

Full Paper

Silver Nanoparticles Dispersed in Polypyrrole Matrixes Coated on Glassy Carbon Electrode as a Nitrate Sensor

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Abstract- Silver nanoparticles dispersed in polypyrrole (PPy) matrixes coated on glassy carbon electrode (GCE), as a novel electrode, was easily synthesized by electro-polymerization of pyrrole on GCE and then electrodeposited silver nanoparticles on PPy electrode. The electrochemical behavior and electro-catalytic activity of silver nanoparticles/PPy/GCE were characterized by cyclic voltammetry. The morphology of electrodes was characterized by scanning electron microscopy. The electrochemical sensor exhibited strong electro-catalytic activity with toward reduction of nitrate. The detection limit of nitrate was found to be 2.0 μM . Moreover, the sensor showed excellent sensitivity, selectivity, and stability.

Key words- Polypyrrole, Silver Nanoparticles, Nitrate, Nanocomposite, Electrocatalytic

1. INTRODUCTION

Nitrogen species play an important role in determining the ecological status and health of freshwater ecosystems. They are one of the most implicated species in water eutrophication. The main anthropogenic sources of nitrates in the environment are municipal and industrial wastes and artificial fertilizers. Nitrogen concentrations in river and ground water increase by

increasing agricultural activity and point-source discharges [1]. Nitrogen forms many inorganic ionic species, of which the most important are nitrate, nitrite and ammonium ions.

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^{3-} , 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 [2].

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 [3,4]. 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 [5].

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 [6] 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* [7].

In the last couple of decades, many strategies have been developed to facilitate the detection, determination and monitoring of nitrate and nitrite [8]. Several instrumental techniques have been reported for the determination of nitrate include chromatography [9, 10], voltammetry [11-14], polarography [15], raman spectroscopy [16], spectrophotometry [17], chemiluminescence [18,19], and spectrofluorimetry [20-22].

However, although they have high sensitivity and good reproducibility, these techniques require large and expensive instruments and extensive pre-treatment of the sample. Electrochemical methods, such as stripping voltammetry and differential pulse voltammetry, have been widely applied for the determination of pharmaceuticals, insecticides pesticides and inorganic ions [23-26]. Modified electrodes are being used frequently in the

voltammetric determination of organic and inorganic compounds because of their efficiency and selectivity that can be obtained by varying the modifier [27,28].

Conducting polymers there has been much interest in their potential use in areas such as battery electrodes [29], corrosion protection [30], and biosensors [31,32]. Among the various conducting polymers, polypyrrole is one of the most frequently investigated [33]. This is due to its ease of preparation by electropolymerization, relative stability compared to other conducting polymers and ready commercial availability of many of its derivatives.

At the end of the 1990s, Jovanovic et al. [34], showed that conducting polymers based on polypyrrole (PPy) doped with a given anion not only displayed a Nernstian-type response toward the dopant anion, but that a molecular impression phenomenon was also induced that afforded a highly selective surface film. Such results encouraged the construction of sensors having a selective polypyrrole membrane doped with nitrate [35] and even bigger anions like dodecyl sulphate [36].

The conducting polymers have the excellent hosts for trapping nanoparticles of metals and semiconductors, because of their ability to act as stabilizers or surface capping agents. The nanoparticles embedded or encapsulated in polymer; the polymer terminates the growth of the particles by controlling the nucleation. Incorporating nanosized metal particles into polymer matrices, such as polypyrrole, is of current interest for many applications [37-39]. The stabilized nanoparticles can then studied for their catalytic, optical, magnetic, mechanical, and electrical properties. On the other hand, the nanoparticles can be stabilized 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 [39].

Furthermore, the nanoparticles can serve as fillers to modify the polymer surface morphology, or even to print nanoelectric circuits using templates or masks. The silver nanoparticles have potential in technological applications due to properties including catalysis, conductive inks, thick film pastes, adhesives for various electronic components, in photonics and in photography [40-42] and their ability to attach bio-molecules to be used in biosensor applications [43,44].

