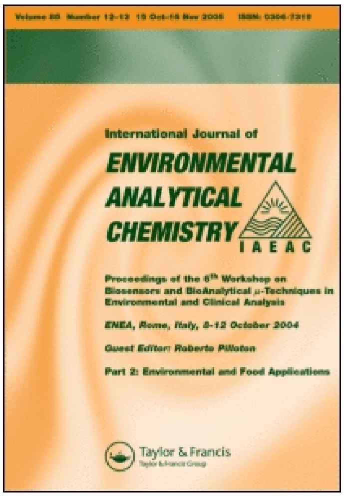

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Determination of nitrite with a nano-gold modified glassy carbon electrode by cyclic voltammetry

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The fabrication and electrochemical characteristics of nano-gold modified glassy carbon (NG/GC) electrode were investigated. The modified electrode showed an obvious electrocatalytic activity for the oxidation of nitrite at 0.850 V *versus* the Ag/AgCl electrode in $0.05\,\mathrm{mol\,L^{-1}}$ H_2SO_4 solution. Some electrochemical parameters, such as the diffusion coefficient, D, electron transfer number, n, and rate constant, k_s, were calculated. The peak current was proportional to the concentration of nitrite in the range of 5.0×10^{-6} to $5.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ for the cyclic voltammogram method with the detection limit of $5.0 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$. The possible reaction mechanism has also been discussed. The NG/GC electrode has a high stability and can be applied to the determination of nitrite in rain water with simplicity, rapidity, and accurate results.

Keywords: Nitrite; Glassy carbon electrode; Chemically modified electrode; Nano-gold

1. Introduction

Nitrite is an important contaminant in water, food products, and environmental matrices. Ingested nitrite can react with amines and amides to form potent carcinogens, nitrosamines [1]. The acceptable daily intake (ADI) recommended by the World Health Organization is < 8 mg of nitrite for an adult of about 60 kg [2]. The environmental impact caused by the buildup of high nitrite and nitrate concentrations, owing to their uses as fertilizers, and the problems caused by the contamination of water sources for human consumption are also of great concern [3, 4]. Therefore, reliable analytical procedures are required for the sensitive determination of nitrite in various matrices. Many techniques such as spectrophotometry [5, 6], fluorescence [7, 8], liquid chromatography [9–11], capillary electrophoresis [12, 13], and chemical luminescence [14] have been commonly used for its monitoring. Despite their efficiency, these methods usually comprise complex, time-consuming, and costly steps. In contrast,

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owing to the rapid response and simple use, electrochemical detection techniques are favourable for nitrite determination [15–17].

Electrochemical determination based on the oxidation of nitrite offers several advantages, namely no interference from nitrate ion and from molecular oxygen, which are usually the major limitations in cathodic determination of nitrite [18]. However, the electrochemical behaviour of nitrite is poor at conventional solid electrode surfaces (platinum, glassy carbon, and gold) because several species may poison the electrode surface and decrease the electrode sensitivity and accuracy [19]. Increasing the sensitivity of the electrode response can be achieved by maintaining a large and highly active surface area on the surface of the electrode [20]. In recent years, nanoparticles materials have been proven to be one of the most powerful tools [21]. Lu *et al.* reported a chitosan-carboxylated multiwall carbon nanotube modified electrode for the determination of nitrite [15]. Liu *et al.* developed a method for the determination of nitrite with a carbon nanotube modified glassy carbon electrode in the presence of cupric ion [22]. Ju *et al.* proposed a nitrite amperometric sensor based on a haemoglobin-colloidal gold nanoparticle modified screen-print carbon electrode [23]. Until now, a direct nano-gold modified glassy carbon electrode used for the determination of nitrite has not been reported.

In this article, we studied the electrochemical oxidation of nitrite at the nano-gold particles modified glassy carbon electrode by cyclic voltammetry (CV). This modified electrode has been proven to have a catalytic effect on nitrite. In addition, some electrochemical parameters, such as the diffusion coefficient, D, electron transfer number, n, and rate constant, k_s, have also been calculated.

