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Short communication

Silver particle-decorated carbon paste electrode based on ionic liquid for improved determination of nitrite

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A B S T R A C T

A simple silver particle-modified carbon paste electrode is proposed for the determination of low concentration levels of nitrite ions. The electrode consists of a carbon powder decorated with silver sub-micrometre particles (AgPs) and a hydrophobic ionic liquid trihexyltetradecylphosphonium chloride as a binder. It has been shown that AgPs exhibit a strong electrocatalytic effect on the nitrite oxidation. For optimal electroanalytical performance the electrode was conditioned via silver oxidation/reduction cycle. The electrode revealed a linear square-wave voltammetric response in a wide examined concentration range of 0.05 to 1.0 mmol L^{-1}, limit of detection (LOD) of 3 μmol L^{-1} and excellent repeatability with RSD of 0.3%.

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1. Introduction

Nitrite is used extensively in food industry to prevent bacterial growth and oxidative food degradation. It is mostly used in cured meat products, although it has also been found in commercially available vegetables [1]. One of the main nitrite sources in soil is fertilizers after nitrogen transformation. Nitrite is toxic and mutagenic to both humans and animals, with a lethal dose for humans of ca. 33 mg per kg body weight [2]. Nitrite consumption has been linked with methemoglobinaemia [3], migraines [4] and chronic obstructive pulmonary disease [5], but most importantly, nitrite has been found to be a precursor in the formation of nitrosamines [6] and aromatic carbocations [7] which are well-known carcinogens.

Hitherto, several different methods for nitrite determination have been reported, most of them based on separation techniques, such as ion and liquid chromatography [8,9] and/or detection mainly based on spectrophotometry, often using the Griess reaction [10–13] and chemiluminescence [14,15]. Although these techniques offer precise measurements and relatively low detection limits, they usually require more complex sample preparation and fairly expensive instrumentation compared to their electrochemical counterparts. Electrochemically, nitrite has mainly been determined using amperometry [16–20], cyclic voltammetry [21–25], and differential pulse voltammetry [26,27]. Both oxidation and reduction reactions have been exploited for nitrite detection

using different electrode materials/modifications. Various electrode modifications, mainly in the form of thin layers on a glassy carbon substrate electrode (e.g. poly(3,4-ethylenedioxythiophene)/graphene nanocomposite, polyaniline/Cu nanocomposite and reduced graphene/Pd nanocomposite to name a few), have been proposed [28–30].

In comparison with solid electrodes, carbon paste electrodes (CPEs) offer several advantages. Their paste consistency allows bulk modification and rapid surface renewal. In combination with ionic liquids (ILs) as binders, improved signal-to-noise characteristics have been observed due to higher ionic conductivity of ILs and their potential interaction (e.g. extraction, ion exchange) with the analyte. A few attempts to determine nitrite using modified carbon paste electrodes have recently been published [31–34], among which there are few employing ionic liquid as a binder/modifier [18,20,35]. For example 1-butyl-3-metylimidazolium bis(trifluorometylsulfonyl)imide combined with paraffin has been used as the binder in CPE, which served as the substrate for a poly(o-anisidine) film [35], n-octylpyridinum hexafluorophosphate and single-walled carbon nanotubes have been used to fabricate a composite CPE [20], and n-octylpyridinum hexafluorophosphate has been used to make a CPE with multi-walled carbon nanotubes, after which the CPE was further modified with haemoglobin and octylpyridinum chloride [18]. ILs have also been used as modifiers on glassy carbon electrodes (GCE), e.g. as a trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide-multi-walled carbon nanotube composite, further modified by electrodepositing AuPt alloy nanoparticles [26], a 1-octyl-3-methylimidazolium hexafluorophosphate-multi-walled carbon nanotube-chitosan composite [22] or as one of the layers in a haemoglobin-ionic liquid (1-ethyl-3-methyl imidazolium

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tetrafluoroborate)-multi-walled carbon nanotube modified glassy carbon electrode [19].

