Contents lists available at ScienceDirect





Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electro-oxidation nitrite based on copper calcined layered double hydroxide and gold nanoparticles modified glassy carbon electrode

Lin Cui, Xiaomeng Meng, Minrong Xu, Kun Shang, Shiyun Ai*, Yinping Liu

College of Chemistry and Material Science, Shandong Agricultural University, Taian 271018, Shandong, PR China

ARTICLE INFO

Article history: Received 23 June 2011 Received in revised form 4 August 2011 Accepted 8 August 2011 Available online 31 August 2011

Keywords: Calcined layered double hydroxides (CLDHs) Gold nanoparticles (AuNPs) Nitrite Non-enzymatic

1. Introduction

Nitrite (NO₂⁻) is a typical inorganic pollutant and its anthropogenic sources include wastes from fertilizers, preservative, and adulterants in food [1]. Nitrite promotes the irreversible oxidization of hemoglobin and reduces the capability of the blood to transport oxygen [2]. In addition, it can react with amines to form Nnitrosamines, many of which are known carcinogens [3,4]. Hence, selective and sensitive methods for nitrite detection have become important. There are many analytical technologies for nitrite detection, and these technologies mainly utilize spectrophotometry, chromatography, capillary electrophoresis chemiluminescence, or electrochemistry. Electrochemical techniques have been proven to be among the most advantageous methods for the determination of nitrite, and nitrite sensors that are based on electrochemical methods [5,6], especially biosensors [7–11], are most favorable. Most nitrite biosensors are dependent on protein catalysis for a reductive reaction by nitrite. However, these kinds of biosensors are complicated and the products are complex [10–12]. Thus, the electrochemical oxidation of nitrite with enzymatic and nonenzymatic nitrite sensors has been studied in recent years. We have constructed two types of nitrite biosensors that are based on the immobilization of Cytochrome c (Cyt c) on multi-walled carbon nanotubes (MWCNT)-poly(amidoamine) (PAMAM)-chitosan (Chit) nanocomposites [13]. This nanocomposite, with the

ABSTRACT

In this paper, a novel nitrite sensor was constructed based on electrodeposition of gold nanoparticles (AuNPs) on a copper calcined layered double hydroxide (Cu-CLDH) modified glassy carbon electrode. Electrochemical experiments showed that AuNPs/CLDH composite film exhibited excellent electrocatalytic oxidation activity with nitrite due to the synergistic effect of the Cu-CLDH with AuNPs. The fabricated sensor exhibited excellent performance for nitrite detection within a wide concentration interval of 1–191 μ M and with a detection limit of 0.5 μ M. The superior electrocatalytic response to nitrite was mainly attributed to the large surface area, minimized diffusion resistance, and enhanced electron transfer of the Cu-CLDH and AuNPs composition film. This platform offers a novel route for nitrite sensing with wide analytical applications and will supply the practical applications for a variety of simple, robust, and easy-to-manufacture analytical approaches in the future.

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incorporation of DNA and Cyt c for the electrochemical oxidation of nitrite [14], and both of the biosensors showed a fast response to nitrite. Although the enzymatic biosensors had good selectivity and high sensitivity, their stability was limited due to easy denaturation by environmental changes because their catalytic activity originated from the intrinsic nature of enzymes [15], and due to leakage of the enzymes during their storage and the immobilization procedure. Moreover, the preparation and purification of the enzymes was usually time-consuming and expensive. Therefore, many efforts have been made to develop non-enzymatic sensors to solve these problems.

It is becoming more and more significant in analytical chemistry to take advantages of various inorganic nanomaterials, because of the following intrinsic advantages: regular structures, chemical and thermal stabilities, high surface reaction activity, high catalytic efficiency, large surface-to-volume ratio, and strong adsorption ability [16]. There are many such kinds of inorganic nanomaterials, such as clay [17,18], macroporous active carbon [19], zeolite [20], sol-gel matrix [21], metallic carbon nanotubes [22–24], transition metal disulfide [25], transition metal oxides [26–31], and conducting polymers [32]. Each of these materials has been used in the construction of non-enzymatic electrochemical sensors because of its unique and particular properties.

