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ORIGINAL PAPER

A conducting polymer/Ag nanoparticle composite as a nitrate sensor

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Abstract A novel electrochemical sensor was fabricated by electrodeposition of silver nanoparticles on pre-synthesized polypyrrole (PPy), to form a PPy/Ag composite matrix on a glassy carbon electrode. The electrochemical sensor exhibited strong catalytic activity with regards to nitrate reduction. Scanning electron microscopy and cyclic voltammetry were used for the characterization of the composite. The detection limit of nitrate was found to be 5 μM. Moreover, the sensor showed excellent sensitivity, selectivity, and stability.

Keywords Nitrate · Polypyrrole · Silver · Nanoparticles

1 Introduction

Environmental pollution is one of the most serious problems in the modern world. Water may become contaminated after the use of fertilizers on crops, by animal wastes, or decaying organic matter. The environmental monitoring of water is of special significance to both human life and livestock. Some inorganic species, such as PO_4^{2-}, SO_4^{2-}, Cl^-, and NO_3^- influence the quality of environmental water and can lead to health risks. Currently, nitrate is the most common chemical contaminant in groundwater and soil, and its levels are increasing [1]. The fate of applied fertilizer nitrate has been well-documented in relation to its conservation and distribution in the soil profile and root zone, availability to the crop, effect on the crop yield during the cropping season, and its leaching after harvest [2, 3]. Both nitrites and nitrates are continuously monitored because of their toxicity. Nitrites can be converted to carcinogenic nitrosamines in food products and also within the human digestive system [4]. Nitrates, although more stable and less toxic than nitrites, are also of concern because they can be readily converted to nitrites by microbial reduction in food products. Infants who are fed with water that has high levels of nitrate can develop a condition called methemoglobinemia (blue baby syndrome). There have been warnings [5] that nitrate contamination of drinking water may increase cancer risks, as nitrate can be reduced to nitrite and subsequent nitrosation reactions give rise to *N*-nitroso compounds which are highly carcinogenic. The quantitative determination of nitrite and nitrate concentration is of rapidly increasing interest, especially for drinking water quality, wastewater treatment, food production, food quality, and for the control of remediation procedures. In particular, the control of water quality is important to avoid contamination of food produced when water is used as a raw material. Moreover, nitrates and nitrites are routinely added to meat products as a preservative against food poisoning microorganisms such as *Clostridium botulinum* [6]. Spectrophotometric methods for the determination of nitrate have been developed over the past several decades [7–11]. Common methods for nitrate analysis utilize ion-exchange chromatography combined with spectrophotometric, conductimetric, or electrochemical detection and are suitable for a wide variety of environmental samples, such as drinking water, ground water, acid rain waters, and wastewater [12–17]. However, although they have high sensitivity and good reproducibility, these techniques

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require large and expensive instruments and extensive pre-treatment of the sample. Biosensors incorporating enzymes, antibodies, and whole cells have also been used for nitrate analysis [18–20]. Enzymatic methods using redox mediators have a relatively high limit of detection (LOD); require pH control and lengthy isolation procedure of the enzyme from bacteria. Immunoassay, even though it has high sensitivity and good selectivity still has associated problems. These include the expense of the materials and difficulty in handling them. A voltammetric method employing a copper-plated glassy carbon electrode is affected by the presence of phosphate ions [21]. In addition several chemical methods have also been investigated [22, 23].

With regards to conducting polymers there has been much interest in their potential use in areas such as battery electrodes, corrosion protection, and biological sensors [24, 25]. Among the various conducting polymers, polypyrrole is one of the most frequently investigated [26]. This is due to its ease of preparation by electropolymerization, relative stability compared to other conducting polymers and the ready commercial availability of many of its derivatives. Incorporating nanosized metal particles into polymer matrices, such as polypyrrole, is of current interest for many applications [27, 28]. On one hand, the polymer can be used as a matrix for stabilizing the growth of nanoparticles and avoiding the agglomeration process [29]. The stabilized nanoparticles can then be studied for their catalytic, optical, magnetic, mechanical, and electrical properties. On the other hand, the nanoparticles can be deposited into polymer matrices to modify the electronic, mechanical, and electrical properties of the polymer. For example, polypyrrole might lose its conductivity over time but with the inclusion of nanometal fillers, this loss in conductivity is not observed [30]. Furthermore, the nanoparticles can serve as fillers to modify the polymer surface morphology, or even to print nanoelectric circuits using templates or masks. Silver nanoparticles are of special interest due to their novel optical properties, surface-enhanced Raman scattering (SERS) and their ability to attach bio-molecules to be used in biosensor applications [31].

