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Highly selective dopamine sensor based on graphene quantum dots self-assembled monolayers modified electrode

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ABSTRACT

The graphene quantum dots (GQDs) were synthesized by a convenient method and immobilized to glassy carbon electrode (GCE) through covalent self-assembled method. The GQDs and the obtained (GQDs–$NHCH_2CH_2NH$)/GCE were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy and atomic force microscopy (AFM), etc. Its electrochemical property of the (GQDs–$NHCH_2CH_2NH$)/GCE was explored carefully by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and differential pulse voltammetry (DPV). It was demonstrated that the modified electrode presents good electrical conductivity and has favorable electrochemical response to dopamine (DA). The (GQDs–$NHCH_2CH_2NH$)/GCE displays a linear range from 1 to 150 μM and a detection limit of 0.115 μM (S/N = 3) to DA, which illustrates that the modified electrode is highly sensitive towards the determination of DA. The (GQDs–$NHCH_2CH_2NH$)/GCE also possesses good anti-interference capability and well stability. Furthermore, the sensor displays satisfactory results in real samples determination which demonstrate its great potential in practical applications.

1. Introduction

Dopamine, 2-(3,4-dihydroxyphenyl)ethylamine (DA) is a neurotransmitter which plays an important role in the communication between neurons. It is linked to arrhythmia, cardiac and hypertension abnormality of dopamine concentrations [1]. Hence a simple, sensitive, and accurate analytical method for detection of DA in vivo/vitro is a subject of great importance. In the past, various methods have been developed for the determination of DA, such as spectrophotometry [2], colorimetry [3], chromatography [4] etc. Among various methods, the electrochemical method has attracted more attention due to its fast, simple, accuracy properties in recent years [5]. However, the selectivity of bare electrode is not high enough when working in the presence of other interferences, such as uric acid (UA) and ascorbic acid (AA) [6] etc. To improve the selectivity of the bare electrode, various kinds of carbon materials have been employed to modify the working electrodes, including graphene-based materials [7], carbon nanotube-based materials [8], carbon microspheres-based materials [9], nitrogen doped carbon materials [10], and so on. These carbon materials have low limit and well sensitivity to the determination of DA, but some of them are time-consuming or expensive, such as C_{60}-functionalized multiwalled carbon nanotube films [11], Laccase-si-MWCTNs composite layers [12] and tyrosinase-SWNTs-Ppy/GCE [13] etc. Therefore, it is essential to explore a suitable material that not only has good selectivity to the determination of DA but also is easy to access, atoxic and practical.

Graphene quantum dots (GQDs) are zero-dimensional with lateral size less than 100 nm and consisted of a single layer or few-layer of carbon atoms in a closely packed honeycomb structure [14]. They are a kind of fragments of graphene, thus not only have the excellent performance of graphene, such as good biocompatibility, suitable conductivity, and low toxicity etc. [15,16], and the GQDs also exhibit new phenomena due to quantum confinement and edge effects. Therefore, GQDs have received more attention recently. The application of GQDs mainly focused on the fields including photovoltaic devices [17], cellular imaging [18], drug delivery [19] and a new generation of detection [20]. Nowadays, many researchers have devoted their efforts to explore sensing systems for biological molecule. For example, Zhao et al. [21] demonstrated that GQDs modified pyrolytic graphite electrode coupled with probe single-stranded DNA for the sensitive and selective detection of various target molecules; Razmi and Mohammad-Rezaei [22] have further developed a new, simple and low cost glucose biosensor based on glucose oxidase–GQDs/GCE; Liu et al. [23] studied GQDs-based fluorescent probe for sensitive and low-cost detection of ascorbic acid; Zhang et al. [24] GQDs/gold electrode and its application in living cell H_2O_2 detection, and so on. However, there still has large developing space of the GQDs in electrochemical sensing application. Based on structure properties and oxygen-containing groups (hydroxyl, carboxyl) [19] of the GQDs, as an alternative strategy, it comes to be a good idea forming self-assembled films with chemical modification, which can further utilize the electrochemical activity of GQDs.

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The self-assembled technique is a popular method which employs a variety of secondary molecular interactions to form complicated multifunctional nanostructured molecular films on any surface [25]. The self-assembled monolayers (SAMs) have conformal ultrathin films and high tunable surfaces which display a better mass transport, electrocatalysis and surface area for well sensitivity, selectivity and high detection ability [26]. During the self-assembled process, secondary molecular interactions such as covalent bond [27], electrostatic interaction [19], Van der Waals and coordination interactions [25] were employed to form nanostructured molecular films. Regretfully, these films have poor stability and reproducibility in electrochemistry application because of the loose interactions like electrostatic adsorption or hydrophobic interaction. However, the rich oxygen-containing groups of GQDs will be easy to form a steady and strong covalent bond. So the GQDs can be used as an appropriate candidate for preparing self-assembled monolayers and then to construct electrochemical sensor.

In this paper, the GQDs were synthesized by convenient method and characterized carefully. Then the GQDs monolayers were obtained by self-assembled method based on amide covalent bond formed between GQDs and ethylenediamine. The GQDs self-assembled monolayers were characterized using AFM images and FT-IR spectra. The electrochemical properties of the GQDs modified electrode were deep studied by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The obtained modified electrode exhibits good electrochemical response to DA, and it also shows excellent selectivity and stability for the determination of DA.

2. Experimental

2.1. Reagents and apparatus

N-hydroxysuccinimide (NHS) and 1-ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride (EDC) were purchased from Yanchang Biotechnology Co., Ltd. (China). UA, AA and DA were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals were analytical reagent grade and were used without further purification. Phosphate buffer solution (PBS) was prepared by mixing 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4. All solutions were prepared with redistilled deionized water.

