



The influence of uric and ascorbic acid on the electrochemical detection of dopamine using graphene-modified electrodes

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ABSTRACT

In this paper, we report on the preparation of gold electrodes modified with graphene-AuAg (Au/Gr-AuAg) or graphene-Au (Au/Gr-Au) composite materials as electrochemical sensors for dopamine (DA) detection. The response of the Au/Gr-AuAg electrode to dopamine was linear within a 3×10^{-7} – 3×10^{-4} M concentration range, and the Limit of Detection was found to be 2.05×10^{-7} M ($S/N = 3$). In contrast, the Au/Gr-Au electrode exhibited a narrower linear range (10^{-5} – 10^{-4} M) and a higher Limit of Detection (3.03×10^{-5} M). Using the Au/Gr-AuAg modified electrode, we have investigated the effect of two interfering species (ascorbic and uric acid), which are considered to be the most problematic species, due to the fact that their oxidation potentials are close to that of dopamine. Their presence in the electrolyte induced no shift in the peak potential of dopamine (+0.24 V) but instead led to an increase in the peak current. Consequently, a change in the calibration plot has occurred most probably due to the regeneration of dopamine under the influence of ascorbic acid. In that case, the Limit of Detection was found to be 2.16×10^{-6} M.

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1. Introduction

Dopamine [4-(2-aminoethyl) benzene-1,2-diol] is a transmitter of the nervous system and a hormone and is involved in many biological processes in the human brain and body. In the brain, dopamine primarily controls the reward-motivated behavior [1], while in the body it is involved in processes such as motor control or the release of other important hormones. Low levels of dopamine are common in those suffering from Parkinson's disease due to the loss of dopamine-containing neurons in the midbrain [2]. Abnormal dopamine concentrations are also related to schizophrenia, attention deficit hyperactivity disorder (ADHD), and restless legs syndrome (RLS) [3–5]. Dopamine does not pass through the brain-blood barrier, and, in the blood vessels, it serves as a local chemical messenger, like a vasodilator, and reduces insulin production or regulates the activity of lymphocytes.

A number of analytical methodologies have been developed to study dopamine detection. These include expensive instruments and many chemical reagents, like colorimetric assay based on the aggregation of silver nanoparticles, due to their high binding affinity for protonated dopamine [6], spectrophotometric [7],

chromatographic [8], or fluorescence sensing [9]. Compared with other techniques, the electrochemical methods are more accessible for dopamine sensing and quantification due to their low price, fast response, trouble-free operation, and high sensitivity. However, the electrochemical detection of dopamine is hampered by the very close oxidation potential of other species (e.g., uric and ascorbic acid) found in the biological fluids, generally at high concentrations. In the past, this difficulty was overcome by using electrodes modified with a self-assembled monolayer. Those chemically modified electrodes were proved to have a very low detection limit (2×10^{-8} M) [10].

Graphene is a two-dimensional, carbon-based material formed by sp^2 bonded carbon atoms, which possesses high thermal conductivity, electric conductivity, and good mechanical strength. Due to its large potential window and high electro-catalytic activity for many redox processes, graphene-modified electrodes have shown good potential for dopamine detection. Hence, several graphene-based materials have been employed including nitrogen-doped graphene [11,12], electrochemically formed flower-like graphene nanosheet clusters [13], electrochemically reduced graphene-oxide [14], or even simple graphene oxide [15]. Also, considerable interest has been devoted to improving the sensing properties by functionalization of graphene sheets with various organic molecules, such as porphyrin, [16] non-covalent cobalt tetraphenylporphyrin [17], sulfonated groups [18], amino-functionalized mesoporous Fe_3O_4 [19], tryptophan [20], trimethyl

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ammonium bromide [21], molecular imprinted polymers [22], and overoxidized polyimidazole [23].

The sensitivity of these sensors is generally reported to be in the micro-molar domain and considered to be independent of the concentration of various species present in biological fluids, such as ascorbic acid, uric acid [11,12,24–26], tryptophan [27], or nitrite [21]. The variation in the detection limits can be attributed to the different nano-structuring properties of the materials, as it is well known that graphene layers are hydrophobic and have a tendency to restack. The decoration of a graphene surface with noble metal nanoparticles proved to be a good method for spacing the graphene layers, while taking advantage of the electro-catalytic properties of the metal. Dopamine detection has been achieved by modifying the electrodes with graphene-supported silver [27], gold [28], or bimetallic Pd-Pt nanoparticles [29]. In the above-referenced papers, graphene-metal nanoparticle composites were prepared by multi-step procedures which involved chemicals that pose possible risks for health and the environment.

Within the last five years, our group has developed an easy procedure to prepare few-layer graphene decorated with metallic/bimetallic nanoparticles by catalytic Chemical Vapor Deposition with Induction Heating (cCVD-IH) [30–33]. The composite materials were proved to have excellent electro-catalytic properties towards the oxidation of various organic molecules [33,34].

In this paper, we report for the first time the electrochemical detection of dopamine using gold electrodes modified with graphene-AuAg (prepared by cCVD-IH) or graphene-Au (prepared by chemical route). The composite materials were characterized by SEM/TEM and FTIR, while the modified electrode which gave the best electrochemical response (Au/Gr-AuAg) was tested in pH6 PBS solution containing dopamine and two interfering species: ascorbic and uric acid. Different electrochemical techniques (Cyclic Voltammetry, Square Wave Voltammetry, Electrochemical Impedance Spectroscopy) were employed to investigate the effect of the ascorbic and uric acid on the electrochemical detection of dopamine.