Calcination products of layered double hydroxides (LDHs), known as calcined layered double hydroxides (CLDHs), owe their popularity to their numerous attributes such as their larger surface areas, higher metal dispersion, smaller crystallite size, greater stability against sintering, and lower diffusion resistance than LDHs [33]. Moreover, CLDHs have the advantages of having porous

^{*} Corresponding author. Tel.: +86 538 8247660; fax: +86 538 8242251. *E-mail addresses*: ashy@sdau.edu.cn, chemashy@yahoo.com.cn (S. Ai).

^{0013-4686/\$ -} see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2011.08.026

structures and both of abundant acidic and basic sites [34], which can bind to an enzyme. The synthesis of sheets of CLDHs that contain transition metal ions is of particular interest because of the strongly enhanced activity of the oxidation properties of these metals in mixed oxides. CLDHs, especially those containing Cu, were investigated for the ability to selectively hydrogenate cinnamaldehyde [35] and for good catalytic properties in the catalytic oxidation of phenol [36–38]. In previous work, we had also used Cu-CLDH as a mimic of peroxidase to detect the hydrogen peroxide [39]. Following this work, we demonstrated the construction of a new amperometric sensor for electro-oxidation of nitrites based on Cu-CLDH and AuNPs.

The AuNPs/CLDH composite film was fabricated and electrochemically characterized to explore its catalytic activity for nitrite oxidation. This material exhibited excellent performance for nitrite electro-oxidation, such as a high electrocatalytic activity, a low detection limit, and good selectivity. The AuNPs/CLDH modified electrode opens up new opportunities for fast, simple, and sensitive analyses of nitrite. With its enhanced stability, ease of preparation, and special properties, AuNPs, coupled with CLDH composite, can be used as a new material for use in a wide range of potential applications in sensors, biotechnology, and environmental chemistry.

2. Experimental

2.1. Reagents and apparatus

Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O, and other chemicals that were obtained from the Chemical Reagent Company of Shanghai (China) were of pure analytical grade and used without further purification. Hydrogen tetrachloroaurate (HAuCl₄·4H₂O) was obtained from Sigma. Phosphate buffer solution (PBS) was prepared by mixing a stock solution of 0.1 M NaH₂PO₄ and 0.1 M Na₂HPO₄ and adjusting the pH either with 0.1 M H₃PO₄ or 0.1 M NaOH. All of the chemicals were of analytical reagent grade, and all of the solutions were prepared with redistilled deionized water.

Electrochemical experiments were performed with CHI660C electrochemical workstation (Shanghai Chenhua Co., China) with a conventional three-electrode cell. A bare glassy carbon electrode (d=3 mm) or a modified glassy carbon electrode was used as the working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the reference electrode and auxiliary electrode, respectively. Scanning electron microscopy (SEM) was performed on a Hitachi S-3000N instrument (Japan), and powder X-ray diffraction (XRD) patterns were carried out with a Rigaku D/MAX 2200PC X-ray diffractometer (Japan) with Cu K_{\alpha} radiation ($\lambda = 0.154178$ nm, graphite monochromator, 28 kV and 20 mA). Additionally, a 2 θ range (from 10° to 80°) was investigated at a scanning speed of 10° min⁻¹.

2.2. Preparation of Cu-CLDH

The Cu-LDH was prepared as in a previous report [40]. Briefly, a 20 mL solution containing $1.208 \text{ g Cu}(NO_3)_2$, $3.846 \text{ g Mg}(NO_3)_2$ and $3.751 \text{ g Al}(NO_3)_3$, was titrated with a 20 mL mixture solution of 2.40 g NaOH and $5.30 \text{ g Na}_2\text{CO}_3$ under vigorous stirring. During synthesis, the temperature was maintained at 25 °C, and the resulting suspension was subsequently kept at 65 °C for 1 h with stirring. The resulting product was filtered and washed thoroughly with deionized water until a neutral pH was obtained and then dried at 60 °C for two days in air. The Cu-CLDH was obtained by heating Cu-LDH in a muffle furnace at 500 °C for 7 h.

