



Simultaneous determination of L-ascorbic acid, dopamine and uric acid with gold nanoparticles- β -cyclodextrin-graphene-modified electrode by square wave voltammetry

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ABSTRACT

Graphene decorated with gold nanoparticles (AuNPs- β -CD-Gra) has been synthesized by *in situ* thermal reduction of graphene oxide and HAuCl₄ with β -cyclodextrin (β -CD) under alkaline condition. The AuNPs- β -CD-Gra product was well characterized by infrared spectroscopy, X-ray powder diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, and selected area electron diffraction. This material was used to fabricate an AuNPs- β -CD-Gra-modified glassy carbon electrode (GCE) which showed excellent electro-oxidation of L-ascorbic acid (AA), dopamine (DA) and uric acid (UA) in 0.10 M NaH₂PO₄-HCl buffer solution (pH 2.0) by square wave voltammetry (SWV). Three well-resolved oxidation peaks of AA and DA and UA were obtained. The AuNPs- β -CD-Gra/GCE exhibits linear responses to AA, DA and UA in the ranges 30–2000, 0.5–150 and 0.5–60 μ M, respectively. The detection limits (based on $S/N=3$ and preconcentration time = 3.0 min) for AA, DA and UA are 10, 0.15 and 0.21 μ M, respectively. The AuNPs- β -CD-Gra/GCE has been successfully applied to determine UA in human urine with satisfactory results. Our work provides a simple, convenient and green route to synthesize AuNPs on Gra which is potentially useful in electroanalysis.

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Introduction

Nanomaterials have shown unique and special properties that are different from the bulk materials, originating from their quantum-scale dimensions [1]. So far gold [2–4], silver [5,6], platinum [7,8], and palladium [9] nanomaterials have attracted considerable interests and studies in the past two decades. Among these, gold nanomaterials have been successfully applied to fabricate various types of optical [10,11], electrochemical [12,13] sensors and biosensors [14], owing to their good conductivity, electrocatalytic ability, and biocompatibility. To our knowledge, a lot of useful materials like polymer [4,15], carbon nanotubes [13,16–18], graphene oxide (GO) and/or graphene (Gra) [19–31] have been used as substrates to assemble gold nanomaterials. In many of the

developed assemble strategies of gold nanomaterials, GO or Gra has received much attention, attributing to its specific nanostructure and ability to enhance the performance of nanocomposites. Tuan et al. [19] immobilized gold nanoparticles (AuNPs) on GO sheet via an amidation reaction. Mao et al. [23] directly assembled AuNPs-antibody conjugates on thermally reduced GO sheet to form a field-effect transistor biosensor which shows high sensitivity and selectivity to specific proteins. Muszynski et al. [24] explored a solution-based approach to anchor AuNPs on octadecylamine functionalized Gra and the hybrid material is very useful for surface plasmon application. Liu et al. [31] developed a co-electrodeposition route to synthesize Gra-Au nanocomposite which shows potential application for electroanalysis. Malola et al. [22] used density-functional theory to confirm that AuNPs could be in-plane adsorbed on Gra. Since this AuNPs-Gra hybrid material exhibits favorable electrochemical properties, it is worth to explore its applications in various fields.

L-Ascorbic acid (AA), a soluble vitamin, is an essential nutrient for humans. In living organisms, AA is an antioxidant which can protect the body against oxidative stress [32]. Dopamine (DA) is a catecholamine neurotransmitter which plays an important physiological role as an extracellular chemical messenger. Uric

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acid (UA) is a relatively water-insoluble end product of purine metabolism in humans and is excreted *via* urine. UA also coexists with AA and DA in biological fluids such as blood and urine. An abnormally high level of UA (DA and/or AA) is usually a symptom of illness. Therefore, simultaneous determination of these compounds is of particular importance [33]. Since these compounds show voltammetric responses on traditional bare electrodes (*e.g.*, glassy carbon electrode) at very close working potentials, it is rather difficult to simultaneously determine their contents in biological samples without sample pretreatment [34]. Various active materials including polymers [6,8,35–42], noble metal/alloy nanoparticles (NPs) [6,8,43–45], oxides [46,47], and carbon-based materials [9,41,48–54] have been applied to simultaneously determine AA, DA and UA with moderate success. Recently Han et al. [53] used a chitosan-Gra modified electrode to well resolve the oxidation potentials of AA, DA and UA. Similarly, Liu et al. [31] demonstrated that Gra–Au nanocomposite is a promising material for simultaneous electroanalysis of AA, DA and UA. As such, to move forward, we incorporated both AuNPs and β -cyclodextrin (β -CD) on Gra to fabricate a modified glassy carbon electrode (GCE). The AuNPs– β -CD–Gra/GCE shows better analytical performance for simultaneous determination of AA, DA and UA.

In this work, we propose a simple green one-pot synthesis of AuNPs on Gra by *in situ* thermal reduction of hydrogen tetrachloroaurate(III) (HAuCl₄) and GO with β -CD in alkaline condition. During the synthesis process, β -CD on Gra sheet not only acts as dispersant and stabilizer for HAuCl₄ but also serves as a reducing agent to reduce GO and AuCl₄[−] to Gra and AuNPs, respectively. The resulting AuNPs– β -CD–Gra composite can be easily purified, stored and redispersed in water without any further chemical treatment. Finally, the GCE modified with AuNPs– β -CD–Gra has been used to simultaneously determine AA, DA and UA by square wave voltammetry (SWV). Additionally, it has been successfully applied to determine the UA content in human urine with satisfactory results. Our work demonstrates that the developed AuNPs– β -CD–Gra/GCE shows potential in biomedical or clinical analysis.