2. Experimental

2.1 *Reagents*

A $0.01\,\mathrm{mol\,L^{-1}}$ nitrite stock solution was prepared by direct dissolution of sodium nitrite in water and stored in the dark. Unless otherwise noted, a $0.05\,\mathrm{mol\,L^{-1}}$ H_2SO_4 solution was used for all the electrochemical measurements. $HAuCl_4$ was purchased from Sinopharm Group Chemical Reagent Co., Ltd (Shanghai, China), and trisodium citrate dehydrate was purchased from Chongqing Nanfang Reagent Factory (Chongqing, China). All other chemicals were of analytical-reagent grade and were used without further purification. Doubly distilled water was used throughout. All the experiments were carried out at room temperature.

2.2 *Instruments*

Electrochemical measurements were carried out on a CHI 660 electrochemical analyser (CH Instruments, Austin, TX). Electrochemical impedance measurement was carried out on a CHI 440 B electrochemical analyser (CH Instruments). The determination of gold nanoparticle size was carried on a N5 submicron particle size analyser (Beckman Coulter, Fullerton, CA) and characterized with a UV-8500 spectrophotometer (Techcomp Ltd, Shanghai, China). A three-electrode system used in the measurements consists of a glassy carbon electrode or a nano-gold modified glassy carbon electrode as the working electrode, Pt as the counter electrode, and Ag/AgCl electrode as the reference electrode. All potentials were given with respect to the Ag/AgCl electrode.

2.3 *Preparation and characterization of nano-gold colloid*

All glassware used in these preparations was thoroughly cleaned in *aqua regia* (three parts HCl, one part HNO_3) and dried prior to use. Au colloids were prepared according to Frens [24] with a slight modification. Fifty millilitres of 0.01% $HAuCl_4$ was brought to a rolling boil with vigorous stirring in a 100-mL round-bottom flask. Then, 1.5 mL of 1% sodium citrate was rapidly added to the vortex of the solution, which resulted in a colour change from pale yellow to burgundy. Boiling was continued for 15 min, the heating mantle was then removed, and stirring was continued until the solution reached room temperature. The Au colloid was characterized by a UV-Vis spectrum, and its maximum absorption appeared at 518 nm (as shown in inset of figure 1). The particle size of Au colloid determined with an N5 submicron particle size analyser was about 14 nm (figure 1).

2.4 *Preparation of the nano-gold modified glassy carbon electrode*

A bare glassy carbon (GC) electrode was polished to a mirror-like surface with 0.3 Al_2O_3 powder and then with 0.05 μm Al_2O_3 powder. Then, the polished electrode was sonicated in 1 : 1 nitric acid, ethanol, and doubly distilled water for 10 min, respectively. Then, it was soaked in a 14-nm nano-gold colloid solution and maintained at +1.5 V for 20 min [25]. The nano-gold modified glassy carbon electrode was obtained, labelled as the NG/GC electrode, and immersed in doubly distilled water before use.

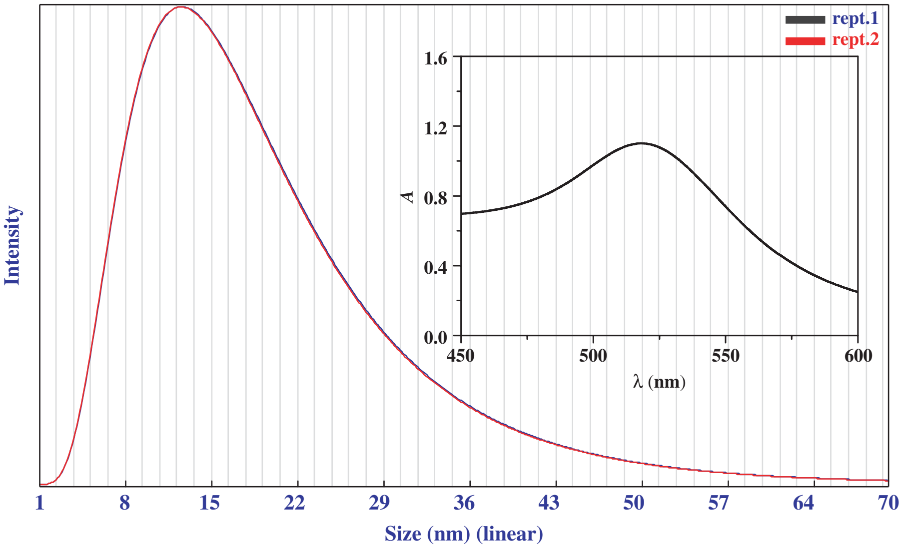

Figure 1. Particle size distribution of gold colloid. Inset: absorption spectrum of colloidal Au solution.