In this article, we investigate the synthesis of a PPy/Ag matrix by two steps. The first step involves the electopolymerization of pyrrole on a glassy carbon electrode, while the second step is the electrochemical deposition of silver on the surface of the polypyrrole. The silver nanoparticles were embedded in the PPy network and also well-dispersed onto the surface of the polymer. The PPy/Ag matrix provides a porous structure with large effective surface area and high electrocatalytic activity toward the reduction of nitrate.

2 Experimental

A conventional three-electrode electrochemical cell was used for all electrochemical experiments. The counter electrode was a platinum wire. The reference electrode used throughout the experiments was a saturated calomel electrode against which all potentials are quoted. The working electrodes were prepared from pure glassy carbon rods supplied by Goodfellow. The electrode materials used were cut into 3 cm lengths. An electrical contact was made between the metal and the external circuit by threading a length of copper wire through the PTFE holder. This was then attached to the rod using conducting resin. Once prepared the electrode was sealed using non-conducting epoxy resin. Before each experiment the exposed electrode surface was polished using a Metaserve Universal polisher and water lubricated silicon carbide paper. The samples were polished to a smooth finish with successively finer grades and rinsed with distilled water. The electrochemical measurements were carried out using a Solartron EI 1285/1287 potentiostat or a CHI 400 EQCM, Model 440.

Cyclic voltammograms were recorded between −0.2 and −2.0 V. Differential pulse voltammetry experiments were conducted under the instrumental conditions of 50 mV pulse amplitude, pulse width of 50 ms, pulse time of 200 ms, and sample width of 16 ms. The supporting electrolyte used was 0.1 M Na_2SO_4.

All solutions used for electrochemical measurements were prepared using distilled water and analytical grade reagents. The pyrrole monomer was supplied by Aldrich with 99.5% purity. It was necessary to distil the pyrrole monomer regularly to prevent solution oxidation. Following distillation the pyrrole monomer was stored at −4 °C and maintained in the dark to reduce decomposition. All experiments were carried out at ambient temperature.

3 Results and discussion

3.1 Electrode preparation

Polypyrrole (PPy) was electrochemically deposited at a constant potential of 0.65 V from an aqueous solution of 0.1 M Na_2SO_4 containing 0.12 M pyrrole. The PPy-modified electrode was treated for 6 h in 0.15 M NaOH. The silver nanoparticles were then electrochemically deposited on the prepared PPy by a double pulse technique. The double pulse technique involves the application of two pulses; the first, the nucleation pulse E_1 and the second, the growth pulse, E_2. The pulse parameters were chosen carefully to avoid degrading the polymer. The pulse parameters were determined as follows $E_1 = -1.353$ V, $t_1 = 0.100$ s, and $E_2 = -0.700$ V, $t_2 = 10$ s. A bare glassy carbon electrode was modified with silver nanoparticles (Ag/GCE) following the same method for comparison purposes.

3.2 Characterization of electrode surface

SEM micrographs of the synthesized PPy/Ag composite on GCE are shown in Fig. 1a, b. Figure 1a shows the image of deposited PPy/Ag matrix, which is sponge-like and consists of the PPy film covered with silver nanoparticles. The silver nanoparticles were mainly dispersed on the surface of the PPy film, Fig. 1b. The silver nanoparticles varied between 100 and 350 nm in diameter. The characterization of PPy films and silver composites was also investigated using cyclic voltammetry. Figure 2 shows the cyclic voltammograms obtained for PPy (a) and the PPy/Ag (b) composite in 0.1 M Na_2SO_4 on a glassy carbon electrode. The cyclic voltammogram of PPy (a) shows the typical redox activity of the deposited PPy film, while the cyclic voltammogram of PPy/Ag (b) composite is characterized by an oxidation peak at 0.20 V that may correspond to the oxidation of Ag. The quantity of silver deposited on the GC surface was estimated from the charge, calculated by integration of the Ag oxidation peak in the cyclic voltammogram. The quantity of silver deposited on the surface of the electrode was estimated to be 2.35×10^{-7} mol Ag cm^{-2} (0.0235 mg).

