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Article

Electroanalysis of Dopamine Using Polydopamine Functionalized Reduced Graphene Oxide-Gold Nanocomposite

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Abstract: A novel polydopamine functionalized reduced graphene oxide/gold (PDA-RGO/Au) nanocomposite modified electrode was fabricated, and applied for electrochemically determine dopamine. UV-vis spectroscopy and FTIR characterizations confirmed the successful reduction of graphene oxide (GO) to RGO during the dopamine self-polymerization process. Then, Au nanoparticles with an average size of 120 nm were electrodeposited onto the PDA-RGO film modified glassy carbon electrode (GCE) was performed. The electrocatalytic activity of the PDA-RGO/Au modified GCE was evaluated by oxidation of dopamine using cyclic voltammetry and linear sweep voltammograms. The results showed that the obtained anodic peak currents were linearly proportional to concentration in the range of 0.05 mM to 1 mM with a detection limit of 3.211 μM (S/N = 3.0). In addition, the effect of co-existing species such as ascorbic acid, uric acid and glucose on the determination of dopamine was investigated. Therefore, the PDA-RGO/Au modified dopamine sensor with excellent sensitivity and selectivity could provide an ideal matrix for clinical applications.

Keywords: Reduced graphene oxide; Polydopamine; Gold; Electrodeposition

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1. Introduction

Dopamine (DA) is an important catecholamine neurotransmitter in the central nervous system. Studies demonstrated the abnormal level of DA could lead to several serious central nervous system disorders, such as Parkinson's, Alzheimer's and schizophrenia diseases [1,2]. Therefore, develop an accurate and sensitive method for DA determination is necessary for the clinical diagnostic purposes. Till now, the methods for the detection of DA including UV-vis spectrometry [3], capillary electrophoresis [4], chemiluminescence[5] and electrochemical analysis[6]. Among these techniques, electrochemical method has been found owing advantages of fast speed, low cost, low detection limits and high accuracy.

Graphene, a two-dimensional sheet of sp^2-hybridized carbon, has been received lots attention in the electrochemical field due to its high electronic conductivity, low mass density and high specific surface area [7-9]. Recently, Qian and co-workers demonstrated a DA sensor based on Au nanoparticles decorated polypyrrole/reduced graphene oxide sheets and exhibits a remarkable sensitivity [10]. However, the graphene used for sensor design usually in its reduced form from graphene oxide (GO) prepared by the oxidation of graphite. One major drawback of reduced graphene oxide (RGO) is the natural tendency of agglomeration, which lower the surface area of product [11]. In order to overcome this problem, polydopamine (PDA) was used for reducing and functionalizing GO to a solution processable RGO [12]. Moreover, coupling carbon based materials with noble metal nanoparticles could highly enhance the electrochemical activity. For example, our group demonstrated the preparation of Ag nanoparticle and carbon nanotube hybrid film by a layer-by-layer self-assembly technique [13]. The fabricated hybrid thin film exhibited excellent electrocatalytic activity to the reduction of hydrogen peroxide.

Herein, we report the construction of PDA-RGO/Au nanocomposite and its electrocatalytic behaviors toward oxidation of DA. The PDA modified RGO nanocomposite was firstly fabricated by self-polymerization process of PDA. The self-polymerization process also simultaneously reduces the GO to RGO. Then, Au nanoparticles were electrodeposition on the PDA-RGO modified glassy carbon electrode. The electrocatalytic activity of the PDA-RGO/Au modified GCE was determined by oxidation of DA using cyclic voltammetry and linear sweep voltammograms.

2. Experimental

2.1 Materials

Uric acid (99%), L-ascorbic acid (99%), $HAuCl_4$, 3-hydroxytyramine hydrochloride (DA) and glucose were brought from Sigma-Aldrich. Graphene oxide powder was purchased from JCNANO. All other chemicals used were analytical grade reagents without further purification. Phosphate buffer solution (PBS) was prepared by mixing 0.2 M KH_2PO_4 and K_2HPO_4 solution to appropriate pH. Milli-Q water (18.2 MΩ cm) was utilized throughout the experiments.