3. Results and discussion

3.1 *Electrochemical characterization of the NG/GC electrode in $Fe(CN)_6^{3-}$ and $[Ru(NH_3)_6]^{3+}$ solution*

$K_3Fe(CN)_6$ was used as an electrochemical probe to investigate the electronic communication behaviour between the immobilized gold nanoparticles and the electrode. Figure 2 shows the CVs of the bare GC electrode and the NG/GC electrode in a 5.0×10^{-3} mol L^{-1} $Fe(CN)_6^{3-}$ solution containing 0.1 mol L^{-1} KNO_3. The CV at the bare GC electrode shows a reversible redox reaction with a peak-to-peak separation of about 60 mV at 100 mV s^{-1}. However, the peak current was greatly decreased at the NG/GC electrode, and the peak-to-peak separation was increased, which showed an inhibitory effect on the electron transfer of $Fe(CN)_6^{3-}$ solution. This result illustrates that nano-gold colloid has been modified on the surface of GC electrode successfully. Under the preparation process of the nano-gold colloid, superfluous sodium citrate was used to deoxidize $HAuCl_4$, and the nano-gold colloid was negative owing to the adsorption of citrate ions. So, the electrode surface was negative by being modified with nano-gold. With the electrostatic repulsion from the negative charge, $Fe(CN)_6^{3-}$ was inhibited to access the electrode surface. Therefore, the electrochemical response was decreased on the NG/GC electrode. In order to further confirm that the surface of the nano-gold modified electrode was negative, $[Ru(NH_3)_6]^{3+}$ was used as an electrochemical probe. Figure 3 shows the CVs of the bare GC electrode and the NG/GC electrode in a 5.0×10^{-3} mol L^{-1} $[Ru(NH_3)_6]^{3+}$ solution containing 0.1 mol L^{-1} KCl. A potential window of +0.1 to −0.5 V was used for the cyclic voltammetry. The CVs results showed that $[Ru(NH_3)_6]^{3+}$ had a good response on the NG/GC electrode. This can be ascribed to the attractive interaction between the positively charged marker $[Ru(NH_3)_6]^{3+}$ and the electrode surface of the negative charge.

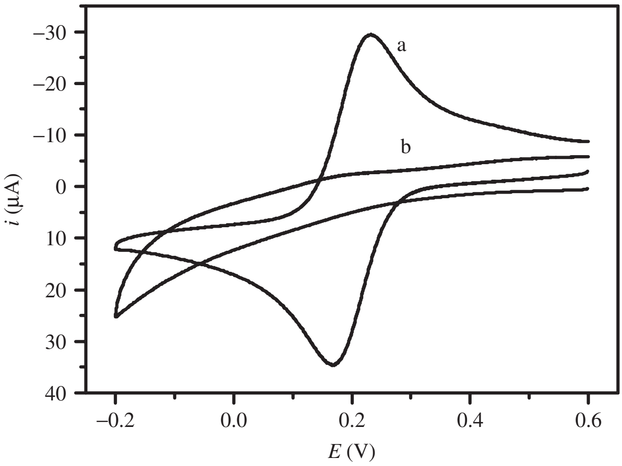

Figure 2. CVs of 5.0×10^{-3} mol L^{-1} $Fe(CN)_6^{3-}$ solution containing 0.1 mol L^{-1} KNO_3 at the bare GC electrode (a) and the NG/GC electrode. (b) Scan rate: 100 mV s^{-1}.

