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Facile synthesis of Au-graphene nanocomposite for the selective determination of dopamine

Minjeong Kwak [a,1,2], Sohee Lee [a,1], Dongwon Kim [a], Seung-Keun Park [a], Yuanzhe Piao [a,b,*]

[a] Graduate School of Convergence Science and Technology, Seoul National University, Seoul 151-742, Republic of Korea
[b] Advanced Institutes of Convergence Technology, Seoul National University, Suwon 443-270, Republic of Korea

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ABSTRACT

We report a facile strategy of graphene/gold nanocomposite based electrochemical biosensor that exhibit good sensitivity and high reproducibility. The graphene/gold nanocomposites were prepared by using sodium hydroxide acting as an accelerator for the reduction of gold ions. The graphene oxide was reduced by chemical and thermal methods after deposition of gold nanoparticles. The composition of the resulting materials was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and thermogravimetric analysis (TGA). Also, transmission electron microscope (TEM) was employed to demonstrate the successful deposition of gold nanoparticles on the surface of graphene sheets. The electrochemical behavior of dopamine (DA) on the surface of the graphene/gold nanocomposite modified electrode was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). In comparison to the reduced graphene oxide (rGO) modified electrode, the graphene/gold nanocomposite modified electrode shows good performance for the selective determination of DA. The nanocomposite modified electrode showed a low detection limit (0.095 μM), an enhanced electrochemical oxidation current for DA, and a good separation of potential of DA and ascorbic acid (AA).

1. Introduction

As one of the most important and representative catecholamine neurotransmitters, dopamine (DA) plays a significant role in central nervous, renal and hormonal systems [1,2]. The abnormal DA levels could indicate some brain diseases such as Parkinson's disease, schizophrenia, and Huntington's disease [3,4]. As a water-soluble vitamin, ascorbic acid (AA) is an essential nutrient for humans. AA is a major redox buffer and a cofactor for enzymes involved in regulating photosynthesis, hormone biosynthesis, and regenerating other antioxidants. Despite the fact that most mammals can synthesize ascorbate, humans are unable to make vitamin C as a result of a mutation to the gene encoding L-gulono-1,4-lactone oxidase, the last enzyme in the ascorbate biosynthetic pathway [5]. Electrochemical methods can be used for DA detection because of its high electrochemical activity. However, the very low concentration of DA in the "extracellular fluid" of the caudate nucleus requires sensitive detection methods for DA. It also coexists with excess AA in real biological samples and both are electroactive compounds. It is quite hard to determine DA with high selectivity [6,7] since the concentration of AA is about 1000 times higher than that of DA and the direct oxidation of AA at the electrodes occurs at a similar potential so that overlap that of DA [8]. Therefore, the diagnostic tool that is capable of selective detection of DA in the excess AA is demanded. Many attempts have been made on the development of highly selective dopamine biosensor but still need more investigations [9–12].

Graphene, a single layer graphite with close-packed conjugated honeycomb lattices, has attracted tremendous attention from scientific communities since the experimental observation of single layers by K. S. Novoselov and A. K. Geim in 2004 [13,14]. Graphene has excellent mechanical strength, and chemical stability. Moreover, it possesses remarkably high charge mobility under ambient conditions with reported values in excess of 15,000 $cm^2/(V \cdot s)$ [15,16]. It is recognized as the basic building block of all-dimensional graphitic materials and one of the lightest, strongest and most conductive materials ever known. It provides a variety of new applications such as field-effect transistor [17], energy storage [18], biotechnologies [19], transparent electrodes [20] and novel nanocomposites [21]. Above all, graphene possess excellent

* Corresponding author at: Graduate School of Convergence Science and Technology, Seoul National University, Seoul 151-742, Republic of Korea.
E-mail address: parkat9@snu.ac.kr (Y. Piao).
[1] These authors contributed equally to this work.
[2] Present address: Center for Nanosafety Metrology, Korea Research Institute of Standards and Science, Daejeon 305-340, Republic of Korea.

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merits in biosensing due to its biocompatibility, large detection area and high electron mobility [22]. Considering a wide-ranging potential applications of the two-dimensional graphene sheet as host material for a variety of nanoparticles, many research works have been made for the fabrication of hybrid nanoparticle–graphene structures endowed with multi-functionalities.

Nanomaterials made of noble metals like Au, Ag, Cu, Pt, and Pd are being widely studied for various applications, such as sensing [23,24], catalysis [25], biological labeling [26], drug delivery [27], and cancer therapy [28]. These nanoparticles show new physico-chemical properties which are different either in the individual molecules or in the bulk metals [29]. Among them, gold nanoparticles (Au NPs) have attracted much attention owing to their high stability, superior electronic conductivities, and great catalytic properties. Due to these unique properties, the studies of Au NPs for electrochemical sensor and biosensor applications have attracted great research interests. In addition, it is also demonstrated that Au NPs could be used to construct interfaces for the electrocatalysis of oxidation and reduction of many important biomaterials [30].

Recently, various methods have been reported to synthesis Au–graphene hybrids for catalytic and optoelectronic applications. There have been several new reports on the construction of electrochemical biosensors using Au/graphene composite nanomaterials [31–33].

In this work, we demonstrate a simple approach to prepare reduced graphene oxide (rGO)/Au/GCE nanocomposite electrode, in which the rGO was chemically reduced from the graphene oxide(GO) and the Au nanoparticles were reduced by thermal processes. The glassy carbon electrode (GCE) was modified with the as-prepared rGO/Au nanocomposite by drop-casting method and the electrode was applied for the determination of DA in the presence of AA. The modified electrode exhibited enhanced electrochemical oxidation current of DA and showed good voltammetric peak separation of DA from AA.