Several variables were examined that may affect the size and the amount of silver deposited on the surface and as a result can affect the sensing of nitrate, these variables are:

1. Film thickness of the PPy on the surface
2. E_1
3. t_1 and t_2

In addition to these, the following conditions were also investigated:

1. Interferent ions like those present in the tap water
2. The effect of acid and bases on the polymer

3.3 The effect of film thickness of PPy on the peak current of nitrate

The film thickness was varied by controlling the charge applied to the electrode and calculated using the following relation as outlined by Diaz et al. [32]: 24 mC cm^{-2} = 60 nm. As shown in Fig. 3a, the peak current for the nitrate reduction peak decreases with increasing the film thickness. However, there was no linear correlation between film thickness and peak current, although it was observed that a higher nitrate peak current was observed at a charge of 0.01 C cm^{-2} (25 nm) while the lowest peak was found at 0.20 C cm^{-2} (500 nm).

3.4 The effect of E_1, t_1, and t_2 on the size and the dispersion of the nanoparticles

The electrodeposition of silver nanoparticles on GC was performed in 0.1 M Na_2SO_4 solution, using a double-pulse technique method to control deposition of Ag nanoparticles. The pulse parameters, $E_1 = -1.353$ V, $E_2 = -0.700$ V, were employed as previously reported by Plieth et al. [33]. The two variables examined were nucleation time (t_1) and growth time (t_2). By controlling these two variables it was possible to control the particle size, the particle density and the polydispersion of the particles. The polymer film thickness was kept constant during these experiments at 25 nm (0.01 C cm^{-2}). The reported results suggested that on increasing t_1, the particle density increases and thus substantially reduces the particle size and slightly increases the polydispersity [33]. The catalytic efficiency of a metal nanoparticle for an electron transfer process is size-dependent. In addition, the redox potential of a metal nanoparticle is dependent on its size and increases proportionally with size [34, 35].

For a given concentration of silver nanoparticles, the smaller particle size results in a more negative potential, which results in a larger potential difference between silver and NO_3^- and hence higher catalytic activity. The highest peak current was obtained when t_1 was 0.1 s. There was no correlation found between the increase of t_2 and peak

