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ORIGINAL PAPER

Electrodeposition of cobalt oxide nanoparticles on carbon nanotubes, and their electrocatalytic properties for nitrite electrooxidation

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Abstract We describe a modified glassy carbon electrode (GCE) for the sensitive determination of nitrite in waste water samples. The GCE was modified by electrodeposition of cobalt oxide nanoparticles on multi-walled carbon nanotubes (MWCNTs) deposited on a conventional GCE. Scanning electron microscopy and electrochemical techniques were used for the characterization of the composite material which is very uniform and forms a kind of nanoporous structure. Electrochemical experiments showed that the modified electrode exhibited excellent electrocatalytic properties for nitrite. Amperometry revealed a good linear relationship between peak current and nitrate concentration in the 0.5 to 250 μM range with a detection limit of 0.3 μM (S/N=3). The method has been applied to the amperometric detection of nitrite. The modified electrode displays good storage stability, reproducibility, and selectivity for a promising practical application.

Keywords Amperometric sensor · Electrocatalytic oxidation · Nitrite · Cobalt oxide

Introduction

Nitrite is ubiquitous within environmental, food and life science and can interact with amines to form carcinogenic nitrosamines [1]. Hence, it is necessary to develop a reliable and sensitive sensor to detect nitrite in food, drinking water and environmental samples. Several techniques, including spectrophotometry [2], chemiluminescence [3], chromatography [4], and capillary zone electrophoresis [5], have been developed. However, it must be pointed out that most of the above methods involve time-consuming and tedious procedures. Owing to the rapid response, cheaper, safer and simple use, electrochemical methods have often been employed for the detection of nitrite [6–10]. For example, Badea [11] presented an amperometric procedure for nitrite determination in cured meat using a carbon paste electrode covered with a cellulose acetate membrane. This probe turned out to be free from interferences by ascorbic acid as present in meat samples. Zhao et al [12] constructed a biosensor for nitrite by immobilization of hemoglobin and a room temperature ionic liquid on a multi-walled carbon nanotubes modified glass carbon electrode. The biosensor has been successfully applied to the determination of nitrite in water samples. Lu et al [13] made use of the synergetic effect of Pd–Fe nanoclusters to investigate the electrocatalysis of nitrite. This modified electrode exhibited excellent stability and high catalytic activity towards nitrite reduction. Gu et al. [14] have described an electrochemical activity towards the reduction of nitrite using a nanometer-sized gold colloid attached to an ethylenediamine monolayer modified electrochemically pretreated glassy carbon electrode.

Cobalt oxide-based materials have been widely used for energy storage system [15], electrochromic thin films [16], magnetoresistive devices [17] and heterogeneous catalysis

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[18]. Cobalt oxides continue to attract considerable attention, mainly due to their excellent electrocatalytic activity toward various compounds, such as glucose, glutathione, carbohydrate, thiol, hydrogen peroxide, arsenic(III) and methanol [19–24]. Several methods have been developed for the preparation of cobalt oxide including solvothermal process [25], solution spray pyrolysis technique [26] and electrochemical method [27]. Among these techniques, the electrochemical method is an attractive and promising method. Casella et al. have prepared cobalt oxide or oxyhydroxide layers on the surface of gold [28] and glassy carbon electrode [29, 30] by electrodeposition technique. In addition, the electrochemical properties of cobalt oxide films deposited anodically or cathodically at conductive boron doped diamond (BDD) or glassy carbon electrodes have been investigated [31, 32].

In this study, cyclic voltammetry was used to form cobalt oxide film on the surface of MWCNTs/GCE. The electrocatalytic activity, stability, pH effect and kinetic parameters of modified electrode were evaluated by electrochemical techniques. The modified electrode for oxidation of nitrite has also been investigated. To evaluate the possible analytical application of the modified electrode, it has been used for amperometric detection of nitrite.

