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One-pot synthesis of graphene–chitosan nanocomposite modified carbon paste electrode for selective determination of dopamine

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ABSTRACT

Background: A simple, rapid, low-cost and environmentally friendly method was developed to determine dopamine (DA) in the presence of ascorbic (AA) and uric acid (UA) based on a novel technique to prepare a graphene–chitosan (GR–CS) nanocomposite and modify it on the surface of carbon paste electrode (CPE). For our design, CS acts as a media to disperse and stabilize GR, and then GR plays a key role to selective and sensitive determination of DA.
Results: Under physiological conditions, the linear range for dopamine was determined from 1×10^{-4} to 2×10^{-7} mol/L with a good correlation coefficient of 0.9961 in the presence of 1000-fold interference of AA and UA. The detection limit was estimated to be 9.82×10^{-8} mol/L (S/N = 3). In order to study the stability and reproducibility, GR/CS/CPE underwent successive measurements in 10 times and then tested once a d for 30 d. The result exhibited 98.25% and 91.62% activities compared with the original peak current after 10-time measurements and 30-d storage.
Conclusion: The GR/CS/CPE has wide linear concentration range, low detection limit, and good reproducibility and stability, which suggests that our investigations provide a promising alternative for clinic DA determination.

1. Introduction

Since we have known that dopamine (DA) plays a key role in the functions of human being, determinations of DA as an important basis of clinical diagnosis have attracted much interest [1,2]. Various methods have been developed to analysis of DA including chromatography, flow-injection chemiluminescence and electrolysis [3,4,5,6,7,8]. Among the methods mentioned above, electrochemical method presents distinctive advantages, such as quick response, low detection limit, low cost, simple operation and the absence of pretreatment. However, interferences of electroactive impurities, especially the interferences of ascorbic acid (AA) and uric acid (UA) that coexist with DA in body fluids, always affect the accuracy of determinations. In order to eliminate these interferences, the technique of chemically modified electrode has been used to determine DA selectively [9,10,11,12,13,14]. As mentioned from Pardavé's work, only simple modification of the electrode surface with sodium dodecyl sulfate micelles has successfully provided a drastic change in the DA oxidation potential peak, and then the electrochemical oxidation overlap of DA, UA and AA has been separated [15].

Attachment of nanomaterials to the surface of electrode has received wide attention because the modified electrode exhibits more favorable properties than bold electrode even simple chemical modification [16,17,18,19,20]. Graphene (GR), as a prototype two-dimensional carbon system, has been considered as an ideal nanomaterial for modified electrode. Particularly, GR that can provide a friend microenvironment is a promising alternative to bioassay [21,22,23,24,25,26,27,28]. Therefore attractive nature of GR permanently leads to extensive concerns for its synthesis and applications. Currently, several methods have been suggested to prepare GR, such as mechanical cleavage of graphite [29], chemical reduction of graphite oxide [30], thermal expanded graphite [31] and liquid-phase exfoliation [32]. Especially the last method, the liquid-phase exfoliation, is very appealing because it is direct, simple and has subsequent easy applications. Due to the strong π–π stacking and Van der Waals interactions, the solvent choice referring to GR disperse and agglomerate became the key parameter for the technique of liquid-phase exfoliation [25].

The driving force in the investigations and applications of chitosan (CS) is from its satisfying film-forming ability, biodegradability and biocompatibility, especially as a naturally abundant product from deacetylation of chitin [33,34,35]. To the end, CS has been already

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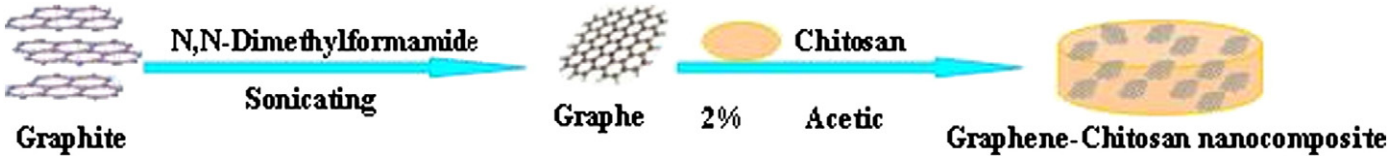

Fig. 1. The procedure for the synthesis of GR–CS nanocomposite.

used to disperse nanomaterials and coat biomacromoleculars [36,37]. Undoubtedly, these intriguing investigations and relative background on the nanomaterials preparation encourage us to continue our efforts for the technique of liquid-phase exfoliation in a convenient and green way. Herein we successfully introduce CS to liquid-phase exfoliation of graphite towards stabilization and solubilization of GR in an aqueous dispersed system. Additionally, the excellent adsorption and viscosity of CS tightens GR modification on the surface of the object.

