Journal of Electroanalytical Chemistry 770 (2016) 56–61

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Graphene coated by polydopamine/multi-walled carbon nanotubes modified electrode for highly selective detection of dopamine and uric acid in the presence of ascorbic acid

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ARTICLE INFO

Article history:
Received 21 January 2016
Received in revised form 22 March 2016
Accepted 24 March 2016
Available online 28 March 2016

Keywords:
Multi-walled carbon nanotubes
Polydopamine
Graphene
Dopamine
Uric acid

ABSTRACT

Graphene (GR) was easily coated with a reactive biopolymer polydopamine (Pdop), and the Pdop functionalized graphene (Pdop@GR) novel nanomaterial was obtained by dispersing graphene in a dopamine solution and mildly stirring at room temperature. Meanwhile, a new modified electrode based on three-dimensional (3D) Pdop@GR-multiwalled carbon nanotubes (MWCNTs) hybrid nanomaterial has been prepared and applied on the simultaneous electrochemical determination of dopamine (DA) and uric acid (UA). The interference test showed that the coexisted ascorbic acid (AA) had no electrochemical interference toward DA and UA. Under the optimum conditions, the calibration curves for DA and UA were obtained in the range of 7.0–297.0 μM and 20.0–320.0 μM with detection limits (S/N = 3) of 1.0×10^{-6} M and 1.5×10^{-5} M, respectively. Importantly, the proposed method offers promise for rapid, simple, selective and cost-effective analysis of small biomolecules.

1. Introduction

Dopamine (DA), the most significant among the class of catecholamines, plays important roles in control of central nervous system, cardiovascular, renal, and hormonal functions [1,2,3]. Serious diseases such as epilepsy, senile dementia, parkinsonism, schizophrenia and HIV infection may result by loss of DA containing neurons [4,5]. Uric acid (UA), the primary end-product of purine metabolism, is another important biomolecule presented in urine and blood [6,7]. Such as for DA, abnormal levels of UA are markers of several illnesses such as gout, Lesch–Nyhan syndrome, rhabdomyolysis, fanconi syndrome, renal disease and cardiovascular problems [8,9]. It is known to all, DA and UA, the electroactive species, usually coexist with AA in the central nervous system and both of them have very close oxidation potentials [10], so selective detection of DA and UA is still a challenge in biological analysis. Besides, many reported detection methods were complicated, expensive, and suffered from sensitivity as well as selectivity. To overcome these obstacles, a variety of materials have been used for the modification of electrode, such as N-doped carbon nanotubes functionalized with Fe_3O_4 nanoparticles [11], multiwalled carbon nanotubes/graphene oxide nanocomposite [12] and one-dimensional MgO nanostructures [13].

As a new member of the family of carbon-based nanomaterials, Graphene (GR), a single layer of sp^2-bonded carbon atoms extended to form a two-dimensional (2D) nanostructure, has attracted great attention recently due to its unique optical, catalytic, mechanical, thermal and electronic properties and large conjugated system [14,15]. Modifying the outer surface of GR is a promising pathway to manipulate them into solutions, hybrid assemblies and nano-devices [16]. Although a variety of chemical modification methods have been reported, many available methods have limitations for widespread practical use, such as the drastic reaction conditions and breakdown of GR sidewalls; the use of complex instrumentation and multistep procedures and the limitations of coating thickness [17]. Therefore, the development of convenient and versatile coating methods for GR remains a challenge for researchers.

Recently, the physical absorption methods has been shown to be an efficient method to modify GR. Especially, the bionics research finds that dopamine and other catechol compounds are able to self-polymerize in aqueous solution as well as perform well as binding agents for coating various substrates such as rocks, metals, polymers and wood [18,19]. So, in this work, we demonstrate a facile and novel approach toward GR directly by in situ spontaneous oxidative polymerization of dopamine at room temperature. This highly wrapping tendency supports the preference of nucleation at GR surfaces, due to the affinity between

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http://dx.doi.org/10.1016/j.jelechem.2016.03.038
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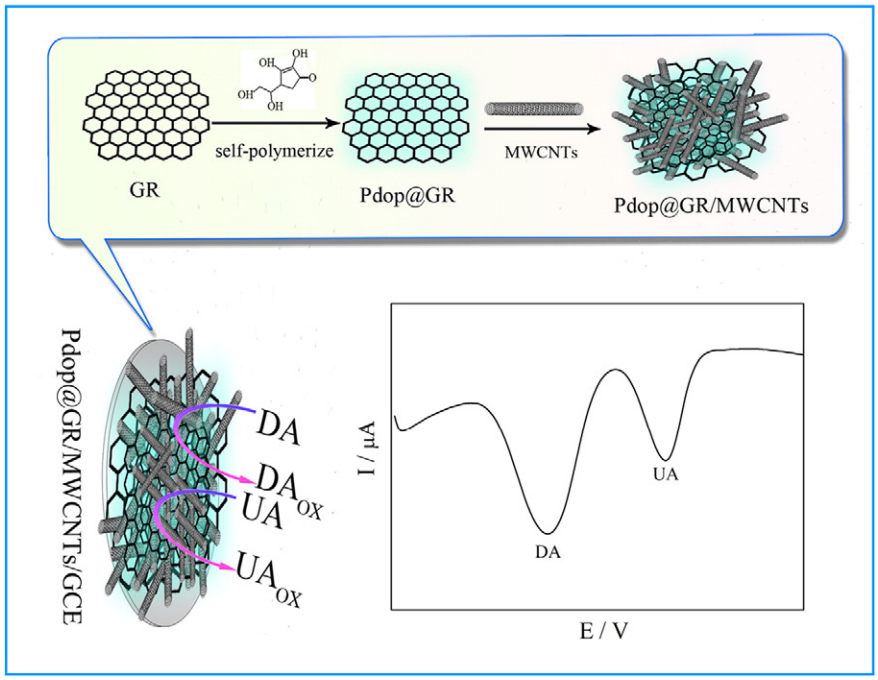

