



A novel free-standing CVD graphene platform electrode modified with AuPt hybrid nanoparticles and L-cysteine for the selective determination of epinephrine

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ABSTRACT

A novel free-standing graphene platform electrode (GPE) was prepared directly by transferring a chemical vapor deposition (CVD) graphene film from Cu foils to polyethylene terephthalate substrates with the aid of poly-methyl-methacrylate. AuPt hybrid nanoparticles (AuPtNPs) and L-cysteine (L-Cys) were electrodeposited simultaneously on the GPE. The successful formation of AuPtNPs-Cys/GPE was confirmed by scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), Raman microscope and X-ray diffraction (XRD). The electrocatalytic activity and enhanced conductivity of AuPtNPs-Cys/GPE sensor was evaluated by determining epinephrine (EP) in the presence of ascorbic acid (AA), dopamine (DA), uric acid (UA) in phosphate buffer solution by various techniques, including cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry. Further, the proposed sensor not only achieved the selective determination of EP, but also separated the voltammetric signals of AA, DA, EP and UA with potential differences of 266, 250 and 183 mV, respectively. The amperometric current response was increased linearly with increasing EP concentration in the range of 0.2 to 1000 μM with a detection limit of 0.0157 μM ($S/N = 3$). In addition, the as-obtained sensor delivered extraordinary stability, reproducibility, as well as high resistance to interferences, and was successfully utilized in determining real samples.

1. Introduction

Epinephrine (EP) is one of the most important neurotransmitters in mammalian central nervous systems, which exists in the nervous tissue and body fluids as large organic cations. This compound controls the nervous system in its performance for a series of biological reactions and nervous chemical processes [1]. It is an essential product to treat cardiac arrest, anaphylaxis, croup, and superficial bleeding. Abnormal levels of EP will trigger hypertension, multiple sclerosis, and Parkinson's disease. EP is often coexisting with ascorbic acid (AA), dopamine (DA) and uric acid (UA) in biological sample [2, 3]. Therefore, the sensitive, reliable, and selective determination of EP becomes an important topic in a variety of fields, such as biochemistry, diagnostics, healthcare and pathology research. Because EP is easily oxidized, electrochemical methods appear to be very suitable for its quantitative determination due to their unique performances of rapidity, simplicity and high sensitivity [4, 5].

Normally, the electrochemical behavior and electron transfer property of electrodes could be improved by the introduction of active

components [6, 7]. Metal nanoparticles have attracted much attention due to their unique properties and numerous potential applications [8, 9]. In particular, gold nanoparticles (AuNPs) and platinum nanoparticles (PtNPs) are widely known as the most promising bimetallic systems for various applications because of their high chemical stability, excellent catalytic ability, good biocompatibility, electrical conductivity and enhanced surface area [10–13]. In addition, many reports showed that L-cysteine (L-Cys) played an important role in forming self-assembled monolayers. The size and crystalline structure of metal nanoparticles could be controlled by using L-cysteine [14].

Graphene (GN), a two-dimensional planar sheet of sp^2 carbon atoms, has attracted growing scientific interest in fundamental as well as practical researches, such as fuel cells, super capacitors, batteries and electrochemical sensors etc., due to its high surface-to-volume ratio and transmission rate [15]. There are many fabrication methodologies that have emerged for graphene: chemical reduction of graphene oxides, mechanical cleavage, chemical vapor deposition (CVD) and so on [16, 17]. Up to now, graphene films on electrodes are usually obtained by drop-casting a graphene homogenous suspension solution, or by

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graphene oxide (GO) solution being first assembled on the electrodes, and then being electro-reduced into electrochemically reduced graphene oxide (ERGO). However, the ease of aggregation and high defect content always degrade the electrical properties [18, 19]. Therefore, a unique approach that can effectively overcome the above disadvantages should be developed.

Both the edge plane and basal plane of CVD graphene have brilliant electrocatalytic activity [20]. Moreover, free-standing electrodes have generated significant interest due to their potential to eliminate electrochemically inactive mass from metal foil current collectors. In our previous work, a linear graphene edge nanoelectrode based on the edge of CVD grown few-layer graphene was fabricated and its electrocatalytic behavior for some biological molecules was studied [21]. Cu nanoparticle was deposited on the edge plane of graphene nanoelectrode to construct a non-enzymatic glucose sensor [22]. We also transferred the basal plane of CVD graphene onto polyethylene terephthalate (PET) surface to establish a free-standing graphene platform electrode (GPE). A cobalt hexacyanoferrate modified GPE as a hydrogen peroxide sensor [23] and a poly-L-Cys/GPE as a DA and AA sensor [18] were fabricated. In the present work, Au and Pt nanoparticles were electrodeposited on GPE with additive L-cysteine to form an AuPtNPs-Cys/GPE. As a result, a new AuPtNPs-Cys/GPE sensor not only detecting EP individually but also determining AA, DA, EP, UA simultaneously was developed. To the best of our knowledge, there was no study on the application of CVD graphene and bi-metallic hybrid nanoparticles for detection of four species so far. Fig. 1 is the schematic illustration of fabrication, modification and analytical procedure of AuPtNPs-Cys/GPE. Electrocatalytic properties of the resultant AuPtNPs-Cys/GPE sensor were evaluated. As expected, the AuPtNPs-Cys/GPE sensor delivered superior electrocatalytic activity for the oxidation of EP with improved sensitivity and selectivity.

