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Application of carbon ceramic modified electrode with prussian blue for electrocatalytic oxidation of nitrite ion

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Abstract

A novel chemically modified electrode containing Prussian blue complex was achieved on the surface of glassy carbon electrode by sol-gel technique. The electrochemical behavior of modified electrode was characterized by cyclic voltammetry in detail. The film electrode obtained was very stable and exhibited electrocatalytic response for oxidation of nitrite. The experimental results showed at the bare GC electrode a small oxidation peak current which was observed at about 740 mV and a well-formed sharp catalytic oxidation peak at about 600 mV which was also observed at Prussian blue complex modified electrode. The transfer coefficient (α) for electrocatalytic oxidation of nitrite and the diffusion coefficient of this substance under the experimental conditions were also investigated.

Keywords: Prussian blue complex; cyclic voltammetry; nitrite; electrocatalytic oxidation.

Introduction

Research in the field of chemically modified electrodes (CMEs) is still an active area, since there exists several compounds whose oxidation or reduction at commonly used electrodes are accompanied with a considerable overvoltage. The application of chemically modified electrodes in electroanalysis offers several advantages. They can decrease the overpotential, increase the reaction rate and sensitivity and improve selectivity [1-5].

The presence of nitrite ion in the environmental samples also indicates the

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extent of pollution and eutrophication of natural waters [6]. Nitrites are of both environmental and biological importance. Nitrites are used as food preservatives and their salts are known to occur in high quantity in soil. Nitrites which are known to react with amines forming nitrosamines are known to be carcinogenic [7]. Oxidation is preferred because reduction of nitrite is known to suffer from interferences such as reduction of nitrate ions and molecular oxygen.

The use of bare electrodes such as carbon, platinum and gold for the oxidation of nitrite requires high potentials and these electrodes tend to be poisoned by the species formed during the electrochemical process. A good way of lowering potentials is by modification of the electrodes [8]. One promising approach for minimizing this effect is the use of chemically modified electrodes (CMEs). Many different strategies have been employed for the electrode modification, such as electrochemical polymerization [9-10], covalent bonding [11-12] and mixing with carbon paste [13-14].

One promising approach is the use of chemically modified electrodes (CMEs) containing specifically selected redox mediators immobilized on conventional electrode surface.

The sol-gel process is very well adopted for coating of thin films on complex shapes. The porosity and pore size of these films can be controlled to maximize the specific surface area and to ensure that permeability of the film remain high. Furthermore, the sol-gel process involves low-temperature hydrolysis and condensation of appropriate monomeric precursors and is suitable inclusion of organic moieties that cannot withstand high temperatures [15].

Prussian blue (PB) is one of the well-studied materials and has been extensively studied with well known eletrochromic, electrochemical [16], magnetic properties [17], photophysical [18] and potential analytical applications [19-20].

But up to now, only a few chemically modified electrodes [21] containing Prussian blue complex that were fabricated by sol-gel technique was reported. In this paper, we used an electrode for electrocatalytic oxidation of nitrite that was developed via an easy and effective sol-gel immobilization method. This electrode which comprises silicon dioxide gel films doped with Prussian blue complex retains its structure, electrochemical activity and electrocatalytic properties to a large extent.

Experimental

Reagents and solutions

Sodium nitrite, Methyl trimethoxy silane (MTMOS), methanol and HCl were of analytical grade supplied by Merck. Deionized water was used for the preparation of all solutions. The background electrolyte solution was prepared from potassium chloride. The pH of solutions was adjusted to 7 with phosphate buffer. The Prussian blue complex (Figure 1) was synthesized, purified and characterized as reported [22].

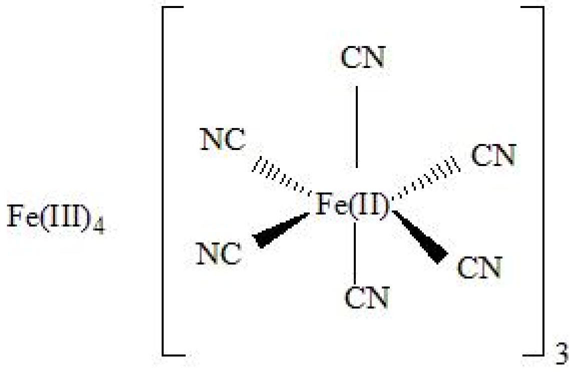


Figure 1. Molecular structure of Prussian blue complex

Instrumentation

Electrochemical measurements were performed with an Autolab potentiostat/galvanostat model PGSTAT 30 (Metrohm, Utrecht, Netherlands) and a system was run on a pc using GPES 4.9 software. An GC electrode was used as working electrode. A platinum wire was employed as counter electrode and a saturated Ag/AgCl (saturated KCl) served as the reference electrode and all potentials in the text refer to it (all electrode obtained from Azar Electrode Co., Urmia, Iran).