2.3. Preparation of the different modified electrodes

Prior to modification, the glassy carbon electrode (GCE) was carefully polished with 0.3 μ m and 0.03 μ m α -alumina powders in sequence. It was then sonicated in anhydrous ethanol for 3 min and then in double distilled deionized water for 3 min. Next, it was dried with nitrogen. A Cu-CLDH (2 mg mL⁻¹) solution was first prepared with redistilled deionized water, followed by ultrasonication for 2 h. With a microinjector, 10 µL of the Cu-CLDH solution was deposited onto the electrode surface. After the solvent had evaporated, the electrode surface was thoroughly rinsed with redistilled deionized water and dried in air, this electrode was denoted as CLDH/GCE. Next, CLDH/GCE was immersed into a 3.0 mM HAuCl₄ solution containing 0.2 M Na₂SO₄. Electrodeposition of Au nanoparticles was carried out at -0.2 V for 45 s, followed by gentle washing in double distilled deionized water and drying by nitrogen blowing. This modified electrode was denoted as AuNPs/CLDH/GCE. Both of the modified electrodes were stored at 4°C in a refrigerator before use.

2.4. Analytical application

In order to investigate the applicability of the proposed analysis method, different ham samples were analyzed to determine nitrite concentration. The pretreatment was performed according to a previous report [41]. In brief, 5 g of crushed sample was mixed with 12.5 mL of saturated borax solution. Next, redistilled deionized water was added, and the mixture was heated until boiling for 15 min. To precipitate the proteins, 2.5 mL of 30% ZnSO₄ was introduced, and after cooling to room temperature, the resulting mixture was diluted to 50 mL with redistilled deionized water and then filtered. The resulting sample solution was stored at 4 °C until it was mixed with 0.1 M PBS (pH 7.0) for nitrite determination using the proposed procedure.

3. Results and discussion

3.1. Characterization of Cu-CLDH

The typical XRD pattern of Cu-CLDH is shown in Fig. 1A. The sample was scanned for 2θ , ranging from 10° to 80° , and the XRD analysis revealed that Cu-CLDH was composed of CuO (JCPDS-ICDD 80-1916), which has a high crystallinity. The calcination of LDH at 500 °C destroyed its layered structure completely and resulted in the formation of spinel phases, which was accompanied by a tenorite phase (CuO). Fig. 1B displays a typical SEM image of the Cu-CLDH and shows that many pores on the surface of Cu-CLDH can be observed. After being calcinated at 500 °C, sample sintering occurred, LDH started to break into smaller pieces and pores appeared due to the loss of water and anions. Therefore, a Cu-CLDH film could give a larger specific surface area, a high surface reaction activity, and an efficient transmission channel for the analyzed molecules to reach the active sites, which will all help to improve the stability and sensitivity of the modified electrode. After electrodeposition of AuNPs onto the CLDH/GCE, the AuNPs were inserted into the porous structure of the CLDH (see supporting information, Fig. 1S).

3.2. Electrochemical impedance spectroscopy characterization

Electrochemical impedance spectroscopy (EIS) was carried out to investigate the changes in electron transfer resistance (R_{et}) that were detected by surface-modified sensors. Fig. 2 shows Nyquist plots for bare GCE (a), CLDH/GCE (b), and AuNPs/CLDH/GCE (c) in 5.0×10^{-3} M [Fe(CN)₆]^{3-/4-} solution containing 0.1 M KCl. As can be seen, curve b presents a larger semicircle domain compared



Fig. 1. XRD (A) and SEM (B) images of the Cu-CLDH.

to curve a, implying a very large $R_{\rm et}$ on the CLDH nanostructures modified electrode. This increase was attributed to the nonconductive properties of CLDH. After the AuNPs were deposited onto the CLDH/GCE, the AuNPs/CLDH/GCE showed a lower interfacial electron-transfer resistance, as seen in curve c, indicating that good conductivity by the AuNPs could hold high electron-transfer efficiency. It also suggested that CLDH was successfully immobilized on the GCE surface.

