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Short Communication

Graphene Oxide - Gold Nanostars Modified Glassy Carbon Electrode for Highly Efficient Sensing for Nitrite

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In this work, a graphene oxide - gold nanostars modified electrode was prepared. The morphology of graphene oxide - gold nanostar films was characterized by scanning electron microscopy. The electrochemical performance of the graphene oxide - gold nanostars electrodes were analyzed by cyclic voltammetry (CV). Tests showed that the final electrode exhibited an obvious electrocatalytic effect for the oxidation of nitrite in 0.1 mol/L PBS (pH=7.0) , the differential pulse voltammetry (DPV) peak current response of nitrite displayed a good linear relationship with the logarithm of the concentration of nitrite in the concentration range of $1.0\times10^{-10}\sim1.0\times10^{-6}$mol/L, the linear equation was i_P (μA) = -40.47lg$c$ - 6.58, and the detection limit was 3.0×10^{-11} mol/L(S/N=3). In addition, the modified electrode was tested by real samples and showed good stability and reproducibility, which provided a new method for the detection of nitrite.

Keywords: Gold nanostars, Graphene oxide, Nitrite, Modified electrode

1. INTRODUCTION

Nitrite is widely used as a preservative and colorant in the industry. After entering the human body, nitrite will oxidize hemoglobin to methemoglobin, which will make hemoglobin lose its ability to transport oxygen and cause human poisoning. In addition, nitrite reacts with amine compounds to form nitrosamines, and the carcinogenic effect of nitrosamines poses a great threat to human health [1]. Moreover, nitrite is widely present in water and atmosphere, which pollutes the environment greatly. Therefore, studies on methods for rapid and accurate detection of nitrite are warranted [2]. There are various methods for the detection of nitrite [3-5], such as chemical method, optical method, chromatography, capillary electrophoresis and electrochemical method. Electrochemical methods have been widely explored for their advantages of high detection sensitivity, simplicity and low cost [6].

Graphene oxide is one of the important derivatives of graphene. Graphene oxide has many advantages such as strong adsorption [7], moisture sensitivity [8], antibacterial [9], photocatalytic performance [10] and electrochemical performance [11]. At present, the application of graphene oxide in electrochemistry has achieved remarkable results. Graphene-based electrochemical biosensor can accurately measure glucose in serum samples [12-13]. In addition, graphene has been developed and applied in fields such as fuel cells due to its efficient electrocatalytic ability [14]. Graphene and ferrite nanomaterial Composites [15], graphene and polyaniline flexible composite materials [16], graphene and lithium iron phosphate three-dimensional structure composite materials [17] and other studies have shown that the electrochemical performance of graphene are greatly improved in this process.

Gold nanostars has excellent biocompatibility, it will not destroy proteins and enzymes in living organisms and can also quantitatively detect the concentration of proteins. At the same time, gold nanostar play an extremely important role in the activity detection between biomarkers and neurotransmitters [18]. Combining gold nanomaterials with graphene, the electrocatalytic activity of gold is further enhanced. Modified electrodes based on graphene and gold nanocomposites can maintain some properties of gold nanomaterials. Due to its excellent electrical conductivity, graphene has a synergistic effect when combined with gold nanomaterials. Compared with a single component, the graphene-modified materials of gold nanomaterials show better electrocatalytic activity [19]. The gold nanomaterials were introduced into the graphene electrode, and the gold nanomaterials penetrated into the gaps of graphene and showed a uniform distribution state. This will also increase the contact range between graphene and gold nanomaterials, so that the electron transfer efficiency is improved [20].

Herein, we utilized the synergistic effect of graphene oxide and gold nanostars to construct a new method for the electrochemically detecting nitrite based on graphene oxide-gold nanostars film [21], and the modified electrode was used for assaying nitrite in the actual samples with the satisfactory results.

2. EXPERIMENTAL

2.1. Chemicals and Instruments

Chloroauric acid, ascorbic acid, graphene oxide (Alfa Aesar), Sodium nitrite (Sinopharm Group Chemical Reagent Co., Ltd.) with analytically pure. The double distilled water used as solvent to prepare 0.1 mol/L phosphate buffer solution (PBS) by mixing NaH_2PO_4 and Na_2HPO_4, after that, the pH of PBS was adjusted by using H_3PO_4 and NaOH.

CHI660A Electrochemical Workstation (Shanghai Chenhua Instrument Company); Three-electrode system was adopted to carry out the electrochemical measurements based on the bare glass carbon electrode (GCE) or modified electrode, saturated calomel electrode (SCE) and platinum wire electrode as working electrode, reference electrode and the auxiliary electrode, respectively. SEM images was obtained by SU1510 Scanning Electron Microscope (Japan Hitachi High-Tech Co., Ltd.).

