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Direct preparation of well-dispersed graphene/gold nanorod composites and their application in electrochemical sensors for determination of ractopamine

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ABSTRACT

Well-dispersed graphene/gold nanorod (G/GNR) composites were synthesized by directly reducing a mixture of graphene and gold growth solution with sodium borohydride. The synthesized G/GNR composites were characterized by ultraviolet-visible spectroscopy and Fourier transform infrared spectroscopy, and the composites were observed by transmission electronic microscopy, which revealed that the GNRs were self-assembled onto the surface of graphene sheets. Glassy carbon electrodes were modified with G/GNR composites to construct a ractopamine electrochemical sensor. A sensitive, rapid, and simple electrochemical method was developed for the detection of ractopamine based on the strong enhancement effect of G/GNRs. The peak currents varied linearly with the concentration of ractopamine over the range of 1×10^{-9} to 2.7×10^{-6} mol L^{-1}, and the detection limit was 5.1×10^{-10} mol L^{-1} (S/N = 3). This method was applied to detect the content of ractopamine in swine urine samples, and the recovery was in the range of 99.2 to 107.3%.

1. Introduction

Graphene, a single-atom-thick sheet of hexagonally arrayed sp^2-bonded carbon atoms [1], has attracted tremendous attention from both experimental and theoretical communities since 2004. Because of its unique properties, including its large surface area, excellent electric conductivity, and mechanical strength, graphene has a wide range of application potentials in many fields, such as in nanoelectronic devices [2], physical, chemical and biochemical sensors [3], transparent conductive films [4], energy storage materials [5], polymer composites [6,7], etc. Graphene can be used not only as a two-dimensional carbon support to anchor various functional materials, but also as a functional component of the composite itself. Thus, graphene-based composites may combine the outstanding properties of graphene with the special functions of the other components. With the advent of nanotechnology, a number of metal nanoparticles have received widespread interest in the field of detection due to their unique optical properties. Gold nanorods (GNR) exhibit strong optical extinction at the longitudinal plasmon band. Slight variation of the refractive index in the vicinity of the GNR will induce a significant change of longitudinal plasmon wavelength, which is a perfect property for sensing specific target binding events [8]. So far, there have been many attempts to synthesize hybrid structures of graphene and gold (or platinum) nanoparticles [9–13], which have been widely utilized in the fields of electrochemical sensing, biosensors, gas sensors, catalysis, surface-enhanced Raman scattering, fuel cells, drug delivery, as well as others [14–20]. However, it is still a challenge to coat GNRs onto graphene sheets with good water dispersibility. In general, graphene reduced by chemical reduction of graphene oxide (GO) is conductive, but its poor dispersibility makes individual graphene sheets almost inaccessible for modification or functionalization due to π-π stacking interactions. Consequently, most resulting graphene-metal composites are in the form of precipitates or aggregates and are unsuitable for applications where good dispersion is required [21]. In order to increase the solubility of graphene-metal nanoparticles, graphene was functionalized by either covalent attachment or noncovalent adsorption of various functional molecules [22–26]. Covalent functionalization is obtained through the chemical bonding of functional molecules with the basal planes and edges of graphene nanosheets. The functional processes are intricate and difficult, and the radical modification of the sp^2 lattice structure of graphene

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will lead to an altered conductivity [24]. In contrast, non-covalent modification not only enables the graphene to retain good conductivity, but may also afford the modified graphene some new properties. The composites may combine the properties of both graphene and the modifier, and the synergistic effects between the graphene and the modifier may also come into play.

Ractopamine, a phenethanolamine with β_2-adrenergic agonist properties, is widely used as a therapeutic drug in humans for the treatment of pulmonary disease, especially asthma [27]. Meanwhile, ractopamine has been shown to reduce fat deposition through a direct action on adipose tissue and promote muscle growth in swine [28]. However, ractopamine is illegally applied as a nutrient-repartitioning agent in the livestock industry to improve the production of muscle tissues [29]. Ractopamine is not licensed for animal use in many countries due to the potential risk to consumers with respect to adverse cardiovascular and central nervous system effects [30–36]. Until now, various analytical methods of ractopamine have been reported, such as gas chromatography [37], liquid chromatography-fluorescence [29], liquid chromatography [38], ultra-performance liquid chromatography-tandem mass spectrometry [39,40], colorimetry [41], capillary electrophoresis [42], immunoassays [43,44], and so on. However, these methods are time-consuming and require expensive instrumentation, and thus they are not suitable for on-site usage. Therefore, it is necessary to build a sensitive and accurate method for detecting ractopamine. Electrochemical methods shave many great advantages, and the well-dispersed composites of graphene/gold nanorods (G/GNRs) are good materials for such applications.

