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ORIGINAL PAPER

Electrochemical determination of nitrite in water samples using a glassy carbon electrode modified with didodecyldimethylammonium bromide

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Abstract The oxidative electrochemistry of nitrite was investigated using a glassy carbon electrode modified with surfactants such as didodecyldimethylammonium bromide (DDAB), Tween-80, and sodium dodecylbenzenesulfonate, respectively. Nitrite oxidation proceeds best in the presence of DDAB. The electrode exhibited good sensitivity and fast response, with a linear dynamic range between 1.0 and 80 μM of nitrite, and a sensitivity of 0.04 $\mu A \cdot \mu M^{-1}$. The electrode was successfully applied to the determination of nitrite in spiked real water samples.

Keywords Modified electrode · Surfactant · Didodecyldimethylammonium bromide · Nitrite determination

Introduction

The nitrite ion is one of the active intermediate species in the nitrogen cycle and a useful indicator of equilibrium state of the oxidative and reductive pathways of the nitrogen cycle. On the other hand, nitrite is a potential toxicity. Once it is taken by human body, the capability of hemoglobin combined with oxygen would decrease because nitrite can oxidize ferrohemoglobin to ferrihemoglobin. In addition, nitrite can react with secondary amine to produce nitrosamine, which could result in cancer [1]. Nitrite is ubiquitous within environment, food and physiological systems and commonly used in some foods as corrosion inhibitor [2, 3] and is an important indicator of water pollution. For these reasons, the World Health Organization (WHO) recommends to never exceeding a nitrite level of 3 $mg \cdot L^{-1}$ in raw waters [4] and the quantitative determination of nitrite concentration has received an increasing interest, especially for drinking water survey, wastewater treatment [5]. Also, the control of water quality is important to avoid contamination of cultivations when water is used for sprinkling [5, 6]. Many methods have been developed to detect nitrite, such as spectrophotometry [7, 8], gas chromatography-mass spectrometry [9], ion chromatography [10], spectrofluorimetry [11, 12], chemiluminescence [13], flow injection analysis [14] and capillary electrophoresis [15].

In addition to these methods, electrochemical approaches are favorable for nitrite determination owing to the rapid response and simple operation [16–18]. In general, the main electrochemical methods involve reduction and oxidation of nitrite on the electrode [19–26]. However, on the bare solid electrode, the determination of nitrite is limited because several species can poison the electrode surface and decrease the sensitivity and accuracy [27]. Hence, oxidation of nitrite at various chemically modified electrodes has been investigated [28–33].

Surfactants are molecules with non-polar regions and charged or polar head groups. These amphiphilic molecules can adsorb strongly at solid/solution interfaces. In recent years, the surfactants have attracted great interests and been used broadly in electrochemical analysis, such as TiO_2 nanoparticles/surfactant polymer complex film on glassy carbon electrode (GCE) for sensing trace dopamine [34], chitosan/cetyltrimethylammonium bromide and chitosan/cetylpyridine bromide modified electrodes for simultaneous

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determination of ascorbic acid and dopamine [35, 36]. However, no reports on surfactant modified electrode for nitrite detection have been published.

In this paper, we present a novel didodecyldimethylammonium bromide (DDAB) modified GCE for nitrite determination by differential pulse voltammetry. DDAB is a kind of cationic surfactant with one positively charged head group and two hydrocarbon tails, which can form steady film on the electrode surface. Besides this, DDAB is relatively cheap, easy to get and the modification process is simple and quick.

Experimental

Reagents

All chemicals used were analytical grade. DDAB was purchased from Sigma-Aldrich (http://www.sigmaaldrich.com/sigma-aldrich/home.html). Tween-80 (TW-80), Sodium dodecylbenzenesulfonate (SDBS), Sodium nitrite ($NaNO_2$), potassium phosphate dibasic trihydrate ($K_2HPO_4 \cdot 3H2O$), potassium dihydrogen phosphate (KH_2PO_4), and orthophosphoric acid (H_3PO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd., China (http://www.reagent.com.cn/index.asp).

0.1 M stock solution of nitrite was prepared by direct dissolution of sodium nitrite in double distilled water and then stored in a dark volumetlric flask in the refrigerator. Phosphate buffer solutions (0.1 M) with different pH values were prepared by mixing the standard stock solutions of Na_2HPO_4 and NaH_2PO_4 by adjusting pH with 0.1 M H_3PO_4. All solutions were prepared with double distilled water. (Assay of nitrite in water samples are shown in the Electronic supplementary material.)