3.2 *Characterization for the NG/GC electrode by complex impedance analysis in the presence of $Fe(CN)_6^{3-}$*

Electrochemical impedance analysis is an effective method for probing the feature of the modified electrode [26]. The impedance spectra follow the theoretical shapes and include a semicircle portion, observed at higher frequencies, which correspond to the electron transfer limited process, followed by a linear part characteristic of the lower frequency attributable to a diffusionally limited electron transfer. Figure 4 illustrates the results of impedance spectroscopy on the bare GC electrode (a) and the NG/GC electrode (b) in a $5.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ $\mathrm{Fe(CN)_6^{3-}}$ solution containing $0.1\,\mathrm{mol\,L^{-1}}$ KCl, which was measured at the formal potential of $\mathrm{Fe(CN)_6^{3-}}$. It can be seen from figure 4(a) that the bare GC electrode exhibits an almost straight line that is characteristic of a diffusion limiting step of the electrochemical process. However, with respect to the modified electrode (figure 4b), the diameter of the high-frequency semicircle was significantly enlarged by the surface deposition of the nano-gold layer, which indicates an increased resistance to the anion redox reaction at the NG/GC electrode. Hence, it was clear that the nano-gold had been modified on the surface of GC electrode successfully. On the other hand, nano-gold modified on the electrode surface generated a negatively charged surface which reduced the ability of the electrolyte to penetrate the electrode surface and eventually effectively eliminated the response of the $\mathrm{Fe(CN)_6^{3-}}$ anion. It was further proved that the electrode surface was negative by modification with nano-gold.

3.3 *Electrochemical response of nitrite at the NG/GC electrode*

It was found that the NG/GC electrode was catalytically active to the nitrite oxidation reaction. Figure 5 shows the CVs of nitrite in $0.05\,\mathrm{mol\,L^{-1}}$ H_2SO_4 solution under the potential windows between 0.5 and 1.1 V at the bare GC electrode and the NG/GC electrode. Figure 5(a) shows that the oxidation peak of nitrite at the bare GC electrode is broad, due to slow electron transfer. At the NG/GC electrode, however, the electrochemical response of nitrite has obviously been improved (figure 5b). The peak

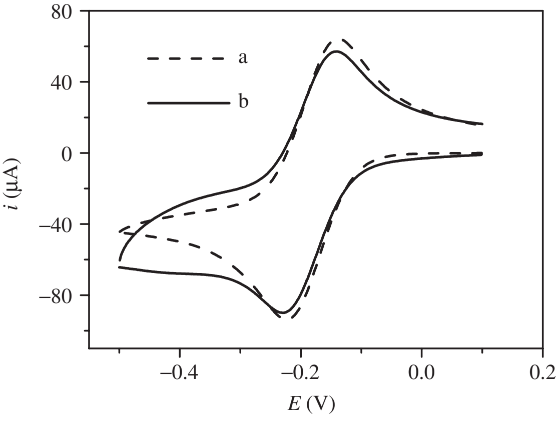

Figure 3. CVs of $5.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ $[\mathrm{Ru(NH_3)_6}]^{3+}$ solution containing $0.1\,\mathrm{mol\,L^{-1}}$ KCl at the bare GC electrode (a) and the NG/GC electrode (b). Scan rate: $100\,\mathrm{mV\,s^{-1}}$.

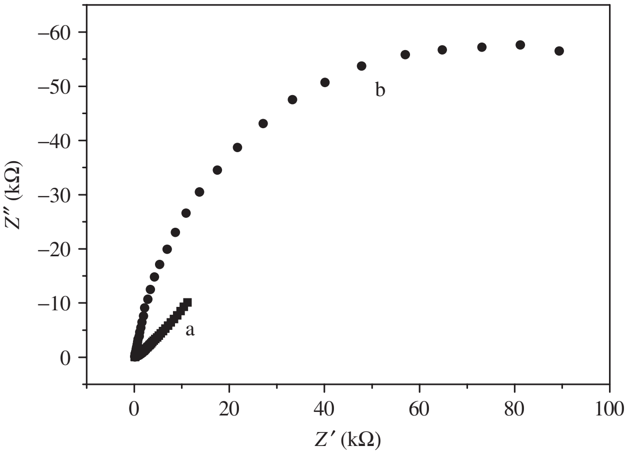

Figure 4. Complex impedance plots measured in a 5.0×10^{-3} mol L^{-1} $Fe(CN)_6^{3-}$ solution containing 0.1 mol L^{-1} KCl at the formal potential of 0.22 V for the bare GC electrode (a) and the NG/GC electrode (b). The frequency range is between 5.0×10^{-2} and 1.0×10^5 Hz with a signal amplitude of 50 mV.