2.2 Synthesis of PDA-RGO nanocomposite.

In a typical synthesis of PDA-RGO nanocomposites, GO was firstly modified with PDA. 10 mg GO was dispersed in 30 mL Tris-buffer (10 mM, pH 8.5) and sonicated for 1 h. 10 mg DA was then added into the dispersion for further 10 min sonication. The resulting mixture was kept stirring for 24 h. The PDA-RGO product was collected and washed three times by water using centrifugation.

2.3 Electrodeposition of Au on PDA-RGO nanocomposite.

Prior to use, the GCE was polished by 0.3 μm and 0.05 μm alumina slurry followed by rinsing with water, ethanol and water, in turn. Then, 5 μL of *PDA*-RGO sample dispersion (0.5 mg/mL) was dropped onto the GCE and dried at room temperature. Before use, the modified electrode was rinsed with water to remove the loosely attached *PDA*-RGO.

Electrochemical measurements were performed on a CHI430a electrochemical workstation (USA), using a three electrode system. A platinum wire was used as the auxiliary electrode and a Ag/AgCl (3M KCl) as the reference electrode. The electrochemical deposition of gold nanoparticles on PDA-RGO modified GCE was performed in 0.5 M H_2SO_4 solution containing 1% $HAuCl_4$ using chronoamperometry at an applied potential of −0.2 V for 30 s. The prepared electrode was defined as PDA-RGO/Au.

2.4 Characterization

The surface functional groups present on the samples were characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet iS5, Thermo Scientific, USA). The optical characterizations were obtained by UV-vis spectrophotometer in the wavelength range from 190 to 700 nm.

3. Results and Discussion

3.1 Characterization of PDA-RGO/Ag nanocomposite

The reduction of GO during the PDA self-polymerization process was firstly confirmed by UV-vis spectroscopy and displayed in Fig 1A. The GO spectrum shows a characteristic absorption peak at 227 nm corresponding to the $\pi \rightarrow \pi^*$ transition of aromatic C═C bonds. After PDA self-polymerization process, this peak red shifted to 278 nm. Moreover, the spectrum showed a significant increase of absorbance at the entire visible range due to the black colour of PDA-RGO nanocomposite. Therefore, the results indicate the successful reduction of GO.

Fig 1B represents the FTIR spectra of GO and PDA-RGO nanocmomposite. It can be observed that the GO spectrum presents typical peaks at 1730, 1620, 1398 and 1047 cm^{-1} which are assigned to the C═O stretching of COOH groups, C═O stretching vibration, C—OH stretching vibration and C—O vibrations from alkoxy groups, respectively. After surface functionalization with PDA, the intensity of these peaks declines significantly, suggesting that the amount of oxygen-containing groups at the surface of GO are greatly reduced. Moreover, two new peaks featured at 1502 and 1356 cm^{-1} are observed on PDA-RGO spectrum, corresponding to the stretching vibration of C=N and C-N-C of the indole ring. They confirm the successful modification of PDA on RGO sheets.