Preparation of modified electrode

The method of immobilizing Prussian blue on GC electrode is described briefly as follows. The GC electrode was polished with emery paper (p 2000) and then by 0.05 µm alumina powder. Then electrode was rinsed by distilled water and sonicated in water and absolute ethanol, respectively (each for 5 min), and then allowed to dry at room temperature. At the first 5 mg Prussian blue was dissolved in 1ml Methanol and homogenized thoroughly by sonication for 5 min until a clear solution was obtained. Then, 0.9 ml of this solution was mixed with 0.6 ml (MTMOS), and 0.1 ml hydrochloric acid (0.1 M) and stirred for 5 min until a homogeneous gel solution resulted. The resulting clear solution was aged for 30 min, and then 10 µl of the freshly prepared mixed solution was pipetted onto the surface of GC electrode. The gel films were dried in an air for 24 h and were ready for use. A few I-E runs were needed at the beginning to stabilize the electrode and obtain reproducible results.

Results and discussion

The Prussian blue -complex modified carbon ceramic electrode was first characterized by

SEM. Scanning electron microscopy (SEM) has been an essential tool for characterizing the surface morphology and fundamental physical properties of the absorbent. A typical scanning electron micrograph image of the carbon ceramic electrode, are shown in Figure 2.

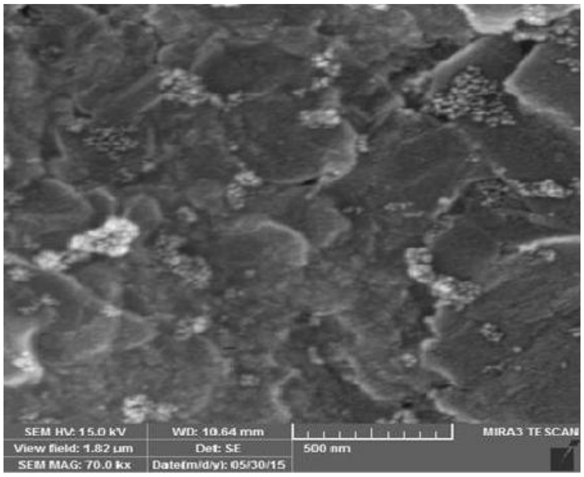


Figure 2. SEM image of Prussian blue modified CCE

The electrochemical properties of the Prussian blue modified GC electrode with sol-gel technique were studied, using cyclic voltammetry. Figure 3 shows typical cyclic voltammograms of the bare and Prussian blue modified GC electrodes by sol-gel techniques in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) at scan rate 10 mV s^{-1} It shows that the oxidation peak areas of Prussian blue modified GC electrodes are much larger than the bare GC electrode. There was an irreversible oxidation peak at …V on bare GCE, which was corresponding to the conversion NO_2^- to NO_3^- through a two-electron oxidation process [23].

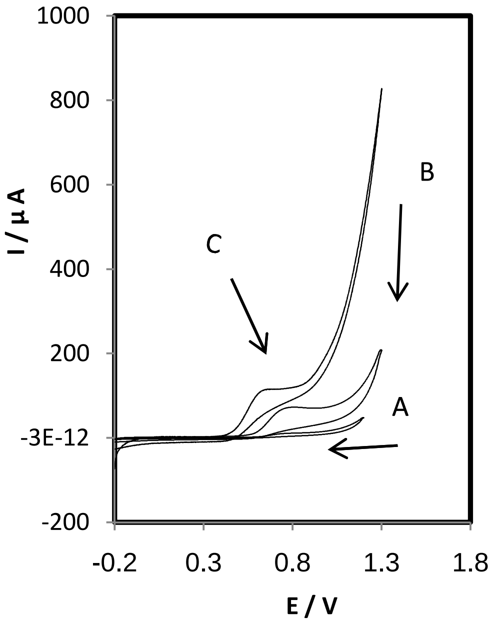


Figure 3. Cyclic voltammograms for 1.0 mM nitrite at (A) bare GC electrode (B) modified GC electrodes by carbon nanotube (C) Prussian blue modified GC electrodes by sol-gel techniques in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) at scan rate 10 mV s^1

The nature of the oxidation process was found to be a kind of diffusion controlled in the buffer system studied, as evidenced from the linear plots of the peak current (i_p) versus square root of the scan rate ($v^{1/2}$) for nitrite. Figure 4A shows the cyclic voltammograms of Prussian blue modified GC electrode in 0.1 M phosphate buffer (pH 7.0) containing 1 mM nitrite ion at scan rates: 10, 20, 30, 40, 50, 60, 70, 80 and 90 mVs^{-1}.