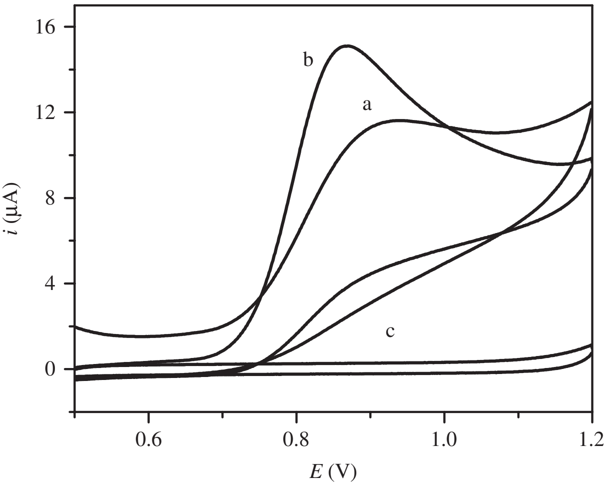

Figure 5. CVs at the bare GC electrode (a) and the NG/GC electrode (b, c) in the presence (a, b) and absence (c) of 5.0×10^{-4} mol L^{-1} nitrite. Supporting electrolyte: 0.05 mol L^{-1} H_2SO_4; scan rate: 20 mV s^{-1}.

potential shifted to a less positive value of 0.850 V with the overpotential having decreased by about 15 mV, and the anodic peak current increased by about 95 mA.

3.4 *Effect of supporting electrolyte on the response characteristics*

As an important factor, the supporting electrolyte influenced the determination of nitrite directly. It was discovered that the anodic peak current of nitrite in H_2SO_4

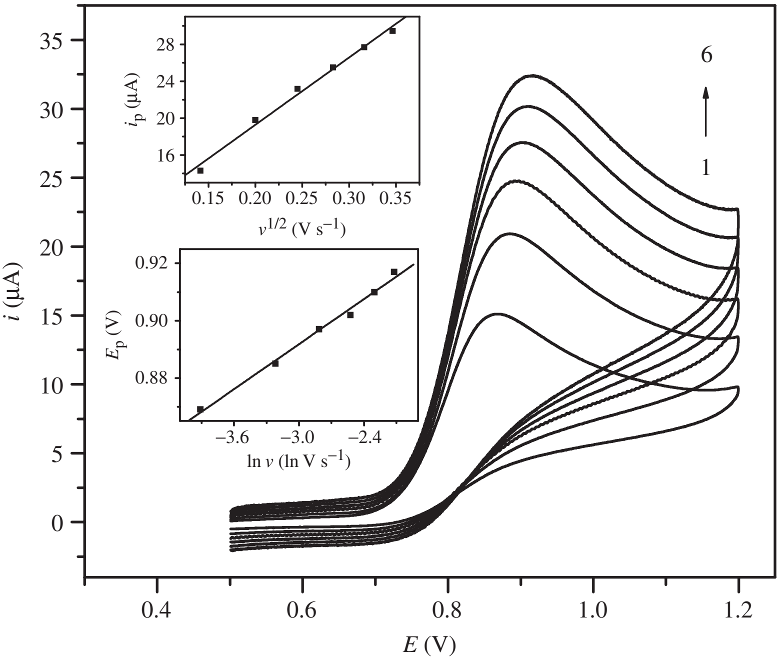

Figure 6. CVs of 5.0×10^{-4} mol L^{-1} nitrite in 0.05 mol L^{-1} H_2SO_4 at the NG/GC modified electrode at different scan rates. (1) 20 mV s^{-1}; (2) 40 mV s^{-1}; (3) 60 mV s^{-1}; (4) 80 mV s^{-1}; (5) 100 mV s^{-1}; (6) 120 mV s^{-1}. The upper inset shows the dependence of peak current on the scan rate. The lower inset presents the relationship between the anodic peak potential and the logarithm of scan rate.