3.3. Electrochemical property of AuNPs/CLDH/GCE

Electrochemical behaviors of the differently modified electrodes in 0.1 M PBS (pH 7.0) were investigated using cyclic voltammetry. As can be seen in Fig. 3, no redox peaks for the bare GCE (curve a) or AuNPs modified GCE is observed (curve b). However, the AuNPs/CLDH modified electrode exhibited a pair of well-defined peaks at +117 mV and +191 mV (curve c), which were attributed to the redox of Cu^{II}/Cu^I in the AuNPs/CLDH conjugate. Moreover, from the inset in Fig. 3, it is evident that the redox peaks current of the Cu-CLDH/GCE was much smaller than that of the AuNPs/CLDH/GCE; meanwhile, a peak separation (ΔE_p) was much larger. This indicated that the AuNPs played an important role in facilitating the electron exchange between the Cu-CLDH and glassy carbon electrode surface.

3.4. Influence of scan rate

Cyclic voltammograms (CVs) of the AuNPs/CLDH/GCE in 0.1 M PBS (pH 7.0) at different scan rates were studied (Fig. 4A). As



Fig. 2. Nyquist plot of the bare GCE (a), CLDH/GCE (b) and AuNPs/CLDH/GCE (c) in 5 mM $\rm [Fe(CN)_6]^{3-/4-}$ containing 0.1 M KCl.

shown in Fig. 4B, the cathodic and anodic peak currents increased linearly with the increase of the square root of the scan rates, from 20 to 200 mV s^{-1} , showing a diffusion-controlled process. This result might be attributed to a slow electron hopping across the matrix of the composite membrane. At higher sweep rates $(300-1000 \text{ mV s}^{-1})$, the peak currents became proportional to the scan rate (inset in Fig. 4C), which indicated that the reaction was a surface-controlled process.

As shown in Fig. 4D, a graph of $E_p = f(\log v)$ yields two straight lines with slopes of $-2.3 RT/\alpha nF$ and $2.3 RT/(1-\alpha)nF$ for the cathodic peak and anodic peak, respectively. Thus, the value of α can be estimated to be 0.52 from the slopes of the straight lines based on the following equation [42]:

$$\log \frac{v_a}{v_c} = \log \frac{\alpha}{1 - \alpha} \tag{1}$$

In order to calculate the value of the apparent heterogeneous electron transfer rate constant (k_s), the following Laviron equation was used [42]:

$$\log k_{\rm s} = \alpha \, \log(1-\alpha) + (1-\alpha) \log \alpha - \log \frac{RT}{nF\nu} - \frac{\alpha(1-\alpha)nF\Delta E_{\rm p}}{2.3RT}$$
(2)

where α is the electron transfer coefficient, *n* is the number of electrons, ΔE_p is the separation of the redox peaks, and *v* is the scan rate. k_s can therefore be calculated to be $1.05 \pm 0.2 \text{ s}^{-1}$.



Fig. 3. Cyclic voltammograms of bare GCE (a), AuNPs/GCE (b) and AuNPs/CLDH/GCE (c) in a solution of 0.1 M PBS (pH 7.0) at 100 mV s⁻¹. Inset: the CV of Cu-CLDH/GCE in 0.1 M PBS (pH 7.0) at 100 mV s⁻¹.



