A facile one-step synthesis of Fe₂O₃/nitrogen-doped reduced graphene oxide nanocomposite for enhanced electrochemical determination of dopamine

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Abstract

Fe₂O₃/nitrogen-doped reduced graphene oxide (Fe₂O₃/N-rGO) was synthesized for enhanced electrochemical determination of dopamine (DA). The nanocomposite was synthesized through a facile one-step hydrothermal method, where ethylenediamine served as reducing agent, nitrogen source and coordinating agent, therefore making the reduction and nitrogen doping of GO and the formation of Fe₂O₃ occur simultaneously. Scanning electron microscopy (SEM), [energy-dispersive X-ray spectroscopy \(EDX\)](#), X-ray diffraction spectroscopy (XRD), fourier transform infrared spectroscopy (FTIR), [Raman spectroscopy](#) and electrochemical techniques were employed to characterize Fe₂O₃/N-rGO. The results showed that large numbers of Fe₂O₃ with spindle morphology were distributed on the surface of N-rGO and the synergetic effect between Fe₂O₃ and N-rGO made the sensor based on Fe₂O₃/N-rGO exhibit an excellent performance toward DA detection with a wide linear range of 0.5 μ M to 0.34 mM, a high sensitivity of 418.6 μ A mM⁻¹ cm⁻² and a low detection limit of 0.49 μ M (S/N = 3). Moreover, the sensor also exhibited good selectivity, reproducibility and stability. Therefore, Fe₂O₃/N-rGO can be applied as a promising type of sensing material for electrochemical detection of DA.

Keywords: Fe₂O₃; Nitrogen-doped reduced graphene oxide; Hydrothermal; Dopamine; Nonenzymatic sensor

1. Introduction

Dopamine (DA) acts as neurotransmitter, which plays important roles in human

bodies [1]. Therefore, the determination of DA is necessary. Electrochemical method can be employed as a promising method since DA can be oxidized electrochemically [2]. However, the oxidation of DA on bare electrode only exhibits a low response [3] and the coexistence of uric acid (UA) and ascorbic acid (AA) usually causes interference [4]. It was reported that nanomaterials can improve the performance of bare electrode [5]. Therefore, in order to improve the analytical properties, studying nanomaterials-based electrodes is necessary.

Currently, large numbers of nanomaterials were employed to modify bare electrode for DA detection [6-10]. Hu [8] fabricated a DA sensor based on Au@carbon dots-chitosan composite. The results founded that the carboxyl groups of carbon dots enabled interaction with amine functional groups in DA through electrostatic interaction and Au nanoparticle could make the surface of the electrode more conductive, therefore making the sensor exhibit an excellent performance toward DA detection. Yang [10] reported a sensitive DA sensor by improving surface adsorption via shape control of hematite α -Fe₂O₃ nanoparticles and the results indicated that shuttle-like Fe₂O₃ nanoparticle surface was covered by high-density atomic steps, which endowed them with the enhanced adsorption and sensor ability toward DA. In particular, Fe₂O₃ attracted much attention due to its advantages of intrinsic enzyme-mimicking activity, low cost, natural abundance and environmental friendliness [10]. However, the poor transport property of Fe₂O₃ usually results in low electrocatalytic activity [11], which limits its application to some extent. On the other hand, reduced graphene oxide (rGO) is a two-dimensional carbon material with large surface area and excellent conductivity [12]. Meanwhile, the surface area and conductivity of rGO can be further improved through doping rGO with nitrogen (N-rGO) [13]. Therefore, it is expected that decorating Fe₂O₃ on N-rGO (Fe₂O₃/N-rGO) not only prevents the aggregating of N-rGO but also enhances the conductivity of Fe₂O₃, which is beneficial to improve the electrochemical response of DA and therefore enables Fe₂O₃/N-rGO a promising sensing material. Up to now, a few examples of synthesis of Fe₂O₃/N-rGO for applications were demonstrated [14-17]. For example, Fu [16] synthesized Fe₂O₃/N-rGO for enhancing the visible

activities of Fe_2O_3 , in which graphene doped with nitrogen was prepared through a one-pot ammonia-modified hydrothermal process and then $\text{Fe}_2\text{O}_3/\text{N-rGO}$ was obtained via a common wet-chemical method. Sun [17] developed a solvothermal-induced self-assembly approach to construct three dimensional macroscopic Fe_2O_3 nanocubes/nitrogen-doped graphene aerogel as anode materials and the nanocomposite exhibited excellent rate capability, outstanding long-term cyclic stability due to the synergetic effect between Fe_2O_3 and nitrogen-doped graphene aerogel. Considering the importance and wide applications of $\text{Fe}_2\text{O}_3/\text{N-rGO}$, developing facile methods to synthesize $\text{Fe}_2\text{O}_3/\text{N-rGO}$ are highly desired. Moreover, although the synergetic effect between Fe_2O_3 and N-rGO enables $\text{Fe}_2\text{O}_3/\text{N-rGO}$ a promising material for wide applications, few studies reported the application of $\text{Fe}_2\text{O}_3/\text{N-rGO}$ as sensing material for DA detection. Therefore, it is necessary to develop a facile one-step method to synthesize $\text{Fe}_2\text{O}_3/\text{N-rGO}$ for DA detection.