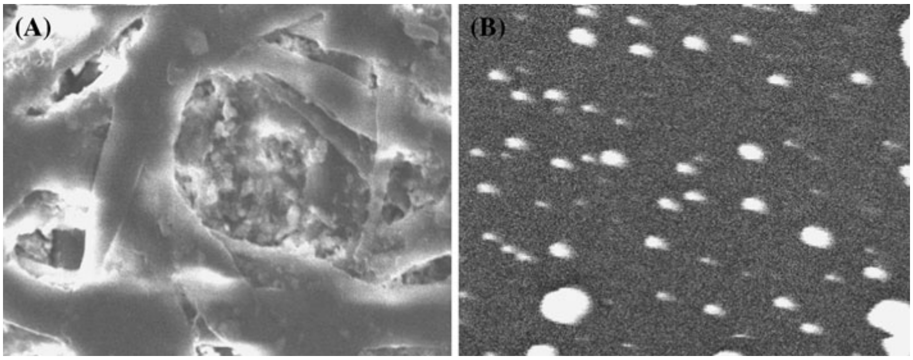


Fig. 1 SEM micrographs of PPy/Ag on GCE

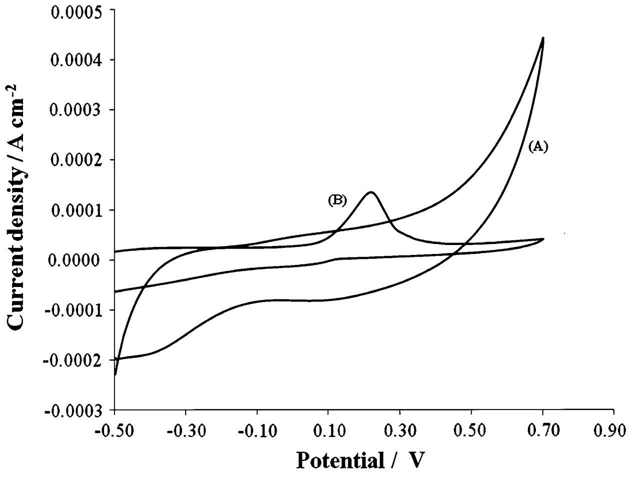


Fig. 2 Cyclic voltammograms of PPy on GC (*A*) and PPy/Ag (*B*) in 0.1 M Na_2SO_4 at 40 mV s^{-1}

current at this potential. The optimum conditions were found to be $E_1 = -1.353$ V, $E_2 = -0.700$ V, $t_1 = 0.1$ s and $t_2 = 10$ s.

3.5 The effect of protonation and deprotonation of PPy on the reduction of nitrate

PPy was polymerized in both acidic and basic media to investigate any variability in the sensitivity of PPy/Ag toward nitrate. PPy synthesized from an acidic medium resulted in poorer nitrate sensing compared to that obtained from a basic medium, as shown in Fig. 3b. Deprotonation/protonation of PPy was carried out prior to deposition of silver using 0.15 M NaOH or 0.1 M H_2SO_4, respectively.

The conductivity and stability of PPy films can be altered by chemical and electrochemical treatments [28, 36]. Treatment of PPy films with a base or acid results in deprotonation or protonation of the polymer, respectively. In addition, the treatment with a base was found to decrease the conductivity of the film by several orders of magnitude, while the acid treatment would restore the conductivity [37, 38]. Van Dyke et al. [39] and Zotti et al. [40] have shown that the reduction in electrical conductivity of PPy tosylate films following treatment with aqueous hydroxide solutions is associated with the replacement of the counter ion by the hydroxide ion. Further, they concluded that PPy films doped with hydroxide ions give rise to a strong negative shift of the oxidation potential of PPy. Hence, in the presence of a metal ion in an acid solution, the polymer is readily reprotonated and oxidized, while the metal ion will be reduced and entrapped in the polymer film. Using this phenomenon, pre-treated PPy films have been used to extract silver from wastewater samples obtained from industry [28].