For measuring nitrite, silver in its various forms has mainly been used for modifying glassy carbon electrodes, e.g. in the form of silver nanoparticles on mercaptopropyltriethoxysilane coated on GCE [24] or silver nanoplates grafted on GCE through carboxymethylcellulose [25]. Silver composites have also been used, e.g. as composite of epoxy resin, expanded graphite and Ag-doped zeolite [23], and as a composite of methacrylate resin, silver and graphite powder [27].

To the best of our knowledge no silver sub-micrometre particle-modified carbon paste electrodes have yet been reported for nitrite determination. Herein, we exploited the advantageous characteristics of IL-based carbon paste electrodes and favourable electrocatalytic effect of silver particles for simple and inexpensive preparation of a sensitive voltammetric nitrite sensor.

2. Experimental

CR-5 carbon powder with an average particle size of 2 μm (Maziva s.r.o., Týn nad Vltavou) was used to produce carbon paste electrodes (CPEs). Two different binders were employed, i.e. paraffin (Merck, Darmstadt) and trihexyltetradecylphosphonium chloride ionic liquid (IL) (Sigma-Aldrich, St. Louis, MO). Milli-Q water (R = 18.2 MΩ) was used to prepare all solutions throughout the work (Millipore, Bedford, MA).

Silver sub-micrometre particle-decorated carbon particles were synthesised in "one pot" using a modified citrate method [36,37]. In a typical experiment 0.5 g of carbon particles were suspended in 40 mL of water with 250 μL of Triton X-100 (Sigma-Aldrich) to prevent agglomeration and precipitation. An appropriate amount of $AgNO_3$ (Kemika, Zagreb), depending on the examined C/Ag ratio, was added and the mixture was sonicated at room temperature for 20 min. The mixture was heated until boiling followed by the addition of aqueous trisodium citrate (Carlo Erba, Milano) (excess amount in 5 mL water). The mixture was left to boil for 30 min and then allowed to cool to room temperature. The silver particle-decorated carbon particles were repeatedly washed with water and ethanol, and finally dried over night at 40 °C. The CPE was made of 70 wt.% decorated or bare carbon particles and 30 wt.% IL or paraffin oil and packed tightly into a Teflon holder.

Electrochemical measurements were conducted using Autolab PGSTAT 10 (Eco Chemie, Utrecht). Unmodified or modified CPE was used as the working electrode, a platinum rod as the counter electrode and an Ag/AgCl/KCl (satd.) as the reference electrode. A 0.1 mol L^{-1} NaCl in 10^{-4} mol L^{-1} HCl (pH = 4) was used as the supporting electrolyte. Appropriate concentrations of nitrite were obtained by diluting a 0.1 mol L^{-1} aqueous solution of $NaNO_2$ (Sigma-Aldrich).