In this paper, $\text{Fe}_2\text{O}_3/\text{N-rGO}$ was synthesized through a facile one-step hydrothermal method, where ethylenediamine served as nitrogen source, reducing agent and coordinating agent. Then, $\text{Fe}_2\text{O}_3/\text{N-rGO}$ was employed to modify glassy carbon electrode for fabricating nonenzymatic DA sensor. The morphology, structure, composition and electrochemical properties of $\text{Fe}_2\text{O}_3/\text{N-rGO}$ were studied in detail.

2. Experimental

2.1. Reagents and materials

Graphite powder, ethylenediamine (EDA) and ferric chloride crystal ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99.0%) were obtained from Xi'an Chemical Reagent. Sigma Company supplied Uric acid (UA), glucose (Glu), ascorbic acid (AA) and DA. Pure double distilled water was used in all experiments.

2.2. Apparatus

Scanning electron microscopic (SEM) images were recorded by JSM-6700F (JEOL, Japan). D/MAX 3C (Rigaku, Japan) and TENSIR 27 (Bruker, German) were employed to record XRD patterns and FTIR spectra, respectively. Raman spectra was obtained on J-Y T64000 Raman spectrometer with 514.5 nm wavelength incident

laser light. Electrochemical measurements were carried out in a three-electrode electroanalysis system controlled by CHI 660 electrochemical workstation (Shanghai CH Instrument Co. Ltd., China), in which glassy carbon electrode (GCE), saturated calomel electrode and platinum wire were employed as working electrode, reference electrode and counter electrode, respectively.

2.3. Synthesis of $\text{Fe}_2\text{O}_3/\text{N-rGO}$

GO was synthesized through modified Hummers [18]. $\text{Fe}_2\text{O}_3/\text{N-rGO}$ was prepared as follows: 15 mg of GO was dispersed in 30 mL of water and 0.1 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added into GO solution with stirring for 30 min. Then, 1.5 mL of EDA was slowly added into above solution and stirred for another 30 min. After that, the mixed solution was transferred into Teflon-lined autoclave (40 mL) and kept at 180°C for 10 h. The product was obtained by centrifugation and washing with ultrapure water. Fe_2O_3 was synthesized by the similar way in the absence of GO.

2.4. Electrode modification

The modified electrode was prepared by casting method. GCE was polished by alumina powder. 2.0 mg of $\text{Fe}_2\text{O}_3/\text{N-rGO}$ was dispersed into 1 mL of water. 6 μL of $\text{Fe}_2\text{O}_3/\text{N-rGO}$ solution and 3 μL of Nafion (0.05% (m:m)) were dropped on the surface of GCE and then dried in air, which was expressed as $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$. GO/GCE and $\text{Fe}_2\text{O}_3/\text{GCE}$ were fabricated in the similar way.

3. Results and Discussion

3.1 Characterizations of $\text{Fe}_2\text{O}_3/\text{N-rGO}$

$\text{Fe}_2\text{O}_3/\text{N-rGO}$ was synthesized through a facile one-step hydrothermal method, where EDA served as nitrogen source, reducing agent and coordinating agent. GO is functioned with large numbers of oxygen-containing groups [19]. Therefore, after adding FeCl_3 and EDA, Fe^{3+} and EDA were adsorbed on the surface of GO through electrostatic interactions. Meanwhile, as the chelating agent, EDA reacted with Fe^{3+} to form $[\text{FeEDA}]^{3+}$ complexes, which was beneficial to prevent the precipitation of iron hydroxide very rapidly [20]. Then, under hydrothermal condition, GO was reduced and doped with nitrogen via the assistance of EDA as reducing agent and nitrogen

source, which was accompanied with the formation of Fe_2O_3 on N-rGO.

