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ARTICLES

Fabrication of Poly(4-Aminobenzoic Acid/*o*-Toluidine) Modified Carbon Paste Electrode and Its Electrocatalytic Property to the Oxidation of Nitrite[1]

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Abstract—The poly(4-aminobenzoic acid/*o*-toluidine) (4-AB/OT) modified carbon paste electrode (CPE) was fabricated by consecutive cyclic voltammetry. The poly(4-AB/OT) CPE shows catalytic activity for the oxidation of nitrite in 0.1 M phosphate buffer solution (pH 7). Due to the electrostatic interaction between the negatively-charged nitrite ions and the positively-charged poly(4-AB/OT) film, the operating potential for nitrite oxidation was shifted about 240 mV to negative side, compared to bare CPE. The catalytic peak current was found to be linear with the nitrite concentration in the range of 6–600 μM, with a correlation coefficient of 0.981, using amperometry. The sensitivity and limit of detection for the poly(4-AB/OT) CPE are about 187.4 μA/mM and 3.5 μM, respectively. The possible interferences from several common ions were tested. The developed sensor was also successfully applied to the determination of nitrite concentration in a mineral water sample.

Keywords: nitrite, electrocatalytic oxidation, carbon paste electrode, modified electrodes

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Nitrite ions are widely used as additives in food, fertilizers in agriculture and as corrosion inhibitors [1], and the problems caused by the contamination of food products, water and environment are significant concerns [2–6]. Nitrite ions can have damaging effects via two mechanisms. They can combine with blood pigments producing methemoglobin in which oxygen is no longer available to the tissues. Also they may interact in the stomach with amines and amides forming nitrosamines, which are well-known carcinogenic substances [4, 7]. Therefore, there has been an increasing interest in the development of methods for the quantitative determination of nitrite concentrations, especially in the supervision of the quality of drinking water, in wastewater treatment, and in the food industry. The simple but highly selective and sensitive methods suitable for fast and reliable field measurements are desirable.

Several techniques have been developed for nitrite determination, including spectrophotometry [8], chemiluminescence [9], chromatography [10] and capillary electrophoresis [11]. However, these determination methods usually have tedious detection procedures and therefore are time-consuming. Compared to these methods, the electrochemical methods can provide cheaper, faster, real-time analysis and thus have attracted more attention.

Electrochemical determination of nitrite is either by reduction or oxidation. Oxidation of nitrite ions offers several advantages, namely no interference from nitrate ion and molecular oxygen, which are usually the major limitations in the cathodic determination of nitrite [12, 13]. The electrochemical determinations of nitrite at traditional electrodes, such as platinum [14] and glassy carbon electrode [15], have been developed. However, the direct electroreduction/oxidation of nitrite ions requires high overpotential at bare surfaces [15, 16]. In addition, these electrodes tend to be poisoned by the species formed during the electrochemical process [17]. A good way of lowering potentials is using modified electrodes. One of the most important effects of any mediator such as metallophthalocyanines and metalloporphyrins [18–24], series of inorganic porous materials [25] and enzyme electrodes [26] is a reduction of the overpotential required for the electrochemical reaction and enhancement of the sensitivity (current) and selectivity of the method.

Recently, conducting polymers have become favorite materials in electroanalysis. Among the various conducting polymers, polyaniline has become the most attractive one because of its facile preparation, high conductivity and good environmental stability [27–30].

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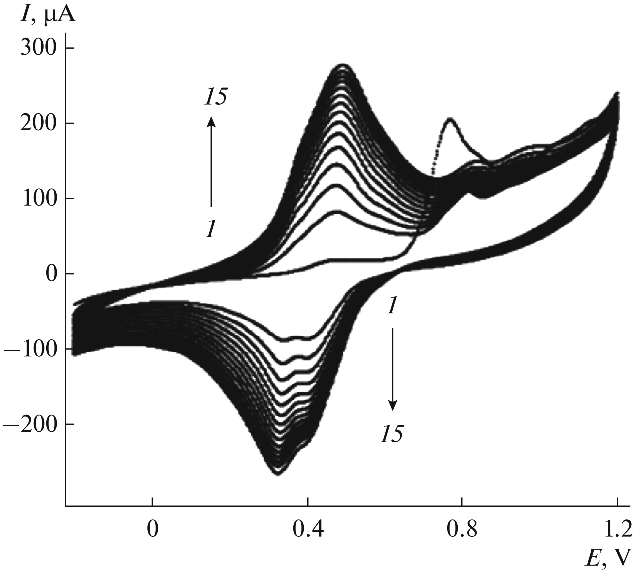

Fig. 1. Cyclic voltammograms (15 cycles) recorded during potentiodynamic growth of poly(4-AB/OT) film in a solution containing 2.5 mM 4-AB, 2.5 mM OT, 5 mM SDS and 0.1 M H_2SO_4; $v = 50$ mV/s.

