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Development of Simple, Reusable and Sensitive Electrochemical Sensor based on Silver Nanoparticles Modified Gold Screen-Printed Electrode for the Detection of Nitrate in Water

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Summary
A simple, reusable and sensitive electrochemical sensor based on silver nanoparticles modified gold screen-printed electrode has been developed for the detection of nitrate in water for animal feed. The sensor exhibited a wide linear response to nitrate from 50 µM to 10000 µM with a detection limit of 4.38 µM (N=4) which is significantly lower than the maximum contaminant level admitted for watering dairy cattle ($3.22X10^3$ µM), and within the sensor linear range. The sensor presented good reproducibility (<10%) and repeatability (2%) as well as selectivity with respect to common interferents found in water.

Keywords: Nitrate; Silver Nanoparticles; Electrochemical sensor; Water monitoring

Introduction

Nitrate (NO_3^-) is widely found in water, resulting mainly from the usage of agricultural fertilizers and the discharge of untreated wastewater from human activities [1]. However, high levels of nitrate can cause serious harms for both aquatic ecosystems and human health [2]. According to regulation EC 183/2005 of the EU [3], the maximum admitted value of nitrate for watering dairy cattle is of $3.22X10^3$ µM. Therefore, there is great interest in developing fast, accurate and portable sensing devices for the determination of nitrate in the field, where electrochemical sensors are one of the most promising. The modification of the surfaces of such sensors with nanomaterials can enhance the sensitivity of those devices, as several have already been reported [4]. However, the pretreatments, preparation and modifications of such sensors in the reported studies are complex and time-consuming. In the present work, a simple, reusable and sensitive electrochemical sensor for nitrate detection consisting of silver nanoparticles (AgNPs) modified gold screen-printed electrode (AuSPE) has been developed. The optimal electrodeposition time of AgNPs has been determined to obtain the highest sensing performances. The electrochemical behavioor of the modified electrode was investigated by Square Wave Voltammetry (SWV). Finally, the selectivity with respect to common interferents in water was demonstrated.

Experimental

Potassium nitrate (KNO_3), silver nitrate ($AgNO_3$) and sodium chloride (NaCl) were purchased from Sigma Aldrich. Stock solution of nitrate and interferents were dissolved in NaCl solution (0.6 M). $AgNO_3$ (3.5 mM) dissolved in KNO_3 electrolyte solution (100mM). Cleaned AuSPEs have been conditioned in H_2SO_4 solution (10 mM) by cyclic voltammetry (CV) between 0 V and 1.5 V at 100 mVs^{-1}. Next, the electrode modification was achieved by the electrodeposition of silver onto AuSPE using the chronoamperometry method at −0.2 V, at controlled time. Thus, t=7s was selected as the optimum time in order to maximise the sensitivity for the determination of nitrate. SWV measurements were carried out at the pulse amplitude of 60 mV with a frequency of 100 Hz. The potential varied from 0.0 V to −1.4 V. Figure 1 shows the fabrication process of the proposed NO_3^- sensor. According to the references, the modification of gold electrodes with AgNPs can lead to the formation of a catalyst that can be used for the selective electrochemical reduction of NO_3^- to NO_2^- according to the following reaction [5]:

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \quad (1)$$

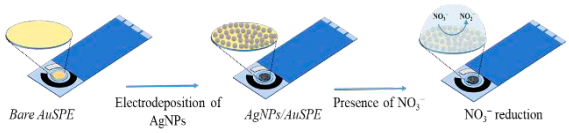

Fig. 1. Schematic illustration of the fabrication process and the detection mechanism of the proposed nitrate (NO3−) sensor.

Results and discussion

The surface of the modified electrode was characterised by Scanning Electron Microscopy (SEM) (Fig. 2). Fig. 2a shows the SEM image,

where the AgNPs deposition was confirmed. The homogeneous distribution of AgNPs (blue color) on the electrode surface is reported in the EDX mapping in Fig. 2b.

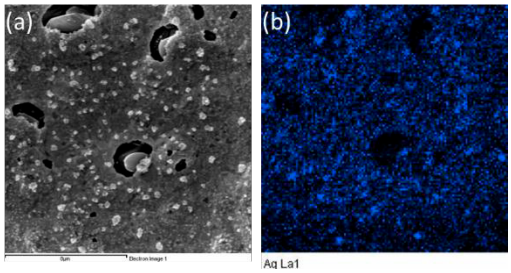

Fig. 2. SEM micrograph (a) and mapping analysis (b) of the AgNPs deposited on the AuSPE electrode surface.

Then, the sensor was characterized by SWV. A significant change of the current value was noted after the modification of the bare electrode with the AgNPs, confirming the surface modification. The influence of scan rate on the reduction of the nitrate was studied by CV (results not shown), indicating that the reduction was controlled by diffusion processes. The electroanalytical determination of NO_3^- using the AgNPs/AuSPE was performed by SWV. The electrochemical curves obtained for varying NO_3^- concentrations are shown in Fig. 3. The calibration plot constructed from the obtained SWV response, illustrated in inset of Fig. 3, shows a wide linear range from 50 to 10000 µM. The calculated detection limit was 4.38 µM (N=4). NaCl electrolyte solution (pH= 7) was used which can provide the opportunity to directly detect nitrate in real water samples without the need to change the electrolyte pH and without interfering with the sensor's performance. Few reported sensors have been developed for nitrate reduction reaction within neutral pH, indeed acidic electrolyte has been used in most cases to obtain better sensitivity. The relative standard deviation (RSD) found for the measurement of 400 µM, 1500 µM and 10000 µM of NO_3^- at four different electrodes, prepared in the same way, was 8.6 %, 5.6% and 5.2% respectively, showing good reproducibility. The repeatability (N= 10) of the sensor was successfully carried out obtaining an RSD of 2.0 %. The selectivity of the sensor towards NO_3^- was investigated in the presence of the most common interfering compounds (Ca^{2+}, K^+, NO_2^-, HCO_3^-, CH_3COO^- and Mg^{2+}) at concentrations 10-fold higher than of NO_3^-. None of the interferents exhibited a significant change in the NO_3^- response.

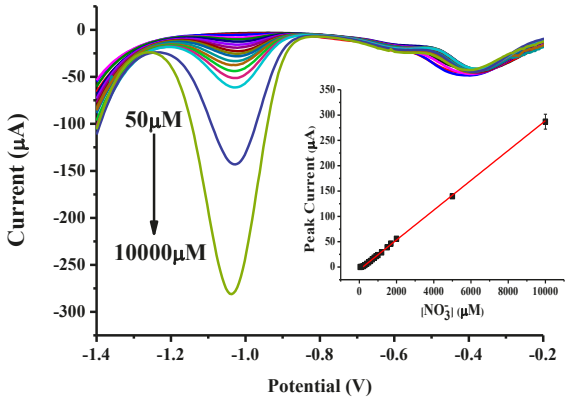

Fig. 3. SWV of different concentration of NO_3^- from 50 µM to 10000 µM at AgNPs/AuSPE in NaCl (0.6M). Inset: corresponding calibration curve.

Conclusion

A simple, reusable and sensitive electrochemical sensor for NO_3^- based on AgNPs has been developed. Important performances such as a low detection limit of 4.38 µM (N=4), wide detection range from 50 µM to 10000 µM and excellent selectivity of the developed sensor were achieved. This could be very promising for the detection of NO_3^- in real water samples.

Acknowledgements

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