The morphologies of GO and $\text{Fe}_2\text{O}_3/\text{N-rGO}$ were characterized by SEM. As shown in Figure 2 (A), GO displayed monolayer nanosheet structure with wrinkles. This structure was beneficial to provide large surface area and anchoring sites. Figure 2 (B and C) showed the SEM images of $\text{Fe}_2\text{O}_3/\text{N-rGO}$, which revealed that large numbers of Fe_2O_3 with spindle morphologies were decorated on the surface of N-rGO. Such structure prevented the aggregating of N-rGO and also enhanced the conductivity of Fe_2O_3 , which was beneficial to improve the electrochemical response of DA. The EDX spectrum of $\text{Fe}_2\text{O}_3/\text{N-rGO}$ was recorded to investigate its composition. As shown in Figure 2 (D), EDX spectrum displayed the peaks of C, O, N and Fe element, which agreed with the characterizations of $\text{Fe}_2\text{O}_3/\text{N-rGO}$.

Moreover, the chemical structures of $\text{Fe}_2\text{O}_3/\text{N-rGO}$ were studied by FTIR spectroscopy and XRD pattern. As shown in Figure 3 (A), GO (curve a) revealed some peaks at 3423 cm^{-1} , 1722 cm^{-1} , 1626 cm^{-1} and 1057 cm^{-1} due to the stretching of $-\text{OH}$, $\text{C}=\text{O}$, $\text{C}=\text{C}$, $\text{C}-\text{O}$ [21], respectively, which confirmed the presence of oxygen-containing functional groups on GO and these functional groups provided large numbers of anchor sites for Fe_2O_3 . Comparing with that of GO, the peak of $\text{Fe}_2\text{O}_3/\text{N-rGO}$ (curve b) at 1722 cm^{-1} almost disappeared, indicating the reduction of GO. Moreover, new peaks at 1560 cm^{-1} and 550 cm^{-1} were observed, which were due to C-N scissoring absorption and Fe-O stretching vibration [14], confirming the successful nitrogen doping and the formation of Fe_2O_3 . In the case of XRD pattern of $\text{Fe}_2\text{O}_3/\text{N-rGO}$ (Figure 3 (B)), some peaks at 24.2° , 33.2° , 35.7° , 40.9° , 49.5° , 54.0° , 57.5° , 62.4° and 64° were observed, which were in good agreement with (012), (104), (110), (113), (024), (116), (122), (214) and (300) planes of Fe_2O_3 [22].

Figure 4 shows Raman spectra of (A) rGO and (B) $\text{Fe}_2\text{O}_3/\text{N-rGO}$. The characteristic D and G bands of rGO appeared at 1331 and 1594 cm^{-1} . In the case of $\text{Fe}_2\text{O}_3/\text{N-rGO}$, the intensity ratio of the D band and G band was higher than that of rGO, which indicated higher concentration of structure defect due to the nitrogen doping and decoration of Fe_2O_3 . Moreover, the peaks at 219 , 283 , 394 and 597 cm^{-1} were assigned as the A_{1g} mode and E_g mode of $\alpha\text{-Fe}_2\text{O}_3$ phase, respectively,

confirming the presence of Fe_2O_3 . Therefore, the results of SEM, EDX, FTIR spectroscopy, XRD pattern and Raman spectra confirmed the successful formation of $\text{Fe}_2\text{O}_3/\text{N-rGO}$.

3.2 Electrochemical properties of $\text{Fe}_2\text{O}_3/\text{N-rGO}$

Cyclic voltammograms (CVs) were employed to study the electrochemical behaviors of different modified GCE. Figure 5 showed the CVs obtained at GCE, GO/GCE, $\text{Fe}_2\text{O}_3/\text{GCE}$ and $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$ in pH 7.5 PBS solution in the presence of 0.05 mM DA at scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$. As shown in Figure 5, a pair of redox peaks were observed at GCE, which was due to the oxidation and reduction of DA since DA can be changed rapidly between oxidized and reduced states during the positive and negative potential scan [23]. Comparing with bare GCE, GO/GCE exhibited a higher oxidation peak, which benefited from the large surface area and the electrostatic interaction between GO and DA since GO is a two-dimensional carbon material with large surface area and large numbers of oxygen-containing functional groups, therefore enabling more DA to absorb and react. In the case of $\text{Fe}_2\text{O}_3/\text{GCE}$, the oxidation peak of DA had a significant enhancement in comparing with that of GCE. This indicates that Fe_2O_3 efficiently catalyzed the electrochemical oxidation of DA. Interestingly, among modified GCE, $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$ exhibited the largest oxidation peak about 16 μA in intensity at 0.18 V, indicating the excellent electrocatalytic activity of $\text{Fe}_2\text{O}_3/\text{N-rGO}$ toward DA oxidation. Therefore, the decoration of Fe_2O_3 on N-rGO not only prevented the aggregating of N-rGO and increased the surface area but also enhanced the conductivity of Fe_2O_3 and improved its electrocatalytic activity, therefore providing more electroactive sites for DA adsorption and reaction. Meanwhile, DA can bind to the Fe-ion more strongly via the chelate catechol-Fe binding, therefore the covalent bond between DA and Fe_2O_3 enabled the number of DA molecules available for the electrooxidation. Furthermore, positively charged aromatic DA molecules can be absorbed on the surface of $\text{Fe}_2\text{O}_3/\text{N-rGO}$ via π - π stacking interaction and electrostatic attraction, which enabled more DA to be absorbed and improved the electrochemical response of DA. The detection mechanism for the electrochemical response of DA can be expressed as