Apparatus

All electrochemical measurements were carried out with a CHI660C electrochemical workstation (Chenhua Instruments, Shanghai, China, http://www.instrument.com.cn/netshow/SH101344/). A conventional three-electrode system, consisting of a DDAB modified glassy carbon working electrode (3.0 mm in diameter), a saturated calomel reference electrode (SCE) and a platinum counter electrode. All potentials were referred to the SCE.

Solartron 1255B Frequency Response analyzer and Solartron SI 1287 electrochemical interface were used for impedance spectroscopy study. Electrochemical impedance spectra measurement was performed in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl using an alternating current voltage of 10 mV. The impedance measurements were recorded at a bias potential of 200 mV within a frequency range of 10^{-2}–10^5 Hz.

Scanning electron microscopy (SEM) was carried out using a JSM-6700F filed emission scanning electron microscopy (Japan).

Preparation of the DDAB modified electrode

Certain amount of DDAB was dissolved in double distilled water and then used of ultrasionic agitation for a few hours to make the solution uniform. Before modification, the GCE was polished with 0.05 µm aluminum slurry, rinsed thoroughly with doubly distilled water, sonicated in a nitric acid solution of HNO_3:H_2O (v/v) = 1:1, alcohol and doubly distilled water successively, and dried under an infrared lamp. And then, required drops of the aqueous DDAB solution were used to cover the electrode surface.

Results and discussion

Electrochemical behavior of nitrite on the surfactant modified electrode

Figure 1 shows the differential pulse voltammograms for the GCE (a), SDBS modified electrode (b), TW-80 modified electrode (c) and DDAB modified electrode (d) in presence of 0.1 mM NO_2^- in 0.1 M phosphate buffer solution. A small oxidation peak current of 0.1 mM NO_2^- was seen on the bare GCE (Fig. 1a). Afterwards, the electrode was modified by anionic surfactant SDBS (Fig. 1b) or nonionic surfactant TW-80 (Fig. 1c), no catalytic current was observed. However, the NO_2^- molecule presents a higher oxidation peak current and a lower oxidation potential on the cationic surfactant DDAB

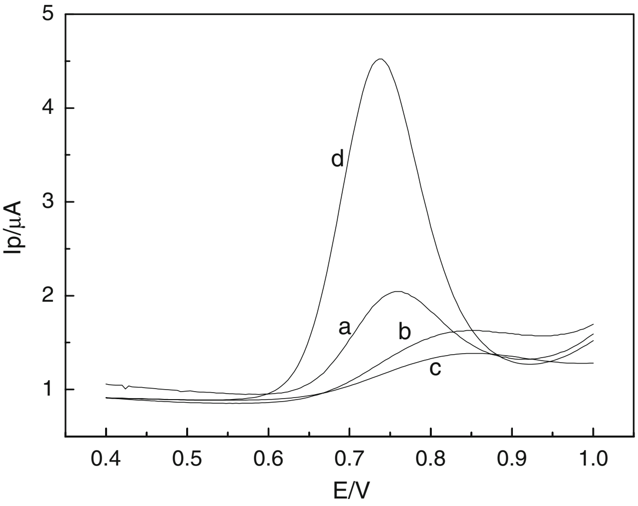

Fig. 1 Differential pulse voltammograms for bare GCE (**a**), SDBS modified eledtrode (**b**), TW-80 modified electrode (**c**) and DDAB modified electrode (**d**) in 0.1 mM NO_2^- + 0.1 M phosphate buffer solution

modified electrode (Fig. 1d). Surfactants have great influence on the rate of electron transfer and mass transport of electroactive species to the electrode surface.

The reason for this probably can be explained as: Nonionic surfactant TW-80 forms a dense film on the electrode surface that prevents the NO_2^- passing. SDBS is a kind of anionic surfactant, which hinders the NO_2^- approaching the electrode surface due to the electrostatic repulsion. Hence the electrode reactions are retarded on these two modified electrode. However, on the cationic surfactant DDAB modified electrode surface, electrostatic attraction occurs between NO_2^- and DDAB, causing increase of the peak current and less shift of anodic peak potential.

Electrochemical and SEM characterization of the modified electrode

Electrochemical impedance of modified electrode

EIS is an effective method for studying the interface feature of surface-modified electrode. The curve of the EIS includes a semicircular part and a linear part. The semicircular part at higher frequencies corresponds to the electron-transfer-limited process and its diameter is equal to the electron transfer resistance (*R*et), which controls the electron transfer kinetics of the redox probe at the electrode interface. Meanwhile, the linear part at lower frequencies corresponds to the diffusion process [37].