Experimental

Apparatus

A Model CHI660A Electrochemistry Workstation (Chenhua Instruments Co. Ltd., Shanghai, China, chi.instrument.com.cn) was employed for all the electrochemical techniques. A three-electrode system was used, where a standard saturated calomel electrode (SCE) served as the reference electrode, a platinum wire electrode as the auxiliary electrode, and a modified glassy carbon electrode (GCE, $\Phi=3$ mm) as the working electrode. All the electrochemical experiments were conducted at room temperature (25°C). Scanning electron microscopic (SEM) measurements were carried out with a JSM-6700F scanning electron microscope (Japan Electron Company, Japan, www.jeol.co.jp).

Reagents

MWCNTs (~95% purity) were purchased from Shenzhen Nanotech. Port. Co., Ltd. (Shenzhen, China, http://www.nanotubes.com.cn/doce/default.html). $CoCl_2$ was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China, http://kermel.b2b.hc360.com). All other reagents were of analytical grade, and all solutions were prepared with water purified in a Milli-Q Millipore system throughout.

Preparation of the modified electrodes

GCE was polished before each experiment with 0.3, and 0.05 μm α-alumina powders (CHI Instrument, Shanghai, China, chi.instrument.com.cn) in sequence, rinsed thoroughly with doubly distilled water between each polishing step, ultrasonicated in 1:1 HNO_3, ethanol, and doubly distilled water, and allowed to dry at room temperature. Then 3.0 mg MWCNTs functionalized with carboxylic acid groups was dispersed in 1.0 mL of N,N-Dimethylformamide (DMF). GCEs were modified by a 5.0 μl drop of MWCNTs-DMF solution and dried in air. Cobalt oxide was electrodeposited on the surface of electrodes from 1 mM cobalt chloride in pH 6.76 phosphate buffer solution, using repetitive potential cycling between 0.5 and −1.1 V [33]. The cycles for the electrodeposition of CoOx nanoparticals had been optimized. The results were shown in Fig. S1 in Supplementary Section. The peak current changed with cycles. At 35 cycles the peak current reached its maximum. Thus, the optimum cycles for further studies was set in 35 cycles at 100 mV s^{-1}. Modified electrode was eventually washed with double distilled water and stored at ambient temperature (25°C) before being used in experiments.

Experimental procedures

Cyclic voltammetric and amperometric measurements were performed in a cell containing 20 mL 0.1 M phosphate buffer solution at room temperature. All solutions were deoxygenated by bubbling highly pure nitrogen for at least 20 min and maintained under nitrogen atmosphere during measurements. The amperometric experiments were carried out with applied potential at +0.75 V for nitrite on a stirred cell at room temperature.

Results and discussions

Characterization of CoOx/MWCNTs composite

In order to investigate the formation of the CoOx, the electrode surface was observed by SEM (Fig. 1). The MWCNTs' tangled ropes with a smooth surface were shown in Fig. 1a. After electrodeposition of CoOx onto the surface of the MWCNTs/GCE, a dense and entangled CoOx/MWCNTs hybrid nanostructure with a three-dimensional network structure was obtained (Fig. 1b). Due to its high surface-to-volume ratio, the three-

