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Macroporous flower-like graphene-nanosheet clusters used for electrochemical determination of dopamine

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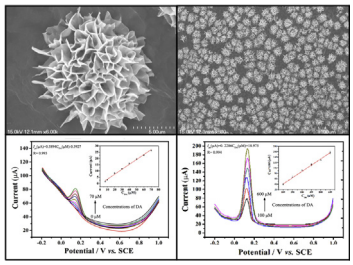
HIGHLIGHTS

- The *f*-RGO/GCE was fabricated by electrochemical method.
- The flower-like graphene framework has a well-defined distributed on GCE.
- The *f*-RGO/GCE shows good responsiveness and high selectivity for DA detection.

GRAPHICAL ABSTRACT



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ABSTRACT

Well-defined flower-like graphene-nanosheet clusters (*f*-RGO) have been facilely and cost-effectively fabricated by electrochemical method on the surface of a glassy carbon electrode (GCE). The obtained *f*-RGO was directly used for the detection of dopamine (DA) via cyclic voltammetry (CV) and differential pulse voltammetry (DPV) technique. The structure of *f*-RGO was confirmed by scanning electron microscopy (SEM). It is observed that the *f*-RGO exhibits typical flower-like interconnected macroporous architecture, which contributes much to the high performance toward DA detection as compared with that of the layer-stacking RGO. For *f*-RGO, DPV measurement gives a wide liner range from 5 μM to 70 μM and 100 μM to 600 μM, respectively, and a good detection limit of 3 μM ($S/N = 3$) for the determination of DA. Moreover, the determination of DA with *f*-RGO is highly selective and reproducible, with a relative standard deviation of 3.0%.

1. Introduction

Dopamine (DA), as a crucial and representative catecholamine neurotransmitter, plays pivotal roles in the function of cardiovascular, metabolism, and central nervous system of mammals [1–3]. It has been proved that abnormal level concentration of DA is related with various neurological diseases, such as Parkinson's disease, Alzheimer's disease, HIV infection, and Huntington's disease [4,5]. So far a variety of analytical approaches, including colorimetry, spectrophotometry, chromatography and eletrochemistry have been developed [6–8]. Furthermore, DA has been detected using electrochemical techniques due to its electroactive nature for a longtime [9–11]. Electrochemical method for quantifying the amount of DA have attracted more attentions due to its a series of advantages such as fast response, high sensitivity, low cost, easy operation, and feasibility of miniaturization. Recently, various materials have been used to modify the working electrode to improve the sensitivity and selectivity of electrochemical senor in electrochemistry detection of DA, such as metal nanoparticles, conducting polymers, carbon nanomaterials and so on [1,12,13].

Graphene (reduced graphene oxide, denoted as RGO), a flexible one-atom-thick sp^2-bonded carbon material, has attracted enor-

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mous attention due to its two-dimensional structure, large specific surface area, high electrical conductivity, perfect biocompatibility, and low cost [1,12–14]. However, the enormous van der Waals force among individual RGO leads to RGO sheets a strong tendency to agglomerate [13], which has a negative effect on its promising applications. In order to overcome this problem, synthesizing three-dimensional (3D) porous RGO is a method to be adopted widely. The 3D porous RGO shows good flexibility, large specific surface area and excellent electrochemical properties in practical applications [15,16]. Amount of effort has been adopted to synthesize 3D porous RGO by various techniques, such as chemical vapor deposition (CVD), hydrogel aerogel techniques, and so on [17–20]. Nevertheless, these methods involve exacting terms, advanced equipments and complicated preparation processes such as high-quality substrate materials, high temperature or accurate control over cooling rates [21]. Therefore, it is significant and necessary to develop a facile and cost-effective method for preparing 3D porous graphene.

In this paper, we report a facile electrochemical method to fabricate the 3D macroporous RGO with flower-like structure (*f*-RGO) on glassy carbon electrode (GCE). The obtained *f*-RGO with large surface area and high electron transfer ability was used to detect DA. For comparison, the electrocatalytic performance of the bare GCE and the layer-stacking RGO modified GCE (RGO/GCE) toward DA detection were also studied.

2. Experimental

2.1. Reagents

Graphite powder (Sinopharm Chemicals Reagent Co., Ltd., China) was used as received. Dopamine was obtained from Acros Organics and used as received. $NaNO_3$, $KMnO_4$, H_2O_2 (30%), $CuSO_4$, Na_2HPO_4, NaH_2PO_4 (Shanghai shiji Chemicals Reagent Co., Ltd., China), were analytical grade. Doubly distilled water was used throughout the experiments.

2.2. Apparatus

The scanning electrode microscopy (SEM) (S-4700, Hitachi High Technologies Corporation, Japan) was used to characterize the morphology of as-prepared electrodes. All the electrochemical experiments were carried out in a conventional three-electrode system using a CHI660D electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China). GCE with a surface area of 0.07 cm^2 was used as the working electrode. A platinum wire and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. All the experiments were performed at room temperature.