3. Results and discussion

The development of a novel nitrite sensor involved preliminary examination of the conventional paraffin binder based CPE; to improve conductivity and overall electroanalytical performance, paraffin was replaced by a hydrophobic room temperature ionic liquid — trihexyltetradecylphosphonium chloride. Further enhancement was achieved via decorating carbon particles with silver sub-micrometre particles as described in the experimental section. The comparison of different electrodes for direct square-wave voltammetric measurements of 0.2 mmol L^{-1} nitrite is shown in Fig. 1. Evidently, bare glassy carbon electrode (GCE) (a) and conventional carbon paste electrode (CPE) (b) exhibited very poor response toward nitrite oxidation. On the contrary, the ionic liquid-based carbon paste electrode (IL-CPE) (c) showed significantly improved signal for nitrite, whereas the ionic liquid/silver particle-decorated carbon paste electrode (AgPs-IL-CPE) (d) revealed a superior performance. The signal of nitrite oxidation was improved by a factor of 3.4 together with a shift of the peak potential of 110 mV toward less positive potentials in comparison with ionic
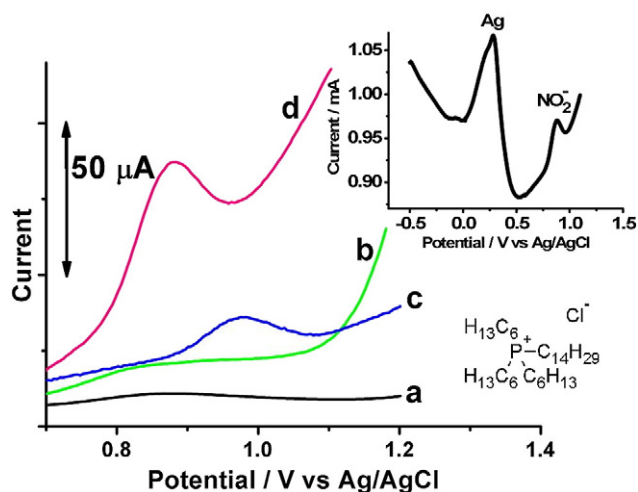

Fig. 1. SWVs of 0.2 mmol L^{-1} nitrite obtained at GCE (a), CPE (b), IL-CPE (c) and AgPs-IL-CPE (d), using two-step conditioning for 30 s at −0.5 V and for 60 s at +0.5 V; step potential of 4 mV, frequency of 25 Hz, amplitude of 100 mV. Insets show the entire potential scan from −0.5 to +1.3 V at AgPs-IL-CPE and the structure of the ionic liquid.

liquid-based carbon paste electrode, i.e. (0.87 V vs. 0.98 V), indicating relatively strong electrocatalytic effect of silver particles.

To get more insights into electroanalytical operation of the novel sensor, several carbon/silver ratios were investigated with 10, 20, 25 and 30 wt.% of Ag^+ added during carbon decoration procedure. The electrode composed of carbon powder with 20 wt.% Ag^+ (Fig. 1d) displayed the most favourable electroanalytical performance, both in terms of nitrite peak height and peak potential shift. The nitrite oxidation signal obtained with AgPs-IL-CPE prepared with 20 wt.% Ag^+ was higher compared to the other three examined electrodes (with 10, 25 and 30 wt.% Ag^+) by a factor of approximately 1.7. The reason for this might be the optimal silver particle distribution in the carbon paste material, as depicted in Fig. 2 showing scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) mapping of silver (white spots). While SEM images show relatively large particles, it is evident from EDX mapping that silver is rather evenly distributed all over the electrode material. On the other hand, higher percentage of silver resulted in considerable agglomeration of silver particles into clusters of several micrometres, whereas lower silver content provided satisfactory silver particle distribution, however, the amount of silver was apparently insufficient (not shown).

Since nitrite was detected using direct square-wave voltammetric (SWV) mode, several key operational parameters were investigated to achieve the optimal electroanalytical performance. Conditioning steps at −0.5 V (30 s, the first step) and +0.5 V (the second step) were shown to have a beneficial effect on the signal height, probably via activating the silver-decorated carbon paste electrode surface. The effect of the second conditioning step was particularly pronounced, thus different conditioning potentials of the second step were further studied. The obtained voltammograms revealed that both the peak height and the peak potential shift were strongly dependent on the selected second conditioning potential, being the most favourable electrode operation obtained after the second conditioning potential set at +0.5 V. Compared to the electrode conditioning only at −0.5 V, the signal was higher by 84% and shifted by 120 mV toward less positive potentials.

Together with the first conditioning step at −0.5 V, the second conditioning at +0.5 V served as the activation of silver, which is evident from increasing peak height and increasing absolute shift of nitrite signal when increasing the conditioning time in the range of 0 to 120 s. The most significant difference was observed between 0 and 60 s, therefore the conditioning period of 60 s was selected as optimal in the second step, as a compromise between sensitivity and time of