Figure 2 illustrates the results of electrochemical impedance analysis on GCE without (a) and with DDAB membrane (b). It can be seen from Fig. 2a that the bare GCE exhibits an almost straight line that is characteristic of a diffusion limiting step of the electrochemical process. However, with respect to the modified electrode (Fig. 2b), significant difference in the impedance spectra is observed. The diameter of the high-frequency semicircle is significantly enlarged, which means that the dynamics of electron transfer in higher frequency range is observed and the current due to voltage excitation is under kinetic control. The low frequency region, which is a straight line, is dominated by mass transfer of the redox species to and from the interfacial region [38]. Hence, it is clear that DDAB film has been formed on the surface of GCE successfully. DDAB can form multi-bilayer films on the electrode surface [39].

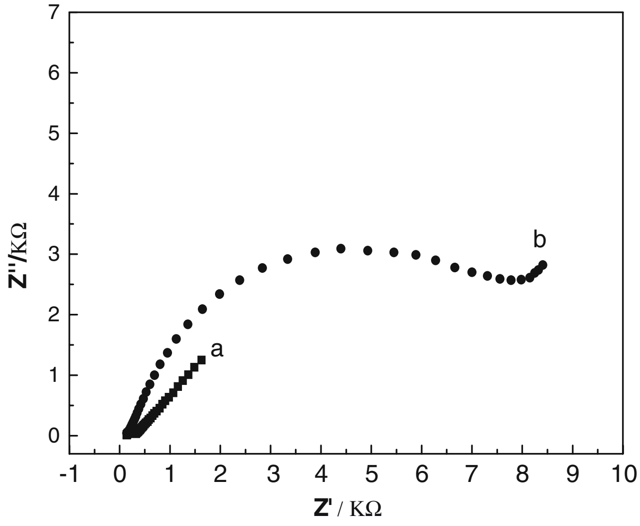

Fig. 2 EIS of bare GCE (**a**), DDAB modified electrode (**b**) in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl

SEM images

SEM is a kind of widely used surface analysis technique. It can examine the surface morphology of the solids rapidly without damage to the surface. To confirm the formation of the DDAB films on electrode surface, we choose SEM technique to characterize the glassy carbon surface. The SEM images were randomly captured at the glassy carbon surface. Some small bright points were clearly seen on the bare glassy carbon substrate after being polished. While on the surface after the glassy carbon substrates modified with DDAB, a clear thin film, instead of the bright points, was visible. This contrast suggests that DDAB form a uniform film on the GCE surface. (SEM images are shown in the Electronic supplementary material of Fig. I)

Optimizing the experiment conditions

Influence of the modifier concentration

The DDAB concentration which is used to modify electrode has a significant influence on the voltammetric response of the same concentration of NO_2^-. The dependence of oxidation peak current and peak potential on the modifier concentration from 2 mM to 10 mM were investigated. The experiment result shows that the oxidation peak current for 0.1 mM NO_2^- increases gradually with the modifier concentration increases from 2 mM to 10 mM. More NO_2^- molecules were attracted by the electrode surface when the higher concentration of modifier was used, and the more molecules reacted on the electrode surface. The result also shows the peak potential dependence on the modified concentration, the peak potential shifts to positive value when the modifier concentration increases from 2 mM to 10 mM. This is because the higher modifier concentration will form the denser film and the denser film has the bigger balk to the electrode reaction.

DDAB is sparingly soluble in water [40]. It can't completely dissolve in water when the concentration exceeds 8 mM. In addition, the incompletely dissolved modifier leads to the electrode surface instability. Therefore, 8 mM of the modifier concentration was chosen in the following experiment.

Influence of the solution pH value

The effect of solution pH on the electrochemical response of NO_2^- was investigated in the pH range from 3.0 to 8.0 in 0.1 M phosphate buffer solution. Figure 3 shows the effect of pH values on the oxidation peak current of 0.1 mM NO_2^-. It can be seen that the peak current increases with pH value from 3.0 up to 5.0, and then a decrease in the current is observed for pH higher than 5.0. At pH 5.0, the peak current gives a maximum. In addition, this study shows that the peak potential is virtually constant in the operating pHs. The peak potential is not affected by the pH. Similar observations were also noticed in NO_2^- oxidation on Prussian Blue [41] and palladium pentacyanonitrosylferrate modified electrodes [42]. From these two papers, this feature can be attributed to a kinetically controlled oxidation process, in other words, a proton independent catalytic step. Thus, pH 5.0 was chosen for further studies.

