

PENCIL CARBON ELECTRODE MODIFIED SILVER NANOPARTICLES FOR DETERMINATION OF NITRITE AND NITRATE

Sarawut Singse¹, Suthasinee Thomporn¹, Anurak Chitbuengphrao¹, Tanin Tangkuaram²,
Anchana Preechaworapun^{1*}

¹Program of Chemistry, Faculty of Science and Technology, Pibulsongkram Rajabhat University, Phitsanulok, 65000, Thailand

²Program of Chemistry, Faculty of Science, Maejo University, Chiang Mai, 50290, Thailand

* E-mail for Corresponding Author; E-mail: anchanaaph@yahoo.com, Tel. +66 5526 7106, Fax. +66 5526 7054

Abstract: The nitrite and nitrate were determined by electrochemical at silver nanoparticles (AgNPs)-modified electrodes. The AgNPs were electrodeposited using cyclic voltammetry with the reduction of a AgNO_3 solution on pencil carbon (PC). The AgNPs/PC electrode was investigated with respect to the oxidation of nitrite and the reduction of nitrate in 0.1 M Na_2SO_4 (pH 2) with 4 mM CuSO_4 . The scanning electron microscopy (SEM) and electrochemical characterization were investigated to confirm the electrodeposited silver nanoparticles on a pencil carbon electrode. The AgNPs/PC working electrode was exhibited the high sensitivity and reproducibility for the electrochemical determination of nitrite and nitrate. The AgNPs/PC electrode provides a long linear dependence on nitrite and nitrate concentration in the range from 0.1 to 25 mM for nitrite and 0.001 to 7 mM for nitrate.

1. Introduction

Nitrites and nitrates can serve as indicators for environmental pollution and for food control. The increasing contamination of water resources for human consumption by nitrates and nitrites due to the anthropogenic activities as agriculture and waste waters is receiving worldwide attention.

In this research improved the sensitivity nitrite and nitrate determination, which can be achieved by AgNPs electrodeposition in Cu^{2+} solution as electrocatalyst with 0.1 M Na_2SO_4 for electrolyte. Also, the electrochemical techniques exhibit specific peculiarities to enhance the performance of electroanalytical detection. Differential-pulsed amperometric (DPA) detection can be an alternative technique to prevent contamination of electroactive compounds.

2. Materials and Methods

2.1 Reagents

Potassium nitrite was obtained. Carlo Erba Reagents, France. Potassium nitrate was obtained analar (England). Hydrochloric acid 37%, copper(II)sulfate pentahydrate and sodium sulfate were purchased Merck (Germany). Potassium chloride was from Australia. Sulfuric acid 98% was purchased. Lapsan analytical science Thailand. Deionized water was from a Milli-Q-gradient system (Millipore, $R \geq 18.2 \text{ M}\Omega \text{ cm}$).

2.2 Apparatus and electrochemical measurements

The electrochemical performances of this electrode for the detection of nitrate and nitrite were studied using cyclic voltammetry (CV) and differential pulse amperometry (DPA). All measurements were carried out using Electrochemical Analyzer (Model 1230A, CH Instruments) at room temperature. Pencil rods (2B), id. 0.5 mm and length 5 cm, were purchased from STAEDTLER, Germany. A conventional three electrode system consisted of pencil carbon, a Ag/AgCl (3 M KCl) and a stainless steel as working, reference, and auxiliary electrodes, respectively.

2.3 Preparation of the AgNPs on a pencil carbon electrode (PCE)

The preparation of PCE was carried out as described earlier. In brief, a mechanical pencil 0.5 was used as a holder for pencil lead. All leads had a total length of 60 mm and a diameter of 0.5 mm. Electrical contact to the lead was achieved by wrapping a metallic wire around the metallic part of the pencil. A total of 0.97 cm of lead was immersed in solution per measurement. Such length corresponds to an active electrode area of 0.19 cm^2 .

The AgNPs-modified pencil carbon (AgNPs/PC) electrode was prepared by immersing PC electrode into a deaerated aqueous solution of 0.25 mM of AgNO_3 and 0.25 mM sodium citrate [1]. Cyclic voltammetry was done with an electrochemical system with cyclic voltammetry from 0 to -0.8 V with different number scan of 0, 1, 2, 3, 4, 5, and 10 cycles. After electrodeposition the electrodes were rinsed with deionised water, ethanol and dried under a stream of air. The AgNPs modified PCE in the same condition was characterized by the Scanning Electron Microscope (SEM; LEO, Model 1400VP).