We here in report the synthesis of an Ag/PPy nanocomposite matrix by two steps. The first step involves the electropolymerization of pyrrole with nanofiber structure on a glassy carbon electrode, while the second step is the electrochemical deposition of silver nanoparticles on the surface of the polypyrrole nanofibers. The silver nanoparticles were embedded in the PPy network and also well-dispersed onto the surface of the polymer. The Ag/PPy nanocomposite matrix provides a porous structure with large effective surface area and high electrocatalytic activity toward the reduction of nitrate.

2. EXPERIMENTAL SECTION

2.1. Chemicals

Pyrrole (Fluka) was purified by distillation under nitrogen atmosphere before use, stored at low temperature and protected from light. All other reagents were of analytical grade and were used without further purification.

All solutions used for electrochemical measurements were prepared using distilled water. All experiments were carried out at ambient temperature.

2.2. Apparatus and characterizations

All electrochemical measurements were carried out with an electrochemical system analyzer (Sama Instruments, Iran). The electrochemical cell contains a three-electrode system, a glassy carbon electrode (GCE) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum (Pt) wire as the counter electrode.

Scanning electron microscope (SEM, model EM 3200, KYKY) was used to characterize the nanostructure of nanomaterials.

2.3. Preparation of PPy nanofiber and PPy/Ag nanocomposite modified electrodes

Before polymerization conducted, electrolyte solutions were desecrated thoroughly with pure nitrogen. Unless stated otherwise, all pyrrole polymerization were conducted at ambient temperature and potentiostatically 0.85 V *vs.* SCE in aqueous solution containing 0.15 M pyrrole, 0.10 M LiClO₄ and 0.10 M carbonate. Freshly prepared PPy nanofibers electrodes were usually conditioned in 0.10 M HClO₄ solution for 24 h to remove the carbonate ions.

The PPy nanofibers modified electrode was treated at 0.85 V for 300 s in 0.15 M NaOH solution. The silver nanoparticles were then electrochemically deposited on the prepared PPy nanofiber in aqueous solution containing 0.001 M AgNO₃ and 0.1 M NaNO₃ 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 $E_1 = -1.35$ V, $t_1 = 0.1$ s, and $E_2 = -0.70$ V, $t_2 = 10$ s.

A bare glassy carbon electrode was modified with silver nanoparticles (Ag/GCE) following the same method for comparisons purposes.

3. RESULTS AND DISCUSSION

3.1. Characterization of electrode surface

Fig. 1 shows the SEM pictures of PPy nanofibers (1a) and Ag/PPy nanocomposite (1b) on GCE. Fig. 1a shows the image of PPy nanofibers with diameters about of 30-80 nm. It can

be seen in fig. (1b) that the silver nanoparticles with diameters about of 50-100 nm are distributed at the surface of the PPy films.

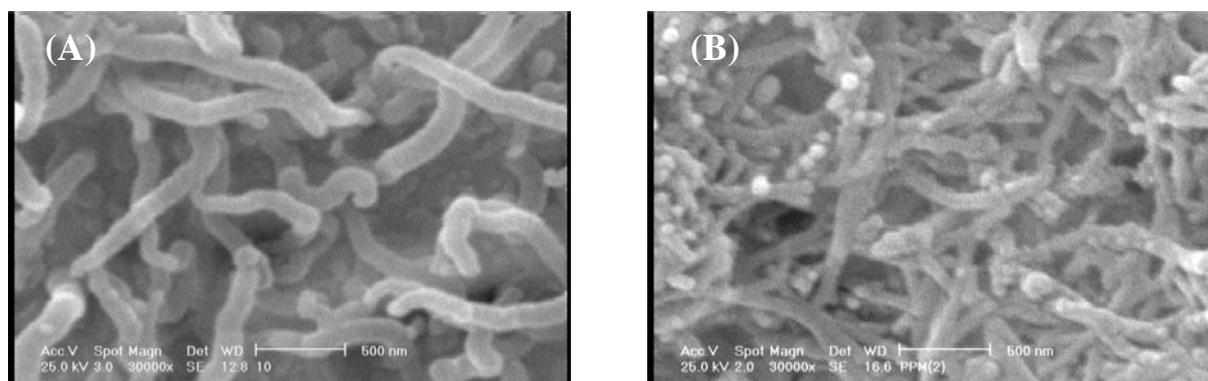


Fig. 1. SEM pictures of PPy/GCE (A) and Ag/PPy/GCE (B)

Fig. 2 shows the cyclic voltammograms obtained for PPy nanofibers (a) and the PPy/Ag nanocomposite (b) in 0.1 M KCl on a GCE. The cyclic voltammogram of Ag/PPy nanocomposite (b) is characterized by an oxidation peak at 0.2 V that may correspond to the oxidation of Ag.