2. Experimental section

2.1. Reagents and materials

Graphite powder (<20 μm), hydrazine, ammonia, *N,N*-dimethylformamide (DMF), H_2SO_4, $KMnO_4$, 0.01 M phosphate buffered saline (PBS; 0.138 M NaCl, 0.0027 M KCl, pH 7.4), sodium hydroxide, dopamine hydrochloride (DA) and L-ascorbic acid (AA) were purchased form Aldrich and used as received. Doubly distilled water was used throughout the whole experiments. Dopamine hydrochloride and L-ascorbic acid solutions were freshly prepared in PBS prior to use. Pharmaceutical sample of DA (Dopamine Injection 40 mg/mL) was obtained from the market.

2.2. Instruments and measurements

The electrochemical measurements were conducted with an AUTOLAB potentiostat (Metrohm, USA) using a conventional 3-electrode system. The electrochemical cell consisted of glassy carbon electrode (GCE, 3 mm diameter, Bioanalytical Systems, Inc.) as the working electrode, Ag/AgCl (Bioanalytical Systems, Inc. filled with 3 M NaCl) as the reference electrode, and platinum wire as the counter electrode. The sweep rate in the cyclic voltammetry (CV) was 50 $mV \cdot s^{-1}$.

X-ray diffraction (XRD) pattern of the as-synthesized rGO/Au NPs nanocomposite was obtained from Bruker D-5005 with Cu Kα radiation ($\lambda = 1.5406$ A) at 40 kV and 40 mA. Transmission electron microscopic (TEM) observations were made on a JEOL EM-2010 microscope at an accelerating voltage of 200 kV and a JEM-3010 (JEOL) at an accelerating voltage of 300 kV. Raman spectra were obtained using Dongwoo DM500i Raman microprobe with a 15 mW Argon laser at 514.5 nm excitation. The composition of each component within the rGO/Au NPs nanocomposite was measured using a thermogravimetric analyzer (TGA, Mettler-Toledo TGA).

2.3. Synthesis of graphene oxide

Graphene oxide (GO) powders were synthesized by oxidation of graphite according to the modified Hummer's method [34,35]. Typically, 72 mL of 95% H_2SO_4 and 8 mL of 85% H_3PO_4 were added into 500 mL beaker filled with 3 g of graphite powder. To avoid rapid heat evolution, 18 g $KMnO_4$ was slowly added. The mixed slurry was stirred mildly at 60 °C for 1 h under ice-cooling. The ice bath was removed and the temperature of the suspension was increased to 90 °C and maintained at that temperature for 24 h. After cooling down, 350 mL of deionized water was slowly added into the reacted slurry and stirred for 2 h. The reaction was finished by adding 5 mL of 30% hydrogen peroxide solution (H_2O_2). The suspension was separated by centrifugation, washed with 2 M HCl solution. Then, the obtained sample was repeatedly washed with deionized water and followed by ultrasonic treatment for 60 min. The final solid product was separated by centrifugation and then dried in a vacuum oven at 60 °C for 24 h.

2.4. Synthesis of rGO/Au NPs nanocomposite

The process for the preparation of GO/Au NPs nanocomposite is outlined in Fig. 1. The GO suspension was prepared by dispersing 0.25 g of GO powder in 250 mL of deionized water. Then, 50 mL of 0.01 M $HAuCl_4$ and 37.5 mL of 0.1 M NaOH were sequentially added to the GO water dispersion at room temperature and the mixture was vigorously stirred for 12 h. The resulting nanocomposite was isolated from residual gold precursor and NaOH by centrifugation (15,000 rpm) and re-dispended in 87 mL of water. Hydrazine (75 μL) was then added and heated using an oil bath at 80 °C with vigorous stirring for 12 h over which the reduced GO/Au NPs nanocomposite were gradually precipitated out. After that, the hydrazine-reduced GO/Au NPs nanocomposite was filtered and dried in a vacuum oven for 3 h. Since the quality of graphene can be improved by thermal treatment, the hydrazine-reduced GO/Au NPs nanocomposite powder was placed into a furnace tube under reducing atmosphere (20% H_2–80% N_2 mixed gas). The temperature was then raised to 300 °C and maintained at that temperature for 1 h. The finally obtained nanocomposite material is referred as thermally reduced GO/Au nanocomposite (rGO/Au NPs).

2.5. Preparation of rGO/Au NPs modified GCE

The GCE was polished successively using 0.3 μm and 0.05 μm alumina powder and rinsed thoroughly with ethanol and deionized distilled water each for 10 min and dried in air before use. rGO/Au NPs nanocomposite powder was dispersed in DMF solvent at a concentration of 0.1 mg/mL and sonicated until a homogeneous suspension was obtained. A 4 μL of the suspension was then pipetted onto the pretreated GCE surface and dried in air.

2.6. Procedure for differential pulse voltammetric (DPV) analysis of DA

All experiments were carried out at room temperature. It was unnecessary to remove dissolved oxygen from the solution before analysis. DPV was performed on the rGO/Au NPs modified GCE in pH 7.4 PBS containing DA and the peak current was measured. DPV was employed for the measurement of DA under the following conditions: scan rate of 50 $mV \cdot s^{-1}$ via a potential scan from −0.2 to 0.6 V, amplitude of 50 mV, pulse width of 50 ms, potential step of 4 mV, and pulse period of 0.2 s. For DPV analysis of pharmaceutical sample, suitable dilution steps for the solution were made with pH 7.4 PBS.