The transmission electron microscopy (TEM) was performed on a FEI Tecnai G2F20 electron microscope and operated at 200 kV with the software package for automated electron tomography. The surface morphology of the modified and the unmodified glassy carbon electrode (GCE, 3 mm diameter) were characterized by atomic force microscopy (AFM, CSPM5500, China). Fourier transform infrared spectroscopy (FT-IR) was recorded on a Bruker IFS66V FT-IR spectrometer. The UV–Vis absorption was recorded by a Mapada UV-1800PC (Shanghai China). Electrochemical experiments were performed with a CHI 660C electrochemical workstation (Shanghai Chenhua Instruments Co., LTD) with a conventional three-electrode system, the modified or unmodified GCE was used as the working electrode, the Pt wire and Ag/AgCl (3.0 M KCl) electrode were used as the counter and reference electrode, respectively.

2.2. Synthesis of GQDs

The GQDs were prepared according to the reported method [28]. Firstly, 2 g citric acid (CA) was put into a 100 mL beaker and then heated to 200 °C using a heating mantle. About 5 min later, the CA was liquated. Following, the color of the liquid changed from colorless to pale yellow, and then orange in 30 min, which implied the formation of GQDs. And then, 10 mg/mL NaOH solution was added into the obtained orange liquid drop by drop under vigorous stirring until the pH of the GQDs solution is up to 8.0. Lastly, the GQDs were dialyzed for 48 h with the dialysis membranes of 1000 cutoffs, and after vacuum freeze drying, the GQDs were stored at 4 °C for using.

2.3. Fabrication of the SAMs GQDs modified electrode

The GCE was sequentially polished with 1.0 μm, 0.3 μm, and 0.05 μm alumina powder and then washed successively with distilled water, ethanol and distilled water each for 1 min, and dried in nitrogen before use. The pretreated GCE was first carboxylated in 20 mM $KMnO_4$ solution containing 2 M H_2SO_4 for 30 min, then immersed in mix solution containing 6.0 mg/mL EDC and 9.0 mg/mL NHS for 1 h, and then kept in ethylenediamine for 1 h, finally dropped 10 μL 2 mg/mL GQDs on the GCE and dried in air. The GQDs were first active by mix solution containing 6 mg/mL EDC and 9 mg/mL NHS for 20 min. The obtained modified electrode was described as (GQDs–$NHCH_2CH_2NH$)/GCE.

3. Results and discussion

3.1. Characterization of the synthesized GQDs and the (GQDs–$NHCH_2CH_2NH$)/GCE

The synthesized GQDs were characterized by TEM, UV–Vis and fluorescence spectra. As shown in Fig. 1A, the GQDs display a small size with diameters about 3–5 nm from the TEM image. According to the UV–Vis absorption spectrum (Fig. 1B), a strong UV–Vis absorption band appears at around 362 nm which is consistent with the previous reports of GQDs [19]. Meanwhile, the fluorescence spectra in Fig. 1B shows that the emission wavelength of GQDs aqueous solution is excitation independent, with the fluorescence excitation and emission wavelengths at 367 and 468 nm, respectively. Fig. 1C shows FT-IR spectra of the GQDs (a) and the (GQDs–$NHCH_2CH_2NH$)/GCE (b). The FT-IR spectra of GQDs appeared absorption of stretching vibration O–H at 3418 cm^{-1}, stretching vibration of C=O at 1611 cm^{-1} and 1395 cm^{-1}, which should be ascribed to the flexure vibration of C–OH [29]. This demonstrates that the GQDs were rich in oxygen groups (hydroxyl, carboxyl). As shown in curve b of Fig. 1C, the FT-IR spectra of the (GQDs–$NHCH_2CH_2NH$)/GCE appeared the stretching vibration O–H at 3356 cm^{-1}, C=O at 1632 cm^{-1} (amid I), C–N at 1243 cm^{-1} (amid II), N–H at 1123 cm^{-1} (amid III), which proved the amide covalent bond were formed successfully between carboxyl groups of GQDs and ethylenediamine.

The morphology of the bare GCE and the GQDs SAMs were characterized by AFM, as shown in Fig. 2. The surface of the bare GCE is relatively smooth with an average roughness of 0.837 nm (Fig. 2A); but the AFM image of the GQDs SAMs shows irregular islands with an average roughness of 6.27 nm (Fig. 2B). Therefore, from the roughness change of the electrode surface, we can conclude that the GQDs were successfully assembled to the GCE surface.

3.2. Electrochemical impedance spectroscopy characterization

Electrochemical impedance spectroscopy (EIS) was used for investigation of the impedance changes in the electrode modified process. The EIS spectrum has two parts included semicircular part and linear part. The semicircular part at higher frequency corresponds to the electron transfer limited process, and its diameter is equal to the electron transfer resistance (Rct). Fig. 3 shows the EIS of the bare GCE (a), the carboxylated GCE (b), the $NHCH_2CH_2NH$/GCE (c) and the (GQDs–$NHCH_2CH_2NH$)/GCE (d) in 0.1 M KCl electrolyte solution containing 0.1 mM $Fe(CN)_6^{4-/3-}$. It is clearly observed that the bare GCE (curve a of Fig. 3) exhibits a small Rct. After carboxylated and further modified with ethylenediamine, the diameter of the semicircular part at higher frequency in the EIS increased, suggesting the obvious increase of the Rct, as shown in curves b and c of Fig. 3. However, after modified with GQDs, the diameter of the obtained (GQDs–$NHCH_2CH_2NH$)/GCE decreased obviously which means the smallest Rct (curve d of Fig. 3), this demonstrates that the existence of GQDs could decrease the resistance of the sensing platform in the solid and solution interface. This