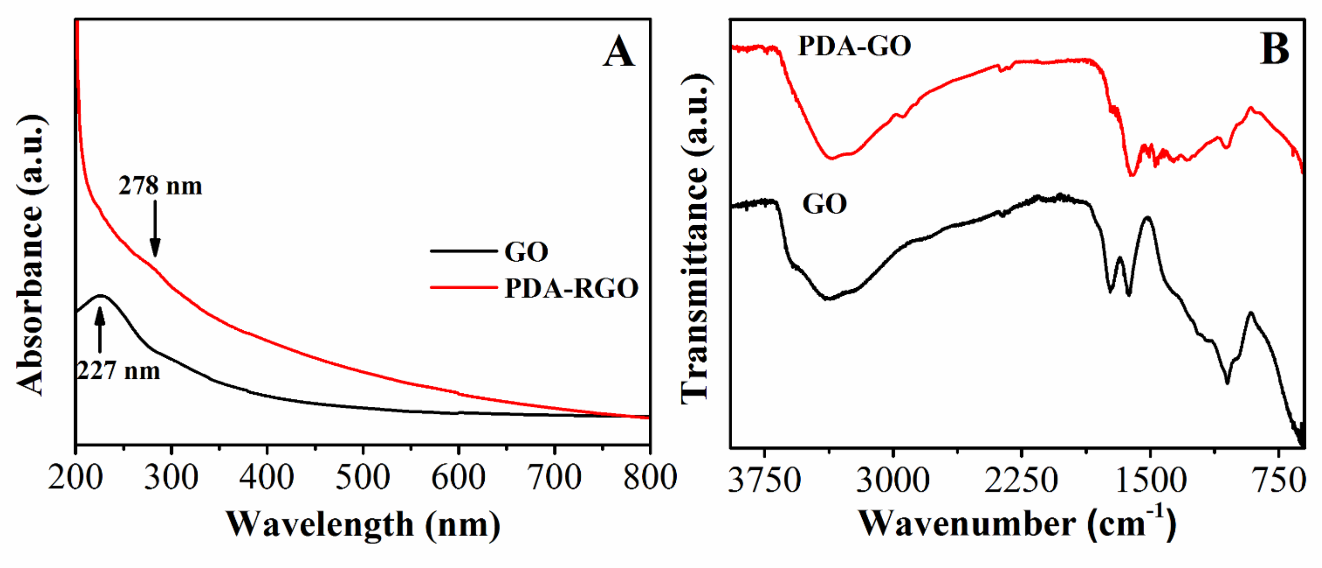

Fig 1. (A) UV-vis and (B) FTIR spectra of GO and PDA-RGO nanocomposite.

The morphology structure of PDA-RGO and PDA-RGO/Au nanocomposites were tested by SEM. It is obvious from the image (Fig. 2A) that the PDA functionalized RGO showed a well dispersibility without sheets aggregation, indicating the PDA surface functionalization could highly improve the dispersibility of RGO and provide a high specific surface area for final nanocomposite. After the electrodeposition, the morphology of the nanocomposite could be seen in Fig. 1B. A number of Au nanoparticles with an average size of 80 nm were observed on the PDA-RGO surface layer as well as inner layers.

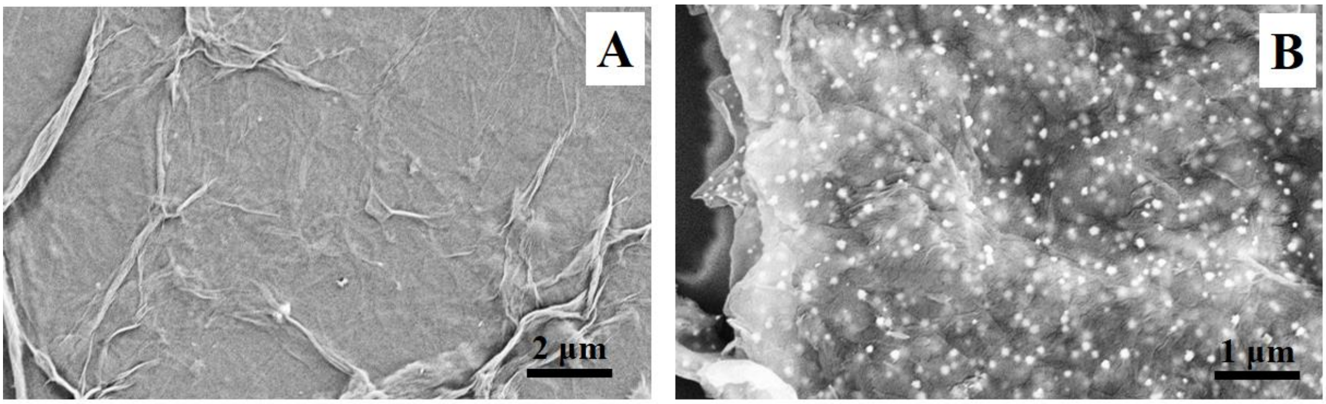

Fig 2. SEM images of (A) PDA-RGO and (B) PDA-RGO/Au nanocomposite.