follows :

The electrocatalytic activity and kinetic mechanism of Fe₂O₃/N-rGO/GCE toward DA oxidation and reduction were studied. Figure 6 (A) showed that the oxidation and reduction current increased with the increasing of DA concentration and a good linear relationship was obtained (Figure 6 (B)), implying the excellent electrocatalytic activity of Fe₂O₃/N-rGO toward DA oxidation and further confirming that Fe₂O₃/N-rGO modified electrode could be employed to detect DA. In addition, as shown in Figure 6 (C), the oxidation and reduction current increased with the increasing of scan rate. Meanwhile, Figure 6 (D) showed the linear relationship between the scan rate and the peak current of DA with a correlation coefficient of 0.9923 and 0.9984 for anodic and cathodic peak currents, respectively. This implied that the electro-oxidation of DA was controlled by diffusion controlled electrochemical process on electrode surface.

The amperometric current-time curve obtained at Fe₂O₃/N-rGO/GCE with successful addition of DA was recorded to study the sensing property of Fe₂O₃/N-rGO/GCE. In order to ensure high signal intensity, lower background noise and less interference of other species, 0.2 V was chosen as the working potential. As shown in Figure 7 (A), the oxidation current increased with the successive addition of DA. Figure 7 (B) showed the calibration curve and the linear regression equation was expressed as $I_p (\mu\text{A}) = 0.2043 + 29.30 \cdot C (\text{mM})$. The linear detection range was from 0.5 μM to 0.34 mM. The sensitivity was $418.6 \mu\text{A mM}^{-1} \text{cm}^{-2}$, which was estimated from the slope of the calibration curve and electrode surface area. The low detection limit of 0.49 μM was obtained at a signal-to-noise ratio of 3 using the equation $\text{LOD} = 3\text{SB}/b$, where SB is the standard deviation of the blank solution and b is the slope of the analytical curve, as shown in Figure 7B. Furthermore, comparing with other DA sensors (Table 1), Fe₂O₃/N-rGO/GCE exhibited an excellent performance for DA detection. Therefore, the synergetic effect between Fe₂O₃ and N-rGO made Fe₂O₃/N-rGO a promising type of sensing material for DA detection.

The selectivity of Fe₂O₃/N-rGO/GCE was investigated. Figure 8 (A) displayed the CVs obtained at Fe₂O₃/N-rGO/GCE in different solutions, which showed that a low electrochemical response appeared after adding 0.1 mM AA or UA and the coexistence of 0.1 mM AA and UA caused only a little effect on the electrochemical response of 0.1 mM DA. Moreover, as shown in Figure 8 (B), an obvious amperometric response appeared after adding 0.005 mM DA. However, only a small electrochemical response was observed after adding 0.5 mM Glu, 0.05 mM UA and 0.005 mM AA, indicating that Glu, UA and AA had almost no interference for DA detection. The possible reason for selective detection of DA may be the strong π - π stacking interaction, electrostatic attraction and covalent bond between DA and Fe₂O₃/N-rGO, which makes more DA absorb on the surface of electrode and leads to an enhanced and specific response of DA. Meanwhile, Nafion film is cation-exchanger polymer which repels electronegative AA and UA toward working electrode and further improves the selectivity of DA. Six Fe₂O₃/N-rGO/GCE were fabricated for detecting 0.05mM DA and a relative standard deviation (RSD) of 6.3% was obtained (Figure 8 (C)). In addition, as shown in Figure 8 (D), Fe₂O₃/N-rGO/GCE ensured 82% of its initial current response after twenty days, indicating the acceptable stability. When the modified electrode was not in use, it was stored in dry conditions in a refrigerator, where the temperature was 4 °C.