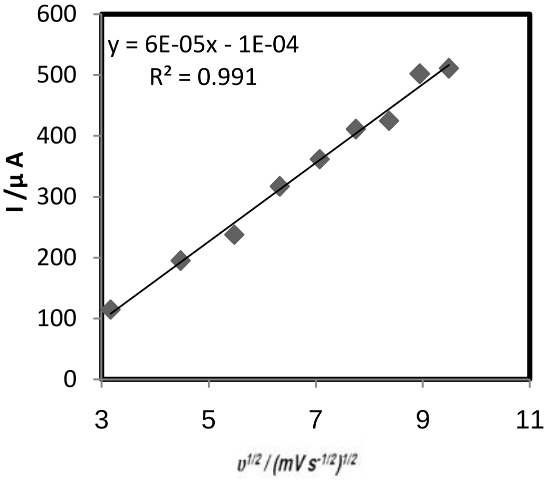


Figure 4. (A) Cyclic voltammograms of Prussian blue modified GC electrodes in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) containing 1 mM nitrite at scan rates of (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, (h) 80 and (i) 90 mV s^{-1} (B) dependence of the peak current with square root of the scan rate

It can be noted from Figure 4B that the anodic currents increase and the peak potential shifts as the scan rate increases. When peak current values were plotted against $v^{1/2}$ (Figure 4B), the following linear relationship was obtained:

$$I_p = 6\times10^{-5}\upsilon^{1/2} - 1\times10^{-4}\ (mV\ /\ s)^{1/2}, \quad R^2 = 0.991 \qquad (1)$$

This behavior suggests that the oxidation process is controlled by diffusion.

Thus, according to the following equation for a totally irreversible diffusive process:

$$I_p = 3.01 \times 10^5 n\ [(1-\alpha)\ n_\alpha]^{1/2}\ ACD^{1/2}\ v^{1/2} \qquad (2)$$

And considering $(1-\alpha)n_\alpha = 0.386$ (see below), $D = 2.61\times10^{-5}$ cm^2s^{-1}(see chronoamperometric studies), A = 0.125 cm^2, it is estimated that the total number of electrons involved in the anodic oxidation of nitrite is n = 1.94 ≈ 2.

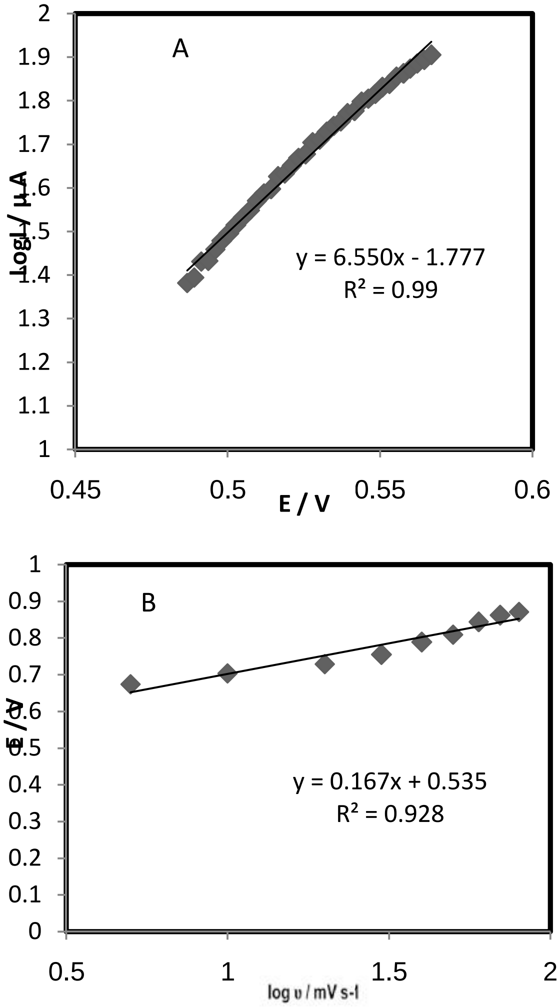


Figure 5. (A) Tafel plot derived from data of the rising part of the E *vs.* log *I* curve at a scan rate of 10 mV s^{-1}. (B) Plot of Ep *vs.* log ν.

