{60}/GCE, Pt NSs/GCE, and Pt NSs/C_{60}/GCE electrodes. As shown in Fig. 1a, C_{60} nanoparticles near evenly attached on electrode with sizes of 50–300 nm in diameter. The Pt nanosheets were electrochemically fabricated by immersing C_{60}/GCE or bare GCE into the solution of K_2PtCl_6 and deposited at a constant potential of −0.35 V (vs. Ag/AgCl). The amounts of Pt loading were controlled by deposition time and 34.7 μg cm^{-2} was used for a typical experiment. It can be seen that the Pt NSs were successfully fabricated on bare GCE (Fig. 1b) and C_{60}/GCE (Fig. 1c). As shown in inset of Fig. 1c, the Pt NSs attached on the surface of C_{60} nanoparticles with sizes of a few hundred nanometers in diameter and ca. 10 nm in thickness. This was further confirmed by TEM (Fig. 1d). From the magnified HRTEM image (inset in Fig. 1d), Pt NSs showed an interplanar spacing of 0.226 nm, corresponding to the (111) lattice spacing of the fcc Pt crystal. That was further confirmed by a 6-fold