solution was more sensitive and its shape was more preferable than those obtained in other supporting electrolytes, such as phosphate buffer, Britton–Robinson buffer, and acetate buffer. Thus, the effect of supporting electrolyte on the voltammetric response of nitrite was studied in H_2SO_4 solution in the concentration range of 0.01–0.1 mol L^{-1}. When the concentration of H_2SO_4 was increased from 0.01 to 0.05 mol L^{-1}, the anodic peak current was increased. However, when the H_2SO_4 concentration increased further to 0.1 mol L^{-1}, the current did not increase any more but decreased. These results were attributed to the proton taking part in the electrochemistry process of nitrite ions. The highest i_p of nitrite was observed in 0.05 mol L^{-1} H_2SO_4 solution, and the anodic peak potential moved in the negative direction. Therefore, the following experiments were carried out in 0.05 mol L^{-1} H_2SO_4 solution.

3.5 *Effect of scan rate on the peak current*

A series of CVs obtained at different scan rates for a typical nitrite concentration are shown in figure 6. It can be seen from figure 6 that the anodic peak current (i_p) was proportional to the square root of scan rate, and a linear regression equation was obtained as $i_p = 0.4679 + 7.2993v^{1/2}$ (i_p: 10^{-5} A; v: V s^{-1}) ($r = 0.9954$), while the anodic peak potential, E_p, shifted positively. In addition, at a lower NO_2^- concentration, the i_p value at the NG/GC electrode did not increase with increasing immersion time. The results suggested that the oxidation of nitrite was undergoing a diffusion-controlled process. In the plot of E_p *versus* $\ln v$, a good, straight line ($r = 0.9960$) was obtained, with a slope of 0.02622.

3.6 *Determination of the electrochemical parameters*

3.6.1 Diffusion coefficient. The time coulomb technique method was used to determine the diffusion coefficient of nitrite. The diffusion coefficient can be calculated according to the following equations [27, 28]:

$$Q = \frac{2nFAC(Dt)^{1/2}}{\pi^{1/2}} \tag{1}$$

$$i_p = 2.69 \times 10^5 A n^{3/2} D^{1/2} C v^{1/2}, \tag{2}$$

where A is the surface area of the electrode, n is the electron transfer number, D is the diffusion coefficient, C is the bulk concentration of nitrite, and F has its usual significance. From the slopes of Q *versus* $t^{1/2}$ and i_p *versus* $v^{1/2}$, D can be obtained if the parameters of A, n, and C are known. In our experiment, from the slopes of the plots between Q and $t^{1/2}$ and between i_p and $v^{1/2}$, $n = 1$ could be obtained, which indicated that there was one electron transfer in this reaction. In addition, the diffusion coefficient, D, was calculated as $5.90 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$.

3.6.2 Standard rate constant and electron transfer coefficient. The standard rate constant (k_s) and electron transfer coefficient (α) can be obtained according to the following equations [29]:

$$E_P = K + \frac{RT}{2(1-\alpha)n_\alpha F} \ln \upsilon \tag{3}$$

$$K = E^{0'} + \frac{RT}{(1-\alpha)n_\alpha F} \times \left[0.78 + \frac{1}{2}\ln\left(\frac{(1-\alpha)n_\alpha FD}{k^2 RT}\right)\right], \tag{4}$$

where α is the transfer coefficient, n_α is the number of electrons involved in the rate-determining step, v is the scan rate, E^0 is the standard electrode potential, k is the heterogeneous electron transfer rate constant, and D is the diffusion coefficient. Therefore, we were able to calculate that $(1-\alpha)n_\alpha$ is 0.490, and k is $0.1128\,\mathrm{cm\,s^{-1}}$.

3.7 *Effect of temperature on response characteristics*

Temperature is one of the important factors that affect the peak current. Figure 7 shows the relationship between the experimental temperature and the oxidation peak current of nitrite. The curve indicates that in the temperature range of 20–30°C, the anodic peak current showed little change, and thereafter decreased gradually with increasing temperature, so the experiment was carried out at room temperature.