Scheme 1. The preparation process of the modified electrode.

the Pdop aromatic rings and GR sidewalls [16]. The novel hybrid nanomaterial polydopamine (Pdop) functionalized graphene (Pdop@GR) has many advantages, such as it promotes the water solubility and reduces the reunication of GR significantly and the resulted coating is a versatile platform for both functional organic adlayers and electroless metallization.

Herein, with the aim of simultaneous detection of DA and UA in the presence of AA, a facile and effective method using one-dimensional (1D) MWCNTs bridged two-dimensional (2D) Pdop@GR that form the three-dimensional (3D) network of Pdop@GR/MWCNTs nanocomposites as an electrode material was put forward. This strategy was provided with following advantages. On the one hand, the loose and porous 3D electrode structures, which not only increased the surface areas but also enhanced electrical conductivity. On the other hand, it also can result in fast electron transfer for sensor applications [20,21]. The results demonstrate that Pdop@GR/MWCNTs exhibits excellent catalytic activity and stability than Pdop@GR and MWCNTs catalyst for small biomolecules oxidation.

2. Materials and methods

2.1. Chemicals

Multiwalled carbon nanotubes, graphene and chitosan were purchased from Sigma Chemical Co. (St. Louis, Mo, USA). 2-amino-2-hydroxymethylpropane-1,3-diol (Tris), Uric acid (UA), ascorbic acid (AA) and dopamine (DA) were purchased from Chemical Reagent Co. (Chongqing, China). Phosphate buffer solutions (PBS) (0.1 M) at various pH were prepared using 0.1 M Na_2HPO_4 and 0.1 M KH_2PO_4. The supporting electrolyte was 0.1 M KCl. Double-distilled water was used throughout the experiments.

2.2. Apparatus

Cyclic voltammetric measurement and differential pulse voltammetry measurement experiments were performed with a CHI660E electrochemical work station (Shanghai Chenhua Instrument Co., China). A conventional three-electrode system was used with a modified glassy carbon electrode (GCE) as a working electrode, a saturated calomel reference electrode (SCE), and a platinum wire auxiliary electrode. The morphological characterization of the composite films was examined using a scanning electron microscope (SEM, S-4800, Hitachi, Japan), transmission electron microscopy (TEM, H600, Hitachi, Tokyo, Japan) and Fourier transform infrared (FTIR) spectroscopy. All measurements were carried out at room temperature.

2.3. Synthesis of graphene coated by polydopamine

Pdop@GR was synthesized according to the literature [16,17]. 10 mg GR, 20 mg dopamine and 12 mg 2-amino-2-hydroxymethylpropane-1,3-diol (Tris) were added into 10 mL deionized water, and dispersed by 1 min sonication in ice water bath. Subsequently, the suspension was stirred for 24 h at room temperature. Finally, the Pdop@GR was centrifuged and rinsed with water.

2.4. Preparation of modified electrodes

Before the modification, a bare glassy carbon electrode (GCE, diameter 4.0 mm) was successively polished to a mirror using 0.3 and 0.05 μm alumina slurry, then sonicated in ethanol and double-distilled water successively and dried at room temperature.

The Pdop@GR/MWCNT nanocomposites were prepared by dispersing 1 mg resulting MWCNTs and 1 mg Pdop@GR in 5 mL 0.5% chitosan (CS) solution, and then the mixture was treated for 1 h with ultrasonication for uniform dispersion. The Pdop@GR/MWCNTs/GCE was prepared by casting 20 μL of the above-mentioned suspension on the surface of the GCE. The preparation process of the modified electrode is shown in Scheme 1. The modified electrode was dried at room temperature and rinsed with distilled water prior to use.

For comparison, MWCNTs/GCE and Pdop@GR/GCE were also prepared under the same conditions.

3. Results and discussion

3.1. TEM and SEM of the modified electrode

The morphologies and microstructures of GR and Pdop@GR composite nanosheets were investigated using TEM. As shown in Fig. 1a, pure