In our previous work, we have demonstrated the ability of copper hexacyanoferrate [31] and poly (N-methylaniline) [32] as catalysts for electrocatalytic reduction of nitrite on the surface of carbon paste electrode. Herein, we report a study of the catalytic properties of poly(4-AB/OT) for the electrocatalytic oxidation of nitrite. The results show that the poly(4-AB/OT) has a very good catalytic activity toward the nitrite oxidation.

EXPERIMENTAL

Reagents and materials. The solvent used in this work was twice distilled water. The electrolyte solutions were 0.1 M phosphate buffer in pH of 0.5, 2, 5, 7, 9 and 11. 2-Toluidine, 4-aminobenzoic acid, sodium dodecyl sulfate (SDS) and sodium nitrite were analytical grade of Merck (New Jersey, US) origin and used without further purification. High viscosity paraffin (density 0.88 g/cm^3) from Fluka (Sydney, Australia) was used as the pasting liquid for CPE. Graphite powder (particle diameter 0.10 mm) from Merck (New Jersey, US) was used as the working electrode substrate. All other reagents were of analytical grade.

Apparatus. Electrochemical experiments were performed with a computer-controlled potentiostat/galvanostat μ-Auto lab type III modular electrochemical system (Eco Chemie BV, Netherlands), driven with general purpose electrochemical system (GPES) software (Nova). Voltammetry was done in a three-electrode cell using the modified CPE as working electrode, a Ag | AgCl | KCl (3 M) from Azar electrode (Urmia, Iran) as reference electrode and a platinum rod from Azar electrode (Urmia, Iran) as counter-electrode. All experiments were carried out at ambient temperature. No action was taken to remove oxygen from solutions.

RESULTS AND DISCUSSION

Electrochemical polymerization. The electropolymerization of 4-AB/OT, onto CPE, was carried out by cyclic voltammetric method in aqueous solution containing 2.5 mM 4-AB, 2.5 mM OT, 5 mM SDS and 0.1 M H_2SO_4 between −0.2 and 1.2 V at a scan rate of 50 mV/s for 15 cycles. Figure 1 shows the typical multi-sweep cyclic voltammograms during the electropolymerization. As can be seen in this figure, in the first anodic sweep, the oxidation of monomers occurs as distinct irreversible anodic peaks ($E > 0.6$ V). A part of the oxidation products of monomers is deposited on the electrode, as a polymer film. In the first reverse cycle, the new cathodic peaks appear at a potential between 0.1–0.6 V, confirming the initial deposition of electrooxidized products. In the second positive scan of potential, a broad anodic peak is appeared at a potential between 0.2–0.8 V. The oxidation peak current of monomer decreases with increasing of the number of potential cycles. The decreasing of oxidation current is due to the loss of activity of the electrode surface when covered with newly formed polymer film.

Electrochemical behavior of poly(4-AB/OT) carbon paste electrode. The cyclic voltammetric response of poly(4-AB/OT) CPE was investigated during several different potential cycles in 0.1 M H_2SO_4 at a scan rate of 50 mV/s. Based on that, currents of anodic and cathodic peaks decrease with increasing of number of cycles (current intensity is constant after 18 consecutive cycles). It can be attributed to the presence of species that not as well as adsorbed. As a result, they separate of surface of modified electrode, easily.