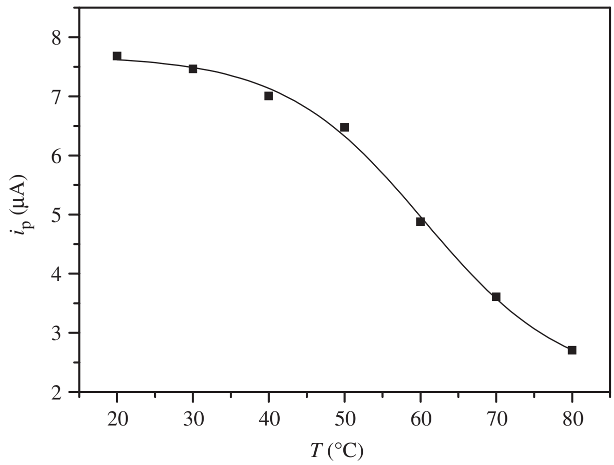

Figure 7. Relationship between oxidation peak current and temperature. Electrolyte: 0.05 mol L^{-1} H_2SO_4; nitrite concentration: 5.0×10^{-4} mol L^{-1}.

3.8 *Kinetic mechanism for the electrocatalytic process*

From our experimental results, it can be seen that the overall electrochemical oxidation of nitrite at this modified electrode might be controlled by the cross-exchange process between nitrite and the redox sites of the gold nanoparticles film and the diffusion of nitrite in solution. The electrocatalytic oxidation of nitrite probably proceeded stepwise. Since the electrocatalytic oxidation of nitrite proceeds in acid solution, nitrite acid can easily lose one electron and produce NO_2 at the surface of nano-gold. Formation of NO_2 will be followed by its disproportionation to give nitrite and nitrate ions [30]. The possible process can be expressed as follows:

$$H^+ + NO_2^- = HNO_2 \tag{5}$$

$$HNO_2 - e = NO_2 + H^+ \tag{6}$$

$$2NO_2 + H_2O = NO_2^- + NO_3^- + 2H^+. \tag{7}$$

3.9 *Calibration plots*

Under the optimum analytical conditions, the linear range of nitrite at the NG/GC electrode has been studied. Figure 8 shows the CVs for nitrite in the concentration range from 5.0×10^{-6} to 5.0×10^{-4} mol L^{-1}. The regression equation was $i_p = 0.2195 + 0.2636C$ (i_p: 10^{-6} A; C: 10^{-5} mol L^{-1}), with a correlation coefficient of $r = 0.9996$. The detection limit for nitrite, considering a signal-to-noise ratio of 3, was 5.0×10^{-7} mol L^{-1}, and the maximum detection concentration was 2.5×10^{-3} mol L^{-1}.

3.10 *Tolerance of foreign substances*

The influence of various foreign species on the determination of 5.0×10^{-4} mol L^{-1} nitrite was investigated. The tolerance limit was taken as the maximum concentration

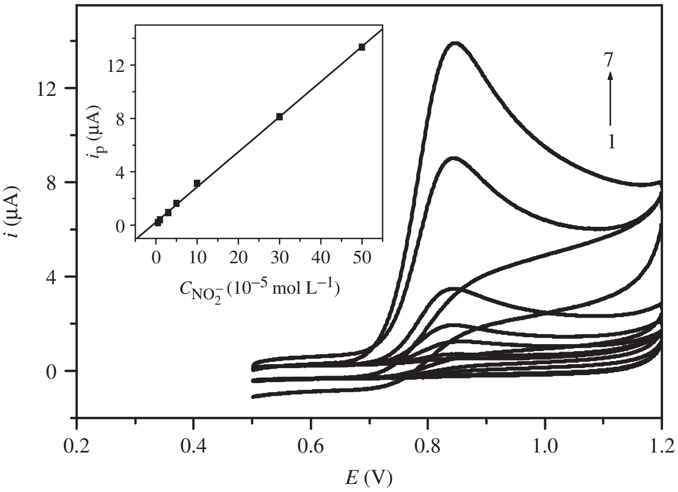

Figure 8. CVs of different concentrations of nitrite in 0.05 mol L^{-1} H_2SO_4 at the NG/GC electrode. Concentration of nitrite (from 1 to 7, mol L^{-1}): 5.0×10^{-6}, 1.0×10^{-5}, 3.0×10^{-5}, 5.0×10^{-5}, 1.0×10^{-4}, 3.0×10^{-4}, and 5.0×10^{-4}. Inset: calibration curve of nitrite. Scan rate: 20 mV s^{-1}.