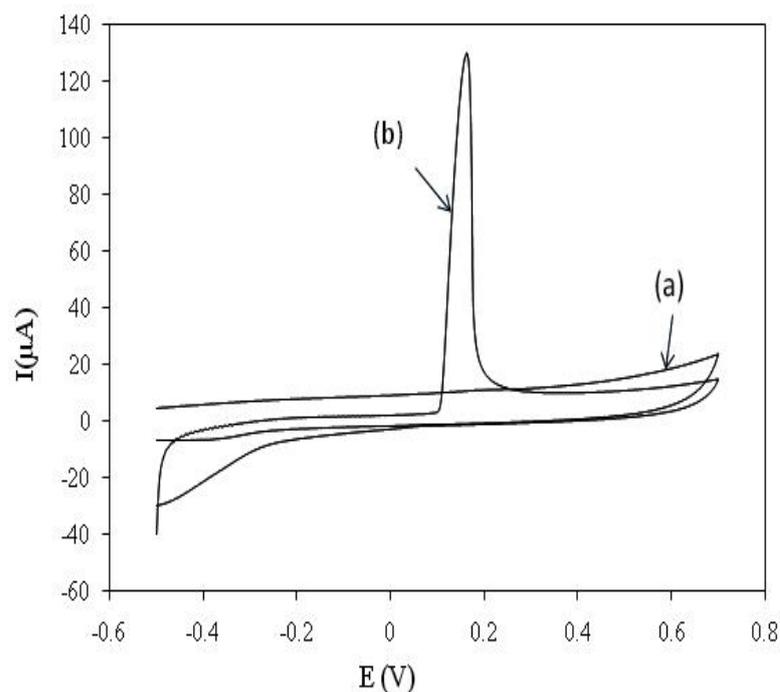


Fig. 2. Cyclic voltammograms of PPy/GCE (a) and Ag/PPy/GCE (b) in 0.1 M KCl, Scan rate: 50 mV s^{-1}

3.2. Electrocatalytic reduction of nitrate ions

In order to study the electrocatalytic behavior of the Ag/PPy nanocomposite toward the reduction of nitrate, cyclic voltammograms were recorded with Ag/PPy/GCE, Ag/GCE, PPy/GCE and bare GCE in the presence of 0.01 M nitrate and compared, as shown in Fig. 3.

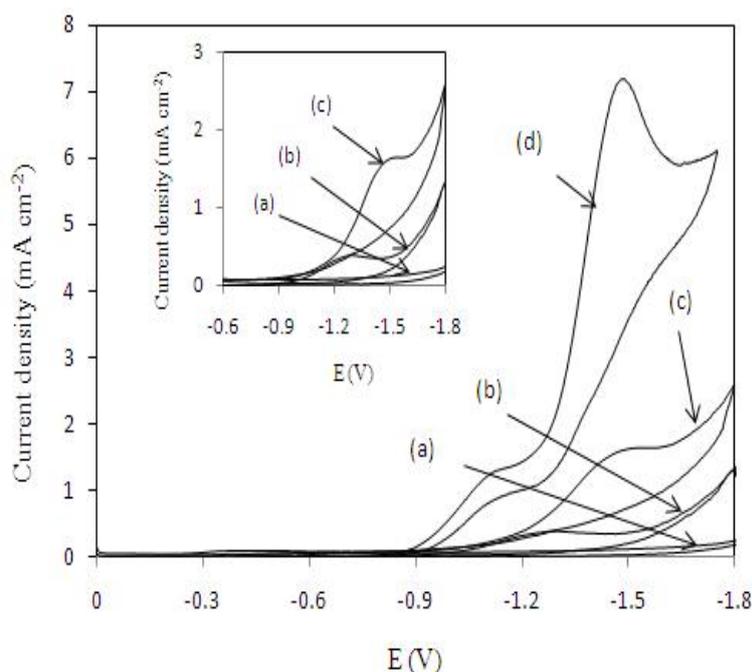


Fig. 3. Cyclic voltammograms of 0.01 M NaNO_3 in 0.1 M KCl solution at (a) bare GCE, (b) PPy/GCE, (c) Ag/GCE, and (d) Ag/PPy/GCE. Inset: Close-up showing a small reduction peak current was observed at about -1.3 V for bare GCE. Scan rate: 50 mV s^{-1}