For this study, hybrid nanocomposite of GR–CS was synthesized by a simple step and then modified on the surface of carbon paste electrode (CPE). The results showed that this modified electrode owns the ability to selectively determine DA with high concentrations of interference. Moreover, this strategy for DA determination was quite accurate and stable. Therefore, the GR–CS modified CPE (GR/CS/CPE) could be a sort of inexpensive and rapid biosensor for DA determination and a good alternative to clinical diagnosis.

2. Experimental

2.1. Reagents and instruments

Dopamine hydrochloride was purchased from Sigma-Aldrich (Germany), and (+)-sodium L-ascorbate, uric acid and chitosan were obtained from Sigma-Aldrich (China). Graphite was obtained from Tianjin Chemical Reagent Factory (China). N,N-dimethylformam was purchased from Sinopharm Chemical Reagent Co., Ltd (China). All the reagents used in this study were of analytical grade, and all solutions were prepared with distilled water. All electrochemical measurements were performed by a CHI650D workstation (Chenhua, Shanghai). A GR/CS/CPE fabricated for a working electrode, a platinum wire and an Ag/AgCl electrode were used to complete the three-electrode system. All the experimental data were the average of three measurements.

2.2. Synthesis of GR–CS nanocomposite

The synthesis of GR–CS nanocomposite is described below: 30 mg graphite was continuously sonicated in 15 mL N,N-dimethylformamide for 30 min, and then 15 mL of 2% acetic acid solution was added for 10 min sonication. The GR–CS mixture was prepared by ultrasonic stirring 60 mg chitosan with the dispersion mentioned above for 1 h. Eventually the resultant dispersion was centrifuged for 90 min at 500 rpm.

2.3. Preparation of GR/CS/GPE

The CPE was prepared by mixing 440 mg graphite powder with 150 mg solid paraffin in an agate mortar and put in incubator until paraffin melted completely. Then the paste was packed into the end of a glass tube, and a copper wire was used as an electrical contact. The surface of the electrodes was polished with Sulfuric acid paper. Eventually, 20 μL nanocomposite of GR–CS was cast to the polished surface of CPE and dried at room temperature.

3. Results and discussion

3.1. Preparation and characterization of GR–CS nanocomposite

GR–CS nanocomposite can be developed in one-pot based on Fig. 1 as described in Section 2.2. While using liquid-phase exfoliation, GR nanosheets show their perfect two-dimensional structure as transparent

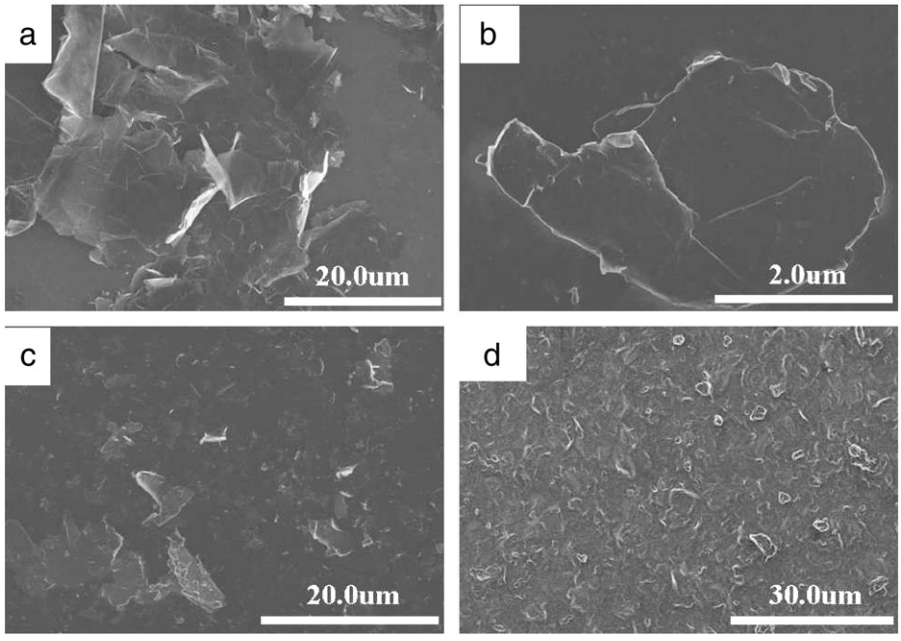

Fig. 2. The images of scanning electron microscope for GR synthesized by liquid-phase exfoliation in N,N-Dimethylformamide (a), one-pot synthesis of GR–CS nanocomposite at low magnification (b) and high magnification (c), GR–CS nanocomposite modified on the surface of CPE (d).