We examined the effect of scan rate at the surface of poly(4-AB/OT) CPE (Fig. 2a). It was found that, with the increase of potential scan rate (10–800 mV/s), the anodic peak potentials shift to more positive and the cathodic peak potentials shift to more negative values, indicating that the redox reversibility of polymeric film was impaired (the peak-to-peak potential separation (ΔE_p) is 120 mV, at $v = 50$ mV/s). Figure 2b illustrates the anodic peak currents are proportional to scan rate. This suggests that electroactive species immobilize on the electrode surface. Also, we used cyclic voltammetry experiments in ferrocyanide solution and the Randles–Sevcik equation [33] to obtain an estimate of the poly(4-AB/OT) CPE real surface area:

$$I_p = 2.69 \times 10^5 D^{1/2} n^{3/2} A c v^{1/2}, \quad (1)$$

where A is the real surface area of the electrode, D is the diffusion coefficient (0.65×10^{-5} cm^2/s), n is num-

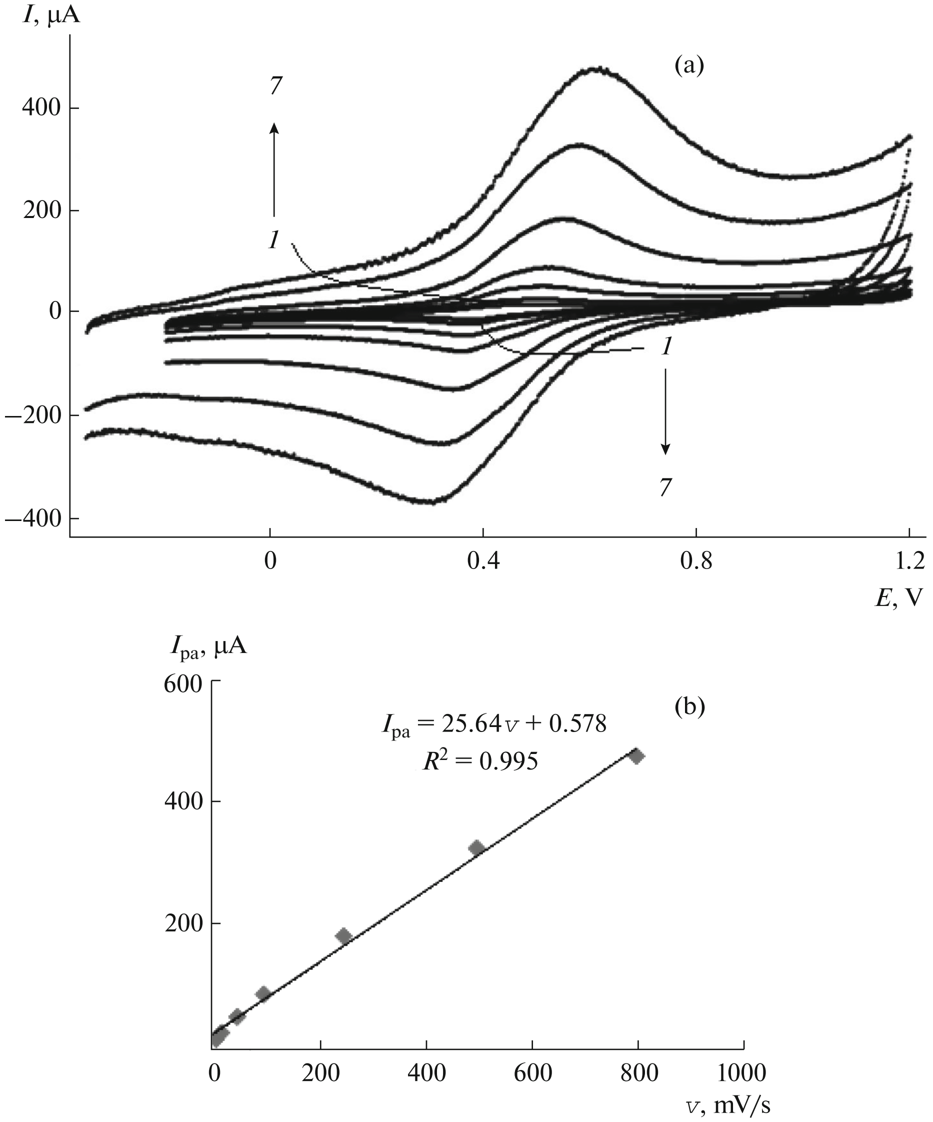

Fig. 2. Cyclic voltammograms of poly(4-AB/OT) in 0.1 M H_2SO_4 at different scan rates: 10, 20, 50, 100, 250, 500 and 800 mV/s from *1* to *7*, respectively (a); relationship between anodic peak currents and scan rates (b).

ber of exchangable electrons for ferrocyanide ($n = 1$) and c is the bulk concentration of ferrocyanide (1 mM). Based on the plots of I versus $v^{1/2}$ for this modified electrode (not shown) and since the other terms are the same in all experiments, the value of the slope can be considered to be an estimate of A. From the slope of this plot, it can be concluded that the real surface area of poly(4-AB/OT) CPE is equal to 0.12 cm^2.

