Synthesis of Fe₃O₄/Graphene oxide/Pristine graphene Composite and Its Application in Electrochemical Sensor

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Abstract. In this work, a Fe₃O₄/graphene oxide (GO)/pristine graphene (PG) ternary composite was synthesized successfully by a two-step method: first graphite was added into GO dispersion to get the GO/PG composite, followed by loading Fe₃O₄ nanoparticles via a co-precipitation method. The structure of Fe₃O₄/GO/PG was characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Compared with the Fe₃O₄/GO binary composite, Fe₃O₄/GO/PG composite shows more excellent properties. An electrochemical sensor fabricated with Fe₃O₄/GO/PG was used to detect dopamine (DA). The linear detection ranges of DA is 5-50 μM with detection limits of 3.37 μM.

1. Introduction
Graphene has attracted great attention since it was discovered in 2004 [1]. Graphene has great advantages of high conductivity, large specific area, and fast charge mobility, so it has been used in many fields, such as sensor, fuel cell, and super capacitor. Graphene oxide (GO) can be prepared by oxidizing graphite powder using chemical method. Thus, oxygen-containing functional groups distributes on the GO, which makes GO show great property of water-solubility. Pristine graphene (PG) is prepared by exfoliating graphite powder. PG represents outstanding conductivity due to its good preservation of graphene structures. As a result, the GO/PG composite might show great electrochemical behavior with the water-solubility of GO and the conductivity of PG [2]. Many materials are used to modify the graphene to achieve a better electrochemical performance, such as noble metal and transition metal oxide. Fe₃O₄ nanoparticles (Fe₃O₄ NPs) are decorated on graphene to achieve a better detect performance due its peroxidase-like activity [3]. Dopamine (DA) secreted by brain is a significant neurotransmitter in message transmission about excitement and happiness. The content of DA in human body has a great relationship to human health. Therefore, it is particularly significant to detect DA efficiently. Electrochemical sensors come into scientists’ sight due to its advantage of convenience and saving time.

In this paper, a Fe₃O₄/GO/PG ternary composite was synthesized by loading Fe₃O₄ nanoparticles on the GO/PG composite by co-precipitation method [4]. The results of scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) both illustrate the Fe₃O₄/GO/PG composite has been synthesized successfully. Besides, electrochemical tests of the sensor based on Fe₃O₄/GO/PG also show good performance on detection of DA.
2. Experimental

2.1. Experimental Materials and Characterization

In this experiment, except graphite powder (1200 mesh, 99.95%), the remaining reagents involved are analytical-level. Phosphorus pentoxide, potassium persulfate, dipotassium phosphate and potassium permanganate were bought from Shanghai Lingfeng Chemical Reagent Co. Ltd. Sulfuric acid, glucose (Glu), and H$_2$O$_2$ were gotten from the Sinopharm Chemical Reagent Co. Ltd. DA, UA, and AA were bought from Sigma-Aldrich. Ultrapure water (≥18.2 MΩ cm) was used throughout this experiment. The morphologies of samples were observed by SEM, which was taken on JSM-5610LV. XPS can explore the types of the elements of composite, which was carried on Thermo Fisher Scientific ESCALAB Xi+. All electrochemical measurements were performed on a CHI660E electrochemical workstation (CH Instruments, Shanghai, China). In this conventional three-electrode system, glassy carbon electrode (GCE), Fe$_2$O$_3$/GO/GCE or Fe$_3$O$_4$/GO/PG/GCE is the working electrode and Ag/AgCl electrode is reference electrode with Pt as the counter electrode. The pH of phosphate buffer saline (PBS) is 7.0, which is close to that of the human body.