In order to evaluate the applicability of Fe₂O₃/N-rGO/GCE, analysis of real sample was investigated. Standard addition method was employed to analyze real sample and the result was added in Table 2. As shown in Table 2, the sensor possessed an acceptable recovery.

4. Conclusion

Fe₂O₃/N-rGO was successfully synthesized for electrochemical determination of DA. The experimental results revealed that the assistance of EDA as reducing agent, nitrogen source and coordinating agent made the preparation method facile without employing other agent or complicated steps. Meanwhile, the decoration of Fe₂O₃ on N-rGO not only enhanced the electron transfer of Fe₂O₃ and improved its catalytic

activity but also prevented the aggregating of N-rGO and increased the surface area for DA reaction, therefore making $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$ exhibit an excellent performance for DA detection. Considering the facile preparation route and excellent experimental results, $\text{Fe}_2\text{O}_3/\text{N-rGO}$ nanocomposite can be applied as a promising type of sensing material and the approach presented in this study may be extended to the fabrication of other metal oxide/N-rGO for applications.

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Figure Caption

Figure 1. Schematic representation of the synthesis procedure of $\text{Fe}_2\text{O}_3/\text{N-rGO}$.

Figure 2. SEM images of nanocomposite: (A) GO, (B, C) $\text{Fe}_2\text{O}_3/\text{N-rGO}$, EDX spectrum of (D) $\text{Fe}_2\text{O}_3/\text{N-rGO}$.

Figure 3. (A) FTIR spectra of (a) GO, (b) $\text{Fe}_2\text{O}_3/\text{N-rGO}$, (B) XRD pattern of $\text{Fe}_2\text{O}_3/\text{N-rGO}$.

Figure 4. Raman spectra of (A) rGO and (B) $\text{Fe}_2\text{O}_3/\text{N-rGO}$

Figure 5. Cyclic voltammograms obtained at bare GCE, GO/GCE, $\text{Fe}_2\text{O}_3/\text{GCE}$ and $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$ in pH 7.5 PBS in the presence of 0.05 mM DA at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$.

Figure 6. (A) Cyclic voltammograms obtained at $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$ in pH 7.5 PBS in the presence of DA with different concentrations (from 0 to 0.06 mM) at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$. (B) Calibration curve of DA versus its concentration. (C) Cyclic voltammograms obtained at $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$ in pH 7.5 PBS containing 0.06 mM DA at different scan rates (from 20 to $200 \text{ mV}\cdot\text{s}^{-1}$). (D) Linear fitting program of DA versus the square root of scan rate.

Figure 7. (A) Amperometric curve obtained at $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$ with successive additions of DA in pH 7.5 PBS at 0.2 V. (B) Calibration curve of DA versus its concentration.

Figure 8. (A) Cyclic voltammograms obtained at $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$ in different solutions, (B) Amperometric curve obtained at $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$ for successive additions of 0.005 mM DA, 0.5 mM Glu, 0.05 mM UA, 0.005 mM AA in pH 7.5 PBS at 0.2 V, (C) Results of the measurements of 0.005 mM DA with five $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$, (D) Current response of 0.005 mM DA at $\text{Fe}_2\text{O}_3/\text{N-rGO}/\text{GCE}$ in twenty days measurement.

Table 1. Comparison of non-enzymatic DA sensors.

Sensors	Linear range (mM)	Sensitivity ($\mu\text{A mM}^{-1} \text{cm}^{-2}$)	Detection limit (μM)	References
Graphene/GCE	0.004 – 0.1	-	2.64	24
rGO/Pd/GCE	0.001 – 0.15	2.62	0.233	6
Pd-MWCNTs	0.012 – 0.278	-	0.63	25
GO-MWCNT/MnO ₂ /AuNP/GCE	0.0005 – 2.5	233.4	0.17	26
Pt/RGO/GCE	0.01 – 0.17	-	0.25	27
Au NP/PANIf/GCE	0.003 – 0.115	384	0.8	28
nano-ZnO/GCE	0.00011 – 0.18	-	0.32	29
SWCNT/Fe ₂ O ₃ /GCE	0.0032 – 0.0318	-	0.36	30
Fe ₂ O ₃ /N-rGO/GCE	0.0005 – 0.34	418.6	0.49	This work

Table 2. Determination of DA in dopamine hydrochloride injection.

Sample	Added (μM)	Found (μM)	Recovery (%)
1	5.0	5.2	104
2	12.0	11.4	95
3	25.0	23.7	94.8

Each value is the average of five measurements.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

A facile one-step hydrothermal method was reported to synthesize $\text{Fe}_2\text{O}_3/\text{N-rGO}$ for enhanced electrochemical determination of dopamine.