In order to get information on the rate determining step, the peak potential, E_p is proportional to log υ as can be seen in Figure 5B. The slope of E_p *vs.* log υ is 0.167 mV. The tafel slope may be estimated according to the equation for the totally irreversible diffusion-controlled process:

$$E_{pa} = b/2(\log \upsilon) + \text{constant} \qquad (4)$$

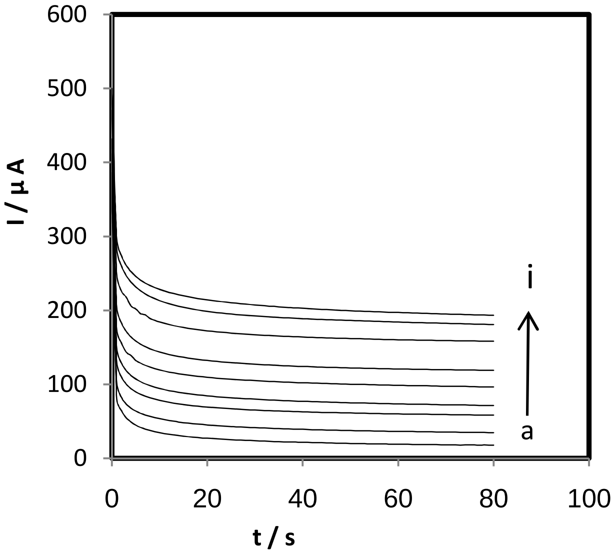
So, b = 0.334 V. this result is close to that obtained from polarization measurement [24].

This slope indicates a one electron transfer to be rate limiting assuming a transfer coefficient of α = 0.64 for nitrite at pH=7.0. the minimum value should be 0.5 indicated that there was an equal probability that the reaction activated transition state can form either products or reactants [25]. Thus the value larger than 0.5 indicates a more favored reaction mechanism [26], which may explain why the electrocatalytic oxidation of nitrite to its oxidation product was more favored on the PB modified electrode compared with the bare GCE.

The tafel slope, b, can be obtained by another method. A tafel plot was drawn (Figure 5A). Derived from data of the rising part of the current-voltage curve at a scan rate of 10 mV s^{-1}, B slope of 6.55 V^{-1} is obtained which indicates that the rate limiting step is one electron transfer (assuming a transfer coefficient of α = 0.62) using the following equation:

$$E/\log I = \text{Slope} = 0.059/(1 - \alpha)n_{\alpha} \qquad (3)$$

The electrocatalytic oxidation of nitrite at the Prussian blue modified electrode was studied by chronoamperometry. The chronoamperograms obtained for a series of nitrite solutions with vaious concentrations as illustrated in Figure 6.