2.2. Sample Preparation

Graphite oxide was prepared using the modified Hummers method [5]. GO was prepared by sonicating graphite oxide (22.5 mg) in water (15 mL) using an ultrasonic cell disruptor (JY92-IID, Ningbo Scientz Biotechnology Co.) at 300 W for 1 min (10 s on, 3 s off). Then, 225 mg graphite was added into above solution and sonicated for 5 min (20 s on, 3 s off) at ice bath. The resulting dispersion was centrifuged at 500 rpm for 20 min using a centrifuge (Hettich Universal 320). The top 4/5 of dispersion was collected. Briefly, 25 mg GO/PG composite was dispersed in 20 mL ultrapure water. Ferric chloride (FeCl$_3$·6H$_2$O) and ferrous sulfate (FeSO$_4$·7H$_2$O) dissolved in 5 mL ultrapure water with molar ratio of 2:1 were added into above solution. Then, the pH of the solution was turned to 11 with the help of ammonia water drop by drop and kept at 90 °C for 2 h. This reaction process was protected by nitrogen. Then the Fe$_2$O$_3$/GO/PG composite was collected by magnet. For comparison, the weight ratio of Fe$_3$O$_4$ to GO/PG varied as 1:1, 2:1, 3:1, 4:1, and 5:1, denoted as X-Fe$_3$O$_4$/GO/PG (X=1, 2, 3, 4, 5). The Fe$_3$O$_4$/GO composite was prepared in a similar way.

2.3. Preparation of Sensor

Before modification, the GCE (diameter: 3 mm) was polished with 0.3μm alumina powder and sonicated in ethanol and ultrapure water successively for 15 seconds, respectively. Then 27 μL X-Fe$_3$O$_4$/GO/PG (1 mg/mL) or 5.4 μL Fe$_2$O$_3$/GO (5 mg/mL) was dropped on the surface of GCE and dried at 25 °C in the atmosphere of air.

3. Results and Discussion

Figure 1 illustrates the preparation of Fe$_2$O$_3$/GO/PG. Figure 2 shows the SEM image of 3-Fe$_2$O$_3$/GO/PG. In figure 2, it can be seen a curled and folded part, illustrating the existence of GO. Some small sheets were anchored on the surface of GO [6]. Besides, the Fe$_2$O$_3$ NPs were scattered on the GO/PG composite. Figure 3 is the XPS spectrum of 3-Fe$_3$O$_4$/GO/PG. The peaks of C 1s, O 1s, and Fe 2p are corresponded to the binding energy at around 284, 531, and 718 eV. The element content of C, O and Fe is 71.13%, 23.35% and 5.52 atom%, respectively. The inset in figure 2 is the Fe 2p spectrum. The peaks at 711 and 725 eV are the characteristic peaks of Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$, which indicates the existence of the Fe$_3$O$_4$ in the ternary composite [7].
Figure 1. Illustration of preparation of Fe$_3$O$_4$/GO/PG composite.

Figure 2. The SEM of 3-Fe$_3$O$_4$/GO/PG.

Figure 3. The XPS of 3-Fe$_3$O$_4$/GO/PG.
Figure 4. (a) CVs and (b) EIS of GCE, 3-FeO₃/O/GO/GCE and 3-FeO₃/O/GO/PG/GCE in 0.1M KCl containing 5mM [Fe(CN)₆]³⁻ /²⁻.

Figure 4a and figure 4b shows cyclic voltammograms (CVs) and electrochemical impedance spectroscopy (EIS) of bare GCE, 3-FeO₃/O/GO/GCE and 3-FeO₃/O/GO/PG/GCE in 0.1M KCl containing 5mM [Fe(CN)₆]³⁻ /²⁻, respectively. The scan rate of CV is 50 mV s⁻¹. The frequency of EIS is from 0.01 to 100 kHz. In figure 4a, a pair of redox peaks all appears on the three electrodes. The peak current of 3-FeO₃/O/GO/PG is highest. The peak current of 3-FeO₃/O/GO is almost same with GCE, even higher. In figure 4b, the diameter of the semicircle at high frequency in EIS displays the electron transfer resistance (Rₓ) on the surface of the electrode [8]. An obvious semicircle can be seen on GCE and the Rₓ is about 23 Ω. The Rₓ for 3-FeO₃/O/GO/GCE is about 20 Ω. However, it could not be seen that a semicircle appears on the 3-FeO₃/O/GO/PG/GCE, illustrating that the charge transfer on the surface of the electrode is fast.