2. Experimental

2.1. Materials

The CVD few-layer graphene grown on copper foil were from Six Carbon Technology Co, Ltd. (Shenzhen, China). Poly (methyl methacrylate) (PMMA) was from Aladdin Industrial Corporation. HAuCl_4 , H_2PtCl_6 , L-cysteine were from BIO BASIC INC. And EP, AA, DA and UA were from Sigma-Aldrich Co. LLC. The phosphate buffer solution (PBS) was prepared by using 0.1 M KH_2PO_4 and Na_2HPO_4 . Human serum

samples were from the Hospital of Renmin University of China. All chemicals were of analytical-reagent grade. All aqueous solutions were prepared with Milli-Q water ($18.2 \text{ M}\Omega\text{-cm}$).

2.2. Preparation of GPE

The large-area high-quality few-layer CVD graphene grown on copper foils was transferred onto PET using the nondestructive polymer-mediated transfer technique [24, 25]. Firstly, 1% Poly(methyl methacrylate) (PMMA) (dissolved in anisole) solution was coated on the CVD graphene and dried at 120°C for 5 min. Secondly, the opposite side was polished to remove the unused graphene layer and the PMMA/graphene/copper sheet was immersed in FeCl_3 solution (1 M FeCl_3 + 0.1 M HCl) to etch away the copper substrate. Then the PMMA/graphene film was transferred to the ultrapure water and washed several times to remove the excess FeCl_3 . Subsequently, a PET sheet was used to support the PMMA/graphene and dried at room temperature overnight to ensure the graphene complete adhesion to the PET. Afterwards, the PMMA/graphene/PET was immersed in acetone for 24 h to remove the PMMA and dried at room temperature. Finally, the insulating tape was used to control the working area, which was $0.3 \text{ cm} \times 0.3 \text{ cm}$. The electrode was connected with the electrochemical instrument through the copper tape contact (Fig. 2).

2.3. Preparation of AuPtNPs-Cys/GPE and electrochemical measurements

The electrodeposition bi-metallic hybrid nanoparticles and L-cysteine were carried out using cyclic voltammetry. A GPE was immersed in 0.5 M H_2SO_4 containing 1 mM HAuCl_4 , 1 mM H_2PtCl_6 , and 0.1 mM L-cysteine, and was scanned in the potential range of -0.4 to 1.2 V at 50 mV/s for 30 cycles. Then the obtained electrode was dried in air.

All the electrochemical measurements including cyclic voltammetry (CV), differential pulse voltammograms (DPV), electrochemical impedance spectroscopy (EIS) and chronoamperometry were carried out on a CHI 660D workstation (Shanghai Chenhua, China) with a conventional three-electrode system at room temperature. The as-prepared AuPtNPs-Cys/GPE was used as the working electrode. A platinum electrode and an Ag/AgCl electrode served as the counter electrode and the reference electrode, respectively. Current density was calculated from the geometric surface area ($0.3 \text{ cm} \times 0.3 \text{ cm}$).

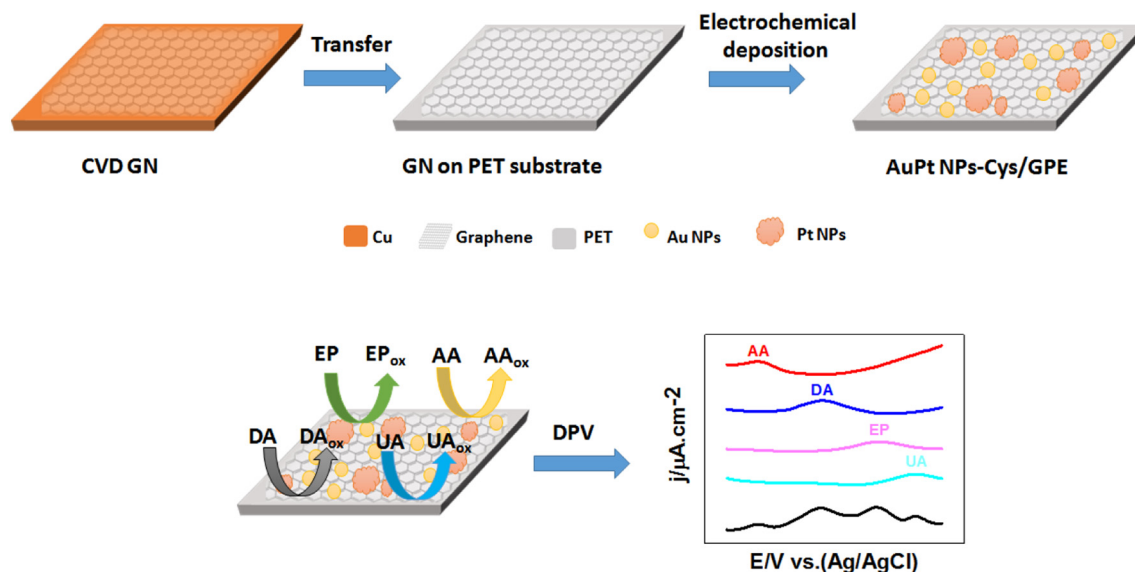


Fig. 1. Schematic representation of the fabrication, modification and analytical procedure of AuPtNPs-Cys/GPE for the simultaneous determination of EP in the presence of AA, DA and UA.

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