At bare GCE, only a very small reduction peak current was observed at about -1.3 V, inset Fig. 3. The cyclic voltammograms obtained at PPy also presented a large overpotential with a very broad peak at about -1.3 V (b), although the current response increased over that observed at bare GCE. Well-formed sharp catalytic reduction peak at -1.57 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 -1.46 V at Ag/PPy/GCE (d) giving a 5-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 $\text{Ag/PPy/GCE} > \text{Ag/GCE} > \text{PPy/GCE} > \text{bare GCE}$. The increase of current response, indicating the surface area of Ag/PPy/GCE nanocomposite was enlarged by dispersion silver nanoparticles in polypyrrole matrix.

3.3. Effect of pH test solution

To determine the influence of the pH on the response of the Ag/PPy nanocomposite nanocomposite electrode, the current density of the sensor was investigated over a pH range of 2.0-9.0 in 0.01 M NaNO₃ solution, varying the pH by means of hydrochloric acid or sodium hydroxide additions. As shown in Fig. 4, the peak current density increased with pH in the range of 2.0-4.0 and decreased at higher pHs than 7.5. The peak current density remained constant within the pH range 4.0-7.5. The decreases in peak current density at pH values higher than 7.5 for nitrate is expected, because the reduction step of nitrate to nitrite takes place in acidic media [44] and consumes proton ion, the increase in pH causes lower reduction of nitrate to nitrite in accumulation step and therefore a decrease in peak current density take place.

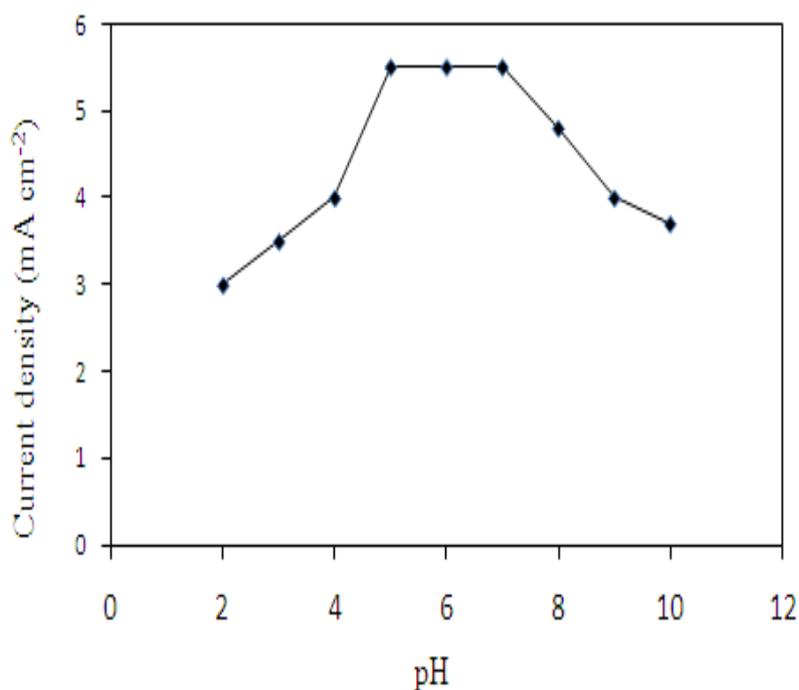


Fig. 4. Relationship between electroreduction current and pH at Ag/PPy nanocomposite modified electrode

3.4. Interference study

Possible interferences for the detection of nitrate at Ag/PPy nanocomposite electrode were studied by adding various ions into a solution containing 0.001 M NaNO₃. The results showed that most of the ions, such as Ca²⁺, Mg²⁺, Al³⁺, SO₃²⁻, SO₄²⁻, Na⁺, K⁺ and HSO₄⁻, even in 150-fold excess over nitrate did not interfere on the determination of nitrate. Thus,

this study reveals that the developed sensor can tolerate a high concentration of interfering ions and, therefore, can be selective in the presence of the more common interfering ions.