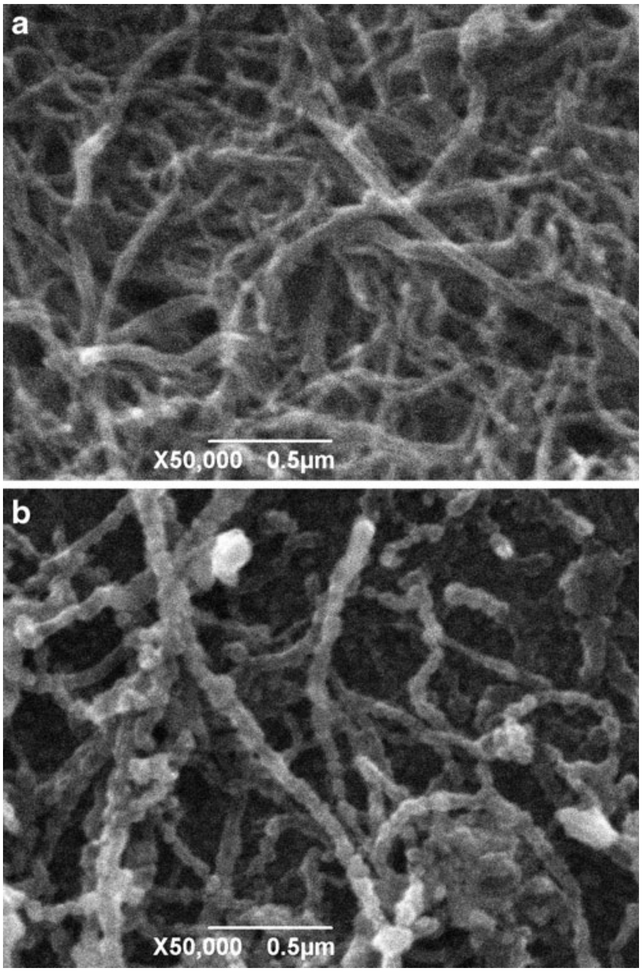

Fig. 1 SEM images of MWCNTs (**a**) and CoOx/MWCNTs nanocomposite (**b**)

dimensional nanoporous structure provided ample space to allow fast mass transport of ions through the electrolyte/electrode interface as well as a conductive network for enhancing electronic conductivity which was favorable to the catalytic application of CoOx [34]. The possible mechanism of the growing process was that the Co^{2+} ions can get selectively adsorbed onto the surface of MWCNTs, and this heterogeneous nucleation process may mainly take place on the surface of CNT.

Figure 2 shows the cyclic voltammograms for the CoOx/MWCNTs/GCE in pH 6.76 phosphate buffer solution in absence (b) and presence of 1.0 mM NO_2^- (a). For comparison, this figure also presents the behavior of bare GCE (d) and GCE modified with MWCNTs only (c) both in presence of NO_2^-. As can be seen, the best response was obtained with the GCE modified with CoOx/MWCNTs nanocomposite (Fig. 2a). This modified electrode presented higher peak current and lower oxidation potential for NO_2^- than the bare GC and MWCNTs modified electrodes. This behavior suggests that the cobalt oxide and MWCNTs can cause a synergic enhancement effect for nitrite oxidation on the sensor surface.

Electrocatalytic behavior of nitrite on CoOx/MWCNTs modified electrode

In order to evaluate the electrocatalytic activity of cobalt oxide film, the cyclic voltammograms of the modified electrode in the presence of different concentrations of nitrite were recorded (Fig. 3). As was shown, with increasing nitrite concentration, the anodic peak currents increased and cathodic peaks decreased due to catalytic oxidation of nitrite. The increased peak current of nitrite oxidation confirmed that cobalt oxide nanoparticles had high catalytic ability for nitrite oxidation. The anodic peak currents of nitrite increased linearly with the increase in nitrite concentrations from 0.25 mM to 1.5 mM. The linear regression equation was obtained as $I_p(\mu A) = 32.76 + 25.90c\,(\mathrm{mM})\,(R^2 = 0.9960)$.

The influence of the solution pH in the electrochemical response of the nitrite using 0.1 M phosphate buffer solution at pH 3–10 were shown in Fig. S2 in Supplementary Section. The peak current changed with pH in the range from 3.14 up to 6.76. At pH 6.76 the peak current reached its maximum. A decrease in the current was observed when the solution pH was higher than 6.76. Thus, the optimum pH for further studies was set in 6.76.

Additional information about NO_2^- oxidation on the modified electrode surface was obtained by using the catalytic current from cyclic voltammograms. According to the theoretical model of Andrieux [35], the catalytic

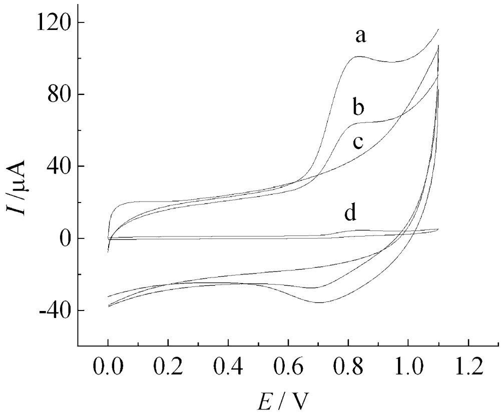

Fig. 2 Cyclic voltammograms for CoOx/MWCNTs modified electrode in the presence (**a**) and absence (**b**) of 1.0 mM NO_2^-; for an electrode with MWCNTs only (**c**) and for a bare GCE (**d**), both in presence of 1.0 mM NO_2^-, in 0.1 M phosphate buffer solution (pH 6.76). Scan rate: 0.10 Vs^{-1}