Experimental

Chemicals and reagents

Graphene oxide was purchased from ACS Material (Warwick, RI, USA). L-Ascorbic acid, β -cyclodextrin, dopamine, hydrochloric acid (HCl), hydrogen tetrachloroaurate(III), sodium dihydrogen phosphate dihydrate (NaH₂PO₄·2H₂O), sodium hydroxide (NaOH), and uric acid were obtained from Sigma–Aldrich (St. Louis, MO, USA). All chemicals of analytical reagent grade or above were used as received without further purification. Buffer solutions were prepared from NaH₂PO₄·2H₂O and HCl in the pH range 1.0–5.0. Freshly prepared solutions of AA, DA and UA were used in all experiments. Double distilled water (DDW) was used throughout the work.

Instrumentation

Scanning electron microscopic (SEM) images were obtained from a Hitachi S4800 SEM (Tokyo, Japan). High-resolution transmission electron microscopic (HRTEM) image and selected area

electron diffraction (SAED) pattern were acquired on a FEI Tecnai G² 20 HRTEM (Hillsboro, OR, USA). X-ray powder diffraction (XRD) was conducted on a TD-3500 XRD (Tongda Instrument Co., Dandong, China) with Cu K α radiation source. Infrared (IR) spectra were collected on a Thermo Scientific Nicolet 6700 Fourier transform IR spectrometer (Sugar Land, TX, USA). The pH measurements were taken on a Thermo Origin 720A+ pH/ion meter (Thermo Electron Corporation, Waltham, MA, USA).

Preparation of AuNPs– β -CD–Gra composite

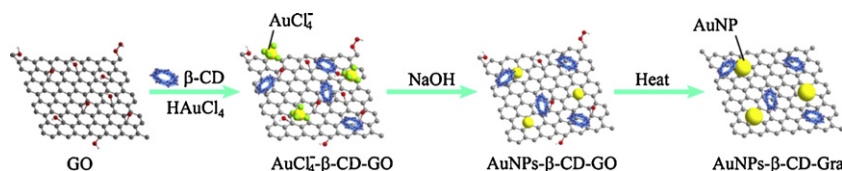
The preparation of Gra [55] and synthesis of AuNPs through β -CD reduction [56] were based on literature methods with modifications to a one-pot synthesis. In essence, GO, β -CD and HAuCl₄ were mixed and heated in an alkaline solution at 60 °C for 2 h. The reaction mixture was then subject to centrifugation, cleaned with DDW and finally vacuum dried to obtain the AuNPs– β -CD–Gra product. The reaction mechanisms are illustrated in Scheme 1 and the preparation details are deposited in Supplementary data. For comparison, AuNPs–Gra, Gra– β -CD and AuNPs– β -CD composites were also prepared in similar procedures.

Fabrication of AuNPs– β -CD–Gra modified electrode

A homogeneous dispersion of AuNPs– β -CD–Gra aqueous solution was prepared by sonication of 1.0 mg AuNPs– β -CD–Gra composite in 1.0 mL DDW for 30 min. Before electrode modification, a GCE (3.0 mm diameter) was polished with 0.1, 0.3 and 0.05 μ m Al₂O₃ slurry sequentially to mirror-like smoothness, rinsed with DDW, and followed by sonication in nitric acid solution (1:1 v/v), absolute ethanol and DDW. Then the clean GC electrode was immersed in a 0.50 M H₂SO₄ and cyclic voltammetry (CV) from −0.20 to +0.80 V for 20 cycles at 50 mV/s were performed. These CV scans aid to remove any impurities/residues and also introduce some active functional groups such as –COOH or –OH on the freshly polished glassy carbon electrode. This typical electrochemical polish procedure permits GCE to have more reproducible and well-defined electrochemical behavior. Afterwards, the GC was rinsed with DDW and dried with a stream of nitrogen (N₂), an aliquot of 5.0 μ L AuNPs– β -CD–Gra aqueous solution was dropped onto the surface of the GCE and dried under an IR lamp for 1 h to obtain the AuNPs– β -CD–Gra modified GCE (AuNPs– β -CD–Gra/GCE). In the control experiments, 5.0 μ L of 1.0 mg/mL Gra– β -CD suspension, AuNPs– β -CD and β -CD solution were also cast onto bare GCEs to obtain the Gra– β -CD/GCE, AuNPs– β -CD/GCE and β -CD/GCE, respectively.

Electrochemical measurement

All electrochemical measurements were performed on a Lanlike LK2006 electrochemical workstation (Tianjin, China). The conventional three-electrode system, comprising a bare or modified GCE as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum foil as the counter electrode, was used. A single compartment electrochemical cell at ambient conditions was used throughout the work. The solutions were deoxygenated with a stream of high purity N₂ (99.99%) at least



Scheme 1. Schematic illustrates the reaction steps of AuNPs– β -CD–Gra.

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