2.2. Preparation of gold nanostars

Preparation of gold seeds: 0.60g PVP was added to 1 mL of 0.05 mol/L $HAuCl_4$ solution, and the mixture was stirred at 500 r/min for 30 min under ice-water bath conditions. 5 mL 0.1 mol/L $NaBH_4$ solution was immediately added into the above solution, the solution changed from light yellow to dark brown, dialyzed for 24 h, washed with water 3 times, and diluted to 100 mL to obtain PVP-coated gold seeds solution, store in a 4°C refrigerator.

Preparation of growth solution: 500 µL 1mol/L HCl and 500µL 0.01mol/L$AgNO_3$ solution were added into 50mL 2.5×10^{-4} mol/L $HAuCl_4$ solution successively and stirred at 500 r/min for 30s to obtain the growth solution.

Preparation of gold nanostars: the gold seeds solution was added into the growth solution under ice bath conditions, take it out after 5 min, add 0.1 mol/L AA solution after the temperature rises to room temperature to obtain a dark blue gold nanostar colloidal solution, centrifuge at 10000 r/min for 15 minutes, wash with water and centrifuge 3 times. The supernatant in the above centrifugation solution was removed.

2.3. Preparation of graphene oxide-gold nanostars modified electrodes

The bare GCE was carefully polished with Al_2O_3 powder suspension to become bright, then sonicated with 1:1 anhydrous ethanol and water for 1 min, then allowing for dry in room temperature. The different ratios (V_{GO} / $V_{gold\ nanostars}$) of the graphene oxide-gold nanostars (3:1, 2:1, 1:1, 1:2, 1:3), and ultrasonically treat for 30 minutes to obtain a mixed solution of gold nanostar and graphene oxide. 10µL of the mixed solution was dropwised onto the glassy carbon electrode surface, and then allowing for dry in room temperature. The obtained electrode was named as graphene oxide-gold nanostars/GCE.

3. RESULT AND DISCUSSION

3.1. SEM Characterization of Gold Nanostars and Graphene Oxide-Gold Nanostar

The prepared gold nanostars and gold nanostars-graphene oxide were characterized by SEM. Figure 1A showed that the synthesized gold nanostars were scattered distributed, which was consistent with previous report[22]. Figure 1B displayed the morphologies of the gold nanostars-graphene oxide. The results showed that the composites were successfully prepared.

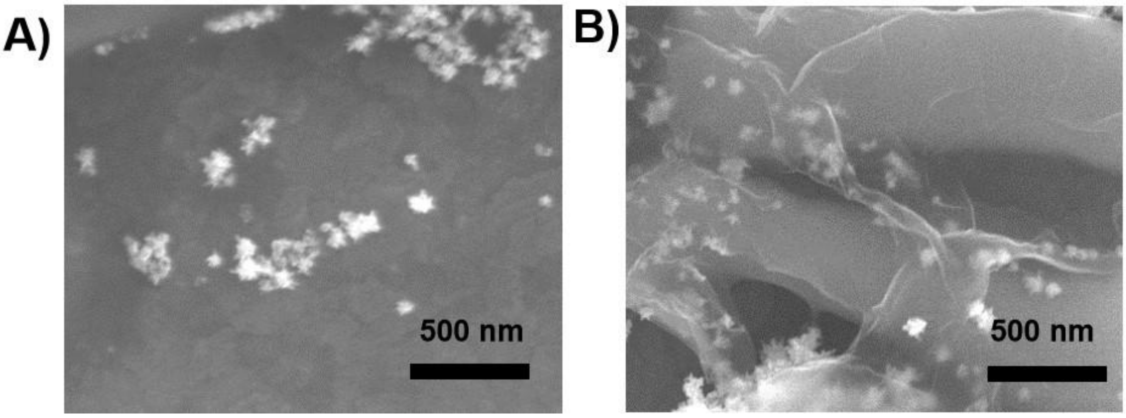

Figure 1. SEM images of gold nanostars and graphene oxide-gold nanostars.

3.2. Electrochemical Behaviors of Nitrite on Different Modified Electrodes

Figure 2 showed the CVs of 1.0×10^{-3} mol/L nitrite at different electrodes in 0.1mol/ L PBS (pH 7.0). According to Figure 2, the bare glassy carbon electrode showed a weak oxidation peak at 0.85 v (a). which was derived from the the oxidation of nitrite at the surface of electrode [23]. For graphene oxide (b) and gold nanostars (c) modified electrodes, a higher response of nitrite was found, respectively. And the oxidation peak potential become more negative. Indicating the graphene oxide (b) and gold nanostars (c) modified electrodes had an electrocatalytic effect for the oxidation of nitrite. Importantly, after graphene oxide-gold nanostars was modified onto electrode surface, an obvious enhancement in oxidation peak current of nitrite was observed, and displayed an obvious negatively shifted. The above results indicated that the graphene oxide-gold nanostars/GCE possessed an electrocatalytic ability for the oxidation of nitrite. It maybe attribute to the synergistic effect of graphene and gold nanostars.