Linear range of nitrite detection

In order to obtain an analytical curve for the sensor, differential pulse voltammograms for oxidation of NO_2^- were carried out at different concentrations in 0.1 M phosphate buffer solution at pH 5.0 (Fig. 4a). Under optimized conditions, the linear dynamic range was comprised between 1.0×10^{-6} M and 8.0×10^{-5} M in terms of the relationship between NO_2^- concentration and the oxidation peak current (Fig. 4b). The equation could be expressed as follows:

$$I_p(\mu A) = 0.04[NO_2^-](\mu M) + 0.14 \quad (1)$$

with a correlation coefficient of 0.9993 (for n = 10) and sensitivity of 0.04 μA·μM^{-1}.

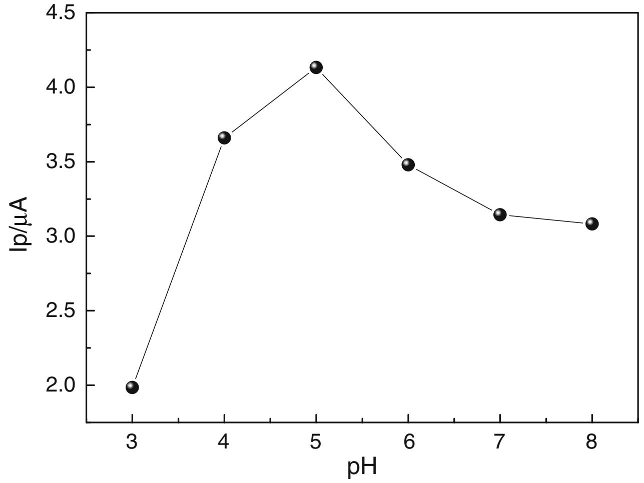

Fig. 3 Dependence of the oxidation peak current on pH values in 0.1 mM NO_2^- + 0.1 M phosphate buffer solution

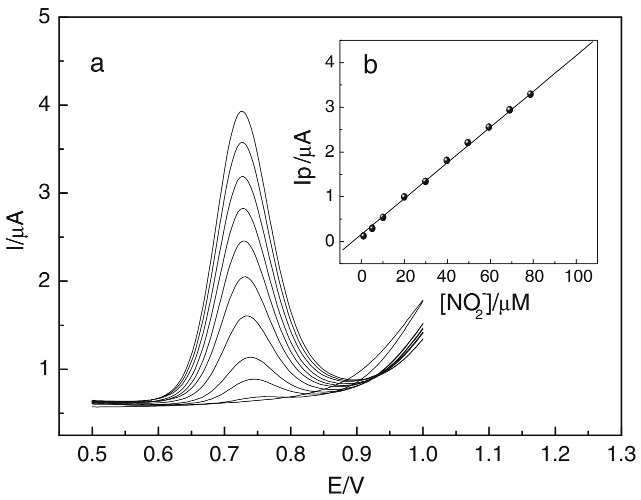

Fig. 4 (**a**) Differential pulse voltammograms recorded in 0.1 M phosphate buffer solution at pH 5.0 before and after addition of NO_2^- to give final solution concentrations in the range 1–80 μM. (**b**) The inset shows the calibration plot

Applications

In order to evaluate the practical utility of the method, NO_2^- was analyzed in real samples using the standard addition method. Water samples were from Weichang Lake in the new campus of Shanghai University and a dirty river near the campus. After filtration to remove the suspension solid substances, the concentration values of NO_2^- in the samples were analyzed by the proposed method. (The figures are shown in the Electronic supplementary material of Fig. II) The NO_2^- amount and the recovery were displayed in Table 1. The results show that the proposed methods could be efficiently used for the determination of the real samples.

Some chemical species were tested to check their levels of interference in the NO_2^- determination. The results showed that most of the ions, such as K^+; Na^+; Mg^{2+}; Ca^{2+}; Zn^{2+}; Cd^{2+}; NH_4^+; F^-; Cl^-; NO_3^-; SO_4^{2-}; Ac^- and PO_4^{3-},

Table 1 Detemination of NO_2^- in water samples (*n*=5)

Sample	Detected (μM)	Added (μM)	Found (μM)	Recovery (%)
Lake water	5.812	8.000	13.72	98.85
River water	46.27	8.000	42.38	104.4

even 100-fold excess concentrations did not interfere in the determination (signal change <5%). However, a small quantity of CN^-; SO_3^{2-} (1×10^{-5} M) will interfere in the NO_2^- assay (signal change >5%) as there are common reductants.

Conclusion

In this work, the SDBS, TW-80 and DDAB modified electrode were all prepared for the NO_2^- detection. Among these modified electrodes, DDAB modified electrode had the highest sensitivity for NO_2^- determination which could detect NO_2^- even at a low level. It also can endure the interference of some common ion. This modified electrode was used to detect NO_2^- in water samples, and satisfactory results were received.

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