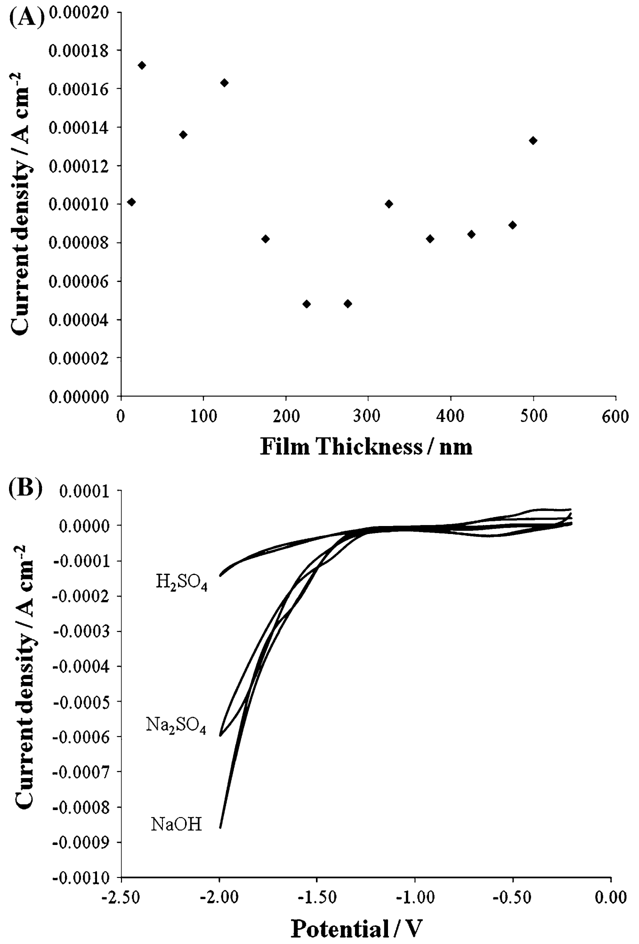


Fig. 3 **a** The change of nitrate peak current with changing PPy film thickness. PPy synthesised from 0.2 M pyrrole in 0.10 M Na_2SO_4. **b** The change of the peak current with protonation/deprotonation of PPy. PPy synthesised from 0.15 M of NaOH in 0.1 M H_2SO_4. The film thickness of PPy was 25 nm

3.6 The effect of interferent ions on the nitrate peak current

The presence of certain ions in water samples can interfere with the determination of nitrate levels. Several of these ions were studied in the presence of nitrate to investigate how they may affect the selectivity of the sensor toward nitrate reduction. The ions chosen, oxalate, EDTA, and NaBr, are well-known interferents with respect to nitrate detection. The affect of the presence of 0.01 M of each ion in 0.1 M $NaNO_3$ was examined. All ionic species were found to have little affect on nitrate measurement. The influence of nitrite on the determination of nitrate was also examined. Figure 4 shows the cyclic voltammograms of 0.1 M $NaNO_3$ with and without the presence of 0.1 M $NaNO_2$ [4, 22, 23]. Initially, it was thought that increasing the concentration of nitrite led to a decrease in the nitrate peak current at −1.4 V. This corresponds well with previous reports that nitrite can become a substantial

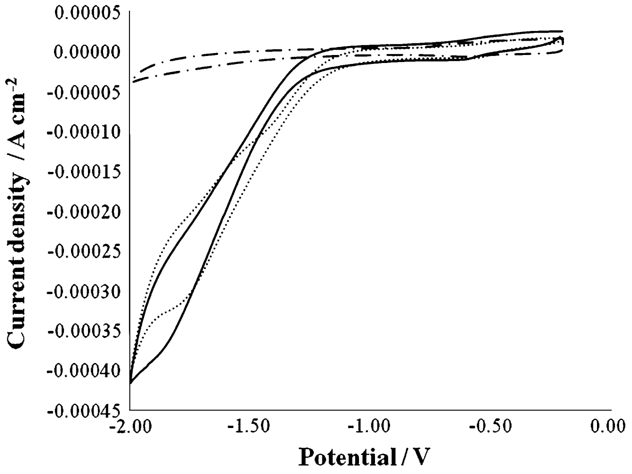


Fig. 4 Cyclic voltammograms of the detection of 0.1 M $NaNO_3$ by PPy/Ag with (*solid lines*) and without (*dotted lines*) the presence of 0.1 M $NaNO_2$. Cyclic voltammogram of PPy/Ag in background electolyte 0.1 M Na_2SO_4 (*dashed dotted lines*)

interferent when it reaches the same concentration as nitrate [4, 22, 23, 41]. However, upon closer examination of the voltammetric traces it was observed that the height of the actual nitrate reduction peak remained essentially unchanged with the presence of nitrite increasing the baseline rather than substantially influencing the nitrate reduction peak.

3.7 Electrocatalytic reduction of nitrate

To evaluate the electrocatalytic activity of the PPy/Ag toward the oxidation of nitrate, cyclic voltammograms were recorded with Ag/GCE, PPy and bare GCE in the presence of 0.01 M nitrate and compared, as shown in Fig. 5. At bare GCE, only a very small reduction peak current was observed at about −1.42 V, inset Fig. 5. The cyclic voltammograms obtained at PPy also presented a large overpotential with a very broad peak at about −1.42 V (b), although the current response increased over that observed at bare GCE. Well-formed sharp catalytic reduction peaks at −1.09, −1.36, and −1.88 V were observed at Ag/GCE (c). The peak current was found to be approximately five times higher than that recorded with PPy. An even sharper catalytic peak appeared at −1.78 V at PPy/Ag (d) giving an 11-fold enhancement of the peak current compared to that recorded with the Ag/GCE electrode. The approximate 0.11 V negative shift of the peak potential indicated the catalytic activity of these electrodes is in the order of PPy/Ag > Ag/GCE > PPy > bare GCE. The increase of current response can be partly attributed to the increase of reversibility of the electron transfer process. However, it may be also generated from a surface accumulation of the electroactive species.

