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A simple preparation of graphite/gelatin composite for electrochemical detection of dopamine

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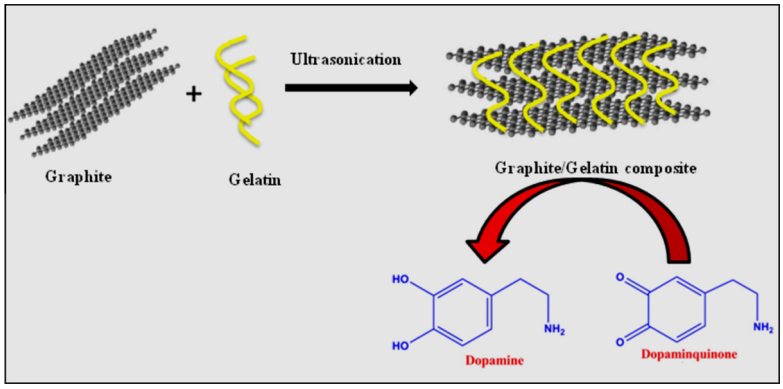
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we demonstrate a simple preparation of graphite (GR) sheets assisted with gelatin (GLN) polypeptide composite was developed for sensitive detection of dopamine (DA) sensor. The GR/GLN composite was prepared by GR powder in GLN solution (5 mg/mL) via sonication process. The prepared GR/GLN composite displays well dispersion ability in biopolymer matrix and characterized via scanning electron microscope (SEM), Fourier transform infrared (FTIR) spectroscopy and electrochemical impedance spectroscopy (EIS) studies. The GR/GLN modified electrode showed an excellent electrocatalytic activity toward the oxidation of DA, suggesting that the successful formation of GR sheets crosslinked with the functional groups of GLN polypeptide. In addition, the GR/GLN modified electrode achieved a wide linear response ranging from 0.05 to 79.5 μM with a detection limit of 0.0045 μM. The calculated analytical sensitivity of the sensor was 1.36 ± 0.02 μA μM^{-1} cm^{-2}. Conversely, the modified electrode demonstrates a good storage stability, reproducibility and repeatability. In addition, the sensor manifests the determination of DA in human serum and urine samples for practical applications.

1. Introduction

In past few decades, the developments of electrochemical sensor for the detection of biological small molecules have received much attention in biosensing application process owing to its vital role in metabolic system of mammals [1,2]. Particularly, dopamine (DA) is an important neurotransmitter in central nervous system, plays a significant role in physiological actions [3]. The low level concentration of DA associated with neurological disorders like Parkinson's disease and schizophrenia as well as the higher concentration of DA leads to some mental disorders or abnormal

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behavior in central nervous system [4]. Hence, the accurate and low level determination of DA is more important to the researcher's from analytical chemistry [5]. To date, different methods have been demonstrated for the determination of DA; however, the electrochemical methods have been widely adapted due to their simplicity, low cost and high efficiency compared with other traditional analytical techniques [6,7]. Thus, numerous modified electrodes have been used for the determination of DA in the previous literatures with excellent sensing performance [8]. However, the development of DA sensor with superior electrocatalytic activity and good sensing performance has received much interest in electrochemical sensor recently [1]. Up to now, various modified electrodes have been constructed for determination of DA using carbon nanomaterials, conducting polymers, metal nanoparticles, metal oxides, metal complexes and etc., [9–13]. Notably, the unmodified electrode has received some major drawbacks continuously such as poor sensitivity, fouling of the electrode response and the oxidation potential is higher [14]. Thus, over come to these problems by fabricating the electrode with suitable material for those requirement including natural polymers, resins and agricultural residues etc. [15]. In addition, the shape-memory polymers are one kind of smart polymeric matrix, which has been used for sensors and actuators, reconfigurable morphing structures, smart textiles, self-healing materials, surgical stents and sutures and implants for minimally invasive surgery in technological applications [16]. However, in recent studies, the researchers have been focused on the biopolymeric matrixes including pectin, cellulose, alginate, chitosan and gurgum etc. for the preparation of efficient composite materials [17–19].