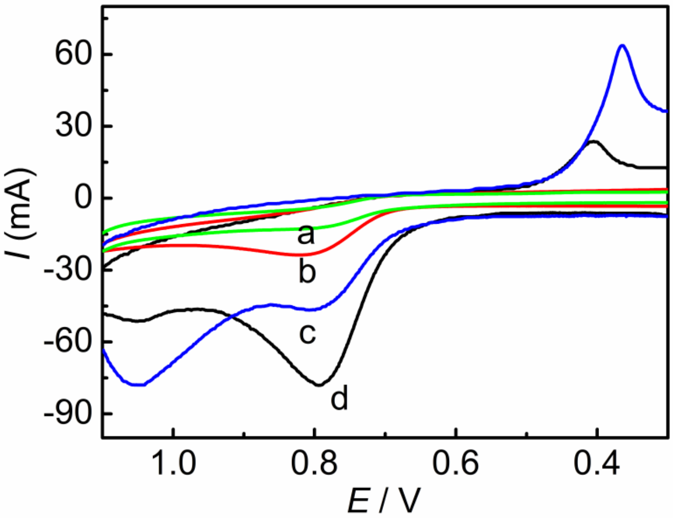

Figure 2. The CV curves of 1.0×10^{-3} mol/L nitrite in 0.1mol/ L PBS (pH 7.0) at different electrodes. Scan rate: 100 mV/s. a - GCE ; b - GO/GCE; c - Gold Nanostar/GCE; d - GO/Gold nanostar/ GCE

3.3. Optimization of graphene oxide and gold nanostars ratios

The electrode modified with different ratios (3:1, 1:1, 2:1, 1:2, 1:4, 1:3) of graphene oxide and gold nanostars were tested by CV using 1.0×10^{-3} mol/L nitrite in 0.1 mol/ L PBS (pH 7.0). The largest peak current was found, when the ratio of graphene oxide:gold nanostar of 1:1. Thus 1:1 was selected as the best ratio to fabricate the graphene oxide-gold nanostars modified electrode.

3.4. Effect of scan rate

The effect of scan rate on the electrochemical behavior of nitrite at graphene oxide-gold nanostars modified electrode was investigated. Figure 3 showed the relationship of the peak current value vs. scan rate. According to Figure 3, the oxidation peak current value increased gradually with increasing scan rate and showed a good linear relationship. The linear equation is i_p (10^{-6}A) = -1.155v -132.34, the correlation coefficient (R^2) was 0.9809, indicating that the reaction process of nitrite at the modified electrode was controlled by adsorption process.

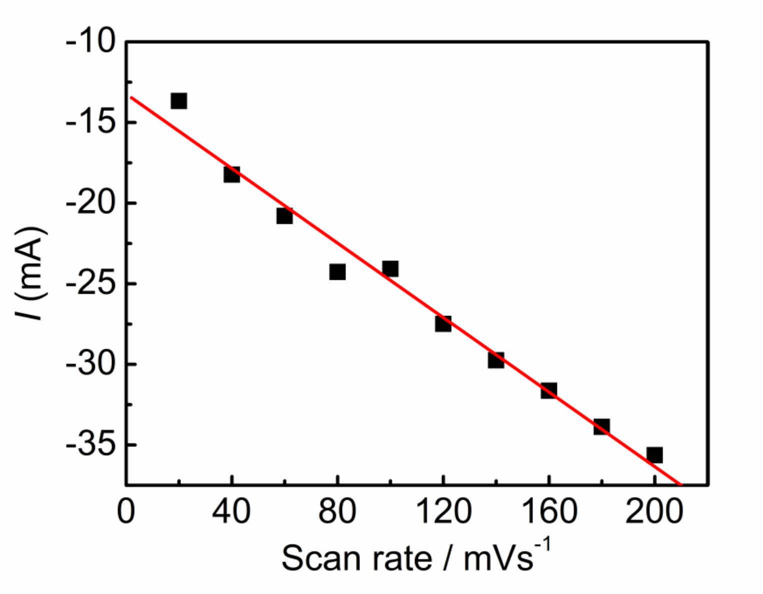

Figure 3. The relationship of scan rate vs. peak current. a-j: 20 mV/s, 40 mV/s, 60 mV/s, 80 mV/s, 100 mV/s, 120 mV/s, 140 mV/s, 160 mV/s, 180 mV/s, and 200 mV/s.