3.5. Reproducibility and stability of the modified electrode in Determination of NO_3^-

Differential pulse voltammetry was used for determination of nitrate at Ag/PPy nanocomposite electrode in 0.1 M KCl solution. As can be seen in Fig. 5, two peaks were seen at -1.0 and -1.46 V. Fig. 6 shows the relationship between electroreduction current and nitrate concentration. From the Fig. 6, we can conclude that there is good linearity over a concentration range of between 10^{-6} and 0.1 M. The limit of detection (LOD) was 2.0 μM .

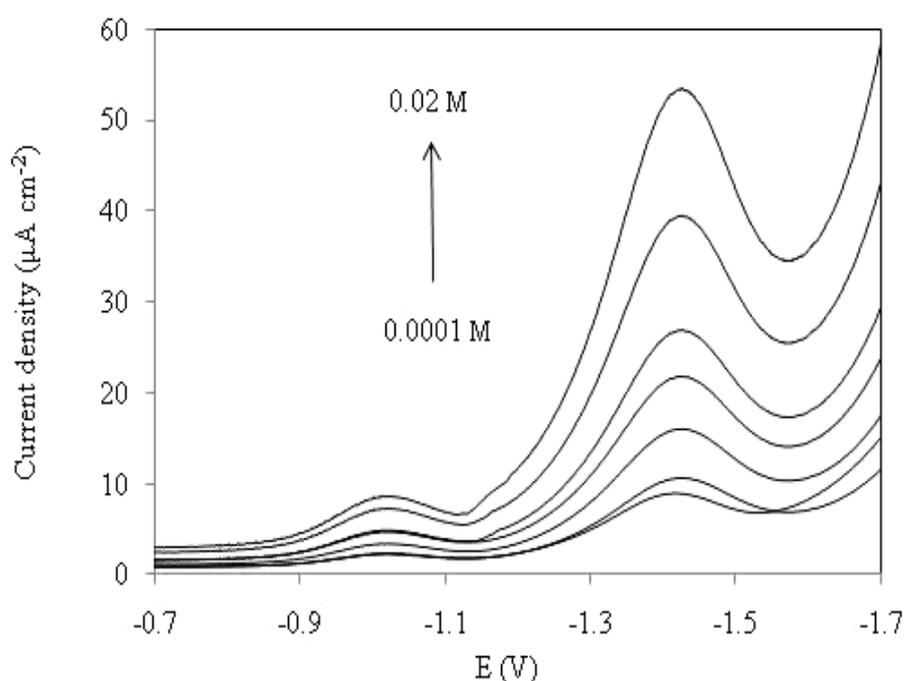


Fig. 5. Differential pulse voltammograms of Ag/PPy nanocomposite electrode in 0.1 M KCl solution with different concentrations of NaNO_3 (from 1.0×10^{-4} to 0.02 M) at 25 °C

The static results from the analytical results ($N=6$) to characterize the reproducibility of the sensor measurements. We can know that the standard deviation of the analytical method is 0.046 and the relative standard deviation for 2×10^{-5} M is 1.167 % ($N=6$). The stability of the Ag/PPy nanocomposite electrode was examined by monitoring the remaining amount of current response after successive cycling of the modified electrode in the potential range of -0.2 to -1.7 V in 0.1 M KCl for 100 cycles. It was found that the peak current for nitrate reduction retained 90% of its initial value and no obvious potential shift was observed. In addition, the storage stability of Ag/PPy nanocomposite electrode was examined with no apparent decrease in the current response to nitrate reduction observed in the first 10 days of

everyday use and storage in 0.1 M KCl at room temperature. A 10% reduction in activity was found after 1 month and 80% 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.

The comparison results of the proposed sensors with some reported sensors for the determination of nitrate are given in Table 1. As can be observed in Table 1, the proposed sensor provides lower limit of detection, wider linear range and selectivity over the most of the reported electrodes.