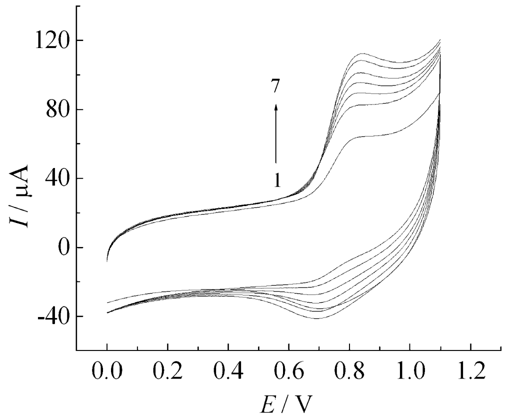

Fig. 3 Cyclic voltammograms of CoOx/MWCNTs/GCE in phosphate buffer solution (pH=6.76) at scan rate 0.10 $\mathrm{Vs^{-1}}$ with increasing NO_2^- concentration: 0.00, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50 mM

current I_p depends on the potential scan rates ν, as is shown in the Eq. 1:

$$I_p = 0.496FAC_oD_o{}^{1/2}(F\nu/RT)^{1/2} \tag{1}$$

where C_o is the substrate concentration, D_o the diffusion coefficient of the substrate, F the Faraday constant, R and T the gas constant and temperature respectively [35, 36]. Firstly, the anodic peak currents of nitrite were proportional to the square root of scan rate in the range of 20–180 mV $\mathrm{s^{-1}}$ in pH 6.76 phosphate buffer solution, $I_p(\mu A) = 16.13 + 62.96\nu^{1/2}(\mathrm{mV^{1/2}s^{-1/2}})\ (r = 0.9980)$ (Fig. 5a), suggesting that the process was controlled by diffusion as expected for a catalytic system. Second, a plot of the sweep rate-normalized current density $I_p\ /\ \nu^{1/2}$ versus the sweep rate (Fig. 5b) exhibited the characteristic shape of a typical EC' catalytic process [37].

As can be seen in Fig. 4, nitrite oxidation was an irreversible process. Thus, the number of electrons, n, involved in the overall reaction could be obtained from the slope of the I_p versus $\nu^{1/2}$ plot according to the equation for a totally irreversible process controlled by diffusion [36]:

$$I_p = (2.99 \times 10^5)n[(1-\alpha)n_a]^{1/2}C_o^*AD_o^{1/2}\nu^{1/2} \tag{2}$$

where α is the electron transfer coefficient, n_a the number of electrons involved in the rate-determining step, D_o ($\mathrm{cm^2\ s^{-1}}$) the diffusion coefficient of the electroactive species and C_o^*($\mathrm{mol\ cm^{-3}}$) the concentration of the electroactive species. Other terms and their meanings were mentioned before. In the present study, the values of the concentration and diffusion coefficient used for NO_2^- in aqueous solution were 0.5 M and 2.1×10^{-5} $\mathrm{cm^2\ s^{-1}}$ [38] respectively. In addition, considering the fact that the (1−α) n_a value has to be known, one approach was employed for the NO_2^- oxidation reaction based on its dependence on the difference between the peak potential E_p and the potential of the half peak current $E_{p/2}$ given by the equation [36]:

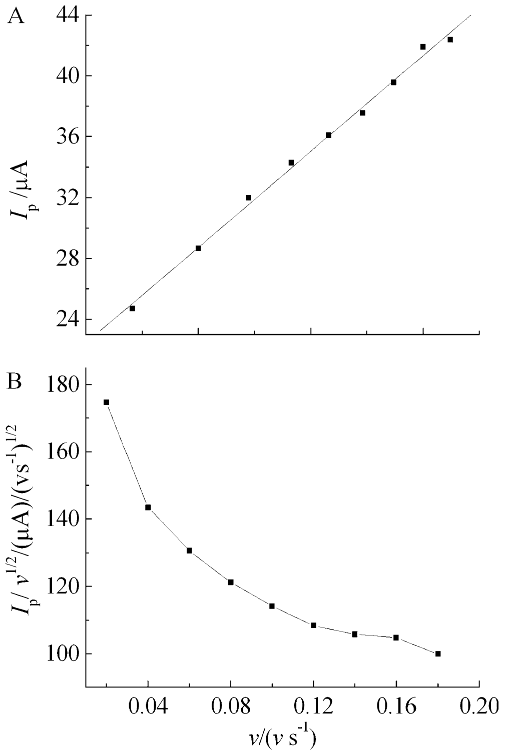

Fig. 4 **a** Variation of the anodic peak current I_p vs. $\nu^{1/2}$ of 0.10 mM NO_2^- at the CoOx/MWCNTs/GCE with scan rate 0.20–0.18 $\mathrm{Vs^{-1}}$ and **b** $I_p\ /\ \nu^{1/2}$ vs. ν plot for NO_2^- at the CoOx/MWCNTs/GCE. Both studies were performed in 0.1 M phosphate buffer solution (pH 6.76)

$$(1-\alpha)n_a = \frac{47.7\mathrm{mV}}{E_p - E_{p/2}} \tag{3}$$

The value of (1−α) n_a was estimated as 0.50. Thus, using its value in the Eq. (2) and the slope of the plot was

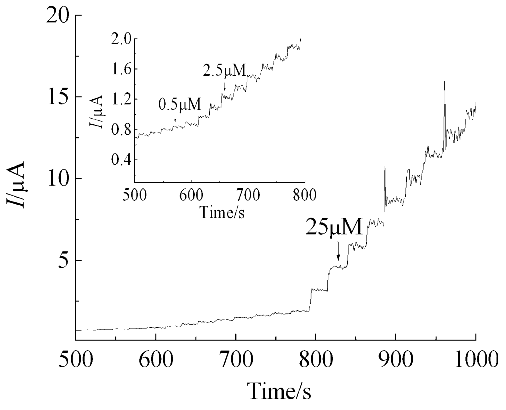

Fig. 5 Amperometric response at the CoOx/MWCNTs/GCE in 0.1 M phosphate buffer solution (pH=6.76) held at 0.75 V for successive addition 0.5 μM, 2.5 μM or 25 μM NO_2^-. Insert for 0.5 μM and 2.5 μM addition

Table 1 Detection limit and linear range of different modified electrodes for the determination of NO_2^-

Electrode	Detection limit (μM)	Linear range (μM)	Reference
Hb/RTIL/MWNTs/GCE	0.81	4–320	[12]
Pd-Fe/GCE	1.0	6–5000	[13]
Au/ethylenediamine/PGCE[a]	45	130–44000	[14]
Nano-Au/P3MT/GCE[b]	2.30	10–1000	[41]
Thionine/ACNTs[c]	1.12	3.0–500	[42]
screen-printed electrode	1.00	2.0–500	[43]
PdPCNF/Al[d]	—	50–100	[44]
VIVO(SB)/CPE[e]	0.61	3.9–405	[45]
Cinder/Prussian Blue/CPE	3.36	3.36–1600	[46]
Au/GCE	2.4	10–500	[47]
CoOx/CNT/GCE	0.3	0.5–249	this work

a: PGCE: Electrochemically pretreated glassy carbon electrode

b: Nano-Au/P3MT/GCE: gold nanoparticles/poly(3-methylthiophene) composite coatedglassy carbon electrode

c: ACNTs: Aligned carbon nanotubes

d: PdPCNF/Al: aluminum electrode modified by palladium pentacyanonitrosylferrate

e: VIVO(SB)/CPE: carbon paste electrode modified with oxovanadium(IV)-4-methyl salophen

62.96 μA / (V $s^{-1})^{1/2}$ extracted from Fig. 5a, the value of *n* was calculated to be 1.8, suggesting two electrons in the oxidation mechanism of nitrite. Hence, the NO_3^- ion was the main product of the reaction, which is in agreement with other works based on the catalytic oxidation of NO_2^- [39, 40]. Therefore, the following mechanism could be suited for the system:

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \qquad (4)$$

Amperometric detection of nitrite

Figure 5 displays the typical steady-state catalytic current time response of CoOx/MWCNTs/GCE with successive injection of nitrite at an applied potential 0.75 V. A well-defined response was observed under the successive addition of 0.5 μM, 2.5 μM and 25 μM of NO_2^-, which suggested a stable and efficient catalytic property through the CoOx/MWCNTs composite film. The oxidation currents at the modified electrode were proportional to the concentration of nitrite in the range of 0.5–249 μM. The linear regression equation was obtained as $I_p(\mu A) = 0.3145 + 56.19 \times 10^{-3} C\,(\mu M)\ (R^2 = 0.9963)$ with the detection limit of 0.3 μM (S/N=3).

The comparisons of the parameters of NO_2^- detection by use of various chemically modified electrodes are listed in Table 1, from which, it can be seen that the detection limit of the method is lower than previously reported [12–14, 41–47]. Meanwhile, the linear ranges of the method for the determination of nitrite are similar to previous methods listed in Table 1. So we think the method has its advantages for the detection of nitrite.

The interference effect of potentially interfering ions on the determination of nitrite was examined by adding various ions into the phosphate buffer solution (pH 6.76) containing 1.0 mM nitrite and the results showed that most of the ions, such as NH_4^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, F^-, Cl^-, NO_3^-, SO_4^{2-} did not interfere the determination. The interference of some oxidable species was also studied. We found that 50-fold amount of Br^-, 20-fold amount of $S_2O_3^{2-}$, and 5-fold amount of I^- showed serious interference. As can be verified, this study reveals that the developed sensor can tolerate a high concentration of interfering ions and,

Table 2 Results of the determination of nitrite in different samples (*n*=6)

Samples	Content /($NaNO_2$, μM)	Added /($NaNO_2$, μM)	Found /($NaNO_2$, μM)	Recovery (%)	R.S.D. (%)
1	2.3	40.0	42.6	100.7	3.2
2	3.2	40.0	43.4	100.5	2.7

therefore, can be stated as selective over the commonly present interfering ions.

Stability and reproducibility of the CoOx/MWCNTs/GCE

In order to investigate the stability of the CoOx/MWCNTs/GCE, the currents of cyclic voltammograms for 1.0 mM nitrite in 0.1 M phosphate buffer solution (pH6.76) was recorded at an interval of every 3 min. It was found that the oxidation current of nitrite remained almost unchanged with a relative standard deviation of 1.6% for 25-time repetitive measurements, indicating that this electrode had a good reproducibility. After voltammetric measurements, this electrode was kept at room temperature. The current response decreased about 2.3% in one week and 3.7% in about two weeks. The above results showed that the present modified electrode was stable and reproducible towards the oxidation of nitrite.

Determination of nitrite in real samples

To examine the possible use of the electrode in practical application, experiments were conducted in samples of waste water for the determination of nitrite. The nitrite concentration was determined. Recovery studies were carried out in waste water samples by using the standard addition method. An appropriate volume of the sample was placed in an electrochemical cell for the determination of nitrite by amperometric determination. From the results listed in Table 2, it can be seen that the method can be successfully applied for the detection of nitrite in real samples.

Conclusions

In this work, a novel sensor for determination of nitrite, which based on cobalt oxide nanoparticles deposited on the surface of MWCNTs/GCE, was successfully constructed. The CoOx/MWCNTs/GCE exhibited good electrocatalytic activity towards the oxidation of nitrite. Compared with previous reports for nitrite response, the method for nitrite determination displayed a lower detection limit of 0.3 μM (*S*/*N*=3). The main reason was ascribed to the large surface area and good conductivity of CoOx/MWCNTs composite, which can enhance the efficiency of the electron transfer between the modified electrode and nitrite. The CoOx/MWCNTs/GCE showed high stability, excellent selectivity, good sensitivity and reproducibility and has been applied to the determination of nitrite in waste water. The reliability and stability gave a good possibility for applying the technique to routine analysis of nitrite in other samples.

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