3.2 Electrochemical behaviour of DA on the PDA-RGO/Au modified electrode

The electrochemical oxidations of DA at various modified electrodes were investigated as shown in Fig 3A. It can be observed that the cyclic voltammogram (CV) of PDA-RGO modified GCE showed an enhanced current response than that of bare GCE. This increased current response is ascribed to the electrode modification of PDA-RGO, which not only increases the conductivity but also provide a higher surface area. Moreover, PDA-RGO/Au modified GCE showed a further increased current response with a lower oxidation potential (+0.21 V), indicating the elecrodeposition Au nanoparticles could facilitate the electron transfer rate for the oxidation of DA at the electrode surface.

The quantitative analysis of DA was investigated by linear sweep voltammograms (LSV). Fig. 3B represents LSV responses of PDA-RGO/Au modified GCE towards different concentrations of DA. Upon increasing the concentrations of DA from 0.05 to 1 mM, the oxidation peak current showed a linear increase. The obtained linear regression equation can be expressed as Ipa (μA) = 9.8684 c (mM) + 2.2215 (R^2 = 0.9884). The detection limit was calculated to be 3.211 μM based on the signal noise ratio of 3.

Fig 3C displays the selectivity of the prepared sensor. The current responses of 1 mM DA, UA, AA, H_2O_2 and glucose at +0.2 were recorded. The results demonstrated that the current responses of interferences are negligible. On the contrary, a much higher current response of DA was showed on the PDA-RGO/Au modified GCE, indicating that the proposed sensor possesses high recognition ability towards DA.

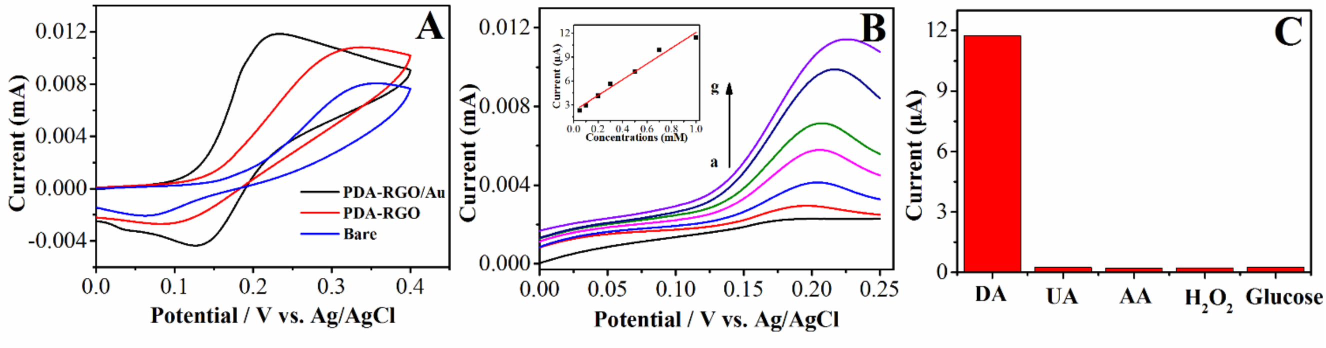

Fig 3. (A) Cyclic voltamograms of bare GCE, PDA-RGO and PDA-RGO/Au modified GCE in PBS (pH 7) with 1.0 mM DA. Scan rate: 50 mV /s. (B) Linear sweep voltammograms of different concentrations (a-g: 0.05, 0.1, 0.2, 0.3 0.5, 0.7 and 1.0 mM) of DA at PDA-RGO/Au modified GCE. Insert: The corresponding calibration plot with current measured at +0.21 V. (C) The selectivity of the PDA-RGO/Au modified GCE.

Conclusion

In this work, we have demonstrated that the preparation of PDA-RGO/Au nanocomposite via a wet chemical approach followed by an electrodeposition process. UV-vis spectroscopy and FTIR results indicated the successful reduction of GO to RGO during the PDA self-polymerization process. SEM characterization reveals the Au nanopartciles with an average size of 80 nm have been electrodeposited on the PDA-RGO sheets. The as-prepared PDA-RGO/Au modified GCE was employed for detection of DA cyclic voltammetry and linear sweep voltammograms. Results showed the PDA-RGO/Au modified GCE had a linear response to the DA in the concentration range of 0.05–1 mM with a detection limit of 3.211 μM (S/N = 3.0).

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Conflicts of Interest

The authors declare no conflict of interest

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