Herein, well-dispersed composites of G/GNRs were obtained without modifying the graphene sheets. The water-dispersible graphene was reduced from GO with sodium hydroxide under alkaline conditions. Subsequently, gold ions were attached to the surface of the graphene sheets and then the GNRs were formed depending on the function of the reductant. On the one hand, water-dispersible graphene was attained without impairing its wonderful properties. On the other hand, the composites of G/GNRs were prepared by a one-step method through electrostatic interaction between negatively charged graphene and positively charged GNRs, which simplified the processing of the graphene-metal composites. The electrochemical behavior of ractopamine was investigated on glassy carbon electrodes modified with G/GNRs. It was confirmed that ractopamine was effectively adsorbed onto the G/GNR-modified electrode surface by differential pulse voltammetry (DPV). A sensitive DPV method was proposed for the detection of ractopamine on account of the strong adsorption of ractopamine on G/GNR-modified electrodes. The method was applied to detect ractopamine in swine urine sample.

2. Experimental

2.1. Materials

Ractopamine was purchased from Dr. Ehrenstorfer GmbH (Germany). Graphite was purchased from Sigma (USA). Hexadecyl trimethyl ammonium bromide (CTAB) was obtained from Kermel (China). Other chemicals were of analytical grade. 0.1 mol L^{-1} phosphate buffer solution (PBS) was prepared and its pH was 6.2. A standard solution of ractopamine (1×10^{-4} mol L^{-1}) was prepared and stored in a refrigerator at 4° C. Deionized water was prepared from Millipore (Bedford, MA, USA).

2.2. Preparation of G/GNRs

GO was prepared from the natural graphite powder according to a modified Hummer's method [45]. The graphite powder was firstly oxidized by concentrated sulfuric acid and potassium permanganate at 80° C for 5 h. The resulting product was oxidized using 0.1 mol L^{-1} sulfuric acid and hydrogen peroxide in an ice bath for 2 h. Finally, the mixture was sonicated for 15 min, centrifuged, and washed with 10% HCl solution to remove ions.

Well-dispersed graphene was reduced from GO with sodium borohydride under alkaline conditions [46]. 200 mg GO was dispersed in water with ultrasonication. The pH value of the dispersed solution was adjusted to 10 with NaOH, and the mixture was sonicating for 1 h until it became yellow-brown. 400 mg $NaBH_4$ was added to the mixture under vigorous stirring at 135 °C for 6 h. The obtained black powder, graphene, was filtered and dried under vacuum.

Gold growth solution was prepared according to the published literature [47]. The growth solutionincluded10 mL of 100 mmol L^{-1} CTAB, 500 μL of 10 mmol L^{-1} $HAuCl_4$, 65 μL of 10 mmol L^{-1} $AgNO_3$, and then 10 mg graphene was added and dispersed.70 μL of 100 mmol L^{-1} ascorbic acid (AA) was mixed with the suspension, followed by stirring for 30 min, and then100 μL of 10 mmol L^{-1} ice-cold $NaBH_4$ was added. The mixture was kept undisturbed at room temperature for 3 h to complete the reaction. The product was centrifuged at 10,000 rpm for 20 min to remove unreacted ions and redundant impurities. The pellet was redispersed in water for subsequent use.

2.3. Characterization

Ultraviolet–visible (UV-vis) absorption spectra were obtained with a VISIONpro USE spectrometer (Thermal Electron, America). Fourier transform infrared (FTIR) spectra were performed on a VERTEX 70 spectrometer (Bruker, Germany) with a KBr plate. Transmission electron microscopy (TEM) was conducted on a Tecnai F30G^2 microscope (FEI, Netherlands).

2.4. Preparation of G/GNR-modified electrode

The 3mm-diameter glassy carbon electrode (GCE) was initially polished with 0.05 μm alumina slurry, and then sonicated in water for 2 min to yield a clean surface. The GCE surface was coated with 8 μL of G/GNR suspension, and dried under an infrared lamp in air.

2.5. Sample preparation

Urine samples were taken from healthy pigs in a countryside hoggery in Xi'an. The samples were processed with a filter to remove any impurities and then each sample was divided into two portions. One portion had standard ractopamine added to it to serve as a spiked sample, and the other portion was the blank sample. The spiked urine samples were diluted with PBS and analyzed directly.

2.6. Analytical procedure

Electrochemical measurements were performed with a CHI 600D electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) with a conventional three-electrode system. The working electrode was a G/GNR/GCE, the reference electrode was a Ag/AgCl electrode, and the counter electrode was a platinum wire.

PBS was used as the supporting electrolyte for the detection of ractopamine. DPV was recorded from -0.6 to 0.2 V after a 3-min accumulation, and the oxidation peak current was measured at -0.43 V. The pulse amplitude was 50 mV, the pulse width was 0.2 s, and the quiet time was 2 s.