2.3. Synthesis of GO

Graphene oxide (GO) was prepared by the Hummer's method [22]. First, 1.0 g graphite powder and 0.5 g $NaNO_3$ were added into a 24 mL H_2SO_4 solution at 0 °C. 3.0 g $KMnO_4$ was slowly added into the solution for 30 min with vigorous stirring at the temperature below 20 °C, and then the mixed solution was stirred for 30 min at 35 °C. Next, 46 mL secondary distilled water was added into the above solution and stirred constantly for 15 min at 98 °C. The reaction was terminated by adding 10 mL H_2O_2 (30%) and 140 mL doubly distilled water. After that, the resulting solution was filtered and washed by HCl solution (5%) until sulfate in filtrate could not be detected with $BaCl_2$. The sample was then dried for 12 h in a vacuum dryer at 40 °C. At last, 10 mg GO product was dispersed into 10 mL of doubly distilled water under ultrasonic homogenizer for 90 min. Impurities were wiped off by centrifuging in GO solution. The concentration of the prepared GO solution was estimated to be 0.5 mg/mL.

2.4. Electrode preparation

The preparation process of *f*-RGO/GCE is described as follow. First, the GO solution (20 μL) was dropped on the surface of a GCE and dried in air. The electrochemical reduction of GO was carried out at −0.9 V vs. SCE for 2000 s in a 0.1 M Na-PBS solution (pH = 4.12). Subsequently, the as-prepared RGO/GCE was used as the working electrode for the electro-deposition of Cu particles at −0.4 V in dilute $CuSO_4$ solution (5 mM) and the deposition charge of metal particles was controlled as 0.01 C. After that, 20 μL GO solution was again dropped onto the obtained electrode (Cu/RGO/GCE) and dried in air, and then reduced at a constant potential of −0.9 V in a 0.1 M Na-PBS (pH = 4.12) solution to obtain a sandwich structure of RGO/Cu/RGO multilayer on the surface of GCE. Finally, the Cu particles deposited on as-prepared electrode were oxidized to Cu^{2+} ($Cu \rightarrow Cu^{2+} + 2e$) at a potential of 0 V for 1200 s, and the Cu^{2+} transported across the exterior RGO layer and diffused into the bulk solution. Simultaneously, the structure of the RGO sheets coated on the copper particles would transform and turn to stand up from the surface of the substrate due to the interactions between the moving Cu^{2+} ions and the exterior RGO sheets. The raised RGO sheets interconnected with each other, and finally the *f*-RGOs formed on the surface of the GCE (*f*-RGO/GCE). In addition, 40 μL GO solution was also dropped on a GCE, dried in air, and followed by electrochemical reduction under the similar conditions as stated above to obtain RGO/GCE for comparison.

3. Results and discussions

3.1. Characterizations of f-RGO/GCE

The surface morphology of the RGO/GCE (A), RGO/Cu/RGO/GCE (B), and *f*-RGO/GCE (C, D) was characterized by SEM. Fig. 1(A) shows the surface morphology of RGO/GCE. It can be seen that many wrinkles are observed on the surface of the electrode, the typical feature of the RGO. Fig. 1(B) exhibits the SEM image of RGO/Cu/RGO/GCE. Through the exterior RGO layer, it is clearly observed that the Cu particles are well dispersed on the surface of the inner RGO layer. As shown in Fig. 1(C and D), the RGO nanosheet clusters with a well-defined flower-like structure are uniformly distributed on the surface of GCE. The 3D macroporous structure as well as the interconnected framework may greatly increase the electrolyte-accessible surface area of as-formed *f*-RGO, and as a result enhance its electrochemical activity and provide more active sites for dopamine oxidation.

The microstructure of as-formed *f*-RGO/GCE was also characterized by Raman spectroscopy. For comparison, the pristine GO and RGO layers on GCE (GO/GCE and RGO/GCE) were also characterized. As Fig. 2 shown, two characteristic peaks known as D-band (1350 cm^{-1}) and G-band (1600 cm^{-1}) are observed in the Raman spectra of *f*-RGO/GCE, RGO/GCE and GO/GCE. The D-band is attributed to the disordered turbostratic structures or defects in the curved graphene nanosheets; the G-band is related to the phonons propagating along the graphitic structures [23,24]. The intensity ratio of the D-band to the G-band, denoted by $R = I_D/I_G$, can be used to predict the amount of defects within the graphene samples. When GO is reduced to RGO, the intensity of D-band will increase, due to more defects introduced into the RGO nanosheets. The R value of *f*-RGO/GCE is 1.18, similar with that of GO/GCE (1.19), but they are higher than that of GO/GCE (0.93). It is indicating that a good reduction degree of RGO both for *f*-RGO/GCE and RGO/GCE, and that the formation of *f*-RGO does not destroy the intrinsic