The electrochernical properties of poly(4-AB/OT) CPE in aqueous buffered solutions were also studied by cyclic voltammetry in the pH range between 0.5–11 at the carbon paste electrode. Cyclic voltammograms show a single reduction peak and a corresponding oxidation peak (Fig. 3a). These results show that the redox behavior of the polymeric film is strongly dependent on the pH of the electrolyte solution. Therefore, the polymer obtained shows a well-defined redox behavior in a less alkaline solution but the response obtained in an alkaline solution (pH 11) shows a complete loss of electrode activity. However, the film was not degraded under these experimental conditions, and its response was recovered when the electrode was immersed in an acidic solution.

Also, the half-wave potentials ($E_{1/2}$) were calculated as the average of the anodic and cathodic peak potentials of the cyclic voltammogrms: $(E_{pa} + E_{pc})/2$ [34], recorded at a potential scan rate of 50 mV/s and then plotted as a function the solution pH (Fig. 3b). This $E_{1/2}$–pH diagram comprises a straight line with a slope equal to −59.7 mV per unit of pH. This means that the electrochemical reaction of the prepared polymer

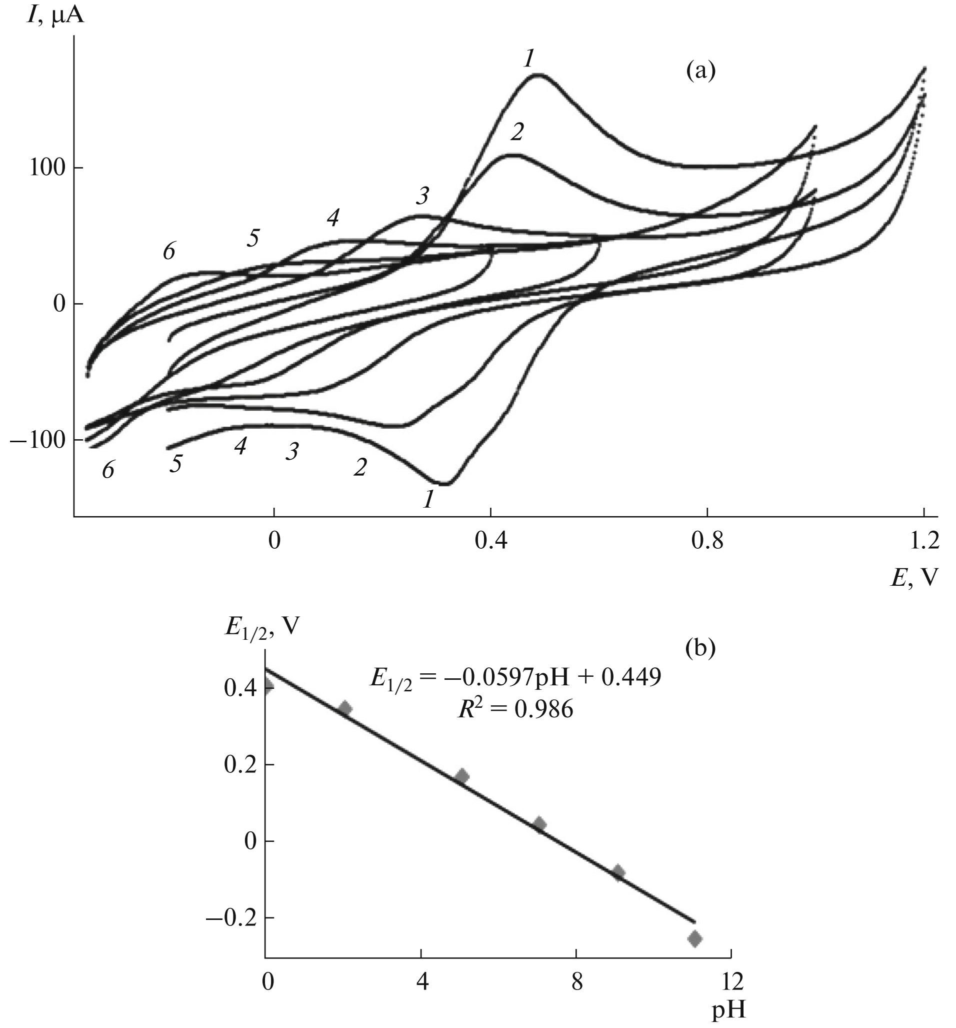

Fig. 3. Electrochemical responses of poly(4-AB/OT) at the surface of CPE at pH 0.5 (*1*), 2 (*2*), 5 (*3*), 7 (*4*), 9 (*5*) and 11 (*6*), v = 50 mV/s (a); pH–potential diagram for poly(4-AB/OT) (b).

occurs with the same number of electrons and protons.

Electrooxidation behavior of nitrite on the modified electrode. The cyclic voltammetric response of CPE and poly(4-AB/OT) CPE is also investigated in the absence and presence of 1 mM nitrite at a scan rate of 20 mV/s. In the presence of nitrite, the values of peak potential on the CPE and poly(4-AB/OT) CPE in phosphate buffer solution are 1.03 and 0.79 V, respectively. As it can be found, oxidation potential of nitrite shifted about 240 mV to the negative side, as the poly(4-AB/OT) film was deposited on the CPE. The results obtained can be attributed to the electrostatic attraction between the oxidized poly(4-AB/OT) film and the negatively charged nitrite anions that resulted in preconcentration of nitrite ions at the electrode surface/solution interface. Ho and et al. recorded the same results for poly(3,4-ethylenedioxythiophene) in the presence of nitrite [35].