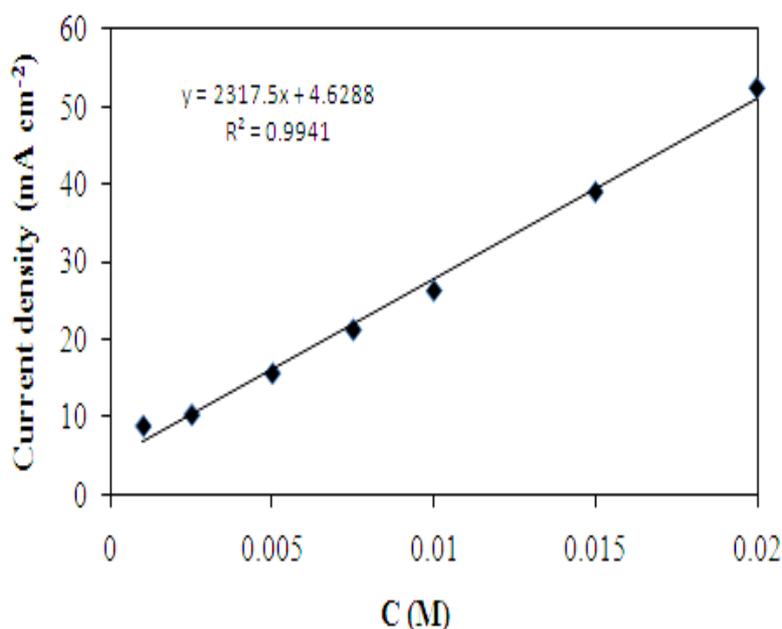


Fig. 6. The plot of nitrate reduction peak current on the Ag/PPy nanocomposite electrode vs. concentration of nitrate

Table 1. The comprehensive results about the voltammetry determination of nitrate.

| Electrode ^a | LOD (μM) | Linear range (M) | Technique | Ref. |
|---|-----------------------|-----------------------------|------------------|-----------|
| CPE modified with L-SCMNPS ^a | 87.0 | - | SWV | [14] |
| PPy composite | 53.7 | 1.56×10^{-4} -<0.1 | ISE ^b | [46] |
| PPy nanowire | 9.98 | - | Amperometry | [47] |
| PPy/Ag composite | 5 | 10^{-6} -0.01 | DPV | [13] |
| PPy/Ag nanocomposite | 2.0 | 10^{-6} -0.1 | DPV | This work |

^aL-SCMNPS:3,6-bis(2-[2-sulfanyl-ethylimino-methyl]-4-(4-nitro-phenylazo)-phenol)pyridazine coated
SiO₂@Fe₃O₄

^b ISE: Ion selective electrode

3.6. Effect of scan rate

To study the electroreduction mechanism of nitrate on Ag/PPy nanocomposite electrode, the cyclic voltammetric curves were recorded at different scan rates in 0.01 M NO_3^- +0.1 M KCl aqueous solutions in the potential range of -0.2 V to -1.7 V as shown in Fig. 7A. It can be seen that the peak current is proportional to the potential scan rate. To investigate the electro-catalytic reaction mechanism of nitrate reduction on Ag/PPy nanocomposite electrode, diagram of peak current density i_p versus square root of scan rate $v^{1/2}$ was constructed. According to the equation (1) which is valid for totally irreversible diffusion-controlled electrode processes [48]:

$$I_p = 3.01 \times 10^5 n [(1-\alpha)n_\alpha]^{1/2} A C_o D_o^{1/2} v^{1/2} \quad (1)$$

Where i_p : peak current, v : scan rate, n : number of electrons transferred, α : coefficient of electron transfer, C_o : bulk concentration of substrate, D_o : diffusion coefficient, A : the electrode surface area. If the concentration C_o is hold constant, the peak current i_p is linearly proportional to the square root of scan rate $v^{1/2}$. While the scan rate is kept constant, the peak current i_p is linearly proportional to the concentration C_o , which indicates that the reaction is controlled by diffusion. It is seen from Fig. 7B that the peak current i_p is linearly related to the square root of scan rate $v^{1/2}$ and the correlation coefficient is $R^2=0.9934$, which ensures that the reduction process of nitrate on the Ag/PPy nanocomposite electrode is a controlled diffusion process.

3.7. Analytical application

The modified sensor was successfully applied to the determination of nitrate in mineral water, sausage and cheese samples. The results are given in Table 2. According to this table, the obtained results are comparable with those obtained by spectrophotometric method. Thus the sensor provides a good alternative for the determination of nitrate in real samples.