of the foreign substances which caused approximately ±5% relative error in the determination. The tolerated ratio of foreign substances to 5.0×10^{-4} mol L^{-1} nitrite was 1000 for Na^+, K^+, Al^{3+}, Ni^{2+}, Mg^{2+}, Cl^-, HPO_4^{2-}, PO_4^{3-}, and SO_4^{2-}, 100 for AA and UA, and 10 for Cr^{3+}, Bi^{3+}, Cd^{2+}, and NO_3^-, respectively. Equal concentrations of Cu^{2+}, Fe^{3+}, phenol, *o*-phenylendiamine, and 4-aminophenol have little effect on the determination of NO_2^-.

3.11 *Repeatability and stability for nitrite at the NG/GC electrode*

To characterize the repeatability of the NG/GC electrode, repetitive measurement–regeneration cycles were carried out in 5.0×10^{-4} mol L^{-1} of nitrite. The results of 10 successive measurements showed that the relative standard deviation (RSD) was 1.3%, which revealed that the repeatability of the NG/GC electrode was excellent. The NG/GC electrode showed a high stability. As shown in figure 9, the signal showed a 4% decrease in the end of the first week; after 2 weeks the current response decreased by about 7%, and in the following month the decrease was 20%. However, if the NG/GC electrode was stored in dry conditions, it showed a low stability; the signal showed a 20% decrease for the first day. Therefore, after experiments, the NG/GC electrode was immersed in water at 4°C for storage.

3.12 *Applications*

The method was applied to determine nitrite in rain water. The experimental conditions were the same as those mentioned above. The recovery studies were carried out on samples added with varying amounts of nitrite standard solutions. The results are summarized in table 1. The recoveries were 99.2–107.0% by the CV method.

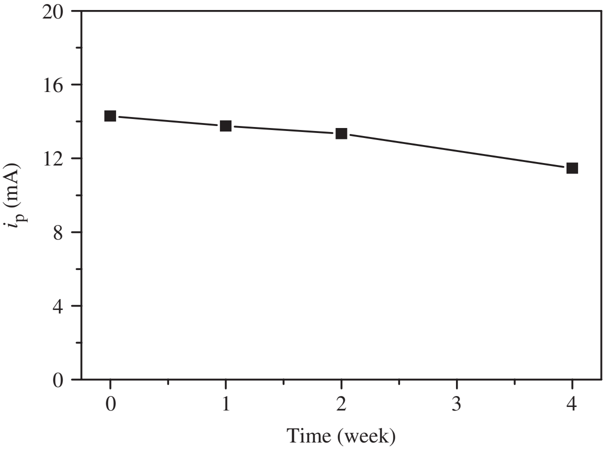

Figure 9. Relationship between oxidation peak current and storage time of the NG/GC modified electrode. Electrolyte: 0.05 mol L^{-1} H_2SO_4; nitrite concentration: 5.0×10^{-4} mol L^{-1}; scan rate: 20 mV s^{-1}.

Table 1. Results for the determination of nitrite in rain water.

Samples	Added (10^{-5} mol L^{-1})	Found after adding (10^{-5} mol L^{-1})	RSD ($n = 6$) (%)	Recovery (%)
Rain water	0.0	0.71	2.8	–
	1.0	1.84	3.4	107.0
	3.0	3.68	2.6	99.2
	5.0	5.81	4.6	102.0

4. Conclusions

The NG/GC electrode exhibited a good sensitivity and selectivity for the determination of nitrite in rain water. The modification procedure was simple, the resulting attachment was stable, and the modified electrode had faster response times to the bare glassy carbon. These features suggest that the modified electrode could be developed as a useful probe for monitoring nitrite.

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