Fig. 4. (A) Cyclic voltammograms of the AuNPs/CLDH/GCE at different scan rates in 0.1 M PBS (pH 7.0). Scan rates from (a) to (q) are as follows: 20, 40, 60, 80, 120, 140, 160, 180, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 mV s⁻¹, respectively. (B) The dependence of current on the square root of the scan rate. (C) Plots of anodic and cathodic peak currents versus scan rate. (D) Variation of anodic and cathodic peak potentials versus the logarithm of the scan rate.

3.5. Electrochemical effective surface area

Fig. 2S (see supporting information, Fig. 2S) shows the plots of Q-t and $Q-t^{1/2}$ at the bare GCE and AuNPs/CLDH modified electrodes in 1×10^{-4} M K₃[Fe(CN)₆] solution containing 1 M KCl. From the slope of the plot of Q versus $t^{1/2}$, the electrochemical effective surface area for the bare GCE and the AuNPs/CLDH/GCE could be calculated by chronocoulometry using 1×10^{-4} M K₃[Fe(CN)₆] as a model complex (the diffusion coefficient D of K₃[Fe(CN)₆] is 7.6 × 10⁻⁶ cm² s⁻¹ [43]) and based on Eq. (3) given by Anson [44]:

$$Q(t) = \frac{2nFAcD^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads}$$
(3)

where *n* is the electron transfer number; *A* is the surface area of the working electrode; *c* is the concentration of substrate; *D* is the diffusion coefficient; Q_{dl} is the double layer charge which could be eliminated by background subtraction; and Q_{ads} is the Faradaic charge. Other symbols have their usual meanings. The plots of Q-*t* and Q- $t^{1/2}$ are shown in Fig. 2S. The linear relationship between Q and $t^{1/2}$ could be expressed as follows: Q=2.165 $t^{1/2}$ – 0.1860 (for the GCE, μ C, $s^{1/2}$, R=0.9948), Q=13.63 $t^{1/2}$ – 13.08 (for the AuNPs/CLDH/GCE, μ C, $s^{1/2}$, R=0.9919). Using these equations, *A* could be calculated to be 0.0721 cm² and 0.164 cm² for the GCE and AuNPs/CLDH/GCE, respectively. These results indicated that the effective surface area of the electrode increased obviously after modification of the GCE with AuNPs/CLDH, which would enhance the current response of NO₂⁻ on the electrode.

3.6. Electro-oxidation behavior of NO_2^- on the AuNPs/CLDH/GCE

Fig. 5 shows typical CVs of the AuNPs/CLDH/GCE in the absence and presence of NO_2^- at a scan rate of 100 mV s⁻¹ in a 0.1 M PBS (pH 7.0) solution. Upon addition of NO_2^- , an obvious anodic peak was observed, and the peak current increased significantly with increasing NO_2^- concentrations (see b–d in Fig. 5). Moreover, the electrocatalytic behaviors of the differently modified electrodes towards the electrochemical oxidation of NO_2^- were also investigated by analyzing the CVs. The cyclic voltammograms for 100 μ M NO_2^- at the bare GCE, CLDH/GCE, and AuNPs/CLDH/GCE are shown in the inset of Fig. 5. At the bare GCE, the CV of NO_2^- demonstrated a wave with an anodic peak potential (E_{pa}) of 1.03 V. The oxidation peak current of NO_2^- at the CLDH/GCE was greater than at the bare GCE, and the potential shifted negatively to 0.942 V. This result might be attributed to the porous structure of CLDH possessing a larger surface area, which could provide a favorable microenvironment for more NO_2^- oxidation. After the AuNPs were deposited onto the CLDH surface, the anodic peak potential shifted negatively to 0.763 V, which was much lower than 0.9 V, as was shown in our previous work [13]. It also showed about a 2-fold larger peak current (i_{pa}) signal than for the bare GCE, indicating that AuNPs facilitated faster electron-transfer kinetics of the NO_2^- oxidation. This result might be explained by CLDH composite film providing abundant active sites and Au nanoparticles improving the



Fig. 5. Cyclic voltammograms for the AuNPs/CLDH/GCE in a 0.1 M PBS (pH 7.0) at various concentrations of NO₂⁻: (a) 0 μ M, (b) 25 μ M, (c) 50 μ M, (d) 75 μ M, and (e) 100 μ M, at scan rate of 100 mV s⁻¹. Inset: CVs of 100 μ M NO₂⁻ using the bare GCE (e), CLDH/GCE (f) and AuNPs/CLDH/GCE (g) in the same conditions.