3.5. Standard curves

DPV was used to study the performance of the modified electrode under optimal conditions. According to Figure 4, when the nitrite concentration increased, the peak current also increased, and the oxidation peak current on the modified electrode had a good linear relationship with the logarithm of the concentration of nitrite. The regression equation was i_p (μA) = -40.47lg$c$ - 6.58 (R^2 = 0.9989), the detection limit was 3.0×10^{-11} mol/L(S/N=3). The linear range and detection limit of graphene oxide gold nanostars/GCE were compared with previously published studies in Table 1. The results displayed that the constructed method had lower detection limit [23-27], it may be have a potential in assay nitrite in real samples.

Table 1. comparison of this paper's linear range and detection limit with published articles

Modified electrode	Linear range （Nitrite:10^{-8} mol/L）	Detection limit （10^{-10} mol/L）	Ref.
Fe_2O_3/rGO	5-78000	150	[24]
f-MWCNT- AuNPs	100-1400	900	[25]
Co_3O_4-rGO/CNTs	800-5600	160	[26]
AuNPs@MoS_2/rGO	20-2600	380	[27]
Graphene Oxide - Gold Nanostars	0.01-100	0.30	This work

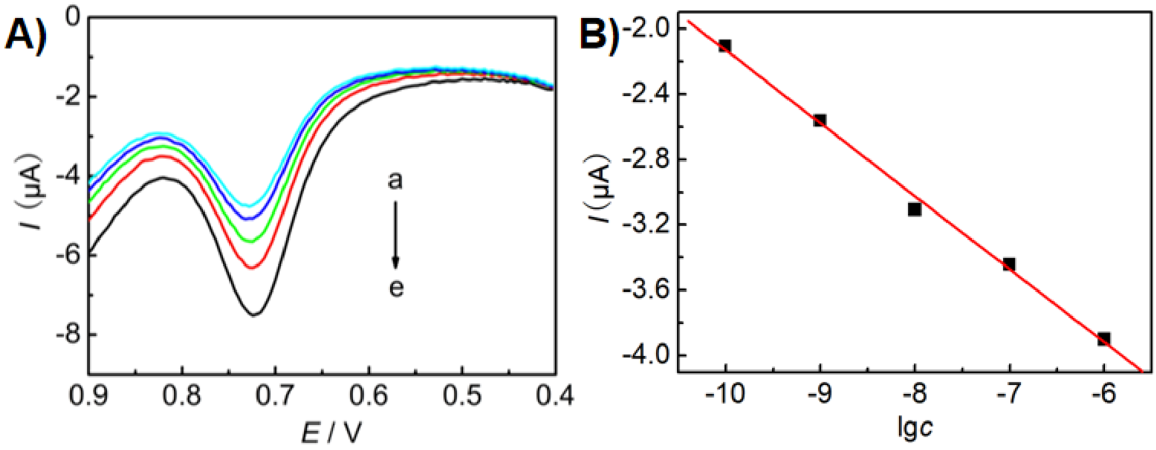

Figure 4. (A) DPVs of the different concentrations of nitrite in 0.1 mol/L PBS (pH 7.0) at graphene oxide-gold nanostars/ GCE. (B) concentration of nitrite vs. the logarithm of the concentration of nitrite.

3.6. Interference experiment

The anti-interference ability test experiments were carried out on the developed method, some common metal ions and some nucleic acid compounds were selected as potential interfering substances. The experiment showed that 100 times concentration of K^+, Ca^{2+}, Zn^{2+}, Na^+, Fe^{3+}, Al^{3+}; 50 times the concentration of dopamine, ascorbic acid; 10 times the concentration of adenine, xanthine; Almost no interference was found for the detection of nitrite. It proved that the graphene oxide-gold nanostars/ GCE had good selectivity and anti-interference ability for the detection of nitrite.

3.7. Sample analysis

Real samples were tested to evaluate the practical application of the proposed method. Taking Pearl lake water and Liuxi water as measured samples, the content of nitrite in water samples was determined by the method of recovery with standard added.The recovery rates were 104.5% and 97.7%, respectively, and a satisfactory recovery was obtained. The results were as follows in table 2.

Table 2. Measurement of nitrite content in real samples

Sample	Added (10^{-9} mol/L)	Found (10^{-9} mol/L)	Recovery (%)
Pearl lake water	2.0	2.09	104.5%
Liuxi water	20.0	19.54	97.7%

4. CONCLUSION

Herein, a new electrochemical method for the detection of nitrite with high efficiency and accuracy was developed. The prepared graphene oxide-gold nanostars modified electrode has good electrochemical catalytic ability for nitrite oxidation. The modified electrode has the advantages of simple preparation, high sensitivity and good selectivity. This study provides a more effective method for the determination of nitrite and has very important application value in the actual analysis of nitrite detection.

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