3. Results and Discussion

3.1. Morphological characterization of the electrodes

Figure 1 (A), and (B) illustrates the SEM images of bare PC, and AgNPs/PC electrodes, respectively. Figure 1 (B) reveals the typical highly spotted AgNPs dispersion on the PC surface. The average size of AgNPs is 100 nm.

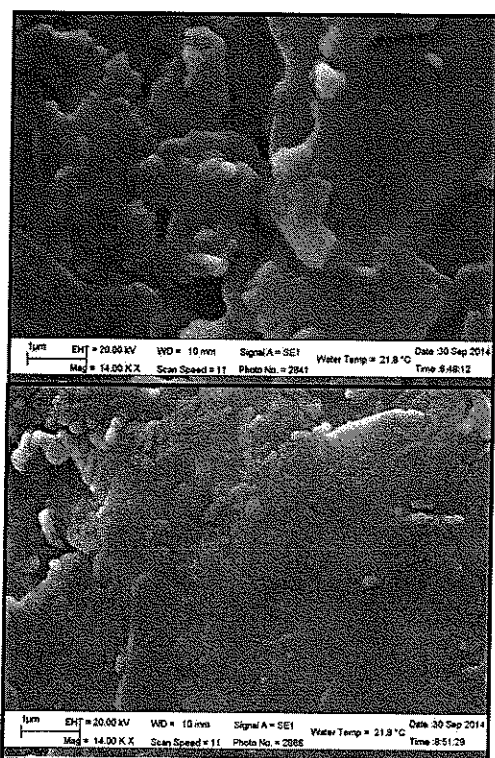


Figure 1. SEM image of (A) bare PCE and (B) PCE after AgNPs electrodeposition by cyclic voltammetry at three cycles.

3.2 Electrochemical characterization of nitrite and nitrate determination

Nitrite electrochemical analysis was studied by CV at the potential 0.2 to 1.2 V, the result showed in Figure 2 (A). Figure 2A show cyclic voltammograms of 0.1 M Na_2SO_4 pH 2.0 electrolyte, 4.8 mM Cu^{2+} in electrolyte solution, and 2.8 mM nitrite in-situ Cu^{2+} in electrolyte solution at bare (Figure 2A(a)) and AgNPs modified PCE (Figure 2A(b)), respectively. The electrolyte and Cu^{2+} solution are not shown at all of electrodes. The nitrite (Figure 4A) are shown oxidation peak at 1.1 V using bare PCE, however when comparison with the AgNPs/PCE shown at 1.0 V, its peak shaper and higher current peak (1.3 times) than bare electrode. In Figure 2B, nitrate electrochemical analysis was investigated by CV at the potential 0 to -1.2 V. The electrochemical behavior of nitrate was investigated as same as nitrite characterization. The Cu^{2+} (Figure 4b) are shown reduction peak at -1.1 V, however when comparison with the reduction peak of nitrate shown clearly peak at 0.8 V at the both of electrode. The cathodic current peak at AgNPs/PCE was shown higher than bare electrode 1.1 times. This result explained to the function of CuNPs as an electrocatalytic in nitrate. This result explained to the function of AgNPs and in-situ Cu^{2+} as an electrocatalytic in nitrite.

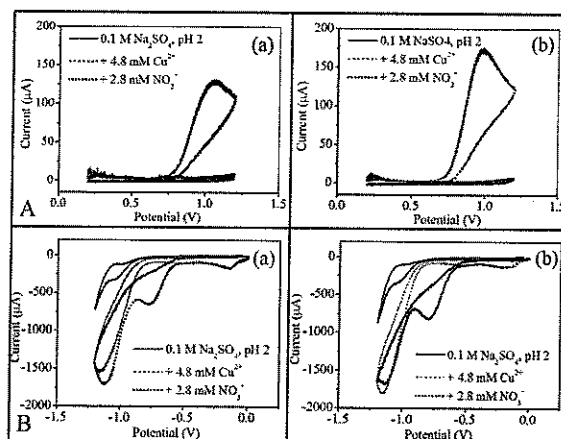


Figure 2. Cyclic voltammograms of electrolyte (0.1 M Na_2SO_4 , pH 2), added Cu^{2+} solution, and added 2.8 mM analyte of nitrite (A) and nitrate (B) using a bare PCE (a) and a AgNPs/PCE (b) at scan rate 50 mV/s.

