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RESEARCH PAPER

Electrochemical Sensing of Nitrite at Aminophenol-Formaldehyde Polymer/Phosphomolybdic Acid Nanocomposite Modified Electrode

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Abstract: An aminophenol-formaldehyde polymer/phosphomolybdic acid nanocomposite modified carbon paste electrode for detection of nitrite was developed. The integration of polymer matrix to form materials is an effective way to harness the electrochemical activity. The aminophenol-formaldehyde polymer/phosphomolybdic acid nanocomposite modified carbon paste electrode showed high electrocatalytic activity for nitrite reduction, enabling the detection of nitrite within a linear range of 10.0–1000 μM (r = 0.998). The limit of detection was 9.8 μM (S/N = 3). The method showed excellent selectivity for nitrite detection in the presence of phosphate, acetate, ammonium, fluoride, chloride and nitrate.

Key Words: Electrochemistry; Nitrite; Phosphomolybdic acid; Aminophenol-formaldehyde polymer

1 Introduction

We have witnessed a gradual increase of social awareness regarding the need of monitoring and controlling environmental and industrial processes in the last few decades. In this connection, it is necessary to get awareness about nitrite ion which is harmful to human health. European Union has issued a number of rules about its maximum permitted residue level in environment[1]. However, due to its wide use as an antimicrobial agent, it has been found in vegetables. It is also used in various types of soups as a preservative[2]. It is found that a portion of nitrate in fertilizers, human waste and animal waste can be converted to nitrite under natural conditions. Epidemiologic studies have revealed that a number of medical issues are associated with excessive exposure of nitrite and nitrate ion in drinking water[3]. For example, "Blue baby" syndrome is resulted from high concentration of nitrite in the bloodstream[4]. Nitrite can also be converted to carcinogenic nitrosamines after reacting with amines under acidic conditions in stomach and may subsequently lead to gastric cancer[5]. Nitrite is easy to migrate in groundwater due to its high water solubility and weak retention in soils[6]. It is an important contaminant in water environment and can be used as a significant indicator of natural water quality[7]. Various methods, such as spectrophotometry, organic chromospheres or fluorophores, mass spectroscopy, capillary electrophoresis and ion chromatography, have been used to determine the concentration of nitrite[8]. However, these methods are time-consuming and with very high cost due to expensive detecting instruments. Therefore, the development of simple and low-cost methods is highly desired.

Electrochemical techniques, which are characterized by low

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cost, easy operation, fast detection and high sensitivity, have aroused widespread interests[4,9,10]. Electrochemical determination of nitrite can be realized based on the oxidation or reduction of nitrite at the surface of glassy carbon electrode[11]. The electrochemical methods based on direct oxidation of nitrite require a very large over potential on most conventional electrodes. In contrast, the electrochemical detection based on the reduction of nitrite can offer several advantages. Firstly, there is no interference from nitrate ion, sulfate ion, bromate ion and molecular oxygen which often coexist with nitrite in water samples under the potential range of nitrite reduction[3,10,12]. Therefore, some modified electrodes were constructed to detect nitrite based on the reduction of nitrite[13,14].

Polyoxometalates (POMs) with interesting structural and physicochemical properties have attracted attention for their use in catalysis, analysis, medicine, biochemistry and materials science[15]. Besides, POMs have fascinated more and more consideration in the field of electrochemistry because of its excellent electrochemical activities. For example, the reversible multi-electron redox behavior can be used for energy storage[16]. Also, POMs have been used to construct POM-carbon composites[17,18]. The structural and functional characteristics of POMs have prompted their transition from inorganic chemistry to material science as functionalized electroactive materials[19].

In this study, we used aminophenol-formaldehyde polymer to fabricate phosphomolybdic acid modified electrode for detection of nitrite for the first time. The aminophenol-formaldehyde polymer/phosphomolybdic acid modified electrode exhibited high electrocatalytic activity toward nitrite reduction. Moreover, this method avoided the interference from other common potential interfering species as well. This study proved that aminophenol-formaldehyde polymer could be used as an effective matrix for immobilization of POMs with fine electrochemical activity.

2 Experimental

2.1 Materials and apparatus

3-Aminophenol, formaldehyde (37%–40%, *w/w*) and phosphomolybdic acid hydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonia solution (25%, *w/w*) were purchased from Beijing Chemical Reagent, China. Electrochemical measurements were performed with a conventional three-electrode cell (volume 1 mL) on a CH Instrument model 830B electrochemical workstation (CHI Inc., China) using an Ag/AgCl reference electrode (saturated KCl) and a platinum wire counter electrode.

2.2 Synthesis of aminophenol-formaldehyde polymer

Aminophenol-formaldehyde polymer was synthesized according to previous literature[20]. In brief, 3-aminophenol (41.9 mg, 0.012 M) and ammonia (0.0227 mL, 0.02 M) were added to 32 mL of deionized water. Then, a formaldehyde solution (0.0568 mL, 0.024 M) was added to the reaction mixture, which was subsequently ultrasonicated for 6 min. The resultant mixture was then incubated in water bath at 80 °C for 0.5 h.

2.3 Preparation of aminophenol-formaldehyde polymer/phosphomolybdic acid nanocomposite modified carbon paste electrode (CPE)

To prepare aminophenol-formaldehyde polymer/phosphomolybdic acid nanocomposite modified CPE, 5 mg of aminophenol-formaldehyde polymer, 1 mg of phosphormolybdic acid, 50 mg of graphite powder and 30 μL of silicon oil were mixed thoroughly to get a homogenous paste. Then the resultant paste was packed firmly into a Teflon tube cavity (3 mm in diameter). A stainless steel screw was twisted into the Teflon tube to establish electric contact. The CPE was polished on a weighing paper to obtain a fresh electrode surface before each experiment.

3 Results and discussion

3.1 Electrochemical behavior of aminophenol-formaldehyde polymer/phosphomolybdic acid modified CPE

Cyclic voltammograms (CV) of aminophenol-formaldehyde polymer/phosphomolybdic acid modified CPE in 2.0 M H_2SO_4 aqueous solution at different scan rates were recorded. As shown in Fig.1, there are three reversible redox peaks, I–I′, II–II′ and III–III′, with the half-wave potentials $E_{1/2}$ = (E_{pa} + E_{pc})/2 at 0.0645, 0.2909 and 0.4227 V in CV curves, which can be ascribed to three consecutive redox processes. Moreover, the cathodic and anodic peak potentials showed negligible shift with increasing scan rates. The peak-to-peak separations between the corresponding anodic and cathodic peaks increased slightly, but the average peak potentials remained unchanged. The peak currents were proportional to scan rates in the range of 0.01–0.20 V s^{-1}, suggesting a surface-controlled redox process.

3.2 Effect of pH value on CV behaviour

Figure 2 shows the CV curves of modified CPE towards different concentrations of sulfuric acid. The anodic (I_{pa}) and cathodic (I_{pc}) peaks potentials shifted towards the negative directions upon decreasing concentrations of H_2SO_4, indicating that proton transfer accompanied the electron transfer of phosphomolybdic acid. Furthermore, the peak-to-peak current (ΔI) between the corresponding anodic and the cathodic peaks remained almost constant for Peaks I, II and III.