Table 2. Comparison between a standard spectrophotometry method and the proposed method for nitrate determination

| Samples | Proposed method* | Spectrophotometry* |
|--------------------------------------|------------------|--------------------|
| Mineral Water (mg L^{-1}) | 7.38±0.21 | 7.12±0.45 |
| Cheese (mg g^{-1}) | 3.25±0.92 | 3.57±0.28 |
| Sausage (mg g^{-1}) | 25.21±1.2 | 26.12±1.43 |

*Average values five determinations

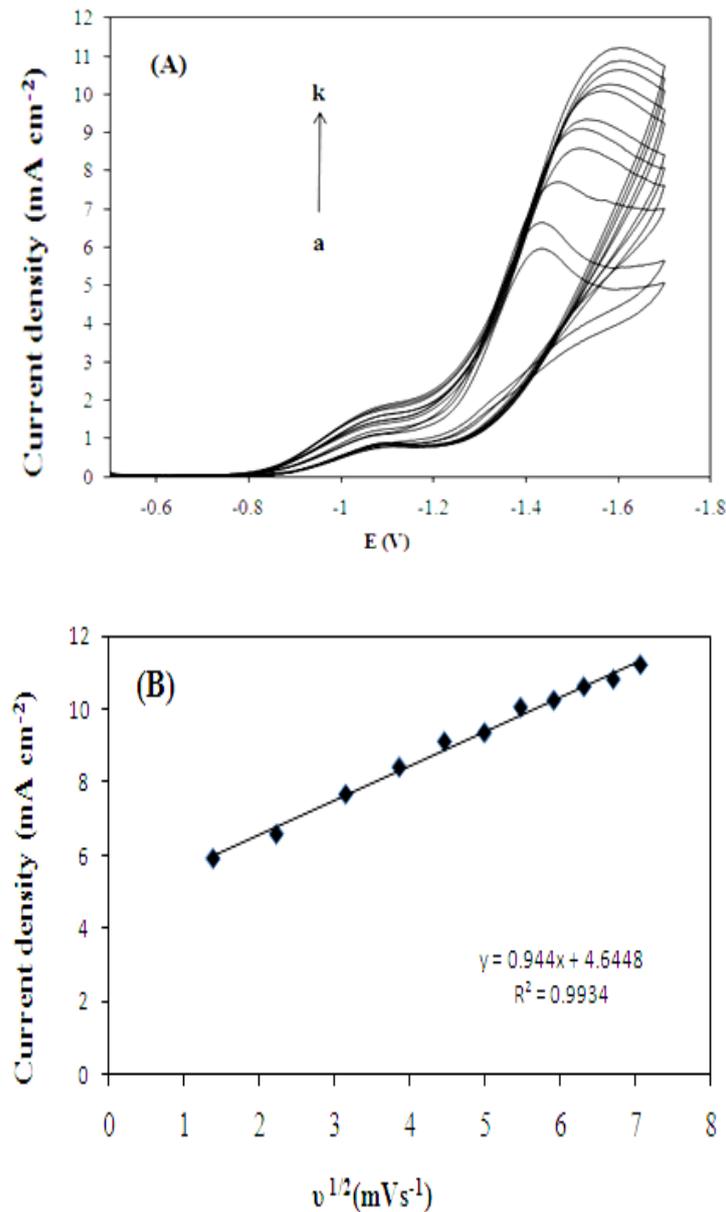


Fig. 7. (A) Cyclic voltammograms of Ag/PPy nanocomposite electrode in 0.01 M nitrate + 0.1 M KCl solution at 25°C with different scan rate (a → k): 2.0, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, 50.0 mV s⁻¹. (B) Plot of nitrate reduction peak current on the Ag/PPy nanocomposite electrode vs. v^{1/2}

4. CONCLUSION

This work demonstrates that Ag/PPy nanocomposite can be used for quantification of nitrate ions in different samples. The proposed electrode exhibits excellent voltammetry performance. It responds to nitrate, presents a good selectivity over most of the anions and showed a low detection limit. The proposed sensor provides lower limit of detection, wider linear range and selectivity over the most of the reported electrodes.

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