2.3 Optimization of parameters of the sensor

In order to get the optimal conditions for achieving highly current sensitive detection of nitrite and nitrate, the number of scan for electrodeposition, the Cu^{2+} concentration, pH value of Na_2SO_4 adjusted with H_2SO_4 and pulse potentials (E1 and E2) in DPA were studied in detail, respectively. The effect of the electrodeposition cycles is illustrated in Figure 3. The current peak from cyclic voltammetry for nitrite and nitrate analyses increased with the increasing of electrodeposition until 1 and 3 cycles, respectively. The results of nitrite determination at AgNPs electrodeposition more than a cycle were shown less difference anodic current. Thus, 3-cycles scan was the optimal condition for AgNPs loading for nitrite and nitrate determinations.

Figure 4 shown the effect of the Cu^{2+} concentration on the performance of the nitrite and nitrate sensors. In nitrite determination in various Cu^{2+} concentrations are not shown difference anodic current. The maximum response current of nitrate was observed when 80 μL Cu^{2+} solution (3.8 mM Cu^{2+}) was used. It may be ascribed to the following reasons: with low Cu^{2+} concentration the AgNPs modified electrode surface could not be thoroughly covered by Cu^{2+} , causing insufficient active sites for nitrite catalysis. However, too high Cu^{2+} concentration was caused the aggregation of analytes determination.

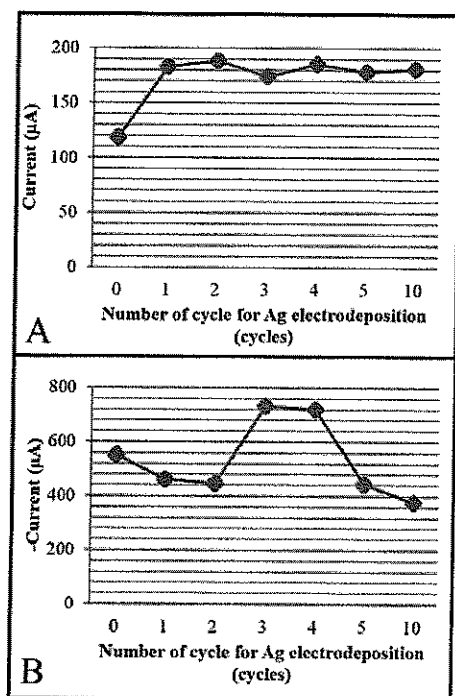


Figure 3. The relationship between the current of nitrite (A) and nitrate (B), and the number of cycle for Ag^+ electrodeposition using 2.8 mM analyte in-situ 4.8 mM Cu^{2+} in electrolyte solution.

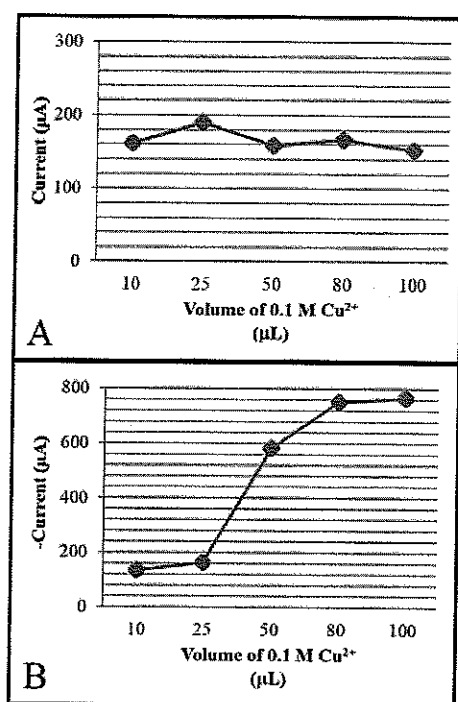


Figure4. The relationship between the current of nitrite (A) and nitrate (B), and the volume of in-situ 0.1 M Cu^{2+} solution using 2.8 mM analyte in electrolyte solution.

The electrochemical behavior of nitrite and nitrate was investigated at the AgNPs/PCE in-situ 3.8 mM Cu^{2+} in 0.1 M Na_2SO_4 solution from pH 1.0 to 4.0 adjust pH with 0.1 M H_2SO_4 by cyclic voltammetry (not shown). It was found that changing pH effected the oxidation and reduction peak potential. The best respond was received at pH 2.0 of Na_2SO_4 and its used hold research experiment.