Since the rate of disproportionation of nitrite in strongly acidic media is significant, the pH effect on the catalytic behavior of the poly(4-AB/OT) CPE toward nitrite oxidation was investigated in the pH range 3 to 9. At this pH range, NO_2^- is the dominant species, and loss of nitrite due to its chemical instability is negligible. However, the peak potential shifted slightly to positive side as the solution pH increased. According to Guidelli [36], the whole process for nitrite oxidation involves two steps, the electrochemical oxidation of nitrite into NO_2 followed by rapid disproportionation of NO_2 into NO_2^- and NO_3^-, as shown below:

$$2NO_2^- \rightleftarrows 2NO_2 + 2e, \quad (2)$$

$$2NO_2 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+. \quad (3)$$

The electro-oxidation of nitrite into NO_2 is the rate-determining step which is proton independent, and therefore, the slight change in peak potential can be attributed to the nature of the poly(4-AB/OT) film. As the pH increased, it seems that the poly(4-AB/OT) film will become dedoped and thus the electrostatic interaction will slightly decrease, resulting in slight increase in peak potential for nitrite oxidation. We chose solution with pH 7 for later experiments due to the maximum oxidation current density (equal to 30, 50, 90 and 75 μA in different solution pH: 3, 5, 7 and 9, respectively).

Effect of nitrite concentration. The effect of nitrite concentration on the cyclic voltammograms of the poly(4-AB/OT) CPE is studied. Based on the results, the height of the anodic peak increases with increasing nitrite concentration. The characteristic shape of cyclic voltammograms in this potential region indicates that the signal is due to the oxidation of nitrite. The catalytic peak current is proportional to the concentration of nitite in the range of 0.01 to 1 mM. The linear regression equation is I (μA) = $(35.0 \pm 0.3)c_{\text{nitrite}}$ (mM) + (17.2 ± 0.5) ($R^2 = 0.989$). The detection limit (LOD) with the signal-to-noise ratio of three, calculated from the calibration graph, was 9 μM nitrite.