Figure 5a shows the effect of the loading amount on 3-FeO₃/O/GO/PG/GCE in PBS (pH=7) containing 1mM DA. As shown in figure 5a, the current intensity is highest when the amount is 27 μg on 3-FeO₃/O/GO/PG/GCE. Figure 5b displays CVs of X-FeO₃/O/GO/PG/GCE in PBS (pH=7) containing 1 mM DA at a scan rate of 50 mV s⁻¹ with the loading amount of 27 μg. It can be seen that the 3-FeO₃/O/GO/PG/GCE shows the largest current response.

Figure 6a shows CVs of bare GCE, 3-FeO₃/O/GO/GCE, and 3-FeO₃/O/GO/PG/GCE in PBS (pH=7) in the presence or absence of 1 mM DA at a scan rate of 50 mV s⁻¹. The peak current of 3-FeO₃/O/GO/PG/GCE is higher than 3-FeO₃/O/GO/GCE and GCE, which can be attributed to the GO/PG composite with the water-solubility of GO and the conductivity of PG. Figure 6b is differential pulse voltammetry (DPV) of 3-FeO₃/O/GO/PG/GCE in PBS (pH=7) with different concentration of DA from 0 to 50 μM. It can be obviously observed that the concentration of DA increases and the peak current near 0.18 V increases correspondingly. Figure 6c exhibits the relationship of the concentration of DA and the DPV peak current on the 3-FeO₃/O/GO/PG/GCE. It can be seen that a corresponding linear relationship appeared in this figure and the linear range is 5-50 μM. Besides, the performance of sensors can be evaluated by the correlation coefficient (R²), the sensitivity, and the detection limit usually set at a signal-to-noise ratio (S/N) of 3. In our work, the sensitivity of the sensor based on 3-FeO₃/O/GO/PG/GCE is 1.97 μA μM⁻¹ and the R² is 0.994. The detection limit is 3.37 μM. All this illustrate the FeO₃/O/GO/PG/GCE sensor shows good detection effect on DA. The anti-interference ability of the sensor is also investigated by DPV signal change as shown in figure 6d. It can be seen that the H₂O₂ has a little influence on the signal change of DA, but the UA, AA, and Glu show more serious signal change of DA compared with H₂O₂. The repeatability of the sensor is estimated with the peak current of six parallel electrodes. The relative standard deviation (RSD) of the six tests results was 7.8% for 20 μM DA. The stability of the sensor is also investigated. After 20 measurements, the value of the peak current based on the FeO₃/O/GO/PG/GCE sensor still maintained 79% in PBS containing 1 mM DA.
Figure 5. (a) The loading amount on 3-Fe$_3$O$_4$/GO/PG/GCE and (b) CVs of X-Fe$_3$O$_4$/GO/PG/GCE (loading amount: 27 μg) in PBS (pH=7) containing 1 mM DA.

Figure 6. (a) CVs of bare GCE, 3-Fe$_3$O$_4$/GO/GCE, and 3-Fe$_3$O$_4$/GO/PG/GCE in PBS containing 0 and 1 mM DA. (b) DPVs of 3-Fe$_3$O$_4$/GO/PG/GCE in 0.1M PBS with different concentration of 0-50 μM. (c) The calibration curve of 3-Fe$_3$O$_4$/GO/PG. (d) The anti-interference ability of the sensor in PBS (pH=7) containing 20 μM DA with the extra addition of 20 μM UA, 20 μM AA, 20 μM Glu, and 20 μM H$_2$O$_2$, respectively.

4. Conclusions
In conclusion, the Fe$_3$O$_4$/GO/PG composite was successfully prepared through a two-step method and fabricated to be an electrochemical sensor to detect DA. Compared with bare GCE and Fe$_3$O$_4$/GO binary composite, the Fe$_3$O$_4$/GO/PG ternary composite shows more excellent properties. The sensor
based on Fe₃O₄/GO/Pt composite has good sensitivity for DA linear detection ranges from 5 to 50 μM and detection limits of 3.37 μM (S/N=3).

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6. References
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