The differential pulse amperometry (DPA) was used quantitative nitrite and nitratedetermination. The DPA, a sequential two-step sampling is executed at two different potentials (E1 and E2). Differential current signal of the duplex sampling events is recorded that functions as time domain. Figure 5A, the effect of potential of pulse E1 and E2 for nitrite was investigated by fixing pulse E1 = 1.0 V for finding pulse E2 and fixing pulse E2 = 0.8 V for finding pulse E1. The optimized pulse E1 and E2 were received 1.3 and 0.8 V for nitrite determination, respectively. Figure 5B, the effect of potential of pulse E1 and E2 for nitrate was investigated by fixing pulse E1 = -0.75 V for finding pulse E2 and fixing pulse E2 = -0.3 V for finding pulse E1. The optimized pulse E1 and E2 were received -0.8 and -0.3 V for nitrate determination, respectively.

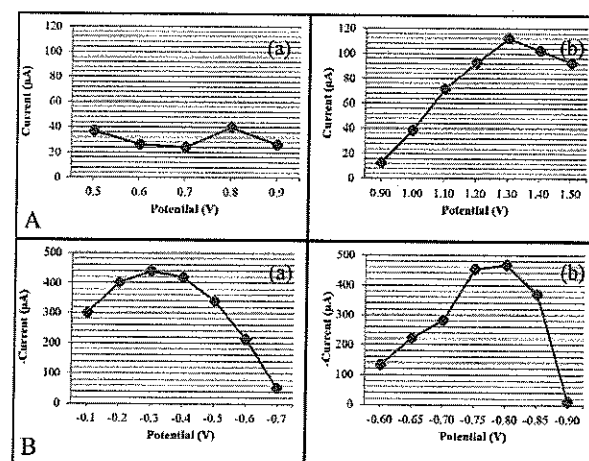


Figure5. Average anodic current of 0.9 mM ($n=3$) nitrite by DPA at nitrite (A) and nitrate (B) various pulse E2 (a) and various pulse E1 (b) in-situ 3.8 mM Cu^{2+} in 0.1 M Na_2SO_4 using AgNPs/PCE.

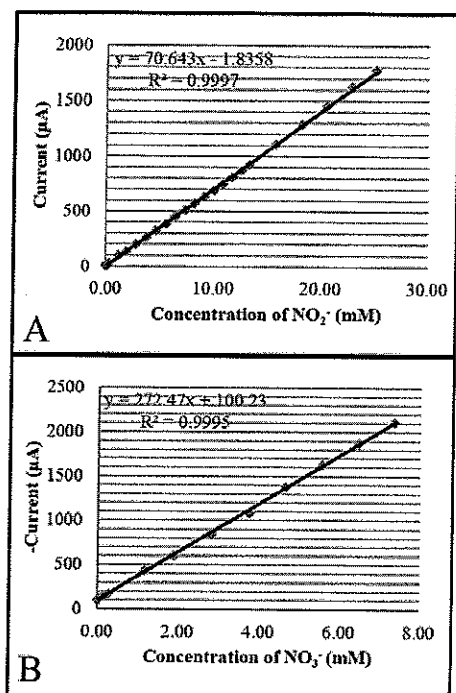


Figure 6. (A) Linearity from differential pulse amperograms of nitrite (A) and nitrate determinations at pulse E1=1.3 and -0.8 V and pulse E2=0.8 and -0.3 V using AgNPs/PCE.

The relationship between the differential pulse amperometric current and the concentration of nitrite was investigated in the range 0.1-25mM and 0.001-7 mM (Figure 6). Using the optimized conditions previously reported, a linear response ($y=70.64x-1.84$, $R^2=0.9997$) and ($y = 272.47x + 100.23$, $R^2 = 0.9995$) was obtained at excellent sensitivity 93.44 and 272.47 $\mu\text{A}/\text{mM}$. The detection limit (3SD) was estimated as 30 and 0.3 μM .

4. Conclusions

In conclusion, we here presented a AgNPs modified PC electrode for electrochemical nitrite and nitrate determinations using DPA. The AgNPs can strongly catalyze the oxidation of nitrite and nitrate in-situ 3.8 mM Cu^{2+} in 0.1 M Na_2SO_4 electrolyte solution (pH 2). The modified electrode provides a sensitive method for the DPA detection of nitrite and nitrate. It is expected the AgNPs/PCE will be a promising material in fabricating nitrite and nitrate sensors.

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References

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