Since amperometry under hydrodynamic condition is much more current-sensitive than cyclic voltammetry, this method was employed to estimate the low detection limit. Figure 4 displays the typical steady-state catalytic current time response of the rotated modified electrode (2000 rpm) with successive injection of nitrite at an applied potential 0.95 V versus reference electrode. As shown in the figure, a well defined response was observed during the successive addition of nitrite. These results demonstrate a stable and efficient catalytic property of poly(4-AB/OT) CPE. There is a linear relation between response current and nitrite concentration in the range 0.006 to 0.6 mM. The linear least squares calibration curve is I (μA) = $(187 \pm 1)c_{\text{nitrite}}$ (mM) + (10.33 ± 0.02) with a correlation coefficient of 0.981. LOD ($S/N = 3$), and sensitivity were 3.5 μM and 187.4 μA/mM, respectively.

Interference studies. The interference effect of the foreign ions (Na^+, K^+, Mg^{2+}, SO_4^{2-}, Cl^-, SO_3^{2-}, NO_3^-) on the determination of nitrite was examined by addition of various ions into the buffer solution (pH 7) containing 0.3 mM nitrite. It was found that 100-fold amounts of the most ions did not show any interference effect during the determination of nitrite by using poly(4-AB/OT) CPE. However, 10-fold SO_3^{2-} was found to have noticeable interference in nitrite determination on the poly(4-AB/OT) CPE. Figure 5 shows amperometric responses of poly(4-AB/OT) CPE in 0.1 M phosphate buffer solution (pH 7) in the presence of 0.03 mM nitrite containing ions such as nitrate and sulfite with different concentrations.

Determination of nitrite in real sample. Finally, poly(4-AB/OT) CPE was applied to determine nitrite concentration in mineral water sample. It should be noted that the original nitrite concentration is undetectable by this method, so we added 19 μM of nitrite in mineral water sample and recorded the results as "value found after adding." The determination of nitrite in a sample was carried out by the standard addition method. The results showed that adding nitrite to the solution caused an increase in the oxidation peak height. Thus, the peak current was attributed to nitrite. In addition, diagram of I_{pa} versus nitrite concentration shows the linear region usable for determination of nitrite ($I_{\text{pa}} = 1.01V + 4.7$, $R^2 = 0.98$). By this method, in mineral water after adding 19 μM NO_2^- was found 20.0 ± 0.3 μM NO_2^- (by five replicate determinations) with mean recovery 105%.

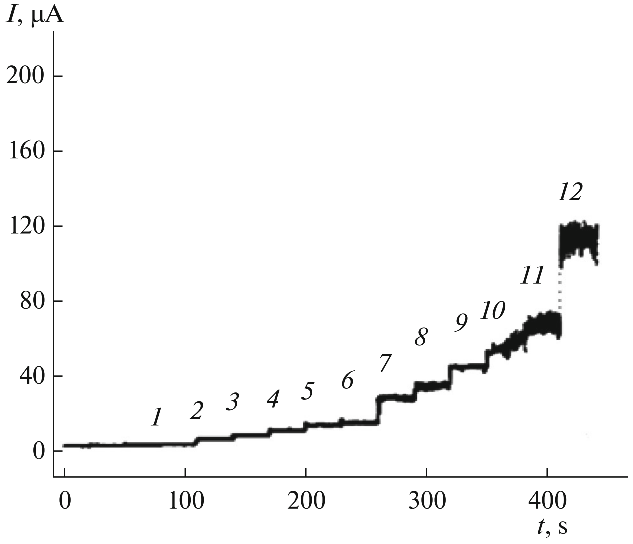

Fig. 4. Amperometric responses of poly(4-AB/OT) CPE in 0.1 M phosphate buffer solution with different concentrations of nitrite, mM: *1*, 0; *2*, 0.006; *3*, 0.009; *4*, 0.01; *5*, 0.02; *6*, 0.03; *7*, 0.06; *8*, 0.09; *9*, 0.1; *10*, 0.2; *11*, 0.3 and *12*, 0.6.

Stability of the modified electrode. The long-term stability of poly(4-AB/OT) CPE was also studied by storing the electrode for 7 days at room temperature. The current response only decreased by 4.5%, which confirms the stability of modified electrode.