Fig. 6. (A) Cyclic voltammograms at the AuNPs/CLDH/GCE in 0.1 M PBS (pH 7.0) and 100 μ M NO₂⁻ at different scan rates (from a to j: 20, 40, 60, 80, 120, 160, 200, 300, 400, 500 mV s⁻¹, respectively). (B) The linear dependence of the anodic peak current on the square root of the scan rate.

electrocatalytic activity for NO_2^- . The catalytic oxidation mechanism can be explained with the following process:

 $NO_2^- \leftrightarrow 2NO_2 + 2e^-$ (4)

 $2NO_2 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+$ (5)

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$
 (6)

First, nitrite loses an electron to form NO_2 [reaction (4)]. Second, this step is followed by a homogeneous disproportionation [reaction (5)] of NO_2 into nitrate and nitrite, which can be written as the total reaction (6) [45,46].

The influence of the Cu-CLDH load, ranging from 0.5 to 4 mg mL^{-1} , on the cyclic voltammetry of 1.0 mM NO_2^{-} in a 0.1 M PBS (pH 7.0) was studied (see supporting information, Fig. 3S). The current response increased with an increasing loaded amount of Cu-CLDH until it reached 2 mg mL^{-1} , but the current response decreased when the Cu-CLDH load amount increased further. This could be caused by the active center being blocked and/or by increasing film thickness. Hence, a Cu-CLDH load of 2 mg mL^{-1} was used throughout this work.

Fig. 6A presents cyclic voltammograms of the AuNPs/CLDH/GCE at different scan rates in PBS (pH 7.0) containing 1.0 mM NaNO₂. The peak current increased linearly with the square root of the scan rate in the range of 20–500 mV s⁻¹; $i_{pa} = -3.629 - 13.92 v^{1/2}$ (μ A, mV s^{-1/2}, *R*=0.9960) (Fig. 6B). The results suggested that the kinetics of the overall process were controlled by a diffusion

process [47]. Having a porous structure, Cu-CLDH together with AuNPs could catalyze the oxidation of NO_2^- .

3.7. Amperometric response of the proposed NO_2^- biosensor

Fig. 7 records the amperometric current-time curves of the AuNPs/CLDH/GCE at an applied potential of +0.763 V upon the successive addition of NO_2^{-1} to a continuously stirred solution of 0.1 M PBS (pH 7.0). With the addition of NO_2^- , a drastic increase in the response current was observed (Fig. 7A). The response to the addition of NO₂⁻ was very fast and reached the steady-state value (95% of the maximum current) in less than 3s. Such a fast response implied that the AuNPs/CLDH could promote the oxidation of NO2-. The faster response was mainly attributed to the synergistic effect of CLDH and AuNPs providing a necessary conductive pathway to transfer electrons of NO₂⁻, which were favorable for nitrite oxidation. As shown in Fig. 7B, the response was proportional to the concentration of NO₂⁻ in the ranges of 1–191 μ M (*R* = 0.999), with a detection limit of 0.5 µM, a signal-to-noise ratio of 3 and a high sensitivity of 382.2 µA mM⁻¹. Although the detection limit was higher than that of a CuNPs/thiol/Au electrode [10], it was much lower than that of inorganic material or protein nitrite sensors, such as the following: a ccNiR/Nf/MV/GCE (60 μ M) [48], a Hb-meso-Al₂O₃- $PVA/GCE(30 \,\mu\text{M})[49]$, a Ferricyanide/CPE(26.3 $\mu\text{M})[50]$, a copper modified electrode $(11 \,\mu\text{M})$ [51], a Mb-ZnO/GCE $(4 \,\mu\text{M})$ [8], a nano-Au/P3MT/GCE(2.3 μM) [6], a catalase/MWNTs/GCE (1.35 μM) [52], and a Hb/nano-Au/TiO₂ sol-gel/GCE (1.2 µM) [10]. This indicated