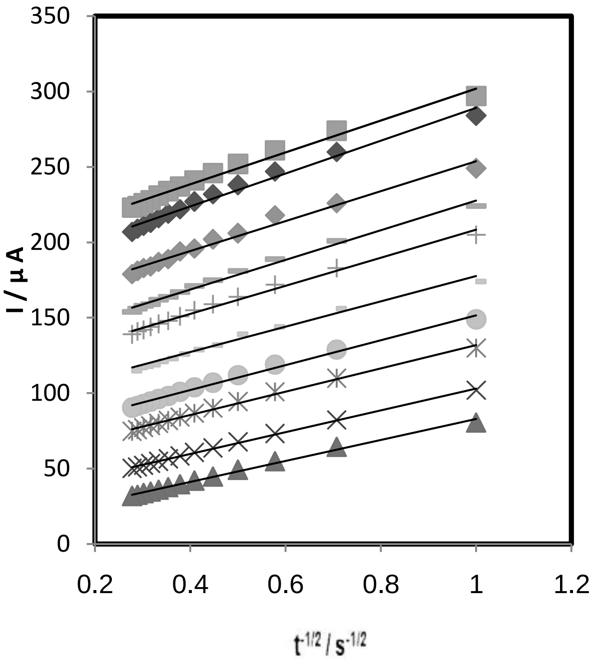


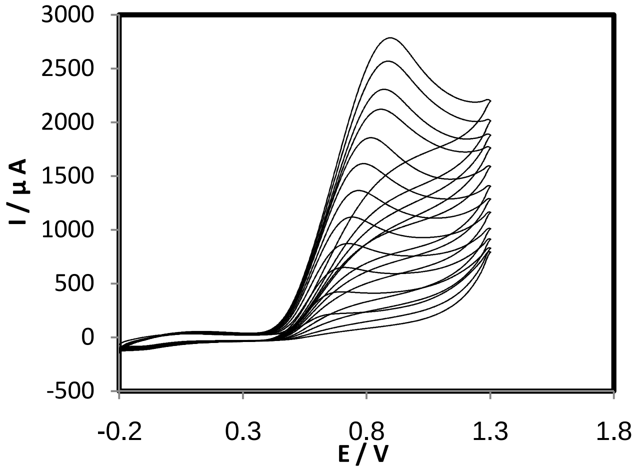
Figure 6. (A) Chronoamprometric response of a Prussian blue modified electrode in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of nitrit for a potential step of 100 mV vs. SCE In the range of 1, 2, 3, 4, 5, 6, 7, 8 and 9 mM (B) Plot of plot of *I* versus $t^{-1/2}$ obtained from chronoamprometric experiments. Inset shows the relationship between the slope of the linear segments and the nitrite concentration.

An increase in concentration of nitrite was accompanied by an increase in anodic currents obtained for a potential step of 100 mV versus SCE. In addition, the level of the Cottrell current, which was measured for 70 s, increase with increasing concentration of nitrite in the range of 1~5 mM. In chronoamperometric studies, the diffusion coefficient of nitrite the modified electrode can be determined. The relationship between current and time can be described by the Cottrell equation [27]:

$$I = nFAD^{1/2}C/\pi^{1/2}t^{1/2} \qquad (5)$$

Where *D* is the diffusion coefficient ($cm^2\ s^{-1}$) and *C* is the bulk concentration (mol cm^{-3}). The plot of *I* versus $t^{-1/2}$ will be linear, and from the slope, the value of *D* can be obtained. Figure 6B shows the experimental plots of the resulting straight line were then plotted versus the concentration of nitrite (Figure 6B, inset), from which we calculated a diffusion coefficient of 2.61×10^{-5} $cm^2\ s^{-1}$ for nitrite.

The cyclic voltammograms at different concentrations of nitrite are shown in Figure 7A. A plot of the peak current values as a function of the concentration was drawn. The plot was linear in the concentration range of 0.5~11 mM nitrite.



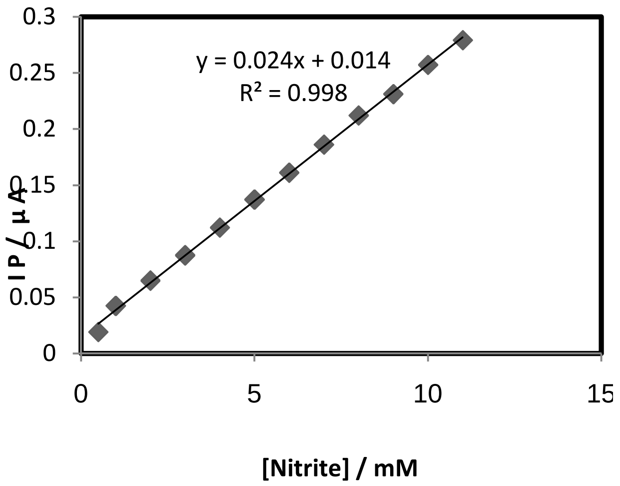


Figure 7. (A) Cyclic voltammograms for increasing concentrations of nitrite from 0.5 to 11 mM (0.5~11) in buffer solution (pH 7.0) containing 0.1 M KCl solutions on Prussian blue modified electrode. Scan rate was 10 mV s^{-1}. (B) Calibration plot for concentrations of nitrite from cyclic voltammograms.

This is the calibration curve for nitrite ion determination.

A comparison of linear range of nitrite ion determination at various electrodes from previous reports is given in Table 1.

The proposed sensor was also successfully applied to the direct determination of nitrite ion in real samples by add found method. The results are compared with each other and are agreement. The results for three replicate are presented in Table 2.

Conclusion

GC electrode coated with a thin film of sol-gel doped with Prussian blue, act as an electrocatalyst for oxidation of nitrite. This film exhibits excellent electrocatalytic behavior toward nitrite oxidation in aqueous phosphate buffer solution containing K$^+$ ion. The overall number of electrons involved in the oxidation of nitrite, the number of electrons involved in the rate-determining step and the diffusion coefficient of nitrite were calculated. Thus, the results obtained for nitrite shows that Prussian blue complex can be used for determination of other compounds.

Acknowledgments

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