Gelatin (GLN) is a translucent colourless soluble polypeptide, which was obtained from most abundant protein in animal skin and bone, while the white tissues are separated by partial hydrolysis of collagens. In addition, GLN is common biopolymer mostly used in pharmaceutical and biomedical applications due to its excellent biodegradability and biocompatibility in tissue engineering [20,21]. The reason for choosing GLN as a dispersing agent, the hydrophilic and hydrophobic segments assisted with the exfoliation of graphite sheets and other carbon layered nanomaterials by sonication process [22,23]. Nabeta et al. used GLN as a dispersing and stabilizing agent for single walled carbon nanotubes in aqueous solution as reported early [24]. Till date, GLN matrix have been made toward reinforcing by different nanomaterials including carbon fibers [25], clay [26] and silk fibers [27] etc. Hence, we have been chosen GLN as a dispersing material for the preparation of GR/GLN composite via sonication method. Like vice, our group recently reported that cyclodextrin as a dispersing agent for the preparation of cyclodextrin entrapped graphite composite for sensitive DA sensor [9]. In addition, the chitosan crafted graphite composite also showed an excellent electrocatalytic activity toward DA sensor in our precious studies [28]. On the basis, in our present work we used GLN as a dispersing agent for the preparation of GR/GLN composite for sensitive detection of DA in biological samples.

In this work, we have prepared a simple and disposable GR/GLN modified screen printed carbon electrode (SPCE) for lower potential detection of DA for the first time. The prepared GR/GLN composite was fabricated within 1 h. Compared with previous procedures, we used an efficient method for preparing GR/GLN composite via sonication process for DA sensor. In addition, the GR/GLN modified electrode shows an enhanced oxidation peak current, higher sensitivity and lower potential detection toward the detection of DA than that of other modified electrodes. The optimization of GR/GLN modified electrode was crucially assessed and discussed in details. The stability, selectivity and practicality of the fabricated sensor also been discussed in detail.

2. Experimental

2.1. Chemicals

Raw graphite, gelatin from bovine skin and dopamine were purchased from Sigma-Aldrich. Screen printed carbon electrode was purchased from Zensor R&D Co., Ltd., Taipei, Taiwan. Ascorbic acid, uric acid and glucose were obtained from Aldrich. The Human blood serum sample was collected from valley biomedical, Taiwan product & services, Inc and the urine sample was collected from Taipei tech students with their permission. The supporting electrolyte phosphate buffer (PBS) pH 7 was prepared by using Na_2HPO_4 and NaH_2PO_4 solutions. All other chemicals were used in this work for analytical grade and all the solutions were prepared using doubly distilled water without further purification.

2.2. Apparatus

The prepared composite was characterized by scanning electron microscopy (SEM) using Hitachi S-3000 H electron microscope. Fourier transform infrared spectroscopy (FT-IR) was recorded from the Thermo SCIENTIFIC Nicolet iS10 instrument. The electrochemical impedance spectroscopy (EIS) studies were performed from IM6ex ZAHNER (Kroanch, Germany) and the impedance data are in the form of Nyquist plots. The electrochemical behavior of the prepared composites was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using CHI1205b and CHI750a electrochemical work stations. A three-electrode system was used for electrochemical experiments; the GR/GLN modified SPCE was used as a working electrode, saturated Ag/AgCl as a reference electrode and platinum electrode as an auxiliary electrode, respectively.

2.3. Preparation of GR/GLN composite and electrode fabrication

First, gelatin (GLN) solution was prepared by dissolving the gelatin powder in DI water (1.5 mg/mL) under continuous magnetic stirring at 60 °C for 2 h [29]. After clear dispersion, the GLN solution was cooled at room temperature and centrifuged to remove the un-dissolved GLN particles. Then, the GR/GEL composite was prepared by sonication of 5 mg/mL of GR in GLN for 10 min via ultra sonic bath with operating frequency of 40 kHz and ultrasonic power output of 150 W. A clear dispersion of GR/GEL composite was obtained and used for further electrochemical studies. Prior to prepare the GR/GEL modified electrode, about 8 μL of as-prepared composite was drop casted on the surface of SPCE and dried at room temperature. For comparison, the GR modified electrode was prepared by the same procedure without using GLN. The GR powder was dispersed in dimethylformamide for electrode preparation. All electrochemical experiments were performed pH 7 (PBS) in an ambient condition.

3. Results and discussion

3.1. Characterisations

The structural analysis of the GR/GLN composite was characterized by SEM. As shown in Fig. 1A, the bundles of GR sheets are assisted with flake like morphology. On the other hand, the SEM image of GR/GLN composite shows that the flake like GR sheets were randomly distributed on the GLN solution, as shown in Fig. 1B. The surface morphology of GR/GLN composite has smooth structural morphology with similar flake like structure. This may be due to the interaction of the GR sheets crosslinked with the hydrophobic amino acid chains of gelatin polypeptide, to form a