The study has described successfully the modification of CPE with poly(4-AB/OT). This modified electrode acts as an active suitable catalyst for the oxidation of NO_2^- ions to NO_3^-. With modification of poly(4-AB/OT), the operating potential can be reduced about 240 mV, compared to CPE. The oxidation currents are directly proportional to nitrite concentration in a wide range, which illustrates the potential applications of this type of electrode for the anodic determination of nitrite ion. Table 1 compared the proposed electrode for nitrite determination with electrodes reported in literature. The proposed electrode is

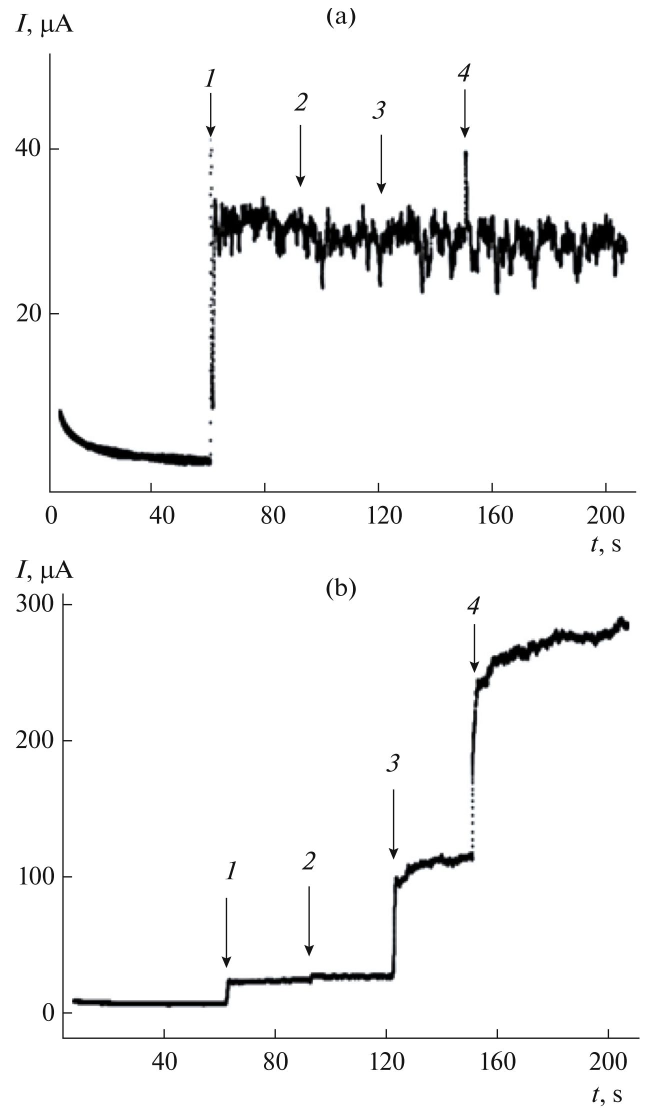

Fig. 5. Amperometric responses of poly(4-AB/OT) CPE in 0.1 M phosphate buffer solution (pH 7): (*1*) in the presence of nitrite without any foreign ion, (*2–4*) with different concentration ratios of nitrite to nitrate, 1 : 1, 1 : 10 and 1 : 1000, respectively (a); as (a) but in the presence of different concentration ratios of nitrite to sulfite (concentration of nitrite 0.03 mM and applied potential 0.95 V) (b).

Table 1. Comparison of performances of some electrodes in determination of nitrite

Electrode	Method	Linear dynamic range, μM	LOD, μM	Reference
PdPCNF/Al	CV	$500–1 \times 10^5$	–	[21]
Thionine/ACNT	DPV	3–500	1.1	[37]
$V^{IV}O(SB)$ /CPE	CV	$3.9–4 \times 10^3$	0.6	[38]
Oxidized GCE	Amperometery	$10–1 \times 10^4$	40	[39]
PEDOT/MWCNT/SPCE	Amperometery	$50–1 \times 10^3$	1.0	[35]
Poly(4-AB/OT) CPE	Amperometery	6–600	3.5	This work

Notations: PdPCNF—palladium pentacyanonitrosylferrate, CV—cyclic voltammetry, ACNT—aligned carbon nanotubes, DPV—differential pulse voltammetry, $V^{IV}O(SB)$—oxovanadium(IV)-4-methyl salophen, GCE—glassy carbon electrode, PEDOT—poly(3,4-ethylenedioxythiophene), SPCE—screen-printed carbon electrodes.

comparable with other electrodes. Also, the proposed method provides a fast, sensitive and simple approach to the determination of nitrite in real samples.

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