2. Experimental

2.1. Preparation of graphene-AuAg composite (Gr-AuAg)

Graphene-AuAg (Gr-AuAg) composite was prepared by catalytic Chemical Vapor Deposition with Induction Heating (cCVD-IH), as described in detail in our recent paper [33]. Briefly, the Au-Ag/MgO catalyst (about 50 mg; 1.5 wt% Au and 1.5 wt% Ag) was dispersed in a graphite support, which was next placed inside a quartz reactor. The reactor was introduced inside a water-cooled copper-tube coil, connected to a high-frequency generator (1.2 MHz; 5 kW). In order to remove the air present inside the reactor, argon gas was flown (300 mL min^{-1}) for 10 minutes. Next, the temperature was increased to 500° C for 5 minutes and then to 1000° C (for 45 minutes) at which point methane gas was allowed into the reactor along with the argon flow (100 mL min^{-1}). After the synthesis process had finished, the methane flow was stopped, and the reactor was cooled to room temperature in argon flow. Throughout the synthesis process, the temperature was monitored with a sensitive infrared thermometer (Pyrometer Impac IGA 8 plus, LumaSense Technologies, Inc Santa Clara, CA, USA).

The catalyst support (MgO) and the amorphous carbon were removed from the synthesis product in two steps. First, the synthesis product was oxidized in the air for 30 minutes at 450° C to remove the amorphous carbon. Second, the MgO support was removed by ultrasound in aqueous HCl (1:1) for 30 minutes at room temperature. After these steps, the carbonaceous product was further kept in HCl for 24 hours and then washed with distilled water. The graphene nanostructures were thereafter denoted as Gr-AuAg.

2.2. Preparation of graphene-Au composite (Gr-Au)

Graphene oxide (GO) was prepared from pre-oxidized graphite powder ($0.125 \mu\text{m}$ obtained from a rod – Pierce eurochemie bv) using a modified Hummers method [35,36]. In a typical pre-oxidation procedure, 4.6 g of graphite powder were added into a solution of concentrated sulfuric acid (8 mL, 80° C) which also contained potassium persulfate (2.5 g) and phosphorus pentoxide (2.5 g). The resultant mixture was heated to 100° C and then left to slowly cool to room temperature. After 5 hours, the mixture was carefully diluted with water, filtered, and washed until the water pH was neutral. The pre-oxidized graphite powder was dried at ambient temperature overnight.

Next, a suspension of the pre-oxidized graphite powder (3.5 g) and sodium nitrite (1.6 g) in sulfuric acid (60 mL) was cooled in an ice-water bath, and potassium permanganate (8 g) was slowly added to the mixture so the temperature would not reach 20° C . The mixture was allowed to stand until the next day, when it was slowly warmed to 35 – 37° C and kept for 2 hours at that temperature. The suspension was diluted with 150 mL water, and the temperature risen to 100° C . After 2 hours, 100 mL of water were added. Next, the reaction was stopped by adding hydrogen peroxide (3%) until no more gas development was observed. The mixture was finally filtered and washed with a diluted HCl solution (5%). The GO product was then suspended in distilled water and dialyzed for 5 days. Exfoliation was achieved by dilution of GO and sonication for 1 hour.

For the preparation of the graphene-gold nanoparticles composite, about 150 mg of GO powder were dispersed in water (50 mL) and sonicated for 15 minutes, resulting in a homogeneous GO dispersion. Next, 1.5 mL solution of HAuCl₄ (1% in water) were added to the mixture and stirred at room temperature for 2 hours. Finally, sodium ascorbate solution (400 mg in 5 ml water) was added in order to reduce both gold ions and GO. The mixture was heated until the temperature reached 90° C and kept at this temperature for 3 hours. At the end of these steps, the resulting homogeneous black suspension was filtered and washed with water several times. The final composite material was denoted as Gr-Au.

2.3. Gold electrodes modified with Gr-AuAg and Gr-Au composite

Prior to modification with one of the composite materials, the gold electrode was electrochemically cleaned by cyclic voltammetry in 0.2 M H₂SO₄ solution (50 cycles from -0.25 to $+1.6 \text{ V versus Ag/AgCl}$, at a scan rate 50 mV s^{-1}) and then by ultrasound in both ethanol and double-distilled water (3 minutes each time). After these steps, 20 μL of colloidal suspension of the desired composite material in DMF (0.5 mg mL^{-1}) were drop-casted onto the gold substrate and dried at room temperature for at least 1 hour. (See Scheme 1.) Following this process, the surface of the gold electrode was fully covered by graphene and ready for the electrochemical measurements. The modified electrodes were subsequently denoted as Au/Gr-AuAg and Au/Gr-Au, corresponding to each composite material.

2.4. Apparatus

The morphological characteristics of graphene-metal nanoparticle composites were investigated by Scanning Electron Microscopy (SEM-JEOL JSM7000F) and Transmission Electron Microscopy (TEM/STEM-JEOL JEM-2100F equipped with X-ray energy dispersive spectroscopy detectors by EDAX, Inc). For Fourier Transform Infrared (FTIR) analysis, 0.2 mg of each composite material (Gr-AuAg or Gr-Au) were mixed with KBr powder and pressed in a pellet. The measurements were performed with a

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