Fig. 7. (A) Typical current-time curve of the AuNPs/CLDH/GCE upon the successive addition of 1, 10 or 20 μ M NaNO₂ into a gently stirred solution of 0.1 M PBS (pH 7.0) at +0.763 V. (B) The linear relationships between the catalytic current and the NaNO₂ concentration.

Table 1	
Determination of nitrite in three different	ent ham samples.

Sample	Content (NO ₂ ⁻ , μ M)	Added (NO $_2^-$, μM)	Found ^a (NO ₂ ⁻ , μ M)	Spectroscopy	R.S.D. (%)	Recovery (%)
1 2	$\begin{array}{c} 1.95 \pm 0.21 \\ 2.02 \pm 0.32 \end{array}$	2.50 2.50	$\begin{array}{l} 4.49 \pm 0.25 \\ 4.58 \pm 0.34 \end{array}$	$\begin{array}{c} 4.53 \pm 0.31 \\ 4.61 \pm 0.43 \end{array}$	3.2 2.8	100.9 101.33
3	1.89 ± 0.20	2.50	4.28 ± 0.23	4.32 ± 0.36	2.5	97.49

^a Mean for five separate measurements.

that this proposed method could potentially be used for sensitively monitoring the concentration of NaNO₂.

3.8. Interference

The potential interference for the detection of nitrite using this biosensor was also examined by adding the following ions into the PBS solution (pH 7.0) at the same concentration that was used for nitrite: K⁺, Na⁺, Mg²⁺, Zn²⁺, NH₄⁺, F⁻, Cl⁻, NO₃⁻, SO₄²⁻, CO₃²⁻, H₂PO₄⁻, HPO₄²⁻ and PO₄³⁻. None of the ions caused interference. Additionally, a 50-fold amount of dopamine was tested and showed no interference.

3.9. Reproducibility and stability of the AuNPs/CLDH/GCE

The fabrication reproducibility of six electrodes, carried out independently, showed an acceptable reproducibility for determining 1.0 mM NO_2^- with a relative standard deviation (R.S.D.) of 6.8%. When not in use, the sensors were suspended in 0.1 M PBS in a refrigerator at 4 °C. The operational and storage stability of the proposed sensor was investigated by measuring the current response of 1.0 mM NO₂⁻ every 3 days for over 1 month. It was found that the peak current for NO₂⁻ oxidation retained 92% of its initial current response, and no obvious potential shift was observed after 1-month of storage. These results implied that the modified electrode was stable.

3.10. Determination of nitrite in real samples

In order to evaluate the performance and feasibility of this method, three different ham samples were prepared using different standard concentrations of nitrite, and each sample solution was tested five times. This method, compared with the recommended spectroscopic method and the results listed in Table 1, showed that the R.S.D. for each sample was less than 5%, indicating that the present sensor could be efficiently used for the determination of nitrite in food samples.

4. Conclusions

The AuNPs/CLDH modified electrode was prepared and it offers a remarkable decrease in the overvoltage for NO₂⁻ oxidation. This sensor was constructed successfully for NO₂⁻ determination, and it exhibited very good analytical performance with low cost, convenient preparation and rapid detection. Furthermore, the AuNPs/CLDH offers an opportunity to build up a more sensitive and selective sensor for the detection of NO_2^- in real samples.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 201075078) and the Natural Science Foundation of Shandong Province, China (ZR.2010BM005).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2011.08.026.

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