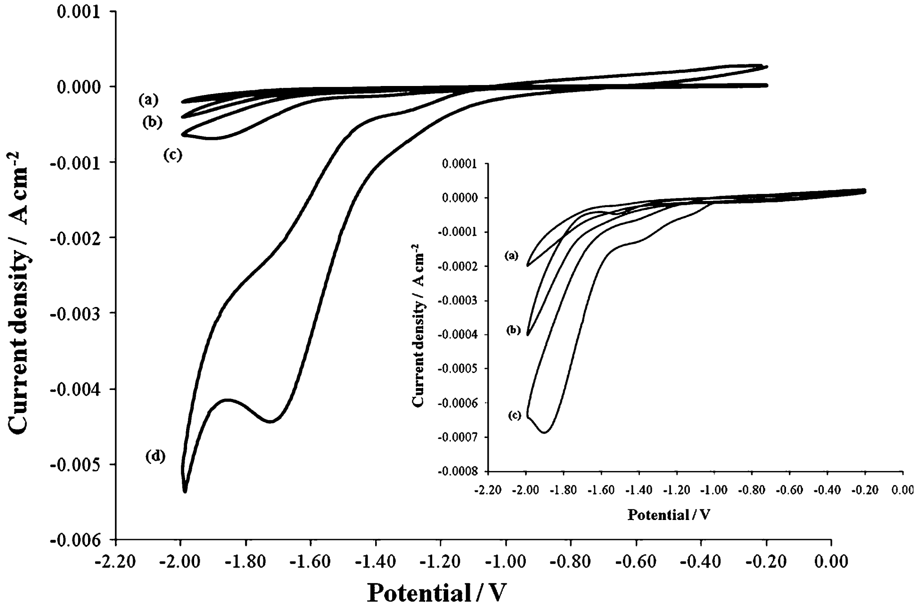
3.8 Determination of nitrate

Differential pulse voltammetry was used for determination of nitrate at PPy/Ag in Na_2SO_4. As can be seen in Fig. 6, two peaks were seen at −1.26 and −1.86 V. The plot of the peak current (i_p) versus concentration of nitrate is shown in Fig. 7. The dependence of the peak current on the concentration measured under given conditions was linear over a concentration range of between 1 and 10,000 μM, as can be seen in Fig. 7.

3.9 Stability and reproducibility of the PPy/Ag matrix

The stability of the PPy/Ag matrix was examined by monitoring the remaining amount of current response after

Fig. 5 Cyclic voltammograms of 0.01 M $NaNO_3$ in 0.10 M Na_2SO_4 at (*a*) bare GCE, (*b*) PPy, (*c*) Ag/GCE, and (*d*) PPy/Ag. Inset: Close-up showing a small reduction peak current was observed at about −1.42 V for bare GCE



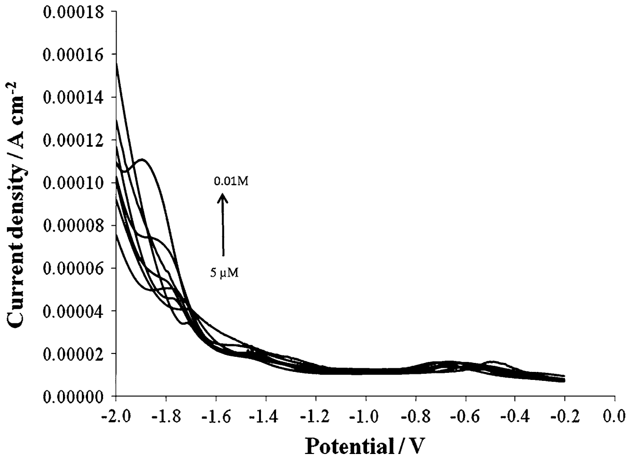


Fig. 6 Differential pulse voltammograms at PPy/Ag in 0.10 M Na_2SO_4, with $NaNO_3$ concentrations between 5 μM and 0.01 M. The film thickness of PPy is 25 nm, scan rate at 40 mV s^{-1}

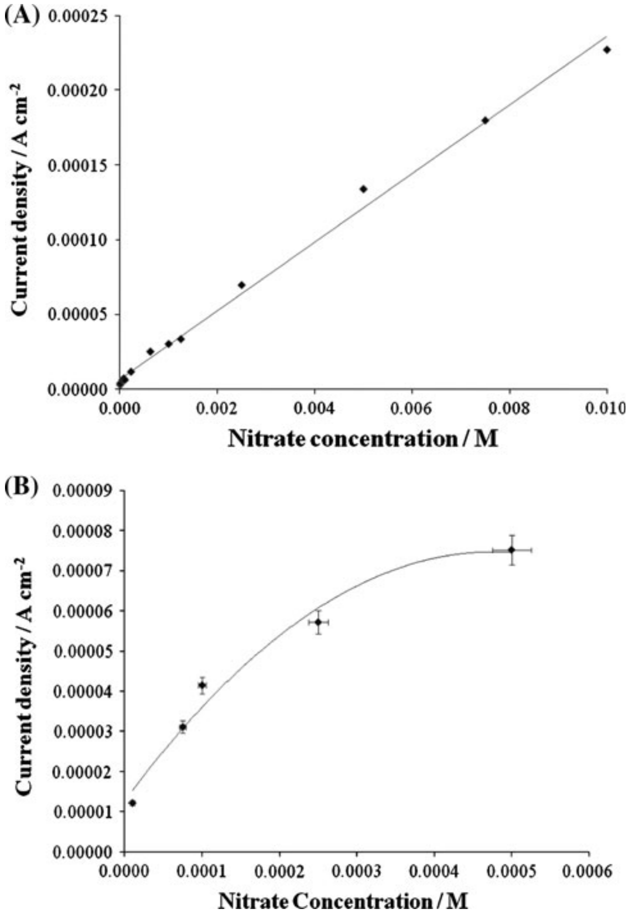


Fig. 7 Peak current dependence on nitrate concentration of PPy/Ag using the following parameters $E_1 = -1353$ mV, $t_1 = 0.100$ s, $E_2 = -700$ mV, $t_2 = 10$ s. The nitrate concentration range was 1–10,000 μM, where **a** shows entire concentration range and **b** lower concentration range 1–500 μM. Scan rate is 20 mV s^{-1}

successive cycling of the modified electrode in the potential range of −0.2 to −2.0 V in 0.1 M Na_2SO_4 for 200 cycles. It was found that the peak current for nitrate reduction retained 96% of its initial value and no obvious potential shift was observed. In addition, the storage stability of PPy/Ag was examined with no apparent decrease in the current response to nitrate reduction observed in the first 7 days of everyday use and storage in 0.1 M Na_2SO_4 at room temperature. A 15% reduction in activity was found after 1 month and 78% of initial activity was observed after 60 days. Under the selected conditions, the method showed that the sensor had good reproducibility and long-term stability. This can be attributed to the PPy matrix, which increases the effective surface area and stabilizes the activity of the silver nanoparticles. In addition, a series of repeat measurements were carried out in 1.0×10^{-5} M nitrate solution to characterize the reproducibility of the sensor measurements. A relative standard deviation of 4% for five replicate determinations for nitrate was observed, indicating that the modified electrode had excellent reproducibility and anti-fouling properties.

4 Conclusions

A novel electrochemical sensor for the determination of nitrate was fabricated using two electrochemical steps: (1) the electropolymerization of pyrrole on GCE and (2) electrodeposition of silver nanoparticles. The PPy/Ag matrix exhibited strong electrocatalytic activity toward nitrate reduction. The PPy/Ag-modified electrode, showed excellent sensitivity toward nitrate using differential pulse voltammetry. The lowest detection limit was estimated to be 5 μM nitrate. The PPy/Ag matrix showed good stability and reproducibility, and demonstrates the synergistic properties of organic and metallic nanoparticles in a composite material for electrochemical sensor construction.

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